

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

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Abstract

Devices featuring electrophoretic displays (EPD) have become extremely popular in recent years because of their low power consumption, high readability and thin display designs, but a product with a full colour gamut comparable with liquid crystal displays (LCDs) has not yet been commercialised. In this article, we demonstrate that staggering the addition of methyl methacrylate (MMA) monomer and low quantities of a coloured dye crosslinker is an effective route to producing well-defined and covalently-linked, strongly coloured PMMA microparticles in one-pot, *via* dispersion polymerisation in supercritical carbon dioxide (scCO₂). This novel methodology is synthetically simple, readily scalable and has the added cachet of being cost effective because the functional molecules can be confined on the microparticle surface such that even at low concentrations, the resulting materials are brightly coloured. We then demonstrate the applicability of this approach to another functional comonomer/crosslinker system in 2-dimethylaminoethyl methacrylate (DMAEMA)/ ethyleneglycol dimethacrylate (EGDMA), in this case allowing hierarchically structured ‘pomegranate-like’ microparticles with polarisable charge to be produced over a range of

DMAEMA loadings as high as 44 wt. %. Finally, the performance of these materials in out-of-plane EPD test cells is compared against analogues synthesised in dodecane. These tests revealed that the coloured microparticles fabricated in scCO₂ performed as well as or better than their dodecane synthesised counterparts, consistently producing the cleanest white state and achieving effective colour switching over ten cycles.

Introduction

Polymer microspheres synthesised by dispersion polymerisation are important materials for a very wide range of applications, including paint fillers, printer toners, chromatography columns and liquid crystal display screens.^[1,2] More recently, such particles have been identified for use in electrophoretic displays (EPD), as found in e-readers such as the Amazon Kindle®.^[3,4] These 'electronic ink' devices have become extremely popular in recent years because of their low power consumption, high readability and thin display designs. The design features of traditional EPD are that the microparticles are black or white, are dispersed in an organic carrier liquid, and that they carry charge so that the pixels in the device can be formed and then switched quickly to refresh the page view. It has been common practice to use carbon black, copper chromite and titanium dioxide as the particles in EPDs.^[5,6] Whilst this tactic is simple and effective, only black and white pixels can be achieved. A key future target for the technology is to introduce colour into such displays. The target is to develop a range of particles carrying different colours that could provide the possibility for very low energy full colour screens using the same EPD technology.^[7] An EPD device with a colour gamut comparable to LCD technology has yet to be commercialised.

A number of approaches have been investigated to produce colour EPD. The first devices on the market used colour filters over conventional black and white EPD technology. This showed some success, but colour filters remove much of the light and so the reflectivity of these

displays is substantially reduced, giving poor colour saturation and low brightness. A more promising approach would be to use coloured particles, as already seen in tri-colour displays for price labelling in supermarkets.^[8] However, this technology only utilises black, white and red particles. A full colour display would require a complete set of primary colours; either red, green and blue, or magenta, cyan and yellow along with the black and white particles. A key problem then is to devise a scalable synthetic route that could provide a simple approach to produce polymeric microparticles with both charge and colour. We hypothesised that this would be readily achievable by exploiting copolymerisation to introduce functional monomers into polymeric microspheres.

Dispersion polymerisation in dodecane has been a preferred route to micron sized particles of poly(methyl methacrylate) (PMMA) for EPD,^[4,9] but other approaches have been explored. Noël *et al.* used various pigment particles to seed dispersion polymerisations of 4-vinylpyridine, which were stabilised by alkyl acrylate macroinitiators.^[10] TiO₂, Fe₂O₃ and CoO·Al₂O₃ were used to produce white, red and light blue particles respectively, before charging the particles either by quaternising the pyridine functionality for positive charge, or using a charging agent such as tridodecylamine to achieve a negative charge. In another example of pigment based particles, Xianwei *et al.* went further, by first producing pigment core/styrene and divinyl benzene shell particles and then coating these with a covalently bound, fluorocene based dye layer.^[11] This method was intended to produce EPD devices that could luminesce in the presence of a backlight in order to overcome the devices dependency on reflected light, making them suitable for use at night. Meanwhile, Chen *et al.* synthesised silica coated organic pigments as a basis to produce particles with exceptionally high reflectivity.^[12] Here the silica coating aided adsorption of surface modifying polymeric species, but also boosted the reflectivity of the pigment due to the way in which the silica particles scatter light.

However, these current approaches come with significant challenges, not least in the environmental acceptability of the processing. An unfortunate limitation of dispersion polymerisation is that it requires use of large quantities of volatile organic compounds (VOCs) as a solvent (e.g. dodecane) for the polymer synthesis. After synthesis, the VOC solvent must then be removed to eliminate residual monomer, initiator fragments, etc. The solvent is then recycled or sent for waste disposal.^[9,13–15] For final application in EPD, the clean dry particles are then dispersed in a hydrocarbon based solvent, such as a high purity dodecane.

Supercritical carbon dioxide (scCO₂) has been successfully employed as an alternative solvent for the dispersion polymerisation of PMMA, and we reasoned that this clean solvent could be exploited to overcome many of these drawbacks.^[16,17] Above its critical pressure and temperature (7.38 MPa and 31 °C)^[18] scCO₂ provides a non-toxic, non-flammable and easily recyclable solvent that is an excellent choice for dispersion polymerisation. It is a good solvent for many vinyl monomers but is a non-solvent for their respective polymers. The exceptions are a small number of amorphous fluorocarbon^[19] or silicone^[20] based polymers that do show high scCO₂ solubility, and these have been utilised in a wide range of successful stabilisers for scCO₂.^[21–27] Very recently, the potential for new stabilisers based on more conventional monomers such as poly(vinylacetate) have been reported.^[28,29]

The use of scCO₂ in the production of electrophoretic particles was reported by Badlia *et al.*, who first produced electrophoretically active particles by a conventional dispersion polymerisation of styrene and divinyl benzene in ethanol.^[30] These particles were then soaked in scCO₂, which caused the polymer to swell and allow CO₂-soluble dyes to diffuse into the particles. This approach was successful and resulted in a range of coloured products. However, there were several drawbacks, namely the multi-step synthesis and that the dye was not chemically bound to the polymer and thus susceptible to leaching out at a later stage.

Thus, a very simple and attractive route to EPD particles should be to use a one-pot free radical polymerisation process to create a dispersion of microparticles in scCO₂ based on PMMA. In addition, we reasoned that the low viscosity and high diffusivity might provide the ideal solvent condition to allow incorporation of small amounts of a second functional monomer to bring charge or colour. This is something that has been trialled in conventional dispersion polymerisations but has not proved viable. Unfortunately, this process often simply does not work. Incorporation of just 2 wt. % of the functional monomer methacrylic acid (MAA) changes the polymer seeding process, destabilises the system, and leads to formation of very poorly defined microparticles.^[4]

However, in scCO₂ the behaviour of the dispersion may well be very different. Mueller *et al.* indicated that new polymer chains initiate mainly in the continuous phase (scCO₂), and then adsorb onto the established particles.^[31,32] Thus, we hypothesised that a better method may be to first establish a stable dispersion of PMMA and only at that final stage to add the second monomer to polymerise on, or in the established microparticles, leading to either a surface coating or perhaps separate polymer domains within the microparticles. Similar multistage techniques for the addition of comonomers were described by Song *et al.* for dispersions of styrene in ethanol,^[15,33] and our group has already demonstrated that the addition of monomers in two-stages affords much greater control over the dispersion polymerisation and is an effective way to control the size of the PMMA microparticles.^[34]

Herein, we describe a novel, staggered, multi-stage monomer addition method for dispersion polymerisation (in scCO₂) that allows the addition of functional co-monomers and crosslinking molecules or coloured dyes to create polymeric microparticles for colour EPD applications. Specifically, we aim to demonstrate the versatility of scCO₂ and exploit its low viscosity, high diffusivity and ability to strongly plasticise polymers.^[35,36] to create well defined and

structurally complex polymethylmethacrylate (PMMA) microparticles incorporating mono- and di-functional monomers containing coloured dye and charged moieties such as 2-dimethylaminoethyl methacrylate (DMAEMA), as well as the common cross-linker ethyleneglycol dimethacrylate (EGDMA).

