

Improved Particle Size Control for the Dispersion Polymerisation of Methyl Methacrylate in Supercritical Carbon Dioxide

Full Paper

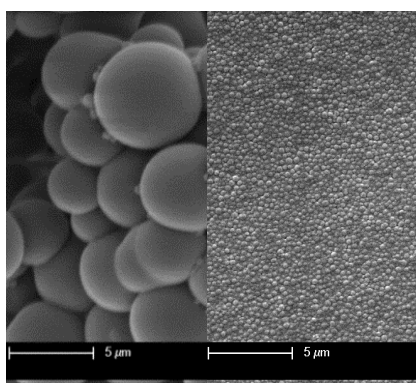
Thomas D. McAllister, Louise D. Farrand and Steven M. Howdle*

T. D. McAllister, Prof. S. M. Howdle
School of Chemistry, University of Nottingham, University Park, Nottingham
NG7 2RD, United Kingdom

Dr. L. D. Farrand
Merck Chemicals Limited, Chilworth Technical Centre, University Parkway,
Southampton, SO16 7QD, United Kingdom

Dispersion polymerisation is a well-established method of producing polymer particles that are easily handled and processed. With careful choice of reaction conditions this technique can yield well defined, spherical particles for a wide range of applications. The use of supercritical carbon dioxide (scCO₂) as a reaction medium offers a route to performing these syntheses without excessive use of volatile organic solvents and minimises work-up and disposal steps. However a significant drawback has been the fact that up till now the control of particle size and morphology from CO₂ have been limited.

Here we present control of particle size and morphology over an unprecedented range for a single stabiliser in scCO₂ by coordinating a few simple parameters to tailor the conditions towards different sizes. Further, we introduce the novel approach in scCO₂ of using delayed monomer addition which allows considerable reduction of the batch-to-batch variability as well as reduced agglomeration between particles.



1. Introduction

Dispersion polymerisation is a method of synthesising spherical particles in the region of 0.1 to 10 μm in diameter. Applications for such particles include fillers in paints, printer toners, chromatography column packing and spacers in liquid crystal display screens.^[1, 2] Renewed interest in the field of dispersion polymerisation has been triggered by potential applications such as in electrophoretic displays.^[3-6] Unfortunately, dispersion polymerisation necessitates the use of large quantities of solvents which are typically volatile organic compounds (VOCs).^[7-13] For many applications this solvent must be removed post-synthesis or transported, both of which represent a substantial energy cost.

An attractive alternative to conventional solvents is to use supercritical carbon dioxide (scCO_2) which is obtained above 73.8 bar and 31 °C. scCO_2 is a good solvent for most common vinyl monomers and a non-solvent for their polymers making it an ideal medium for dispersion polymerisation. However, the field has been limited to amorphous fluoropolymers or silicone based polymers which have been found to be sufficiently soluble in scCO_2 to function as stabilisers.^[14-26] Regardless, various controlled radical polymerisation techniques have been successfully applied including reversible addition/fragmentation chain transfer (RAFT), atom transfer radical polymerisation (ATRP) and nitroxide mediated polymerisation (NMP).^[27-33] Very recent examples have demonstrated the possibility of creating particles for potential drug delivery applications and even unique control of internal particle morphologies in block copolymer samples.^[34-38] There are ongoing efforts to synthesise hydrocarbon based stabilisers, in particular using copolymers of poly(vinyl acetate) and poly(vinyl pivalate), but these have so far only shown success for a limited range of polymerisation systems and have not yet been applied successfully for PMMA.^[39, 40]

One of the underlying limitations seen in dispersion polymerisation in scCO₂ is the reduced range of control over particle sizes. For PMMA, particles between 0.3 and 6 µm have been synthesised using a wide range of different stabilisers.^[14-26] However, the range achieved for any individual stabiliser has so far proved to be much narrower, typically within a factor of three. In addition, the smallest PMMA particles (ca. ~500 nm) could only be synthesised in scCO₂ using fluoropolymer based stabilisers which are both expensive and considered environmentally undesirable.^[18] By contrast in conventional solvents, Antl *et al.* demonstrated that particles between 0.173 - 2.6 µm could be synthesised using a single poly(12-hydroxystearic acid) based stabiliser in a mixed alkane solvent by varying the initial monomer concentration between 35 - 50 % v/v.^[12]

In this work we set out to show that greater control is possible in scCO₂ by varying a few simple parameters to create an unprecedented range of particle sizes using a single stabiliser. For these studies we chose to use methacrylate terminated poly(dimethyl siloxane) PDMS-MA as a stabiliser (Error! Reference source not found.). This is the most commonly used stabiliser for dispersion polymerisation in scCO₂ largely because it is commercially available and non-fluorinated.^[21, 22] Further, we present the use of delayed monomer addition to gain further control over the size and reproducibility of the particles produced from scCO₂.

