Supporting Information for Chemical Communications:

'From Well-defined Macromonomers to Sterically-Stabilised Latexes to Covalently Cross-linkable Colloidosomes: Exerting Control over Multiple Length Scales'

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Experimental Details

Materials. Glycerol monomethacrylate (GMA) was kindly donated by Cognis UK Ltd (Hythe, UK) and used without further purification. 4-Vinylbenzyl chloride (4-VBC; 90 %), Cu(I)Cl (99.995 %) 2,2′-bipyridine (bpy, 99 %), *n*-dodecane, sunflower oil, Triton X-100 and tolylene 2,4-diisocyanate-terminated poly(propylene glycol) [PPG-TDI] were all purchased from Aldrich and were used as received. Styrene (Aldrich) was passed through a column of basic alumina to remove inhibitor and then stored at -20 °C prior to use. 2,2'-Azobisisobutyronitrile (AIBN; BDH) was used as received. Methanol and ethanol were purchased from Fisher and were used as received. De-ionized water was used in all experiments. Silica gel 60 (0.0632-0.2 mm) was obtained from Merck (Darmstadt, Germany). NMR solvents (D_2O, CD_3OD, $CDCl_3$ and d_5-pyridine) were purchased from Fisher.

***N*-(Dimethylamino)ethyl-2-bromoisobutyrylamide ATRP Initiator Synthesis.** N,N-Dimethylethylenediamine (6.00 g, 0.068 mol), triethylamine (27.27 g, 0.27 mol) and dichloromethane (120 mL) were placed in a 500 mL three-necked round-bottomed flask and purged with nitrogen for 30 minutes. A white precipitate of triethylammonium bromide was formed on addition of 2-bromoisobutyryl bromide (15.49 g, 0.067 mol) to this reaction mixture, which was stirred for a further 5 h. The precipitate was removed by filtration, the solution was then dried over $MgSO_4$ and the dichloromethane was removed by rotary evaporation to give a pale brown liquid (11.5 g; yield = 72 %).

^{1}H NMR (400 MHz, CD_3OD): δ 1.88 (6H, s, 2 x CH_3), 2.26 (6H, s, $N(CH_3)_2$), 2.45 (2H, t, J = 7.0 Hz, $(CH_3)_2NCH_2$), 3.31 (2H, t, J = 7.0 Hz, $CH_2NHCOO(CH_3)_2Br$).

Homopolymerisation of GMA. *N*-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator (0.30 g, 1.25 mmol), bpy (0.39 g, 2.5 mmol) and GMA (10.0 g, 62.4 mmol) were weighed into a 25 ml round-bottomed flask and degassed. Methanol (12 ml) was degassed and transferred into the reaction solution under nitrogen. The Cu(I)Cl catalyst (0.120 g, 1.25 mmol) was added to the stirred solution which turned dark brown, indicating the onset of polymerisation. After 24 h, the reaction solution was diluted with methanol and passed through a silica column to remove the spent Cu(II) catalyst. The product was then dried on a vacuum line overnight to afford a white powder (8.0 g; yield = 77 %).

Homopolymer Quaternisation. The $PGMA_{50}$ homopolymer (7.0 g, 0.85 mmol) was dissolved in methanol (20 ml). 4-VBC (0.43 g, 2.55 mmol; 4-VBC/tertiary amine molar ratio = 3:1) was added and the reaction solution stirred at room temperature for 48 h. The excess solvent was removed by rotary evaporation and the resulting solid was then dissolved in water. The excess 4-VBC was extracted three times with cyclohexane. The aqueous solution was then freeze-dried from water overnight to afford a white powder (6.0 g; yield = 84 %).