Results and Discussion

Synthesis and characterisation of magenta coloured PMMA microparticles in scCO₂ and dodecane.

Dispersion polymerisation represents an ideal methodology for introducing colour into polymer particles. A single synthetic process could enable the formation of microparticles with excellent particle size control, reproducibility and, at the appropriate point, a range of colours or other functionalities could be added by simply swapping one functionalised monomer for another, keeping the particle size and chemistry uniform.

We utilised the organic diacrylate dye MM12 which gives a strong magenta colour, ideal as a primary colour in display screens (**Figure 1a**). Moreover, the diacrylate functionality increases chemical incorporation into the polymer (relative to a monofunctional dye) and will prevent leaching from the particles. However, it is well known that addition of a cross-linker introduces further challenges. Shin *et al.* showed that just 0.4 wt. % of the cross-linker ethyleneglycol dimethacrylate (EGDMA) was enough to completely disrupt the growth of PMMA particles in scCO₂.^[17] This happens because in the early stages of the dispersion it is essential that the growing particles are able to swell, to accommodate monomer from the scCO₂ phase and to allow growth of the particle. At the same time the scCO₂ plasticises the polymer, enabling retention of the spherical morphology. Introduction of crosslinking at this early stage disrupts this process and leads to a loss of good dispersion.^[33]

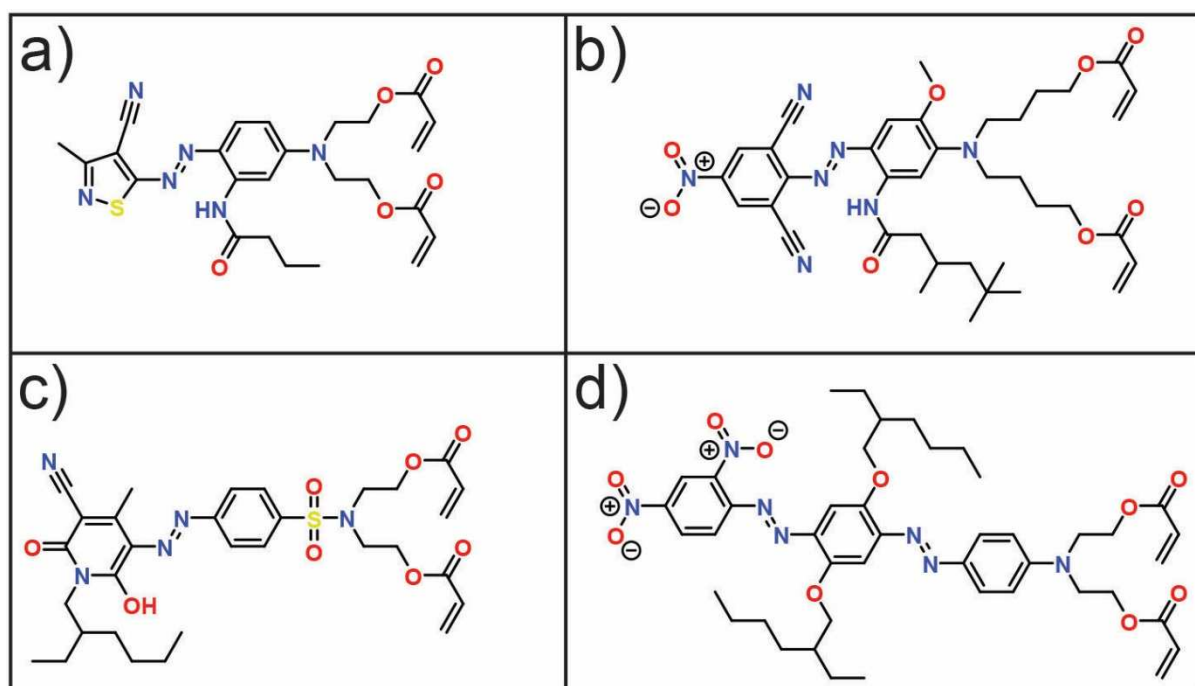


Figure 1: The structures of coloured dyes used to produce the different coloured microparticles reported here. a) Magenta (MM12), b) Cyan (MC10), c) Yellow (MY13) and d) Black (MK6, which is also mixed with MY13).

In order to circumvent this problem, we present a three-stage process to synthesise PMMA particles with excellent size and morphology control, and with the addition of up to 5 wt. % of cross-linking dye. Based upon the two-stage dispersion polymerisation methodology,^[34] we began the process by initially loading half of the MMA into the autoclave along with a radical initiator (2,2'-Azobis(butyronitrile), (AIBN) at 1 wt. % relative to initial charge of MMA) and a methacrylate terminated poly(dimethylsiloxane) macro monomer (20 wt. % relative to initial charge of MMA), which acts as a steric stabiliser. This lower monomer concentration, coupled with a high stabiliser concentration, produces a large number of small nuclei. After one hour the dispersion is well established and a further one-quarter of the total monomer volume is injected directly into the system. This increase in MMA concentration boosts the kinetics of the reaction, leading to high yields after a further 4 hours, excellent particle formation and control of particle size. In the final step, the dye compound is dissolved in the remaining aliquot of MMA (one-quarter of the total MMA volume) and the solution is added to the autoclave and reacted for a further 16 hours. In this way, free-flowing magenta coloured powders comprised

of uniform spherical microparticles are produced. (**Table 1, Entry 1**). Full details for this procedure are given in the experimental section of the supporting information.

Table 1: Characterisation of polymer particles synthesised by two and three-stage dispersion polymerisations in scCO₂ and dodecane. Also included is a donated research sample from Merck Chemicals Ltd.

Entry	Solvent	Steps	Cross-linker		Yield (%) ^b	d _n ^c (nm)	PSD ^c
			Type	(wt. %) ^a			
1	scCO ₂	3	MM12	5	88	393	1.08
2	scCO ₂	3	-	-	96	421	1.14
3	scCO ₂	2	MM12	5	62	313	1.29
4	Dodecane	3	MM12	5	62	583	1.01
5	Dodecane	3	-	-	63	646	1.01
6	scCO ₂	3	EGDMA	10	92	424	1.10

Each entry reports the average of experiments performed in triplicate. ^aBy weight relative to MMA. ^bDetermined gravimetrically. ^cObtained by SEM. The terms d_n and PSD represent the number average diameter of 100 particles and the particle size distribution, respectively, as described by equations 1 – 3 in the supporting information.