2. Experimental

2.1. Materials

Methyl methacrylate (99 %) was obtained from Acros Organics. 2,2'-Azobis(butyronitrile) AIBN, and SPAN-85 were purchased from Sigma-Aldrich. Methacrylate terminated

poly(dimethyl siloxane) (PDMS-MA) ($M_n \sim 10$ KDa) was purchased from ABCR GmbH & Co. Dodecane (99+ %) was purchased from Alfa. SFC grade 4.0 CO₂ (≥ 99.99 %) was purchased from BOC Special Gases.

2.2. Synthesis

2.2.1. One-stage Dispersion Polymerisation

For the initial studies concerning monomer and stabiliser concentration effects, 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 onset 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 ~90 % or higher.

2.2.2. Two-Stage Dispersion Polymerisation

In a typical reaction MMA (5 mL, 46.7 mmol) and an AIBN/PDMS-MA (0.0468 g, 0.29 mmol AIBN and 1.404 g, 0.14 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 onset of the reaction was taken as the moment at which this temperature was reached. The pressure was then increased to 20.7 MPa. 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. 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.

2.3. Characterisation

Scanning electron microscopy (SEM) was carried out on a Philips XL30 microscope. All samples were washed three times by centrifuge in dodecane to remove residual stabiliser before being dropped onto a glass slide, dried and coated with platinum. Particle sizes reported from SEM are the number average (mean) of 100 particles as described by Richez *et al.*^[4]

Proton nuclear magnetic resonance (¹H NMR) was undertaken using a Bruker DPX 300 MHz NMR spectrometer. All samples were dissolved in CDCl₃.

Gel permeation chromatography (GPC) was performed in THF (HPLC grade) at room temperature using two Agilent PL-gel mixed-D columns in series with a flow rate of 1 mL min⁻¹. Detection was facilitated by multi angle light scattering (MALS) detector coupled with a refractometer. All samples were washed with hexane prior to analysis to remove residual PDMS-MA.

Dynamic light scattering (DLS) was carried out with a Malvern Zetasizer. Before analysis each sample was washed by centrifuge in dodecane three times. From this a 5 wt. % solids

dispersion in dodecane was made with 3 wt. % span-85 as a dispersing agent. This mixture was then homogenised using a Silverson L5M rotor stator.

3. Results and Discussion

The size range of PMMA polymer particles that have been reported in scCO₂ (0.3 to 6 μm) is much more limited than in conventional solvents. Additionally, the largest particles are reportedly prone to agglomeration and the smallest show poor control and broad size distributions.^[18] Furthermore, this range has only been achieved using very different stabilisers, no single stabiliser has been used to deliver more than a small portion of this range. Here we aim to show that it is possible to significantly extend range of particle sizes produced by free radical dispersion polymerisation of MMA using a given stabiliser, in this case PDMS-MA (10 KDa) (**Figure 1**), by optimising the reaction conditions to target the maximum range of different sizes.

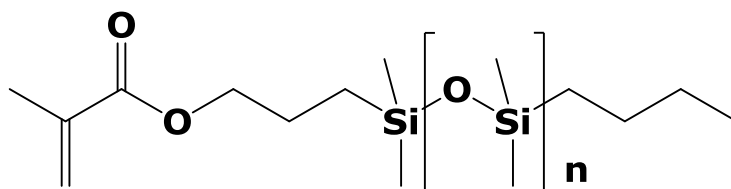


Figure 1: Structure of methacrylate terminated poly(dimethyl siloxane) (PDMS-MA).

