Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for: One-pot synthesis of micron-sized polybetaine particles; innovative use of supercritical carbon dioxide

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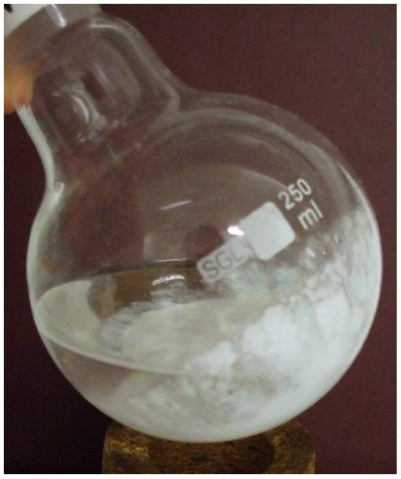
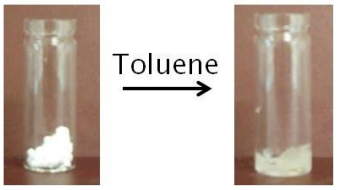
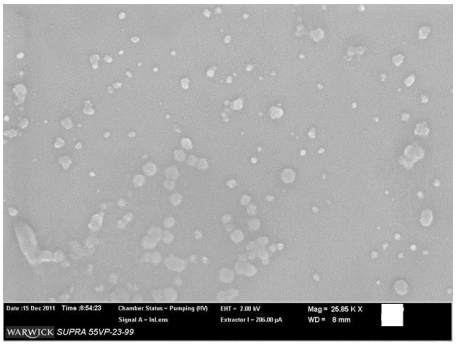
S1 – Overview of conditions attempted for inverse emulsion polymerisations

Sample #	Conditions						Observations Particle size (nm) *DLS*, **SEM**
	Monomer (wt% of aq phase)	Crosslinker (wt% of aq phase)	Aq phase (wt% of total emulsion)	Oil phase (wt% of total emulsion)	Surfactant (wt% of total emulsion)	Initiator (wt% wrt monomer)	
EMUL 1	DMAPS (9.5)	PEGDMA (0.5)	0.5M NaCl (20)	Toluene (80)	TWEEN 80 (2.5)	ACVA (0.1)	Separated after heating *35*
EMUL 2	DMAPS (41.3)	PEGDMA (2.2)	0.5M NaCl (5.5)	Toluene (94.5)	TWEEN 80 (2.5)	ACVA (0.1)	No emulsion formed Higher surfactant concentration required
EMUL 3	DMAPS (21.9)	PEGDMA (1.1)	0.5M NaCl (10)	Cyclohexane (90)	TWEEN 80 (0.5)	ACVA (0.1)	Separated before heating
EMUL 4	DMAPS (21.9)	PEGDMA (1.1)	0.5M NaCl (10)	Cyclohexane (90)	TWEEN 80 (2)	ACVA (0.1)	Separated after heating
EMUL 5	DMAPS (21.9)	PEGDMA (1.1)	0.5M NaCl (10)	Cyclohexane (90)	TWEEN 80 (0.5)	AIBN (0.1)	Separated before heating
EMUL 6	DMAPS (21.9)	PEGDMA (1.1)	0.5M NaCl (10)	Cyclohexane (90)	TWEEN 80 (2)	AIBN (0.1)	Separated after heating
EMUL 7	DMAPS (21.9)	PEGDMA (1.1)	0.9mM NaCl (10)	Cyclohexane (90)	TWEEN 80 (8)	ACVA (0.1)	Gel formed before polymerisation. Surfactant concentration too high
EMUL 8	DMAPS (21.9)	PEGDMA (1.1)	Pure water (10)	Toluene	TWEEN 80 (2.5)	ACVA (0.1)	Emulsion reversed *Erratic data – 150-220*, **70-155**
EMUL 9	DMAPS (21.9)	PEGDMA (1.1)	Pure water (10)	Toluene	TWEEN 80 (4)	ACVA (0.1)	Emulsion reversed
EMUL 10	DMAPS (21.9)	PEGDMA (1.1)	Pure water (10)	Toluene	TWEEN 80 (3)	ACVA (0.1)	Emulsion reversed

S2 - Images of destabilised inverse emulsion after polymerisation (top left), dispersion of product in water rather than oil phase (top right) and wetting of polymer by the oil phase (right), SEM image of "best" irregular particles formed in EMUL 8 (scale bar 200 nm, bottom).