The presence of dye in the particles is verified by the strong magenta colour of the product, which is retained even after thoroughly washing with either dodecane or hexane (**Figure 2a**). The analogous syntheses performed in the absence of dye (**Table 1, Entry 2**) show that the yield is consistently lower in the presence of the cross-linking dye (between 82 and 90 % with dye compared to 88 to 96% without). This minimal effect is likely a result of the poor swelling that will be encountered in the final stage after the injection of dye because of induced cross-linking. However, the effect has been minimised by the three-stage approach because most of the polymer is formed before this stage. This is also evident in the scanning electron microscopy (SEM) images of particles synthesised with and without dye (**Figure 2b and c** respectively).

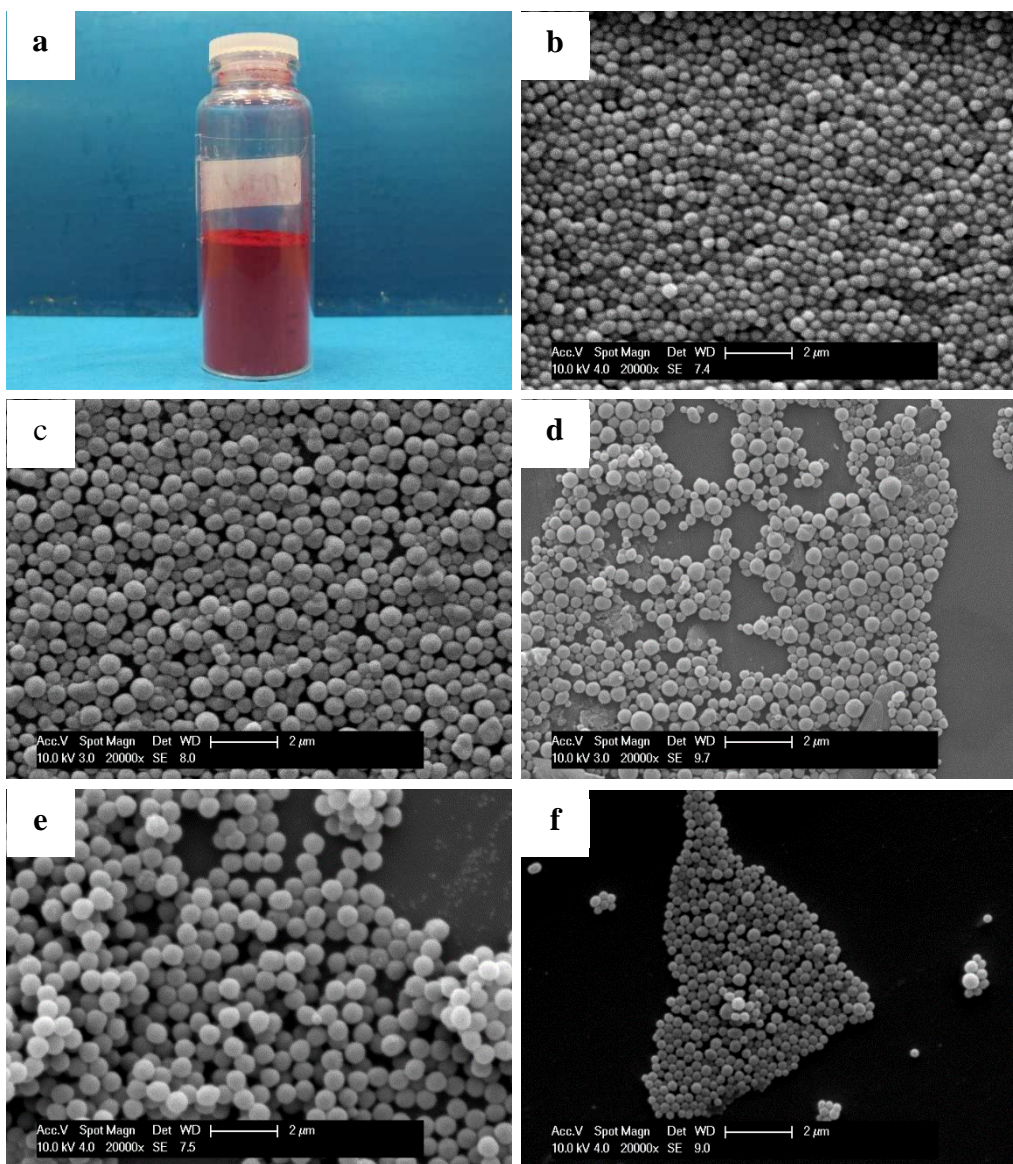


Figure 2: a) A photograph of PMMA particles synthesised in the presence of 5 wt. % MM12 in $scCO_2$ shows strongly dyed particles even after extensive washing with dodecane. Also shown are SEM micrographs of b) the dye containing particles synthesised using the three-stage process, c) PMMA particles synthesised by the three-stage approach in $scCO_2$ without the addition of dye, d) irregular particles synthesised in the presence of 5 wt. % MM12 using a simpler two-stage approach, e) PMMA particles synthesised in dodecane using an analogous three-stage technique and f) PMMA particles synthesised with 10 wt. % EGDMA in $scCO_2$ by the three-stage method.

The significance of the third stage is made more apparent by comparing dyed PMMA particles synthesised by the two and three-stage polymerisations. In the two-stage process the dye was added with the first injection of monomer, 1 hour after the start of the reaction (**Table 1, Entry 3, Figure 2d**). Although the injection of dye was delayed, it still had a significant effect

on the polymerisation kinetics, leading to a yield of just 62 %. Additionally, whilst spherical particles were obtained, they were considerably less uniform, with a particle size distribution of 1.29. Thus, the three stage approach is essential for the synthesis of homogeneous cross-linked particles.

Although developed for use with scCO₂, the principles of this method also seemed to be applicable to conventional solvents. We successfully demonstrated a three stage dodecane reaction for comparison (**Table 1, Entry 4 and Figure 2e**). Polymerisations in dodecane gave lower yields and larger particle sizes compared to scCO₂. However, the lower yields in this case are not entirely the influence of the cross-linking dye, but an artefact of the higher dilution of the monomer and initiator (initial charge of 5 mL MMA in 91 mL dodecane). In dodecane, discrete particles could not be obtained at the same high concentrations that were possible in scCO₂ (5 mL MMA in 60 mL total volume). This higher solids content for scCO₂ would be a significant advantage for commercialisation as it would increase yield per batch for a given reactor volume. The greater particle sizes are predominantly the result of differences in the solubility and concentrations of MMA, PMMA and stabiliser in dodecane and scCO₂ and it is not necessarily meaningful to compare particle sizes between the two solvents.

The scope of this technique is demonstrated by use of a simple cross-linker such as EGDMA (**Table 1, Entry 6 and Figure 2f**). Using this technique, up to 10 wt. % EGDMA could be added to the polymerisation in scCO₂ without any measurable negative effect on the particle morphology. To the best of our knowledge, the successful addition of such high levels of EGDMA to dispersion polymerisations of MMA have not been previously reported in any solvent system and this strongly illustrates the versatility of this method.

Internal morphology of dye containing polymer microparticles from scCO₂ and dodecane.

In addition to creating new materials for use in electrophoretic displays, it is also interesting to consider opportunities to exploit the three-stage dispersion polymerisation in scCO₂ as a synthetic route to structurally controlled particles. As discussed above, Mueller *et al.* have suggested that new chains are initiated predominantly in the continuous phase during dispersion polymerisation and quickly adsorb onto the polymer particles.^[31,32] In this case, it should be expected that in polymerisations that incorporate the dye towards the end of the synthesis, a core-shell type structure will be produced. This was confirmed using transmission electron microscopy (TEM) images of the sectioned particles. Selective staining of the conjugated dye using RuO₄ produces a clear ring of material around the core of the particles (**Figure 3**). Thus, the three-stage approach not only enables the incorporation of significant levels of a cross-linker without detrimentally affecting the particle morphology, but is also a simple route to core-shell type structures.