3.1. The Effect of PDMS-MA Concentration

The concentration of stabiliser used in dispersion polymerisations has been shown to have a direct influence on the final particle diameter.^[23, 25, 41] Increasing the concentration allows a greater surface area of the polymer phase to be stabilised which results in a larger number of smaller particles. Stabiliser concentration was varied between 1 and 20 wt. %. Each reaction was carried out in triplicate to determine the reproducibility of this technique and average results are shown below (**Table 1**).

Table 1. The results of dispersion polymerisations with varying amounts of PDMS-MA stabiliser.

PDMS-MA (wt. %)	Yield ^a (%)	d_n^b (nm)	PSD ^b	M_n^c (kg mol ⁻¹)	\bar{D}^c
0	22	-	-	26	2.6
1	75 ± 9	3807 ± 1636	1.25 ± 0.08	124 ± 11	1.7 ± 0.4
5	91 ± 1.5	1809 ± 100	1.13 ± 0.06	150 ± 16	1.9 ± 0.1
10	90 ± 6	843 ± 276	1.13 ± 0.03	199 ± 14	1.7 ± 0.25
20	95 ± 3	574 ± 81	1.13 ± 0.07	218 ± 20	1.6 ± 0.15

All reactions were carried out using 10 mL of MMA and 1 wt. % AIBN at 20.7 MPa and 65 °C. Values presented are the mean of three results. ^aObtained gravimetrically. ^bFrom SEM. ^cFrom GPC.

There is a clear trend showing that particle size falls from 3.8 to 0.6 µm as stabiliser concentration is increased from 1 to 20 wt. % (**Table 1**, Entries 2 – 5). This is in agreement with previous work by DeSimone who showed a very similar trend using the same PDMS-MA for dispersion polymerisation of MMA in scCO₂.^[21] Successful dispersion polymerisation was confirmed by SEM (**Figure 2**).

The micrograph for particles synthesised using 1 wt. % PDMS-MA shows a bimodal distribution which is indicative of insufficient stabiliser (**Figure 2a**).^[42] This leads to aggregation towards the end of the particle growth stage which hugely reduces the total surface area of the polymer phase. This releases enough stabiliser to allow for a second crop by nucleation of new particles. This poor control is also exhibited by the broad range of particle sizes resulting from these reactions (± 1636 nm).

