

## Electronic Supplementary Information for:

### RAFT Miniemulsion Polymerisation of Benzyl Methacrylate Using Non-ionic Surfactant

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#### Synthesis of 2-cyano-2-propyl phenethyl trithiocarbonate (PETTCCP)

The synthesis of 2-cyano-2-propyl phenethyl trithiocarbonate (PETTCCP) RAFT chain transfer agent (CTA) was conducted according to a modified procedure described by Kocik et al.<sup>1</sup> Sodium hydride (60% in oil, 7.6 g, 191 mmol) was gradually added to diethyl ether (350 mL) at 5 °C to obtain a grey suspension. 2-Phenylethanethiol (25.1 g, 182 mmol) was added dropwise to the grey suspension and hydrogen gas was generated. A white viscous slurry of sodium phenylethanethiolate was formed over a 30 min period. Carbon disulfide (14.5 g, 191 mmol) was added dropwise to the reaction mixture and gradually transformed into a thick yellow precipitate of sodium 2-phenylethanetrithiocarbonate over 30 min. The precipitate was collected *via* filtration and then utilised in the next step without further purification. Sodium 2-phenylethanetrithiocarbonate (44.0 g, 186 mmol) was slowly added to diethyl ether (350 mL) at ambient temperature to obtain a suspension and subsequently solid iodine (24.1 g, 95 mmol) was added. The reaction mixture was stirred at ambient temperature for 60 min and an insoluble white precipitate of sodium iodide was formed and removed *via* filtration. The yellow–brown filtrate was washed using a sodium thiosulfate aqueous solution three times to remove excess iodine and subsequently dried over sodium sulfate to remove residual water. The filtrate was further dried under vacuum at 35 °C to remove volatiles and yield bis(2-phenylethanesulfanylthiocarbonyl) disulfide.

Bis(2-phenylethane sulfanylthiocarbonyl) disulfide (6.0 g, 14 mmol) and azobisisobutyronitrile (AIBN, 3.5 g, 21 mmol) were dissolved in ethyl acetate (100 mL) and deoxygenated *via* purging nitrogen for 30 min. This reaction mixture was immersed into a preheat oil bath at 92 °C and heated for 18 h under nitrogen atmosphere. The organic phase was evaporated under vacuum and the crude product was purified *via* silica chromatography utilising a mixed eluent (7:3 petroleum ether/ethyl acetate, gradually increasing to 3:7) to isolate 2-cyano-2-propyl phenethyl trithiocarbonate (PETTCCP) as a viscous orange oil. The oil was further dried under vacuum at 35 °C to evaporate residual solvent. The purified PETTCCP product was an orange oil at ambient temperature and solidified when stored at 5 °C (74 % yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), d [ppm]: 1.89 (s, 6H), 2.94–3.05 (m, 2H), 2.51–3.63 (m, 2H), 7.17–7.37 (m, 5H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>), d [ppm]: 27.18 (CH<sub>3</sub>), 34.23 (CH<sub>2</sub>Ph), 37.95 (CH<sub>2</sub>S), 42.60 (C(CH<sub>3</sub>)<sub>2</sub>CN), 120.53 (CN), 126.95 (p-Ph), 128.70 (o-Ph/m-Ph), 128.81 (o-Ph/m-Ph), 139.36 (Ph–CH<sub>2</sub>), 217.49 (CS).

### **Synthesis of 4-cyano-4-(2-phenylethanesulfanyl thiocarbonyl) sulfanylpentanoic acid (PETTC)**

The synthesis of 4-cyano-4-(2-phenylethane sulfanylthiocarbonyl) sulfanylpentanoic acid (PETTC) RAFT CTA was conducted according to a procedure reported in our previous work,<sup>2</sup> and first described by Semsarilar et al.<sup>3</sup>

### **Nuclear magnetic resonance spectroscopy (NMR)**

Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) NMR spectra were acquired on a Bruker Advance III 400 MHz spectrometer with 128 scans averaged per spectrum. Samples were dissolved in CDCl<sub>3</sub> prior to NMR analysis.