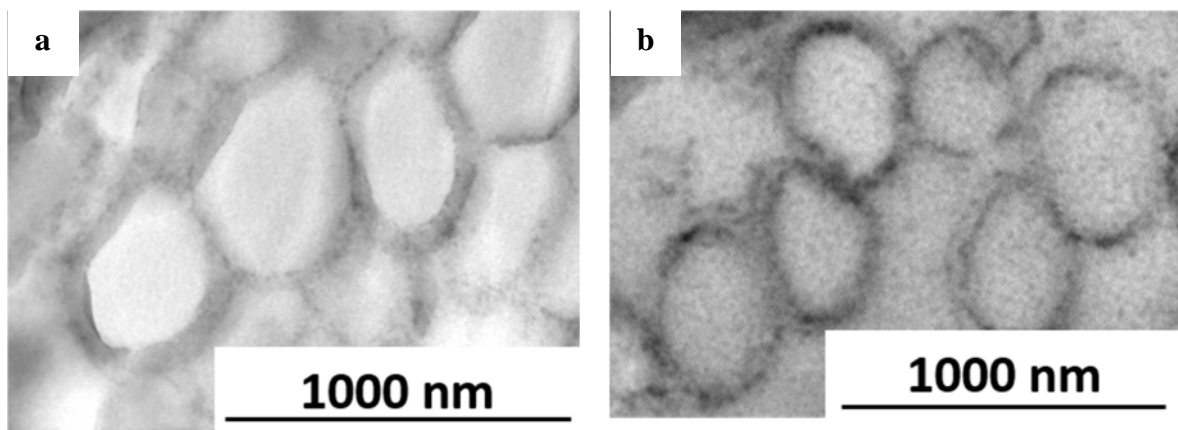


Figure 3: TEM images of particles produced using the three-stage dispersion polymerisation process with final stage addition of the cross-linking dye material (a) in scCO₂, and (b) in dodecane. In both cases, after staining with RuO₄ there is a clear ring of dyed polymer around the unstained PMMA core.

Synthesis of hierarchically structured polymer microparticles from PMMA and DMAEMA via the staggered multi-stage addition process.

One of the key differences between scCO₂ and dodecane as the continuous phase for dispersion polymerisation is that many polymers are significantly plasticised by scCO₂.^[35,37,38] Jennings *et al.* showed that this effect could be used to achieve a number of different internal structures during the dispersion polymerisation of block copolymers, where the individual blocks were selected to be immiscible.^[39-41] We therefore reasoned that by replacing the cross-linker with a monofunctional monomer, it should be possible to produce structured particles. For this investigation we selected dimethylaminoethyl methacrylate (DMAEMA), because the polar amine should strongly phase separate from the relatively non-polar PMMA. Additionally, the incorporation of polarisable moieties might be used to obtain higher particle charge, and this could result in faster switching in EPD. To test this opportunity, a series of three-stage dispersion polymerisations were performed to which 13, 27, 40 and 67 wt. % DMAEMA was injected at the final stage of the polymerisation (**Table 2**).

Table 2: Representative results of three-stage dispersion polymerisations incorporating DMAEMA. The corresponding SEM images are available in SI Figure S 4.

Entry	Solvent	Additive (wt. %)		Yield ^b (%)	d _n ^c (nm)	PSD ^c
		Feed	Actual ^a			
1	scCO ₂	13	20	85	370	1.13
2	scCO ₂	27	27	73	504	1.07
3	scCO ₂	40	37	89	780	1.07
4	scCO ₂	67	44	78	439	1.13
5 ^d	scCO ₂	40	37	71	-	-
6	Dodecane	13	5	56	556	1.01
7	Dodecane	27	5	62	578	1.01
8	Dodecane	40	10	51	636	1.03
9	Dodecane	67	16	29	531	1.09

^aDetermined by ¹H NMR. ^bMeasured gravimetrically. ^cObtained by SEM. ^dSynthesis performed as a one-stage dispersion polymerisation.

In scCO₂, discrete particles could be synthesised at every DMAEMA loading (**Table 2, Entry 1-4**). However, it is clear from these data that both the particle size and yield are significantly affected. In all previous polymerisations using this procedure in scCO₂, the particle size was consistently between 300 and 450 nm, with yields above 85 %. Each reaction was repeated at least in duplicate, and in the presence of DMAEMA the yield varied between 73 and 91 %, whilst the number average particle diameter fluctuated from 346 to 780 nm (**Figure S 4**). There was no discernible correlation between these properties and the amount of DMAEMA added.

However, what is clear is that the multi-stage approach works very effectively to incorporate high levels of DMAEMA into the PMMA microparticles. This fact is demonstrated clearly by comparison with a one-stage approach (**Table 2, Entry 5**). When 40 wt. % DMAEMA was added at the beginning of the reaction, morphology control was completely lost and no particles were obtained, despite reaching a comparable yield (71 %) and the same level of DMAEMA incorporation (37 wt. %) as the three-stage synthesis. Similar observations were made by Wang *et al.*, who showed that for one-stage dispersion polymerisations of MMA/DMAEMA in scCO₂, anything more than 5 wt. % DMAEMA leads to agglomeration, with higher levels producing no particles at all.^[16]

ScCO₂ also showed some advantages over the conventional polymerisations in dodecane, giving higher overall yields and a significantly higher uptake of DMAEMA (**Table 2, Entry 8**). In addition, we found that for the dodecane reactions a much lower level of 16 wt. % of PDMAEMA relative to PMMA was sufficient to cause agglomeration of the particles (**Table 2, Entry 9**). To explain the reduced stability of the particles in dodecane, the internal structures were analysed by taking TEM images (**Figure 4**).