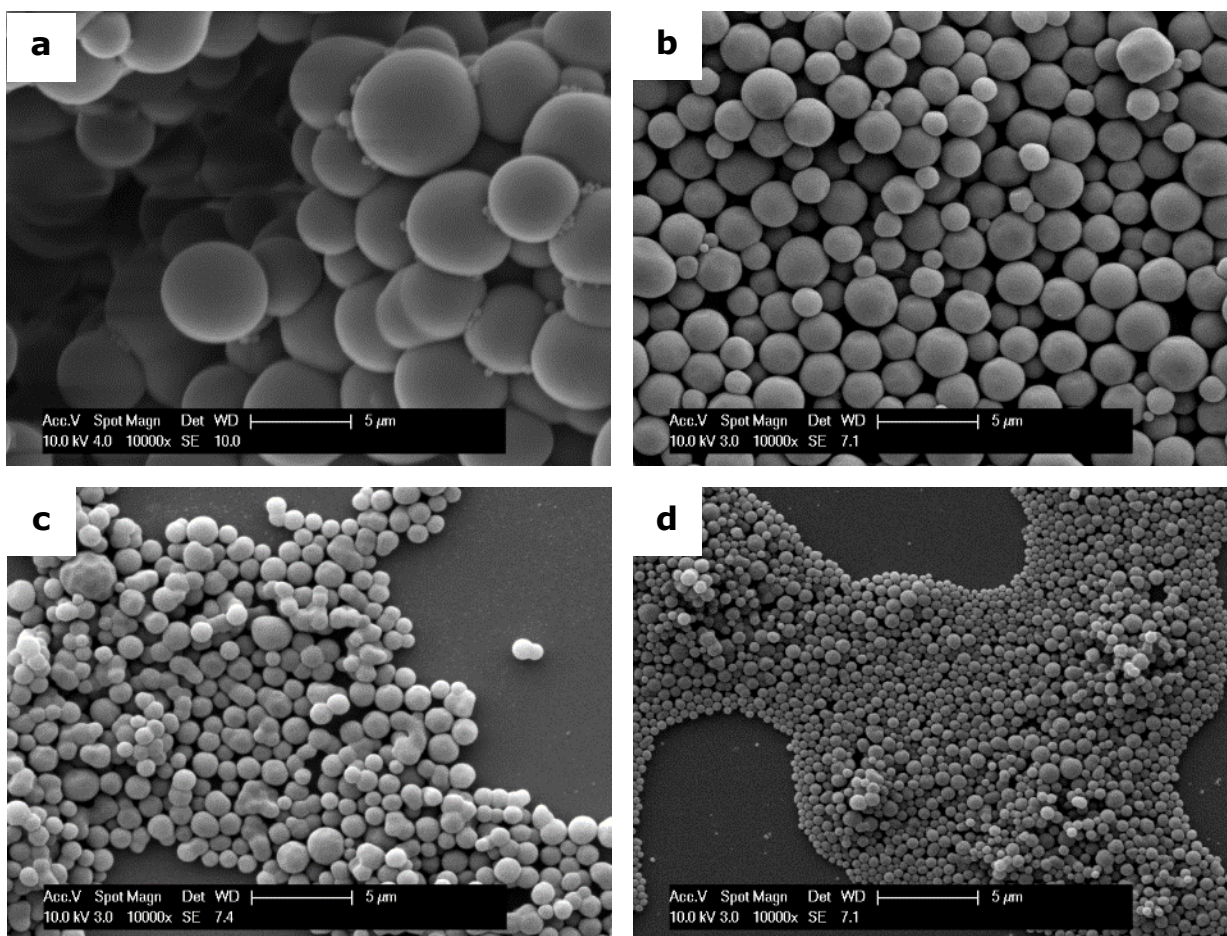


Figure 2. SEM images showing PMMA particles synthesised with a) 1 wt%, b) 5 wt%, c) 10 wt% and d) 20 wt% PDMS-MA stabiliser. The number average diameters are 3966, 1815, 1047 and 508 nm respectively.

As a control experiment, a further reaction was performed in the absence of any PDMS-MA. In this reaction particles were not obtained and only a low yield of low molecular weight PMMA was obtained (22 % yield, $M_n = 26$ KDa, $\bar{D} = 2.6$) showing that a successful dispersion was not established during the polymerisation (**Table 1**, Entry 1). However, just 1 wt. % stabiliser was sufficient to increase both the yield and molecular weight of the polymer formed significantly (75 % yield, $M_n = 124$ KDa, $\bar{D} = 1.7$) which demonstrates the role of PDMS-MA as a stabiliser for dispersion polymerisation (**Table 1**, Entry 2).

With further increases in PDMS-MA loading in the reaction, yield and molecular weight continue to rise which is unusual for dispersion polymerisation where the reaction kinetics are typically independent of stabiliser concentration.^[43] This trend has been observed before

for this same stabiliser in scCO₂.^[22] Ordinarily, dispersion conditions are analogous to bulk polymerisation where viscosity of the polymer phase is high enough that diffusion of radicals through the polymer phase is limited and so the rate of termination is reduced. However, in scCO₂ the polymer phase is significantly plasticised which allows enhanced diffusion of radicals.^[44] In this case, if all the radicals in the reactor are divided into a greater number of particles, then the number of radicals in each particle will be lower, thereby reducing the chance of two radicals terminating one another. Thus, a larger number of smaller particles will lead to higher yields and molecular weights. This effect is well known as compartmentalisation in conventional emulsion polymerisation where the particles are typically much smaller.^[45] Compartmentalisation is not usually observed for the large particles produced by dispersion polymerisation showing that the use of scCO₂ has an important effect on the kinetics of the polymerisation.

Incorporation of the PDMS-MA macromonomer into the PMMA was investigated by ¹H NMR where it was found that for all stabiliser concentrations less than 15 % of the initial PDMS-MA remained in the samples after washing in dodecane. That the majority of the PDMS-MA is not incorporated into the final product has previously been reported by both the DeSimone and Howdle groups.^[21, 22] At low initial stabiliser loadings (1 wt.%) as much as 40 % of the PDMS-MA remained after washing.