Aqueous Emulsion Polymerisation. $PGMA_{50}$ macromonomer (0.500 g) was weighed into a 100 ml round-bottomed flask and dissolved in water (50.0 g). This solution was purged with nitrogen for 30 minutes before being heated to $70^{o}C$ under a nitrogen blanket. The AIBN initiator (0.050 g) was dissolved in styrene (5.00 g) and purged with nitrogen before being injected into the reaction vessel. The solution turned milky-white within 1 h and was stirred for 24 h. The latexes were purified by three centrifugation/redispersion cycles, replacing each successive supernatant with pure water. The mean diameter of the resulting latex particles was assessed by both DLS and SEM.

Alcoholic Dispersion Polymerisation. $PGMA_{50}$ macromonomer (0.500 g) was weighed into a 100 ml three-necked round-bottomed flask fitted with a condenser and nitrogen inlet and dissolved in a 90:10 methanol/water mixture (50.0 g). This solution was purged with nitrogen for 30 minutes before being heated to $70^{o}C$ under a nitrogen blanket. The AIBN initiator (0.050 g) was dissolved in styrene (5.00 g) and purged with nitrogen before being injected into the reaction vessel. The solution turned milky-white within 1 h and was stirred for 24 h. The latex was purified by three centrifugation/redispersion cycles replacing each successive supernatant with the 9:1

methanol/water mixture, followed by three redispersion cycles into pure water. The mean diameter of the purified latex particles was assessed by both DLS and SEM.

Colloidosome preparation. Tolylene 2,4-diisocyanate-terminated poly(propylene glycol) (0.020 g) was weighed into a sample vial and then dissolved in 5.0 ml of oil (e.g. *n*-dodecane, sunflower oil, paraffin oil or 1-undecanol, see Table S2). This solution was then homogenized with 1.0 - 5.0 wt % aqueous latex (120 nm or 1100 nm $PGMA_{50}$-PS particles) for 2 min using either an IKA Ultra-Turrax T-18 homogenizer with a 10 mm dispersing tool (12,000 rpm) or a Silverson stirrer (9,000 rpm). The resulting stable milky-white emulsion was allowed to stand at room temperature for 10-30 minutes to allow the cross-linking reaction to proceed.

In principle, we note that cross-linking is at least as likely to occur between OH groups on the same latex particle as between neighbouring latex particles. However, it is very difficult to calculate the effective isocyanate / OH molar ratio used during the preparation of these cross-linked colloidosomes, since this depends on the precise contact angle made between the latex particles and the oil phase (and this parameter is not known). If we assume that this oil-latex contact angle is 90^o, which is almost certainly an over-estimate, we calculate an isocyanate / OH molar ratio of approximately 1:1 for the 120 nm $PGMA_{50}$-PS latex at 1.0 wt % (this calculation assumes that all of the $PGMA_{50}$ macromonomer chains are located at the latex surface and all the latex is adsorbed onto the oil droplets). Thus there is certainly sufficient polymeric cross-linker present to react with every single hydroxy group that is present at the oil droplet surface. Hence significant wastage of the polymeric cross-linker can occur via intra-particle cross-linking while still allowing efficient inter-particle cross-linking to be achieved.

Cyclohexane annealing. Colloidosomes were prepared as described above, but using a 4:1 *n*-dodecane/cyclohexane mixture as the oil phase instead of pure *n*-dodecane. The resulting stable milky-white emulsion was split between five vials, with four of these samples being heated to 50^oC in an oven for 15, 30, 45 and 60 minutes, respectively.

Polymer Characterization

^{1}H NMR spectroscopy. All ^{1}H NMR spectra were recorded in either $CDCl_3$, D_2O, CD_3OD or d_5-pyridine using a 400 MHz Bruker Avance-400 spectrometer.

DMF GPC. The molecular weight and polydispersity of the PGMA homopolymer precursor were determined by DMF GPC at 70°C. The GPC set-up comprised three Polymer Laboratories PL gel 10 μm 'Mixed B' columns in series with a Viscotek TriSEC model 302 refractive detector. The flow rate was 1.0 mL min^{-1} and the mobile phase contained 10 mmol LiBr. Ten near-monodisperse PMMA standards (M_p = 2,000 – 300,000 g mol^{-1}) were used for calibration purposes and data were analyzed using Viscotek TriSEC 3.0 software.