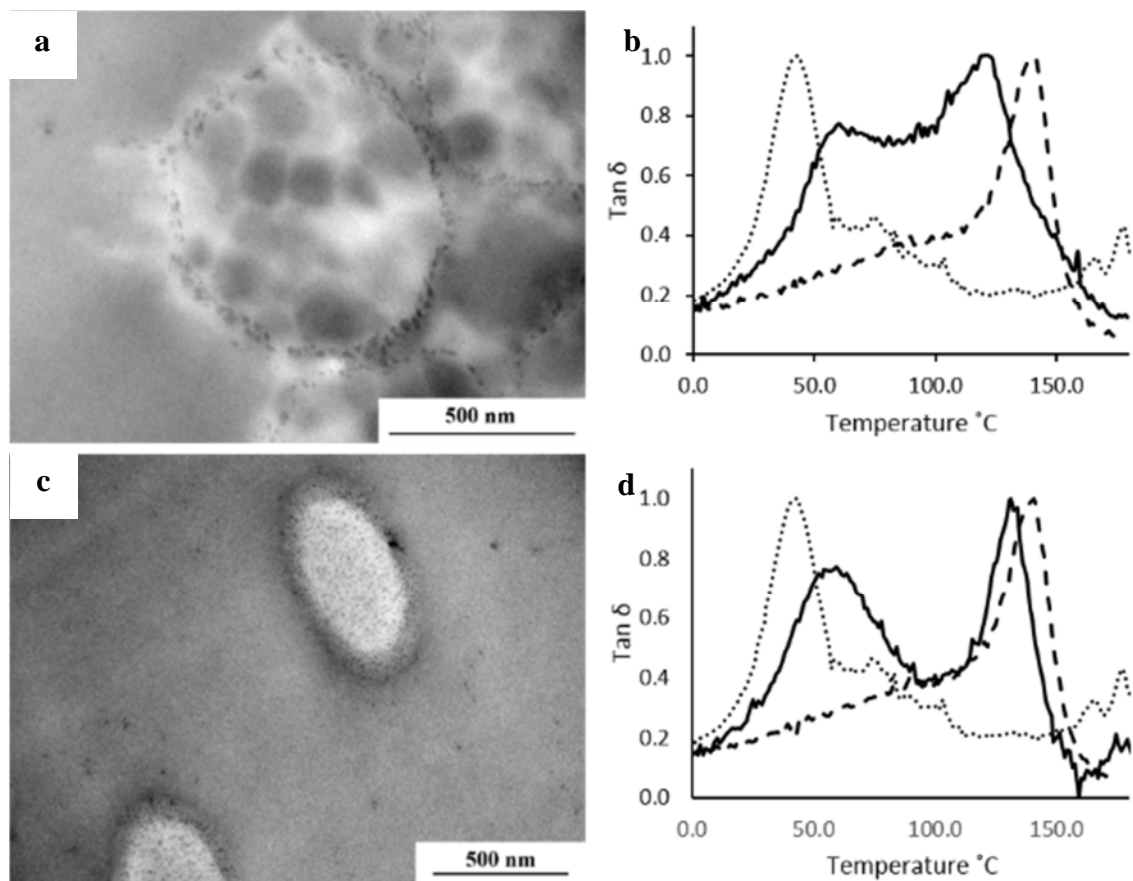


Figure 4: a) TEM image of the stained section of PMMA particles synthesised by three-stage dispersion polymerisation in $scCO_2$ incorporating 37 wt. % DMAEMA and b) the accompanying DMA $\tan\delta$ trace. Also shown are c) the TEM image of the dodecane synthesised analogue incorporating 10 wt. % DMAEMA and d) the corresponding DMA $\tan\delta$ trace. $\tan\delta$ traces for the PDMAEMA (dotted line) and PMMA (dashed line) are also shown for reference. The double-peaks demonstrate that there are two separate polymer domains within the particles, and these are clearly visible in the TEM images.

The surface of the particles synthesised in $scCO_2$ is defined by a ring of small dark spots (**Figure 4a**). We attribute these to the PDMS-MA stabiliser present at the particle surface. Similar EM data were previously reported by Minami *et al.*, who also used a PDMS based stabiliser for the dispersion polymerisation of PMMA in $scCO_2$.^[42] Within the particle, there are clearly defined PDMAEMA rich regions which are preferentially stained by ruthenium. The staining indicates these features are caused by differences in polymer composition within the particles and this is corroborated by dynamic mechanical analysis (DMA) (**Figure 4b**). Here, a peak in the DMA $\tan\delta$ trace indicates the glass transition temperature (T_g) of the

polymer. There is a clear double peak, denoting separate PDMAEMA-rich and PMMA-rich regions. That the two polymers likely do not predominantly exist as separate particles is proven by the significant shift of both the PDMAEMA and PMMA T_g peaks towards each other and their partial merging.

Since new polymer chains initiate almost exclusively in the continuous phase, PDMAEMA must adsorb onto the polymer particles and then migrate towards the centre. This configuration should be thermodynamically preferred in order to minimise interactions between the polar amine groups and the non-polar CO_2 . The use of scCO_2 is essential in achieving these unusual particle structures because the PMMA core is well below its ambient pressure T_g of $126\text{ }^\circ\text{C}$ during the reaction at $65\text{ }^\circ\text{C}$.

This point is clearly demonstrated in the TEM particles synthesised in dodecane, which show a very well defined dark, DMAEMA-rich halo around the pale, PMMA core (**Figure 4c**). This is the conventional structuring that we might have expected when the second monomer is added late in the polymerisation. Dodecane will not significantly plasticise the PMMA microparticles at the reaction temperature ($80\text{ }^\circ\text{C}$ – slightly higher than required in scCO_2 due to slower reaction rates). Thus, new polymer chains will be located only around the surface of the particles. This clear lack of blending and migration is confirmed by the DMA data, where the T_g of the PMMA-rich and PDMAEMA-rich regions are almost separate, and thus largely unchanged from those of the homopolymers. Our method achieves up to 44 wt. % DMAEMA in scCO_2 but only 10 wt. % in dodecane. This is because PDMAEMA is very soft and discrete particles cannot be obtained in scCO_2 . However, by assisting the DMAEMA-rich regions to migrate into the protective PMMA matrix, higher levels of overall incorporation can be stabilised using scCO_2 . In dodecane, the soft DMAEMA layer is trapped at the particle surface and is prone to agglomeration.

Similarly, the same small dark spots which are seen only at the surface of the particles synthesised in scCO₂ are present throughout those produced in dodecane. This is because the polymer is plasticised very effectively and can rearrange in scCO₂ so that grafted PDMS is able to remain at the polymer/solvent interface where it is thermodynamically preferred. In dodecane this is not possible, and so regions of trapped PDMS are seen to be present throughout the particle.

Thus, the use of scCO₂ provides an opportunity to be much more targeted when placing functional monomers onto or into polymer particles. The above examples show us that monomers can be selected to migrate into the interior on the particle, or arrested at the surface by the use of a cross-linking monomer. This choice is not available in dodecane since the PMMA core does not swell sufficiently to allow rearrangement into different structures.

Functional testing of coloured PMMA microparticles in EPD test cells.

Finally, a series of coloured PMMA particles were assessed for use in EPD using out-of-plane and in-plane electrophoretic test cells. The samples that were planned for this analysis are shown below (**Table 3**), where the chosen colours of magenta, cyan, yellow and black match those used in classic subtractive colour printing models.

Table 3: List of planned coloured PMMA particles for testing in EPD test cells.

Entry	Solvent	Colour	Dye mol % ^a	wt % ^a	Yield %	d _n ^b	PDI ^b
1	scCO ₂	Magenta	1	5	88	393	1.08
2	scCO ₂	Cyan	0.7	5	- ^c	- ^c	- ^c
3	scCO ₂	Yellow	0.3	2	80	- ^c	- ^c
4	scCO ₂	Black	0.2	2	73	- ^c	- ^c
5	Dodecane	Magenta	1	5	62	583	1.01
6	Dodecane	Cyan	0.7	5	62	506	1.01
7	Dodecane	Yellow	0.3	2	85	440	1.01
8	Dodecane	Black	0.2	2	82	358	1.02

^a Values based on feed ratio. ^b Obtained from SEM. ^c Product not obtained.

The dyes used for these syntheses were MM12 for magenta, MC10 for cyan, MY13 for yellow and a mixture of MY13 and MK6 for black. Not all planned syntheses could be completed due to the limited solubility of MC10 in MMA, and of MY13 and MK6 in scCO₂ (**Table 3, Entry 2, 3 and 4**). In order to be added to the reaction vessel at the correct stage, the dyes must first dissolve in MMA, and then in the continuous phase. However, these dyes are large, non-polar molecules and mixtures of dyed and undyed polymer resulted, with coloured material settled on the bottom of the reactor. All dyes could be incorporated in dodecane, as the dyes are soluble in dodecane and can be poured directly into the reaction vessel if required, which is not possible with scCO₂ due to the high pressures involved.