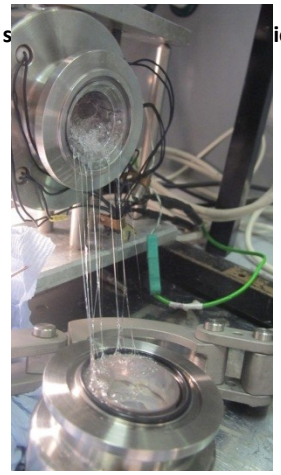




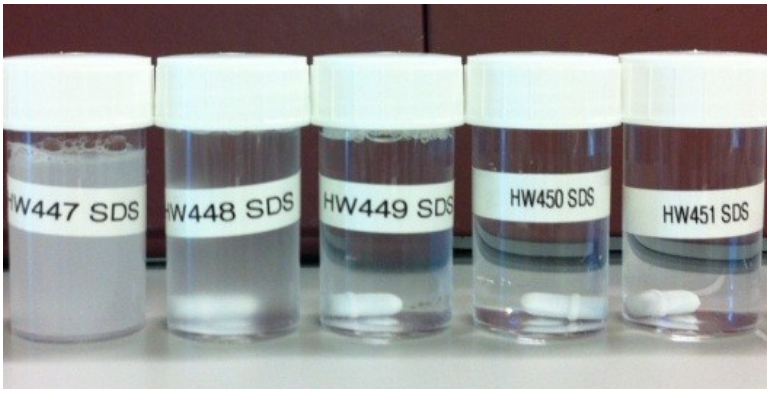
S3 - Overview of conditions used for dispersion polymerisations.

Sample #	Conditions						Observations Particle size (nm) *DLS*, **SEM**
	Monomer (wt%)	Crosslinker (wt% wrt mon)	Surfactant (wt%)	Solvent	Initiator (wt%)	Reaction temperature (°C)	
DISP 1	DMAPS (5)	MBAc (0.5)	TWEEN 80 (1)	H_2O	V50 (0.04)	50	Aggregation
DISP 2	DMAPS (5)	MBAc (0.5)	TWEEN 80 (2)	H_2O	V50 (0.04)	50	Aggregation
DISP 3	DMAPS (1)	MBAc (0.5)	TWEEN 80 (0.2)	H_2O	V50 (0.008)	50	Less aggregation occurs *erratic data,* **500-900nm**
DISP 4	DMAPS (1)	MBAc (2)	PEGMA (0.2)	H_2O	V50 (0.008)	50	Clear solution
DISP 5	DMAPS (1)	MBAc (2)	TWEEN 80 (0.2)	H_2O	V50 (0.008)	50	Aggregation
DISP 7	DMAPS (2)	MBAc (2)	SDS (0.04)	H_2O	KPS (0.02)	65	
DISP 8	DMAPS (2)	MBAc (2)	SDS (0.04)	H_2O	KPS/TEMED (0.02)	25	Aggregation
DISP 9	DMAPS (1)	EGDMA (2)	TWEEN 80 (0.2)	H_2O	V50 (0.008)	50	Clear solution
DISP 10	DMAPS (1)	MBAc (0.5)	TWEEN 80 (0.2)	80% H_2O, 20% MeOH	V50 (0.008)	50	Aggregation
DISP 11	DMAPS (2)	MBAc (2)	SDS (0.04)	80% H_2O, 20% MeOH	KPS/TEMED (0.02)	25	Aggregation
DISP 12	DMAPS (1)	MBAc (2)	PEGMA (0.02)	H_2O	KPS/TEMED (0.02)	25	Aggregation
DISP 13	DMAPS (1)	MBAc (2)	TWEEN 80 (0.2)	95% H_2O, 5% MeOH	KPS/TEMED (0.02)	25	Aggregation
DISP 14	DMAPS (2)	MBAc (2)	SDS (0.04)	H_2O	KPS/TEMED (0.02)	4	Aggregation

