Supporting Information for

Poly(glycerol monomethacrylate)-poly(benzyl methacrylate)

diblock copolymer nanoparticles via RAFT emulsion polymerization:

synthesis, characterization and interfacial activity

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RAFT aqueous emulsion polymerization of PEG$_{113}$-PBzMA$_{200}$

AIPD azo initiator (6.10 mg, 0.0189 mmol), PEG$_{113}$-DB macro-CTA (0.2996 g, 0.0568 mmol; [CTA]/[AIPD] molar ratio = 3.0) and BzMA monomer (2.00 g, 11.4 mmol, target DP = 200) were weighed into a round-bottomed flask containing a magnetic stir bar. These reagents were dissolved in previously deoxygenated water (9.20 mL, 10% w/w solids formulation) and purged with nitrogen for 30 min at 20°C. The flask was sealed using a rubber septum under a positive nitrogen flow and immersed in an oil bath at 50°C for 24 h, after which the reaction was quenched by exposure to air and cooling to 20°C. (N.B. The synthesis and characterization of the PEG$_{113}$-DB macro-CTA has been described elsewhere, see N. J. Warren et al. *J. Am. Chem. Soc.*, **2014**, *136*, 1023).
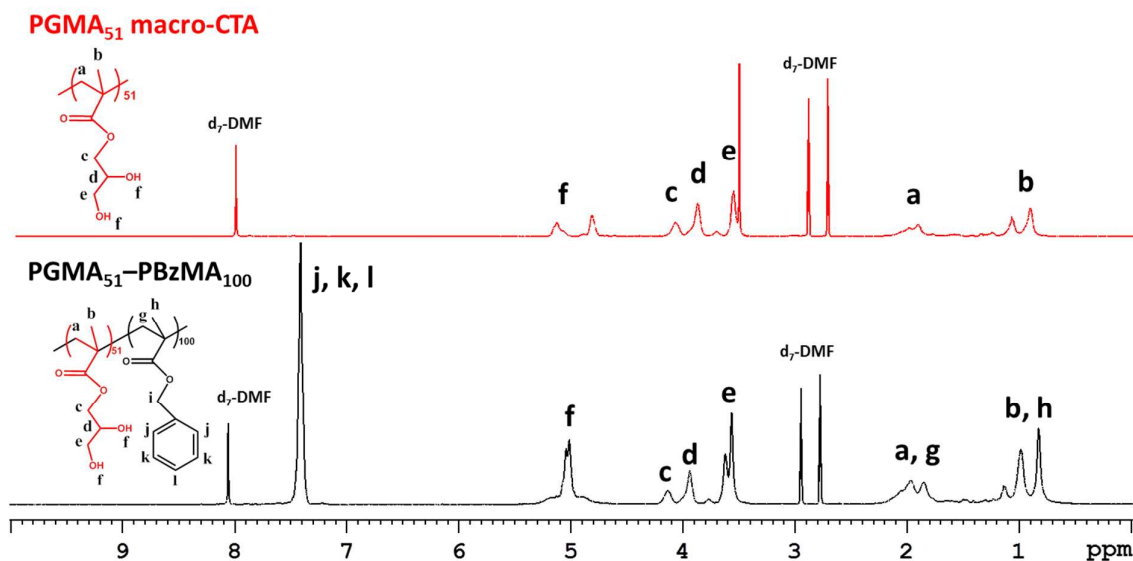
Figure S1. Assigned NMR spectra of the PGMA$_{51}$ macro-CTA and PGMA$_{51}$-PBzMA$_{100}$ diblock copolymer in d$_7$-DMF. PGMA$_{51}$-PBzMA$_{100}$ was freeze-dried prior to dilution in d$_7$-DMF.
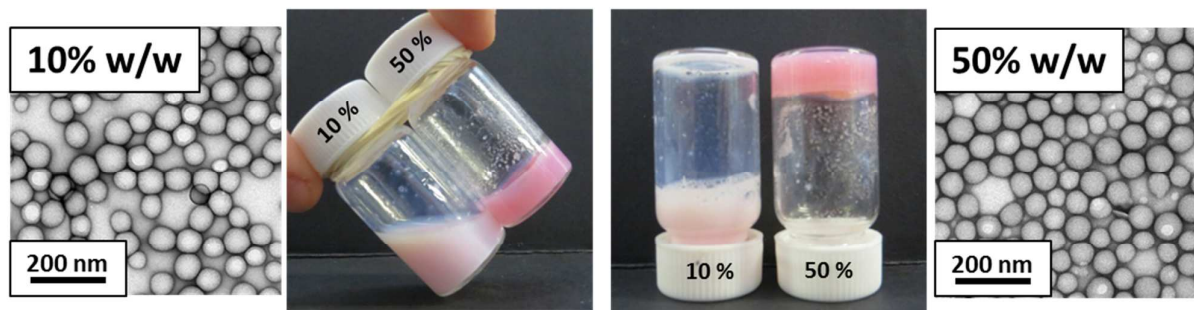