### **Surface interfacial tension (IFT)**

IFT measurements were determined by the pendant drop technique using a Drop Shape Analyzer DSA-100 from KRÜSS GmbH (Hamburg, Germany) and Drop Shape Analysis software (DSA/V 1.9). Stock solutions were prepared for all surfactants, which were diluted down to the required concentration using deionised water. All samples were stirred at 150 rpm for 30 min before analysis. A 15-gauge needle (external diameter of 1.835 mm) was used to produce a drop profile at the tip. A setscrew was used to extract the solution with controlled flow rate and volume at ambient temperature (~23 °C). The pendant drop configuration was fitted using the Young-Laplace model to determine interfacial tensions. IFT values were averaged over 7 measurements.

### **Number of particles per unit volume ( $N_p$ )**

The number of particles per unit volume ( $N_p$ ) was calculated from the Z-average particle diameter ( $D_h$ ) obtained *via* DLS and polymer concentration using Equation S1:<sup>4</sup>

$$N_p = \frac{6m}{\pi\rho D_h^3} \quad \text{Equation S1}$$

Where  $\rho$  is the density of poly(benzyl methacrylate) (PBzMA, assumed to be 1.179 g mL<sup>-1</sup>)<sup>5, 6</sup> and  $m$  is the mass of polymer per unit volume.

### Rate of polymerisation ( $R_p$ )

The conversion-time plots for PBzMA synthesised *via* RAFT miniemulsion polymerisation indicate that these are *pseudo* first-order kinetic reactions. Therefore, the overall polymerisation rate was calculated using the concentration change of monomer in a certain polymerisation time using Equation S2:<sup>6</sup>

$$R_p = - \frac{dM}{dt} \quad \text{Equation S2}$$

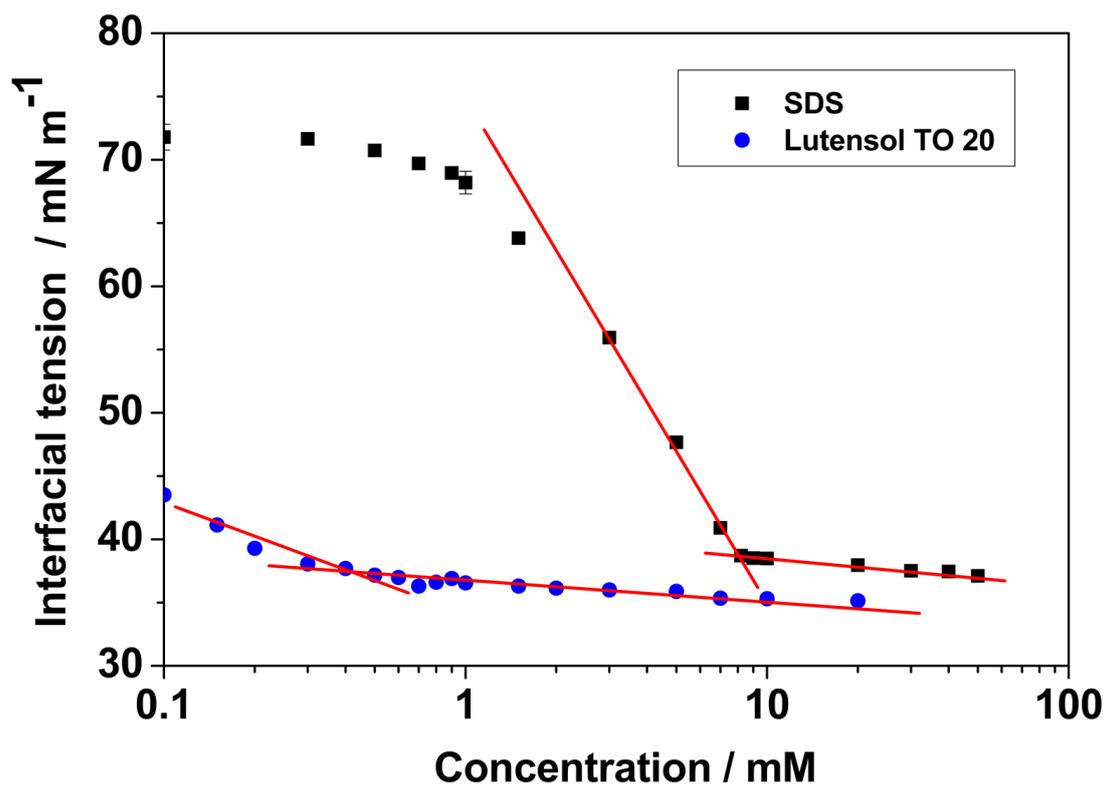
Where  $dM$  represents the disappearance of monomer (benzyl methacrylate, BzMA) calculated using gravimetry and  $dt$  represents the polymerisation time.