Dynamic light scattering (DLS). Intensity-average hydrodynamic diameters of the latex particles were obtained by DLS using a Malvern Zetasizer NanoZS instrument. Aqueous solutions of 0.01 wt % latex were analyzed using disposable curvettes, and the results were averaged over three consecutive runs. The deionized water used to dilute each latex was ultra-filtered through a 0.20 μm membrane so as to remove dust.

Colloidosome Characterization

Conductivity Measurements. The conductivities of the emulsions immediately after preparation were measured using a digital conductivity meter (Hanna model Primo 5). The emulsions were classified according to their conductivities. A high conductivity (typically > 10 μS cm^{-1}) indicated a water-continuous emulsion, while a low conductivity (< 1 μS cm^{-1}) indicated an oil-continuous emulsion. These results were confirmed using the so-called 'drop test': one drop of the emulsion was added to both pure water and oil, and its ease of dispersion was assessed by visual inspection. Relatively rapid dispersion indicated that the continuous phase of the emulsion was the same as that of the diluent.

Lazer Diffraction. A Malvern Mastersizer 2000 instrument equipped with a small volume Hydro 2000SM sample dispersion unit (ca. 50 mL), a HeNe laser operating at 633 nm, and solid-state blue laser source operating at 466 nm was used to size the emulsions. The stirring rate was adjusted to 1,000 rpm in order to avoid creaming of the emulsion.

Optical Microscopy. Optical microscopy images were recorded with a James Swift MP3502 microscope, (Prior Scientific Instruments Ltd.) fitted with a digital camera (Nikon Coolpix 4500).

Scanning Electron Microscopy (SEM). SEM studies were performed using a FEI Sirion field emission scanning electron microscope (using a beam current of 244 μA and a typical operating voltage of 5 kV). Samples were dried onto aluminium stubs and sputter-coated with a thin layer of gold prior to examination so as to prevent sample charging.