Here we have demonstrated that significant particle size control of almost an order of magnitude can be achieved by varying stabiliser loading between 1 and 20 wt. % (3807 – 574 nm). However, a plot of diameter against stabiliser loading shows how the trend plateaus indicating that further increase to stabiliser loading is unlikely to result in smaller particles (**Figure 3**). We have also seen that at 1 wt. % of stabiliser the control of the dispersion is poor and so further reducing the stabiliser content is unlikely to be meaningful. Thus it is

clear that further control of particle size is not possible through varying stabiliser amounts alone.

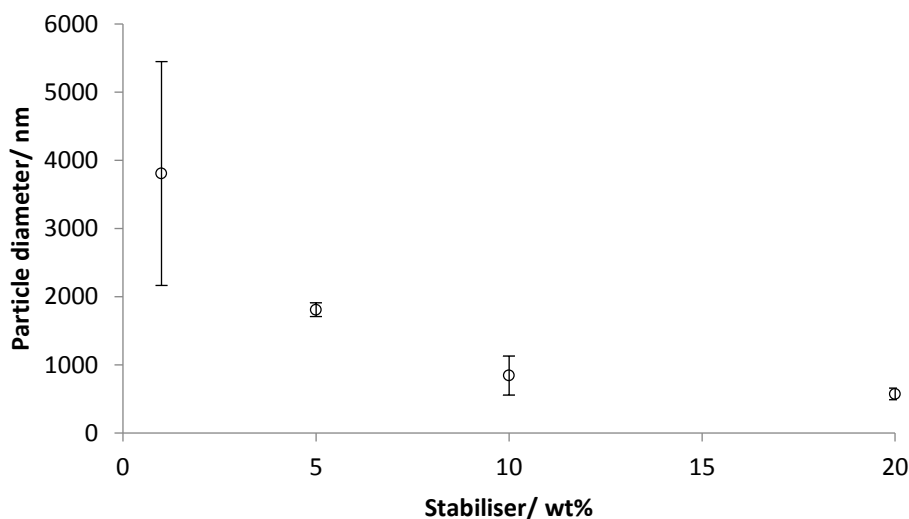


Figure 3. Variation of PMMA particle diameter with stabiliser loading. There is a clear decrease in particle size with increased stabiliser loading.

3.2. The Effect of Initial MMA Concentration

An alternative methodology for manipulating the size of polymer particles is to vary the initial concentration of monomer present which strongly affects the solvency of the continuous phase. The extent to which this approach can be applied to our system was investigated by charging a 60 mL autoclave with 5, 7.5, 10 and 12.5 mL of MMA. In all reactions stabiliser and initiator were kept constant at 5 wt. % PDMS-MA and 1 wt. % AIBN relative to monomer. All reactions were carried out in triplicate to demonstrate the reproducibility of the technique and average results are presented below (**Table 2**).

Table 2. The results of dispersions polymerisations with varying amounts of MMA.

MMA (mL)	Yield ^a (%)	d _n ^b (nm)	PSD ^b	M _n ^c (kg mol ⁻¹)	Đ ^c
5	45 ± 10	-	-	23 ± 5	2.7 ± 0.2
7.5	76 ± 10	1275 ± 228	1.15 ± 0.05	161 ± 11	1.5 ± 0.1
10	91 ± 1.5	1809 ± 100	1.13 ± 0.06	150 ± 16	1.9 ± 0.1
12.5	86 ± 4	-	-	166 ± 44	1.6 ± 0.1

All reactions were performed using 5 wt% PDMS-MA relative to MMA and 1 wt% AIBN at 20.7 MPa and 65 °C. Values presented are the mean of three results. ^a)Obtained gravimetrically. ^b)From SEM. ^c)From GPC.

The results show a narrow range of conditions in which successful dispersion polymerisation occurs. Only reactions carried out with 7.5 mL (12.5 % v/v) and 10 mL (17 % v/v) MMA gave good quality, spherical particles (**Table 2**, Entries 2 and 3). With 7.5 mL MMA, a clear decrease in particle diameter is observed relative to 10 mL MMA (1275 ± 228 against 1809 ± 100 nm) which is in agreement with previous work.^[13] This is a consequence of the monomer working as a cosolvent for the polymer in the reaction medium. Higher monomer concentrations allow longer polymer chains to remain soluble, resulting in fewer particle nuclei and correspondingly larger particles.^[6]