The yields for these particles were typical for the three-stage syntheses in scCO₂ (88 %) and dodecane (62-65 %), with the exception of the yellow and black particles in dodecane which were much higher (85 and 82 % respectively). This is because MY13 is a suspected radical trap and inhibits polymerisation, so additional initiator was injected along with the final charge of monomer and dye. Almost unimodal particles were obtained from all dyes in dodecane (**Table 3, Entries 5 to 8**).

The applicability of these dyed particles for EPD was investigated by use of out-of-plane test cells. These consist of two parallel indium tin oxide (ITO) transparent electrodes which are separated by a distance of 50 µm, between which the particles are suspended in the industry standard dodecane (**SI Figure S 2**). A potential difference of 20 V was applied across the cell and the behaviour of the particles was observed. In order to facilitate colour switching, a dispersion of both coloured polymer particles and a surface modified TiO₂ (white particles) was made. This dispersion also contained 3 wt. % SPAN-85 and 1 wt. % dioctyl sulfosuccinate sodium salt (AOT) as charge control agents (CCA). These surfactants form inverse micelles in

dodecane which can stabilise charge at their core and allow the particles to develop surface charge in order to be manipulated by an electric field.^[43–45]

Dual particle switching was successfully achieved using all the samples tested, and the resulting test cells are shown below (**Figure 5**). When a voltage was applied across the electrodes the cells could be switched between white and coloured states by reversing the voltage. The optical change for all samples took between 500 and 1000 ms under the application of a DC field at $0.4\text{V } \mu\text{m}^{-1}$. A short video of this process for the magenta particles synthesised in dodecane (from **Figure 5b**) is given in the supporting information (**Video 1**).



Figure 5: Out-of-plane electrophoresis test cell images of magenta particles synthesised by three-stage dispersion polymerisation in scCO_2 (a) and magenta, cyan, yellow and black by analogous synthesis in dodecane (b, c, d and e, respectively). The coloured state is shown above and the white state (from TiO_2 particles) below.

Although dual colour switching was achieved for all samples tested, it is evident that they do not all perform to the same standard. Clear examples include the white state for magenta particles synthesised in dodecane, which retains a strong pink hue (**Figure 5b**), and the coloured

state for the black particles synthesised in dodecane, which is only mild grey (**Figure 5d**). A more complete understanding of these results is given by comparing them through in-plane electrophoresis (**Figure 6**).

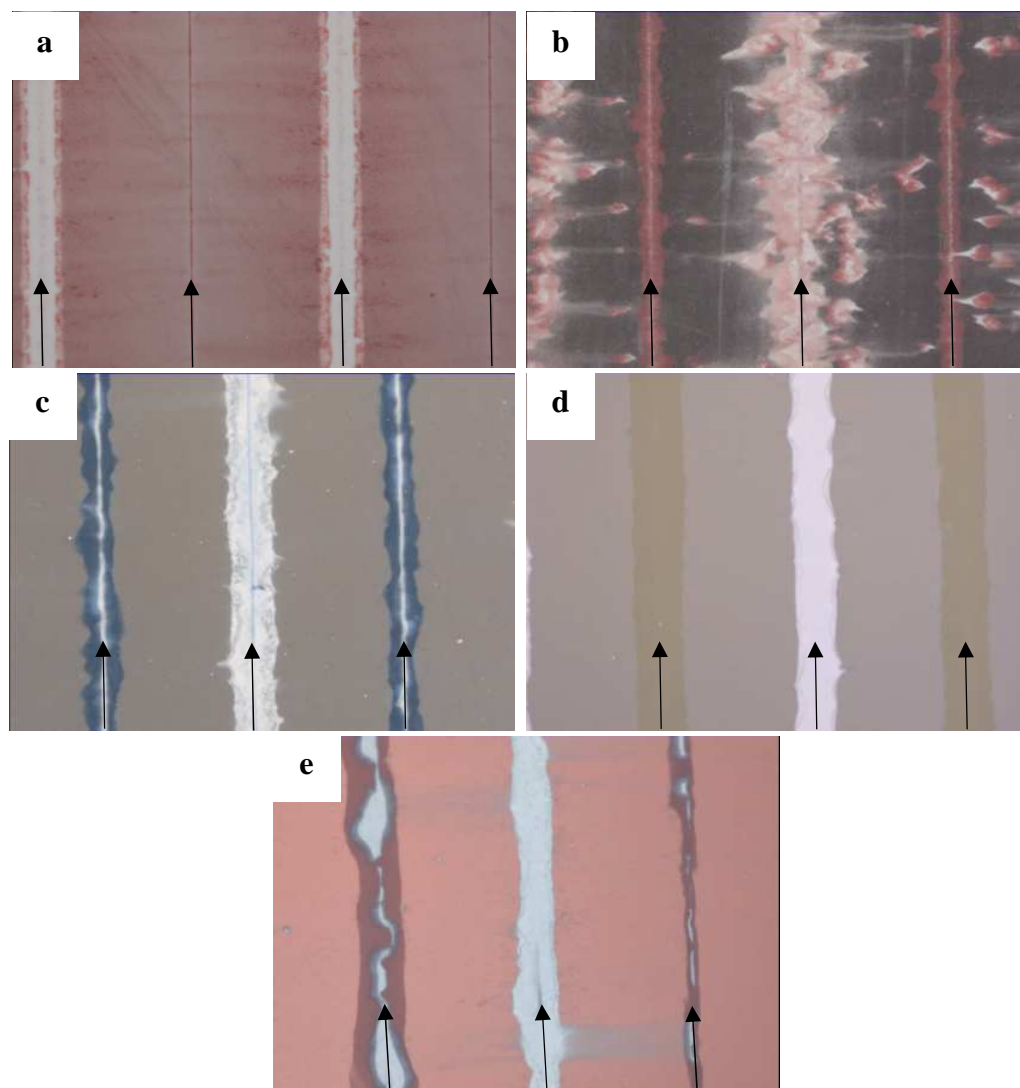


Figure 6: In-plane electrophoresis test cell images showing magenta particles synthesised by three-stage dispersion polymerisation in $scCO_2$ (a) and magenta, cyan, yellow and black by analogous synthesis in dodecane (b, c, d and e, respectively). Each electrode, indicated by the black arrows, carries a potential difference of ± 20 V relative to its neighbours on either side. These images show how effectively the coloured and white particles are separated by the potential difference. The different background colours are simply contrast settings of the microscope used to obtain clear images.

A full description of this analysis is given in the supporting information, however a brief account is as follows: The sample is loaded between two glass plates which are separated by a

distance of 50 μm . Inside the cell there are two electrodes which have a comb-like structure and are placed such that the comb teeth are interleaving (**SI Figure S 1**). A potential difference of 20 V is then applied to separate the charged particles. It can be seen that the magenta particles synthesised in scCO_2 performed well, and although the coloured and white particles were both attracted to the same electrode, the white particles moved much faster and easily displaced the magenta. This corresponds to a clean white state in the out-of-plane cell, when the top electrode is coated with only white particles (Figure 5a). A strong colour state is seen when the voltage is reversed and the white particles coat the back electrode and are covered by the magenta particles. A short video of this process for the magenta particles synthesised in scCO_2 (from **Figure 6a**) is given in the supporting information (**Video 2**).