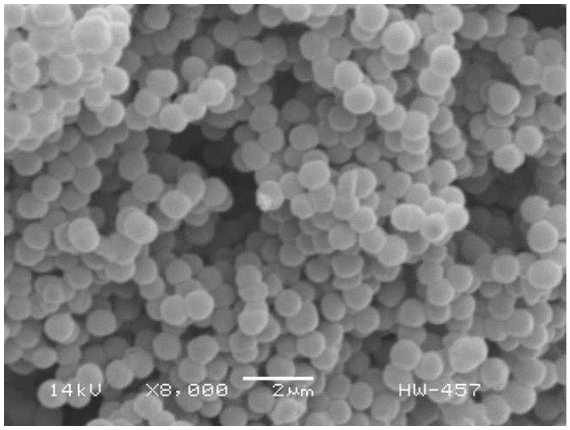
S4 – Image of water swollen gel formed when s ion system was attempted showing issues with

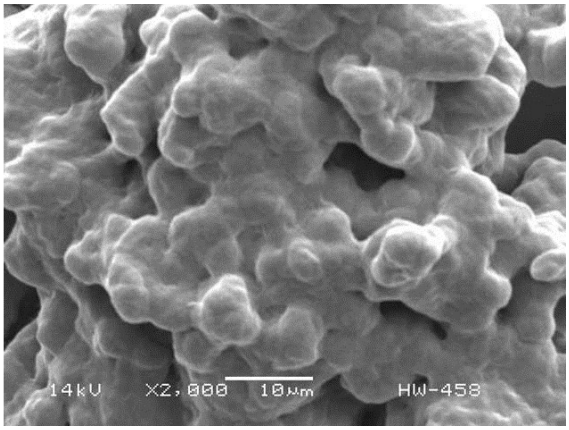


S5 – Image of redispersions of particles with varying crosslinker densities (left to right) – 6 (10 wt%), 5 (5 wt%), 4 (2.5 wt%), 3 (1 wt%), 2 (0.5 wt%).



S6 – SEM images of particles formed with 10wt% MBAc (left) and PEGDMA (right) as crosslinker in the place of EGDMA.





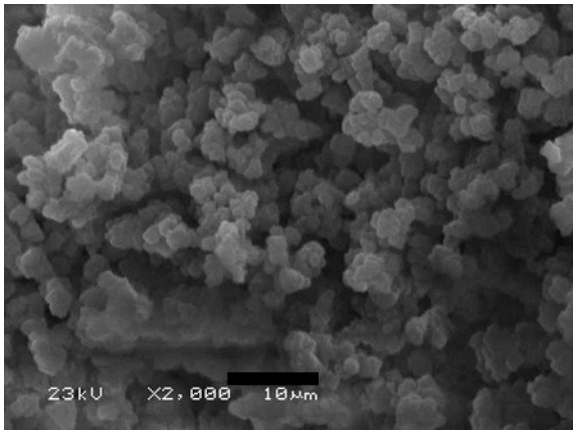
S7 - Effect of varying the concentration of initiator in the polymerisation of DMAPS in $scCO_2$.