At lower concentrations (5 mL MMA, 8.3 % v/v) only low yields and highly disperse, low molecular weight polymer is obtained and no particles were observed (**Table 2**, Entry 1). We attribute this to over dilution of the monomer leading to slow reaction kinetics. Even after 48 hours only 75 % yield could be obtained although no distinct particles were present in the product despite 4 hours being sufficient to obtain good particles when more monomer is used. The half-life of AIBN was calculated to be 24.6 hours in scCO₂ at 65 °C and 207 bar using parameters presented by Guan *et al.*^[46]

The synthesis of polymer particles was also largely unsuccessful at high monomer loadings due to heavy agglomeration (**Table 2**, Entry 4). The resulting polymer appears in SEM images to be agglomerated particles indicating that the reaction proceeded through the dispersion mechanism before becoming unstable and coalescing (**Figure 4a**). It is possible that the high monomer content encourages too few particles to nucleate and so they grow very large. It has been shown for MMA in scCO₂ that above a certain size particles are destabilised by eddy currents which are caused by reactor stirring.^[47] This maximum size is determined by the reactor geometry as well as the stirrer shape and speed. In all three reactions a second crop of particles is seen (**Figure 4b**). These particles almost certainly form late in the reaction and therefore do not grow large enough to become unstable. These particles were approximately 1200 nm in diameter in all three reactions.

These results show that it is indeed possible to influence the particle size significantly by varying the initial monomer concentration within certain limits. Although this offers a much smaller range of size control, it provides an important second tool for tailoring particle sizes for specific applications.

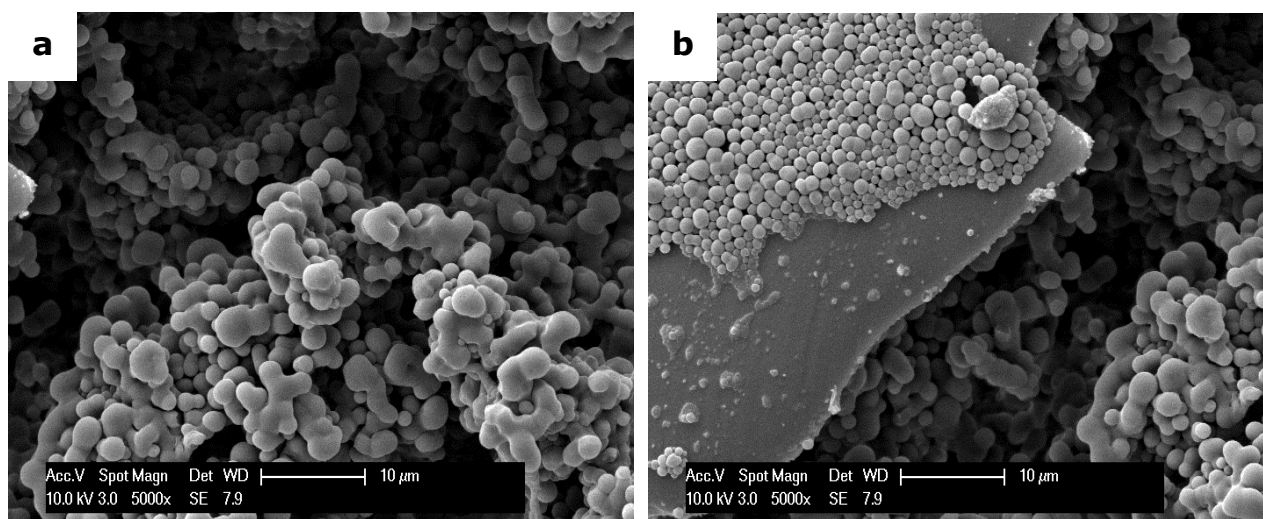


Figure 4. SEM micrographs of PMMA synthesised from a high initial monomer loading (12.5 mL, 20.8 % v/v) showing highly agglomerated nature of the polymer (left) and isolated regions of spherical particles (right).

3.3. Combining Both Monomer and Stabiliser Concentrations

The range of particle sizes accessible by this synthesis technique could be extended by combining both the methods of control discussed above. Further polymerisations were performed using high stabiliser content and low initial monomer content (20 wt% PDMS-MA and 7.5 mL of MMA). Four repeats of this reaction were conducted (**Table 3**).

Table 3. Dispersion polymerisation on MMA in scCO₂ targeting smaller particles.