The above observation is fundamentally different to the mechanism for all particles we synthesised in dodecane, where the white and coloured particles are attracted to opposite electrodes (**Figure 6b - e**). This result was confirmed by two further repeat syntheses of the magenta particles, which behaved in the same manner. It has been shown already that the majority of the PDMS stabiliser is bound at the surface of the particles synthesised in scCO_2 , but is found throughout the whole of the particles from the dodecane based synthesis (**Figure 4**). Assuming a similar amount of PDMS-MA has reacted in each case, then this would ensure a much higher surface concentration of PDMS for particles synthesised in scCO_2 and a much less polar surface. This change in surface environment may well lead to differing particle charge and cause the different behaviour seen in these in-plane test cells.

The magenta particles synthesised in dodecane show considerable deviation from either those synthesised in scCO_2 or from other colours also produced in dodecane (**Figure 6b**). The white and magenta particles can be seen to have aggregated irreversibly around one electrode and are no longer mobile. This white and magenta mixture corresponds to the pink hue in the white

state of the out-of-plane test cell. Such aggregation has been reported before and is even used to advantageous effect by Telfer *et al.*, who then managed to break the aggregates when those colours were required to move by the application of a greater potential difference.^[7] However, the aggregates seen here could not be broken by increasing the voltage.

The in-plane tests also reveal poor separation between the cyan and white particles and the black and white particles. In the case of the black sample, there is a clear correlation between this result and the grey, rather than black, colour state in the out-of-plane cell. This is more subtle for the cyan sample, but only the yellow particles remained completely separated for at least 13 switches, after which the test was stopped. One possible explanation is the different chemical functionalities of the dyes, which we have demonstrated are largely concentrated near the particle surface. As the polymer particles will therefore vary in surface charge and chemistry, they will need to each be balanced against different types of TiO₂ particle for optimal performance. This can be achieved by careful control of the surface charge of both particle types, as well as size ratios between them and selection of the CCA.^[46] Further empirical studies of this phenomenon, in addition to the identification of alternative dye molecules that are compatible with the polymerisations in scCO₂, are beyond the scope of this article and will be investigated in the future.

Conclusions

We have developed a staggered, three-stage dispersion polymerisation technique in scCO₂ and dodecane that enables the free radical polymerisation of covalently dyed PMMA particles for use in EPD. Using this method, it was possible to add up to 5 wt. % of the magenta coloured cross-linking dye MM12 and up to 10 wt. % EGDMA without any negative effect on the particle size and morphology control. Furthermore, we have shown conclusively for the first time that such multi-stage free-radical techniques can produce polymer particles with core-

shell type internal structures. This has allowed the placement of functional monomers, in this case a dye, onto the particle surface where their properties (e.g. colour) might be exploited most efficiently. Although such approaches are commonly used in emulsion polymerisation, translation to dispersion polymerisation has hitherto not been achieved.

We then demonstrate the versatility of this approach for creating particles with more complex internal morphologies by switching to a second functional monomer (DMAEMA) whose polymer is known to phase separate from PMMA. For these samples a ‘pomegranate-like’ structure was achieved, and comparison with dodecane clearly confirmed the pivotal role of scCO₂ as the continuous dispersion medium in producing such alternatively structured materials. In this way up to 44 wt. % DMAEMA could be incorporated into the polymer particle in scCO₂, while only 10 wt. % was possible in dodecane as a result of agglomeration at higher loadings.

Finally, we have evaluated the initial performance of these materials in out-of-plane test EPD cells, achieving very effective colour switching between the magenta dyed particles synthesised in scCO₂, and white TiO₂ particles. Superior white states were also observed when compared with analogous magenta samples that were synthesised in dodecane. As a result, the series was then expanded to include dyes representing the remaining colours used in a traditional subtractive colour printing model, namely cyan, yellow and black. However, due to a lack of solubility of the available coloured dyes in MMA and/or scCO₂, particles with these colours were only successfully synthesised in dodecane. Of these samples, each demonstrated switching between the coloured and white states with varying degrees of effectiveness, with only the yellow sample showing complete reversibility over the 13 cycle tests. Future studies will aim to identify more scCO₂ and monomer soluble crosslinking dyes so that the different

switching properties between the microparticles synthesised in scCO₂ and dodecane can be studied in more detail.

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Supporting Information

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 RuO₄. In the case of iodine, this was achieved by placing the samples in a sealed container with 2-3 iodine crystals. RuO₄ was made *in-situ* by dissolving KIO₄ (12 mg) in DI water (3 mL) and cooling the solution. This was then added to RuCl₃ (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 CDCl₃. 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 $13\ \mu\text{m}$ and the gap between the electrodes is $500\ \mu\text{m}$. 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.

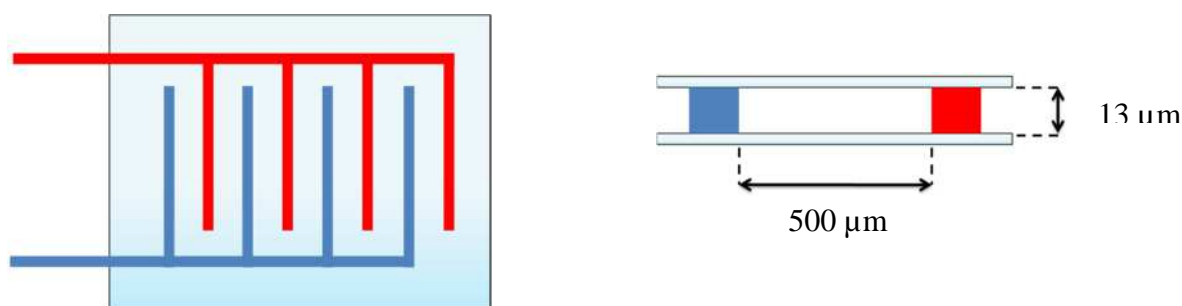


Figure S 1: Plan view (left) and cross-section (right) of in-plane electrophoresis cell with electrodes shown in red and blue.

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 $50\ \mu\text{m}$ (**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. 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.

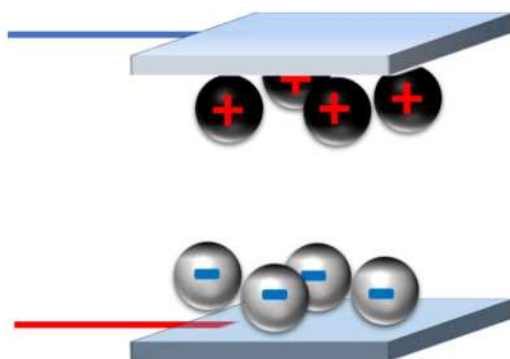


Figure S 2: Schematic of an out-of-plane test cell. The cell will appear the colour of the particles which are attracted to the top electrode when viewed from above.