### Polymerisation rate per particle ( $R_N$ )

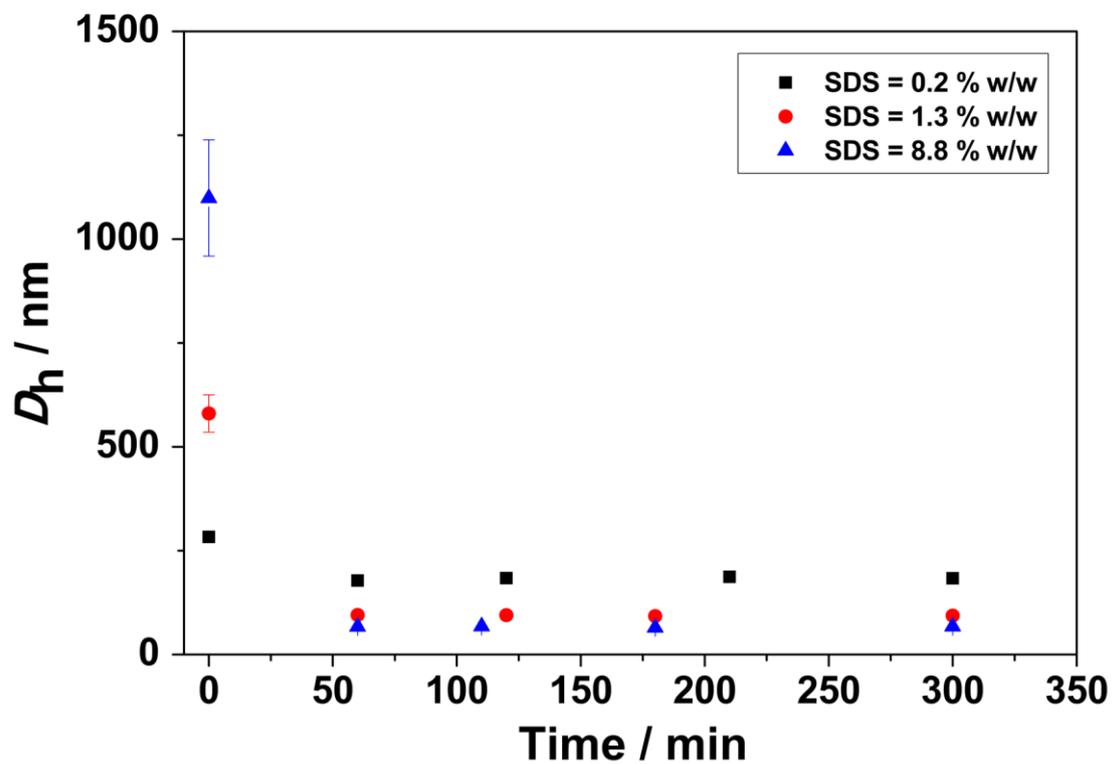
Polymerisation rate per particle ( $R_N$ ) was calculated using Equation S3:

$$R_N = \frac{R_p}{N_p} \quad \text{Equation S3}$$

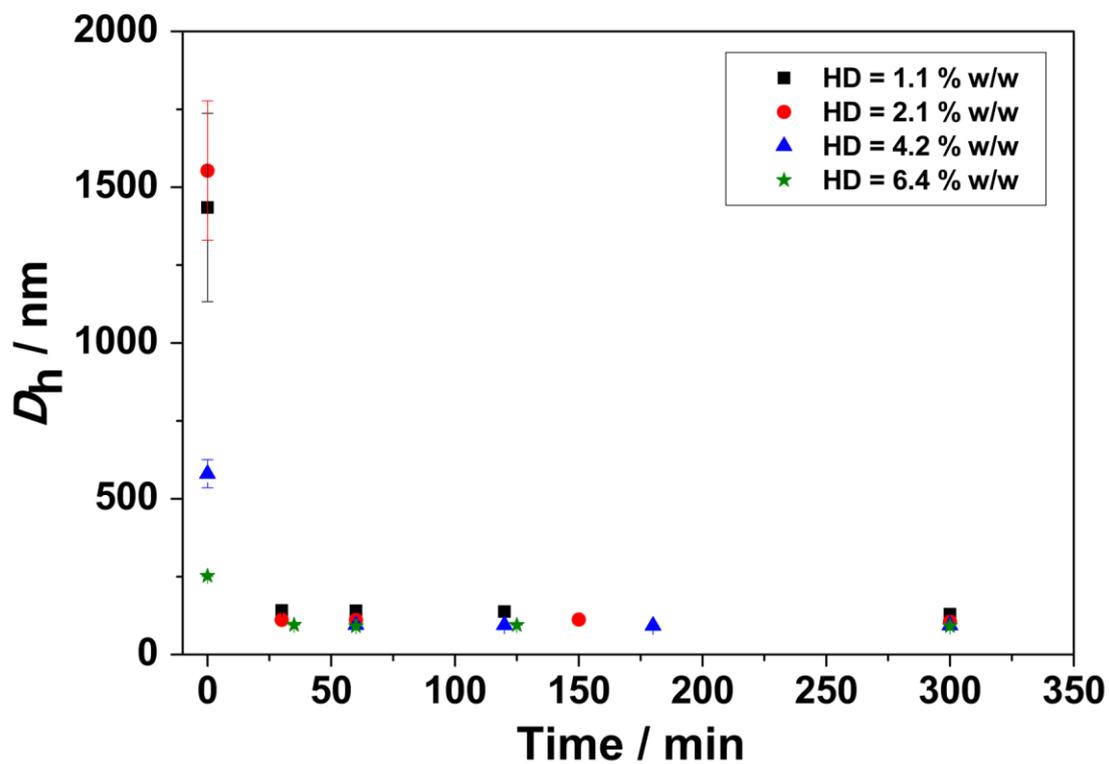
Where  $R_p$  is rate of polymerisation calculated using Equation S2 and  $N_p$  is number of particles per unit volume calculated using Equation S1.