Sample	AIBN / wt% [b]	Obtained Yield / g [c]	Morphology [d]
Init 1	1	93	Highly agglomerated microparticles
Init 2.5	2.5	94	Well defined spherical microparticles
Init 5	5	84	Well defined spherical particles
Init 10	10	87	Highly agglomerated microparticles

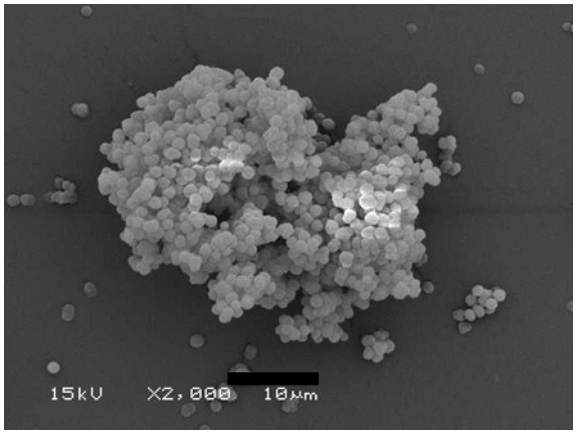
[a] Reactions performed with DMAPS (2 g), EGDMA (190 µL, 10 wt% with respect to monomer), 4.5 mL methanol in a 60 mL autoclave at 65 °C and 27.6 MPa for 2 h, followed by supercritical fluid extraction of methanol at 45 °C and 27.6 MPa; [b] Initiator concentration with respect to monomer; [c] Yield determined gravimetrically after drying *in vacuo*; [d] Determined by SEM

S8 - Effect of varying the concentration of initiator in the polymerisation of DMAPS in $scCO_2$.

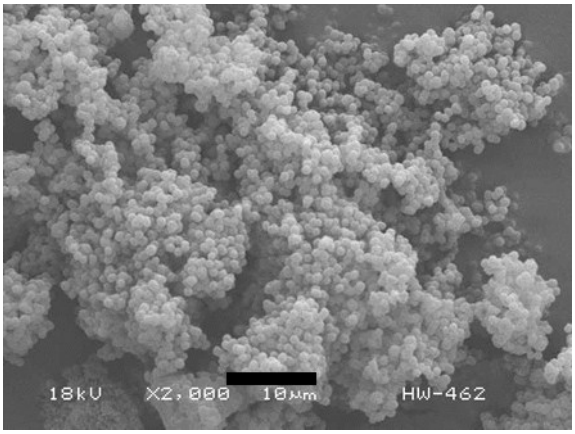
1 wt% AIBN



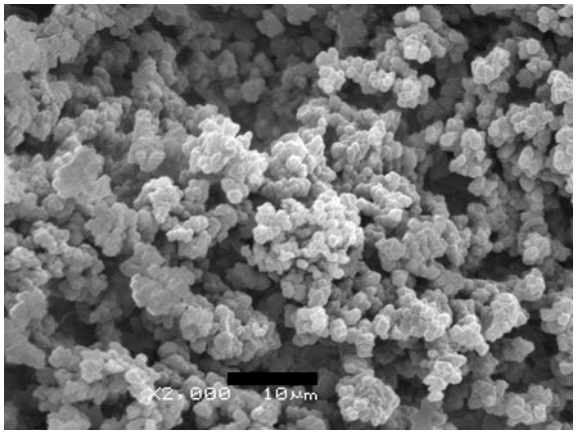
2.5 wt% AIBN



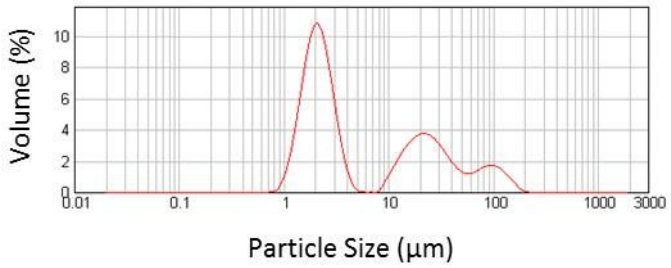
5 wt% AIBN



10 wt% AIBN



S9 – Broad PSD of Sample 11 dispersed in water with SDS, d(0.5)volume = 2.85 µm.



S10 - SEM images of cast film of particles, sample 6 – Table 1 (scale bar 20 µm left, 1 µm right).