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

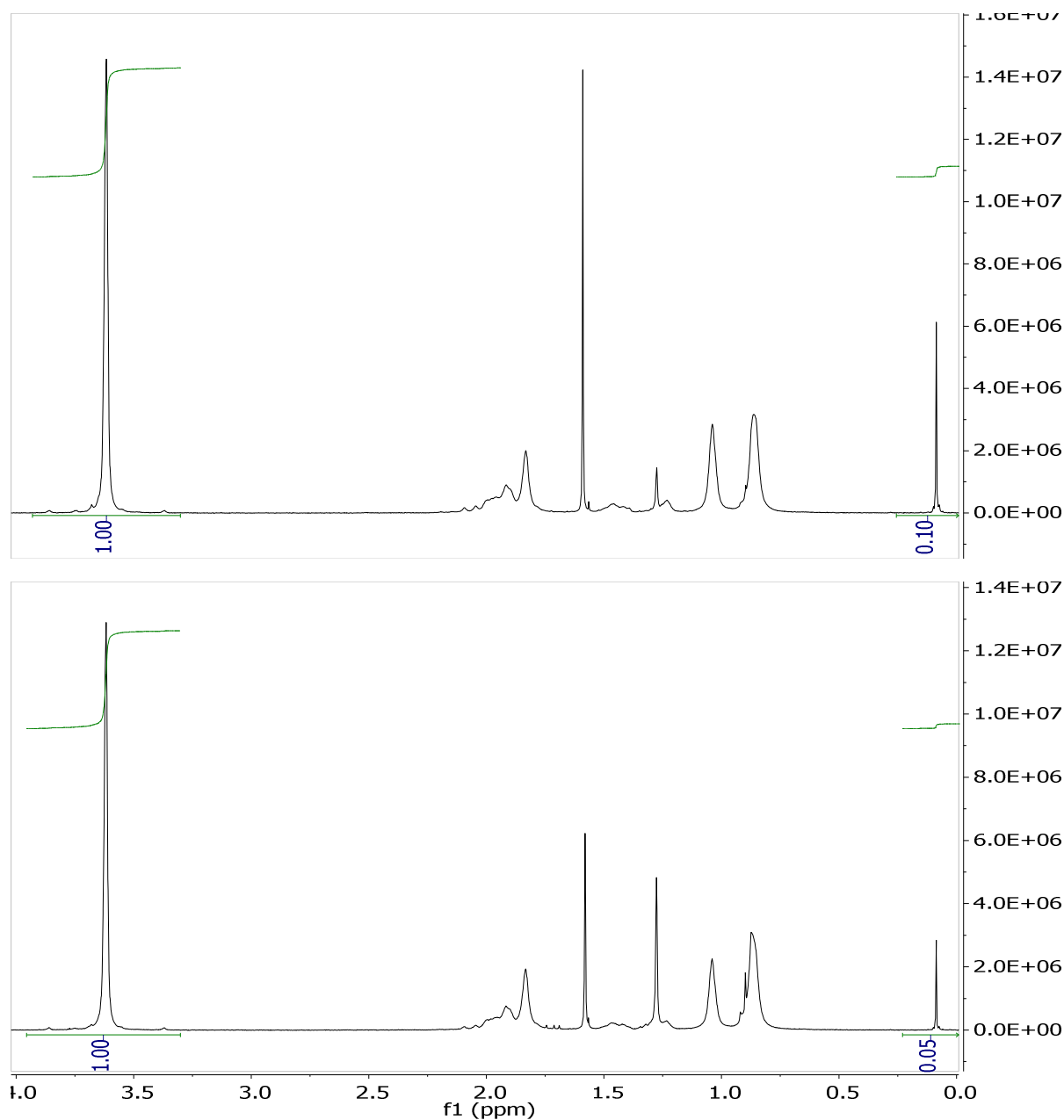
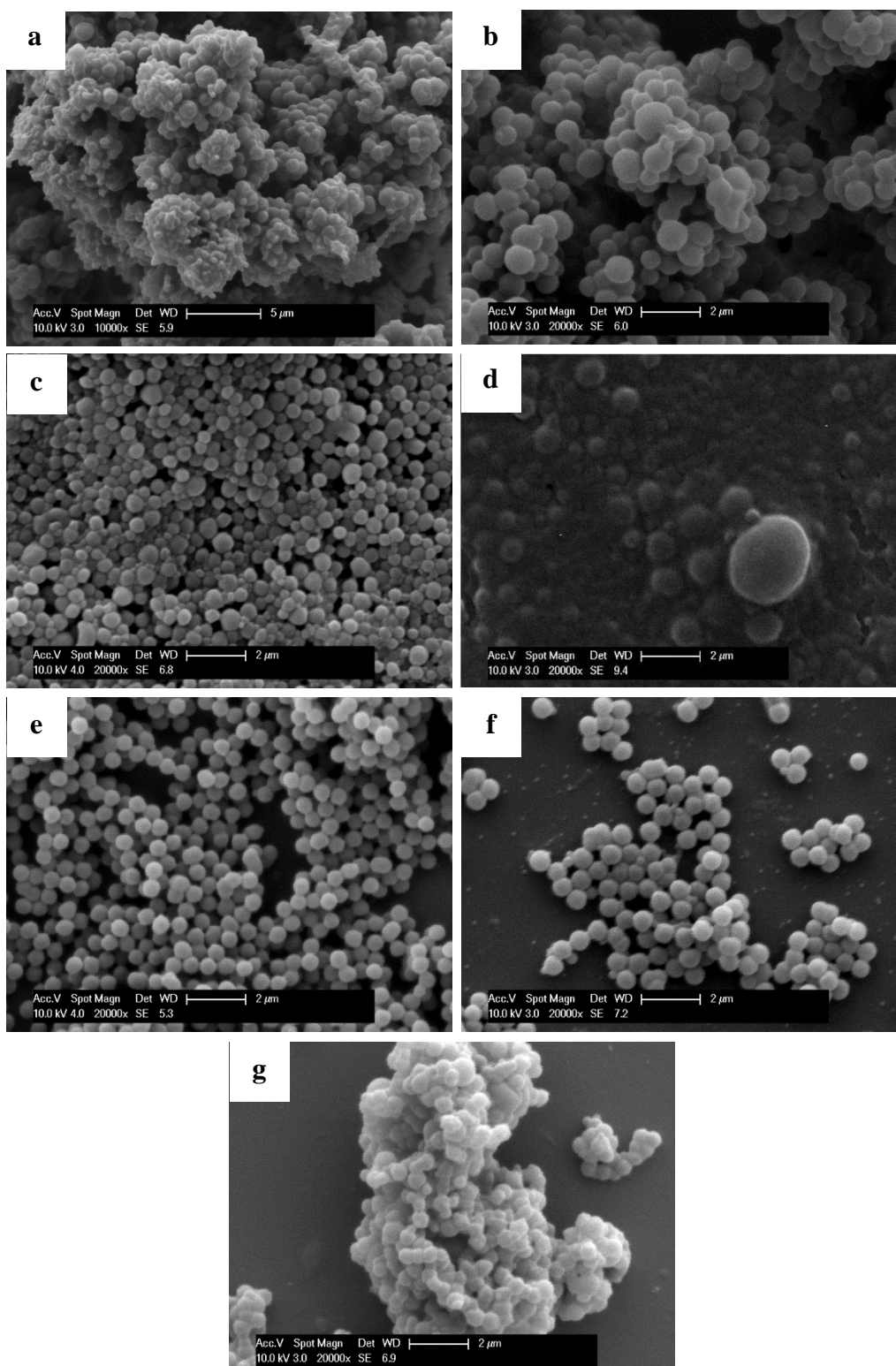


Figure S 3: ^1H NMR spectra of PMMA in CDCl_3 synthesised by one-stage dispersion polymerisation in scCO_2 (top) and dodecane (bottom) after washing with hexane. Comparison of the PDMS peak (δ 0.09) to the pendent methyl group of the PMMA (δ 3.62) shows that the particles synthesised in dodecane contain 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