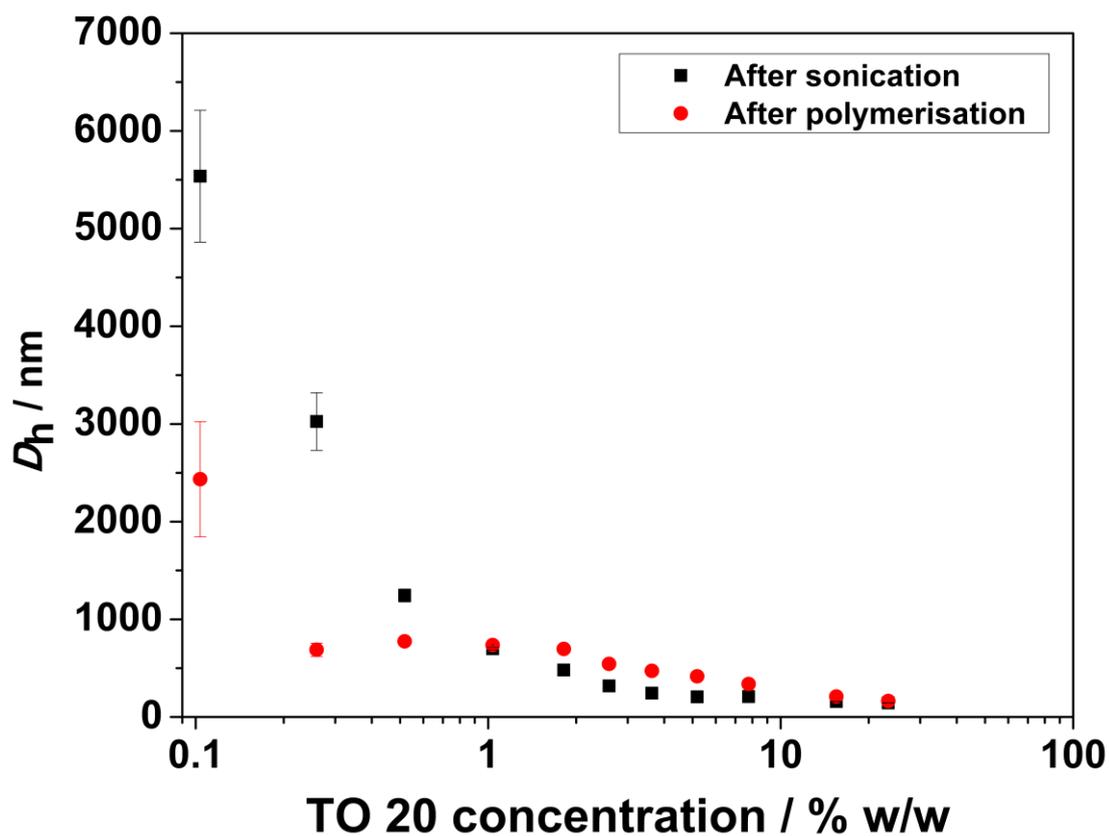
**Figure S1.** Critical micelle concentration (CMC) determination using pendant drop analysis of interfacial tension for sodium dodecyl sulfate (SDS) anionic surfactant and Lutensol TO 20 non-ionic surfactant in deionised water at 23 °C.