Figure S2. Digital photographs and transmission electron microscopy (TEM) images obtained for PGMA$_{51}$-PBzMA$_{250}$ diblock copolymer nanoparticles prepared at both 10% w/w and 50% w/w. Both samples contain spherical particles, see corresponding TEM images. However, the reaction mixture has a paste-like consistency at 50% w/w solids, whereas free-flowing liquids are obtained at 10-40% w/w solids.

Table S1. Summary of solids contents, conversions, number-average molecular weights (M_n), polydispersities (M_w/M_n) and mean DLS and TEM diameters determined for PGMA$_{18}$-PBzMA diblock copolymer nanoparticles and the corresponding PGMA$_{18}$ macro-CTA. (N.B. for the sake of brevity 'G' denotes PGMA and 'B' denotes PBzMA).

	Target Composition	Solids Content (w/w%)	Conversion[a] (%)	M_n[b]	M_w/M_n[b]	Particle Diameter DLS (nm)	TEM (nm)
S1	G$_{18}$	40	68	6,500	1.12	N/A	N/A
S2	G$_{18}$-B$_{50}$	20	>99	10,700	1.10	38 (0.161)	29
S3	G$_{18}$-B$_{100}$	20	>99	16,800	1.10	97 (0.209)	78
S4	G$_{18}$-B$_{150}$	20	>99	21,600	1.14	215 (0.044)	215