Yield ^a (%)	d _n ^b (nm)	PSD ^b	M _n ^c (kg mol ⁻¹)	Đ ^c
90	648	1.09	209	1.5
96	379	1.11	193	1.6
87	626	1.18	153	1.9
87	317	1.10	170	1.6

Four repeats are shown for reproducibility. ^aObtained gravimetrically. ^bFrom SEM. ^cFrom GPC.

In all cases the reaction yielded relatively small, discrete, spherical polymer particles falling below 650 nm in diameter with acceptably low PSD values. However, repeat syntheses show that this method gives poor batch-to-batch reproducibility with average particle diameters falling anywhere between 317 and 648 nm. The smallest particles had a number average diameter of just 317 nm placing them amongst the smallest PMMA particles ever synthesised by dispersion polymerisation in scCO₂ despite the use of a commercial stabiliser that has previously been shown to give only average particle sizes (**Table 3**, Entry 4). Particles in a similar size range were reported by Lepilleur *et al.* who synthesised a fluorinated graft copolymer stabiliser, yielding particles in a similarly small but broad size range (300 - 500 nm).^[18] This is the first time that the commercially available PDMS-MA stabiliser has been used to produce particles this small in scCO₂ and extends the range of particles synthesised during this work to an order of magnitude.

Dispersity varies significantly between batches, resulting in correspondingly varied M_n. These differences do not appear to correlate to particle size or yield although in all reactions

the molecular weight remains high which is expected for free-radical dispersion polymerisation of MMA.

3.4. Greater Control by Two-stage Dispersion Polymerisation

In order to optimise conditions towards the smallest possible particles a new and innovative approach was developed. The smallest particles will be formed when using minimal initial monomer concentrations. However we have shown that monomer loading only operates within a very narrow window in scCO₂ because over-dilution (less than 7.5 mL MMA) slows the reaction kinetics and prevents particles from becoming large enough to produce the gel effect (**Table 2**, Entry 1). In order to circumvent this limit we began the polymerisation with an exceptionally small amount of monomer (5 mL MMA) to allow ideal nucleation conditions and the creation of seed particles, before increasing the rate of polymerisation by adding a second aliquot of MMA (2.5 mL) *via* an HPLC pump.

Initial results for this method showed agglomerated, large particles with a very broad size distribution (**Figure 5a**). This was attributed to the fast injection of the additional monomer leading to rapid changes in polymer solubility and inhomogeneous monomer concentrations

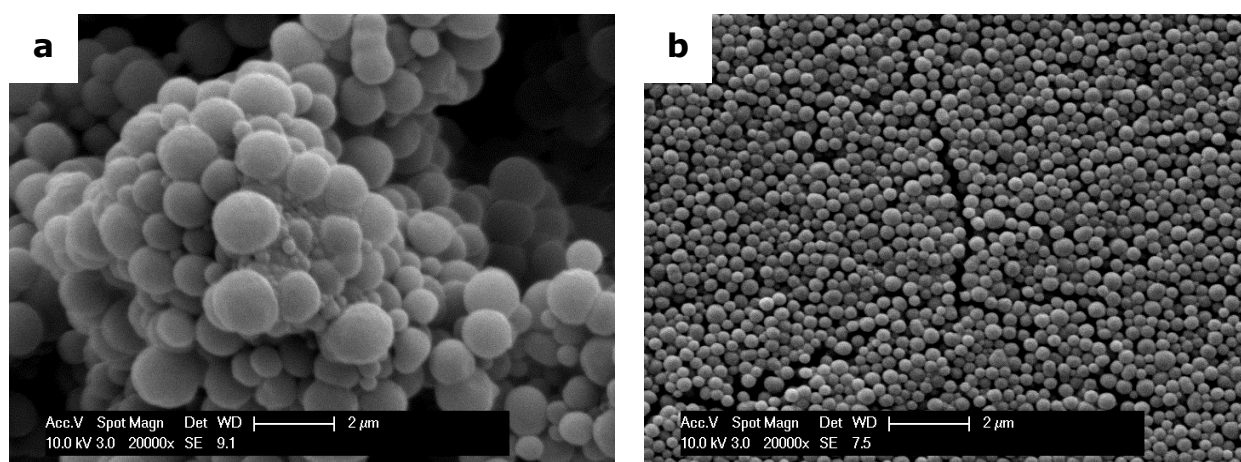


Figure 5. PMMA particles synthesised using the two-stage method. The injection rate was reduced from a) 1 mL min^{-1} to b) 0.2 mL min^{-1} with a marked improvement to particle quality.

in the continuous phase during the injection process. Reduction of the injection rate from 1 mL min⁻¹ to 0.2 mL min⁻¹ allowed much more controlled addition of the second aliquot of monomer and yielded uniform, small particles in the desired size range (**Figure 5b**).