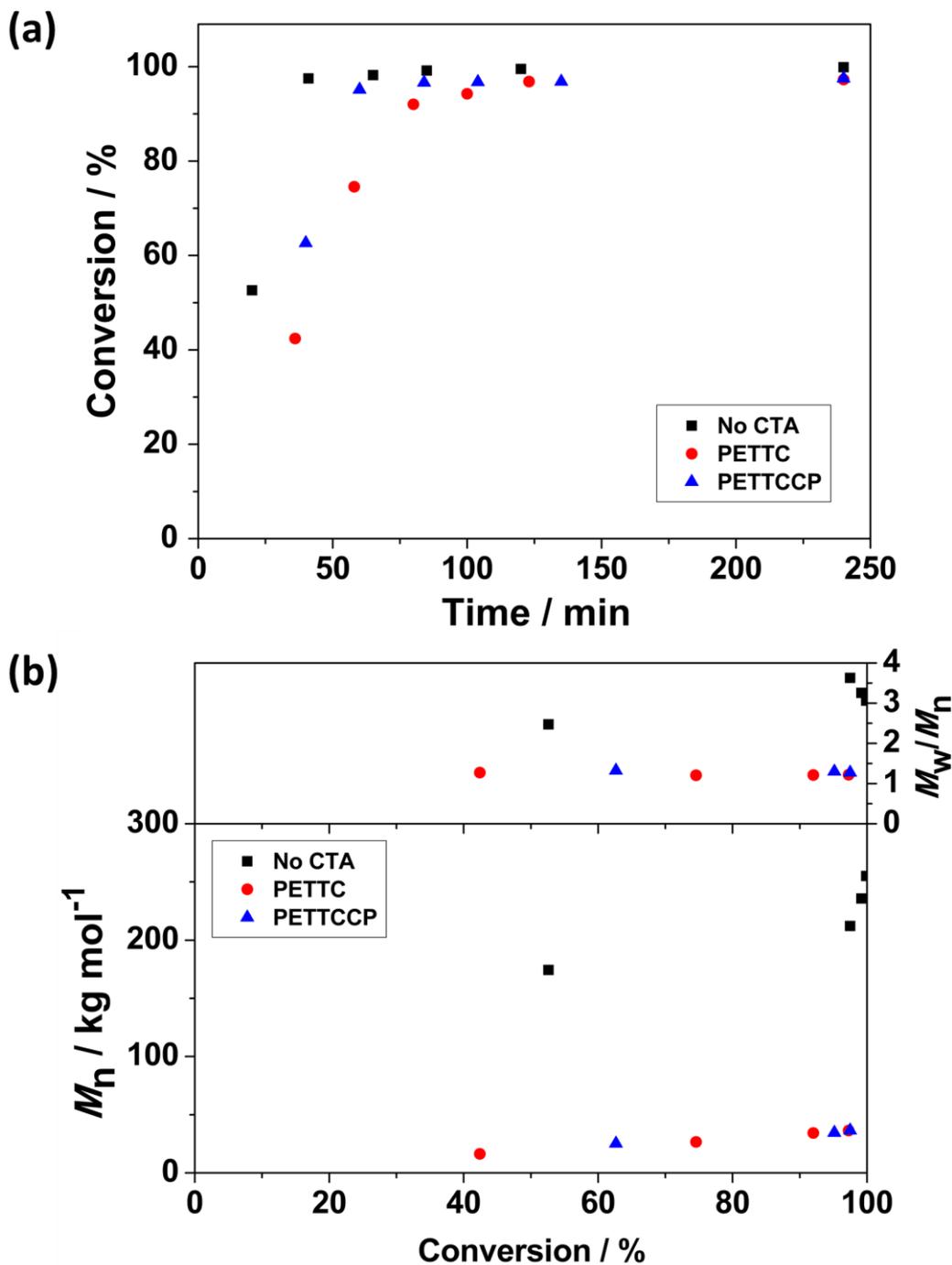
**Figure S2.** Mean hydrodynamic diameter ( $D_h$ ) versus reaction time for PBzMA latexes synthesised *via* conventional miniemulsion polymerisation with varying SDS concentration at 70 °C. Polymerisations were conducted at a dispersed phase content of 20 % w/w with the concentration of hexadecane (HD) fixed at 4.2 % w/w relative to BzMA (see Table S1, Entries 1-3).



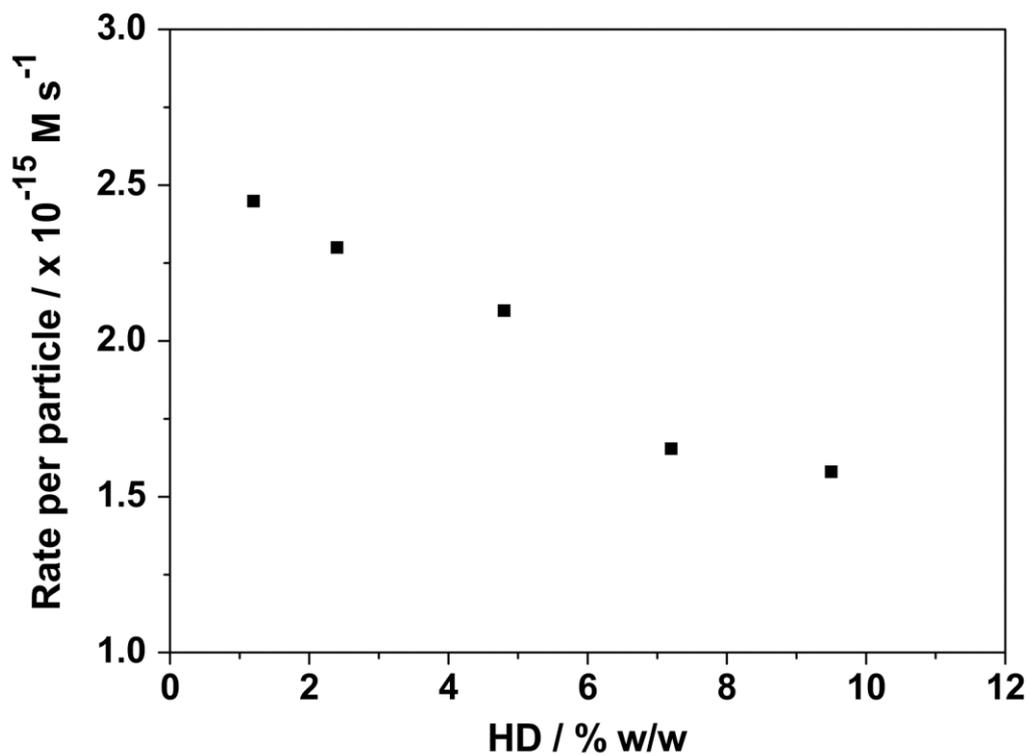
**Figure S3.** Mean hydrodynamic diameter ( $D_h$ ) versus reaction time for PBzMA latexes synthesised *via* conventional miniemulsion polymerisation with varying HD concentration at 70 °C. The concentration of SDS was fixed at 1.3 % w/w relative to BzMA (see Table S1, Entries 2 and 4-6).