a. Monomer conversion determined by ^{1}H NMR spectroscopy.
b. Determined by DMF GPC using a series of near-monodisperse poly(methyl methacrylate) calibration standards
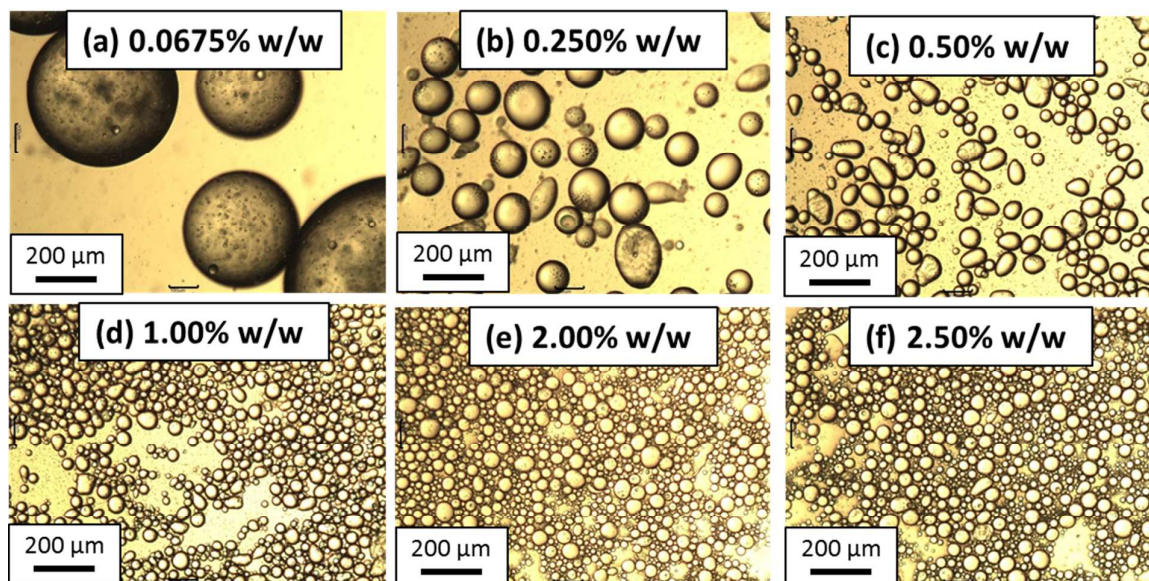
Figure S3. Representative optical microscopy images obtained for sunflower oil-in-water Pickering emulsions prepared using PGMA$_{51}$-PBzMA$_{250}$ nanoparticles as the sole emulsifier at 0.0675, 0.250, 0.500, 1.00, 2.00 or 2.50% w/w. Scale bar = 200 μm in each case.
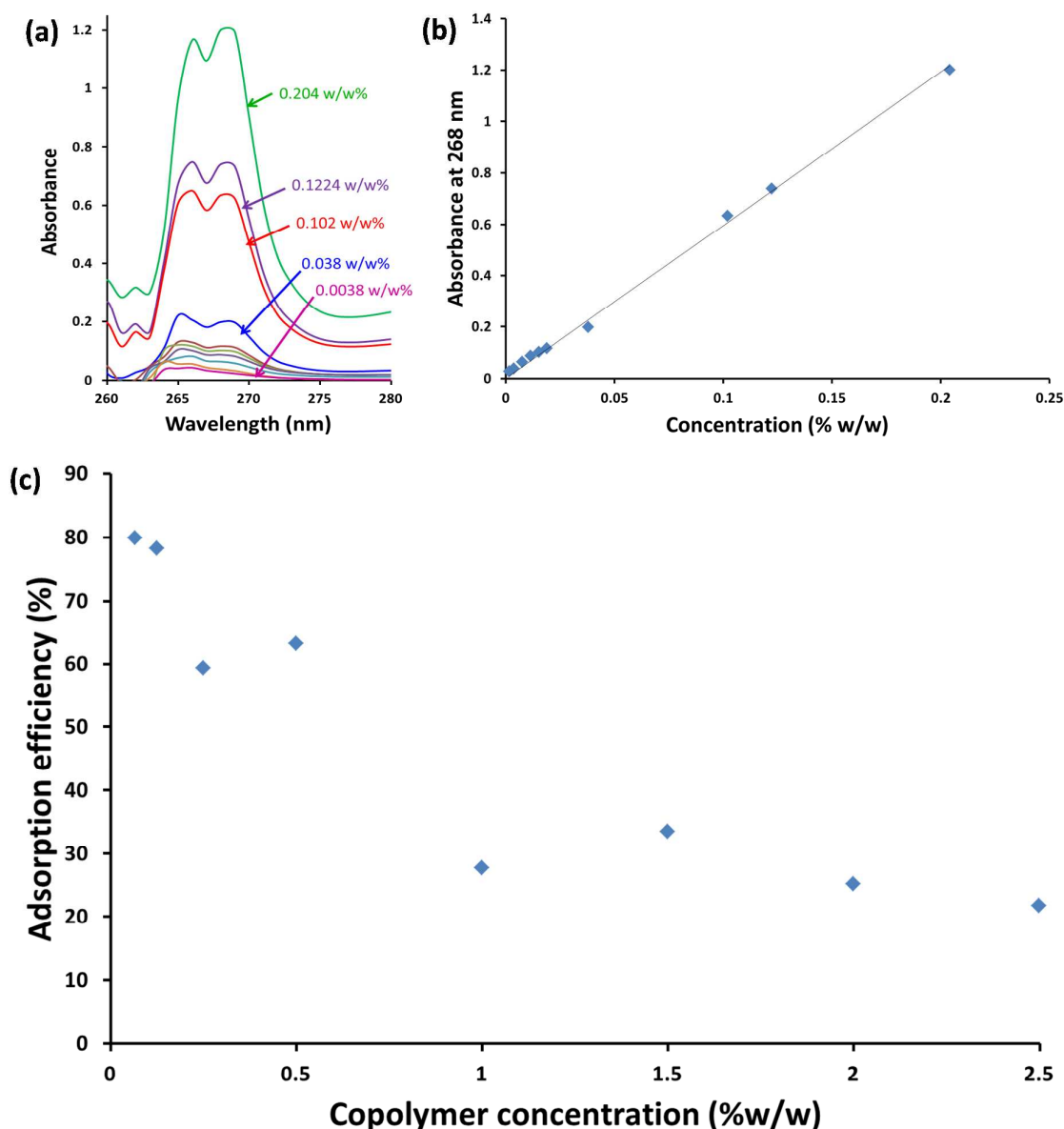
Figure S4. (a) UV absorption spectra recorded for various concentrations of $PGMA_{51}$-$PBzMA_{250}$ diblock copolymer dissolved in DMF. The chromophore at 268 nm is the aromatic benzyl group on the PBzMA block. (b) Beer-Lambert plot obtained for $PGMA_{51}$-$PBzMA_{250}$ diblock copolymer dissolved in DMF. (c) Adsorption efficiency vs. nanoparticle concentration for $PGMA_{51}$-$PBzMA_{250}$ nanoparticles when used as the sole Pickering emulsifier for sunflower oil, as determined using a supernatant depletion assay. This UV spectroscopy-based assay involves nanoparticle dissolution in DMF to avoid UV scattering problems at shorter wavelengths.