Again, this reaction was carried out in triplicate and the results of each reaction are presented below in order to facilitate discussion of reproducibility (**Table 4**).

Table 4. Results from two-stage dispersion polymerisation of MMA in scCO₂ aimed at producing reproducibly smaller particles.

Yield ^a (%)	d _n ^b (nm)	PSD ^b	d _z ^c (nm)	M _n ^d (kg mol ⁻¹)	Đ ^d
99	432	1.07	526	193	1.5
89	317	1.10	425	213	1.6
87	363	1.11	520	214	1.5

a) Obtained gravimetrically. b) From SEM. c) From DLS. d) From GPC.

In all reactions a high yield and molecular weight (≥ 87 %, ~ 200 kg mol⁻¹) indicates a successful dispersion polymerisation following the injection of additional monomer. Without this addition stage, reactions with such low initial monomer loadings were not successful (**Table 2**, Entry 1). Perhaps most importantly, the average particle diameters are all much more tightly grouped than had previously been obtained when targeting particles of this size. Since it is known that nucleation is completed very early on in a dispersion polymerisation (<0.1 % conversion) the addition of monomer after one hour did not interrupt this delicate stage of the reaction. It is interesting to note that these particles are in the same range as those obtained by using higher initial monomer loading (**Table 3**, Entry 2 and 4). This indicates that the conditions that we have chosen produce the maximum number of stable nuclei possible for this solvent/ stabiliser combination. But by allowing nucleation to occur under more ideal conditions, e.g. high stabiliser concentration and low monomer concentration, and then carefully adding more monomer we have overcome the lack of reproducibility that was apparent and we have successfully developed a simple and reproducible synthesis of particles smaller than 450 nm using a commercially available, non-fluorinated stabiliser.

Another important outcome from this synthesis is that the particles were now of such good quality that it was now possible to obtain meaningful DLS measurements. Many of the powders produced using the one-stage process could not be analysed in this way which was attributed to a large number of agglomerates dominating the analysis. By contrast, these particles could be measured by DLS without the need for a filtration step, showing that the particles produced are discrete with far fewer aggregates. In all cases, the diameters obtained from DLS are larger than those measured from SEM images. This is expected because the diameter measured by DLS is the hydrodynamic volume which includes the PMMA particle plus the swollen stabiliser layer. In the vacuum of an SEM this outer layer is flattened to the particle surface making these particles appear smaller. This effect is potentially enhanced if the PMMA shows any swelling in the solvent chosen for DLS measurements, in this case dodecane. Secondly, DLS will not distinguish between particles and small aggregates, pushing the average particle size up. Despite the disparity between these two techniques, it is possible to conclude that the application of our new two-stage process in scCO₂ has led to a very significant improvement in product quality and the fact that the resulting powders can be re-dispersed indicates a significant enhancement of the polymer synthesis.

4. Conclusions

The range of particle sizes synthesised by dispersion polymerisation in scCO₂ for any given stabiliser has typically been very small, generally less than a factor of three, compared to those obtained in conventional solvents where well over an order of magnitude is sometimes achievable.^[12] We have shown that it is indeed possible to synthesize particles over a comparable size range in scCO₂ using a commercially available PDMS-MA stabiliser with particles ranging from 5.3 down to 0.3 µm in diameter. This was achieved by combining control of both the initial monomer and stabiliser loadings, demonstrating that this approach

should be easily applicable to many other stabilisers. Furthermore, we used the addition of a second aliquot of monomer to reach high molecular weight and conversion using starting conditions which otherwise led to poor molecular weight and yield. This innovative step improved the batch-to-batch variability considerably as well as reducing the degree of aggregation in the system, which allowed particles to be redispersed and analysed by DLS.

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