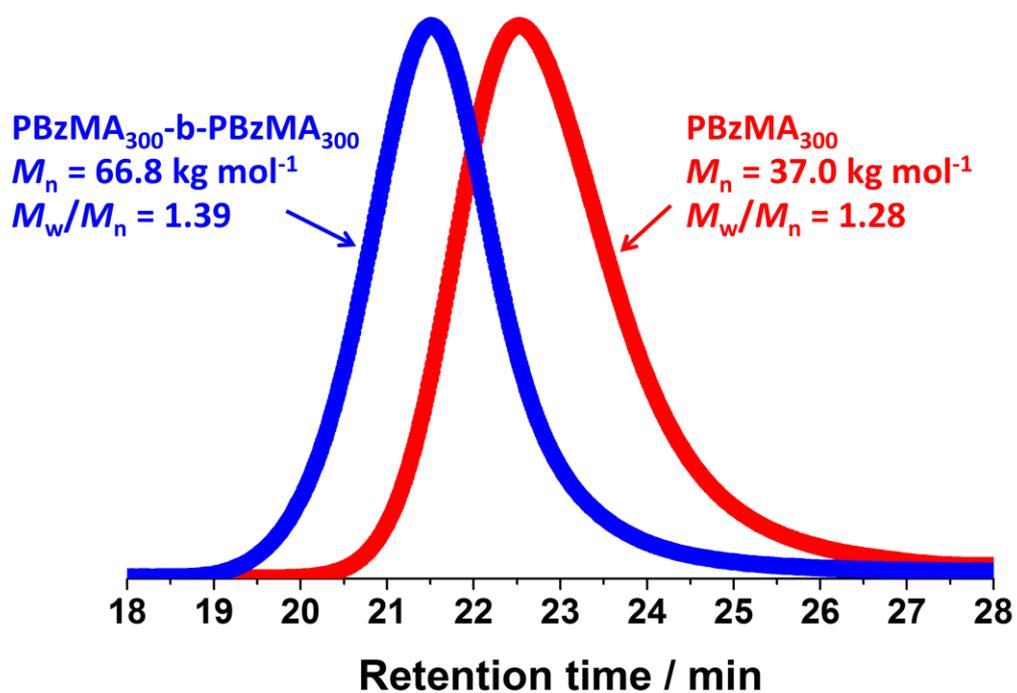
**Figure S4.** Effect of Lutensol TO 20 non-ionic surfactant concentration on the mean hydrodynamic diameter ( $D_h$ ) of PBzMA latexes synthesised *via* conventional miniemulsion polymerisation at 70 °C for 240 min. Polymerisations were conducted at a dispersed phase content of 20 % w/w and the concentration of HD was fixed at 2.4 % w/w relative to BzMA (see Table S1, Entries 7-17).



**Figure S5.** (a) Monomer conversion versus reaction time and (b)  $M_n$  and  $M_w/M_n$  versus monomer conversion for PBzMA synthesised *via* RAFT miniemulsion polymerisation in the presence of no CTA, PETTC, and PETTCCP at 70 °C. The target PBzMA degree of polymerisation (DP) in the presence of RAFT CTAs was 300 and  $[CTA]/[AIBN]$  was 0.4. Polymerisations were conducted at a dispersed phase content of 20 % w/w, with the concentration of HD and TO 20 fixed at 2.4 % w/w and 7.8 % w/w relative to BzMA, respectively. Monomer conversions using no CTA, PETTC, and PETTCCP CTA were 99.9%, 97.3%, and 99.6%, respectively (see Table S2).



**Figure S6.** Effect of HD concentration on the rate of polymerisation per particle for PBzMA synthesised *via* RAFT miniemulsion polymerisation with varying HD concentration relative to BzMA at 70 °C. [BzMA]:[PETTCCP]:[AIBN] = 300:1:2.3. The concentration of TO 20 surfactant was fixed at 7.8 % w/w relative to BzMA.



**Figure S7.** GPC chromatograms obtained for a PBzMA<sub>300</sub> latex prepared by RAFT miniemulsion polymerisation and its subsequent chain extension after 12 months of storage using BzMA at 70 °C (20 % w/w, target DP of second block = 300).

**Table S1.** Monomer, hydrophobe, initiator and surfactant concentration for PBzMA latexes synthesised *via* conventional miniemulsion polymerisation at 70 °C.

Entry	BzMA <sup>a</sup> / % w/w	HD <sup>b</sup> / % w/w	AIBN <sup>b</sup> / % w/w	SDS <sup>b</sup> / % w/w	TO 20 <sup>b</sup> / % w/w
1	18.9	4.2	1.7	0.2	—
2	18.9	4.2	1.7	1.3	—
3	18.9	4.2	1.7	8.8	—
4	18.9	1.1	1.7	1.3	—
5	18.9	2.1	1.7	1.3	—
6	18.9	6.4	1.7	1.3	—
7	19.3	2.4	1.2	—	0.1
8	19.3	2.4	1.2	—	0.3
9	19.3	2.4	1.2	—	0.5
10	19.3	2.4	1.2	—	1.0
11	19.3	2.4	1.2	—	1.8
12	19.3	2.4	1.2	—	2.6
13	19.3	2.4	1.2	—	3.6
14	19.3	2.4	1.2	—	5.2
15	19.3	2.4	1.2	—	7.8
16	19.3	2.4	1.2	—	15.5
17	19.3	2.4	1.2	—	23.3

<sup>a</sup> Concentrations given are relative to total weight. <sup>b</sup> Concentrations given are relative to BzMA.

**Table S2.** Summary of latexes and initial droplet diameter ( $D_{h,droplet}$ ) for miniemulsion polymerisation of BzMA at 70 °C for 240 min using various RAFT chain transfer agents. Polymerisations were conducted at a dispersed phase content of 20 % w/w with the concentration of HD and TO 20 fixed at 2.4 % w/w and 7.8 % w/w relative to BzMA, respectively.

CTA	Conversion <sup>a</sup> / %	$D_h^b$ / nm	$M_n^c$ / kg mol <sup>-1</sup>	$M_w/M_n^c$	$D_{h,droplet}^b$ / nm
No CTA	99.9	338 (0.14)	255.1	3.06	210 (0.18)
PETTC <sup>d</sup>	97.3	577 (0.16)	36.4	1.22	208 (0.19)
PETTCCP <sup>d</sup>	99.6	325 (0.12)	36.5	1.27	190 (0.19)

<sup>a</sup> Determined *via* gravimetry. <sup>b</sup> Obtained *via* DLS analysis, PDI values are indicated in brackets. <sup>c</sup> Determined by THF GPC analysis. <sup>d</sup> Target DP = 300; [CTA]/[AIBN] = 0.4.

## References

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