Supporting Information: Figs and Tables

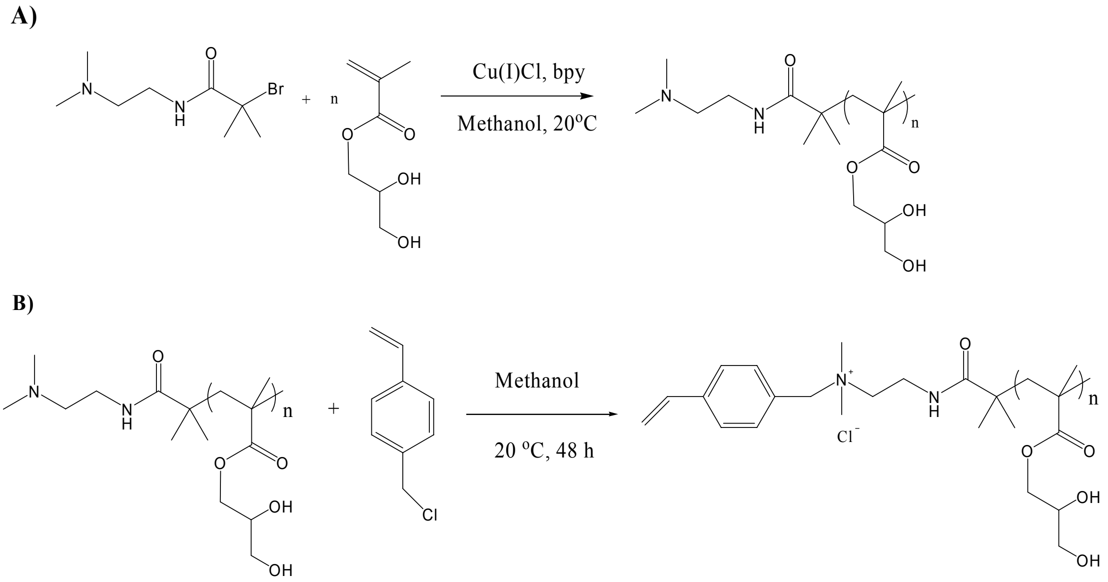


Fig S1. Two-step synthesis of PGMA-based macromonomer: (a) ATRP of GMA monomer at 20 °C in methanol for 16 h followed by (b) post-polymerisation quaternisation of the tertiary amine end-group of the PGMA homopolymer precursor at 20°C in methanol for 48 h.

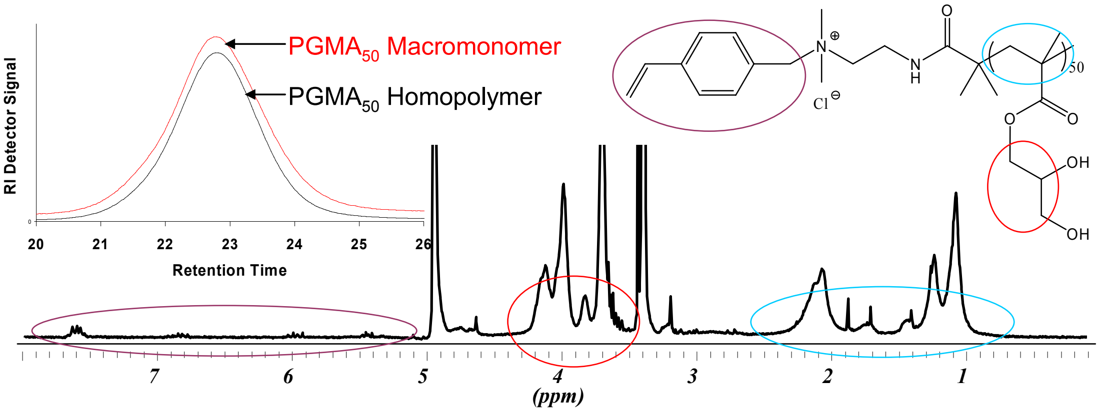


Fig S2. Chemical structure and assigned ^{1}H NMR spectrum for the styrene-functionalized PGMA$_{50}$ macromonomer and GPC data obtained for both the PGMA$_{50}$ homopolymer precursor (M_n = 49,000, M_w/M_n = 1.21) and final PGMA$_{50}$ macromonomer (M_n = 49,300, M_w/M_n = 1.25).

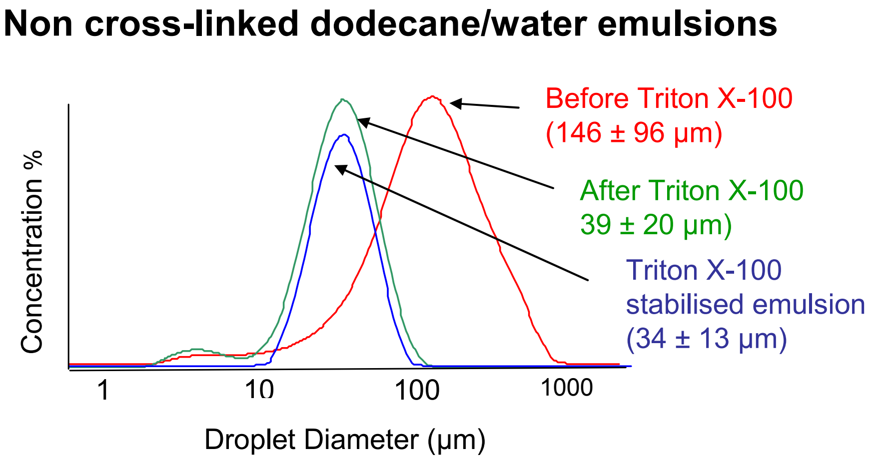
Polymerisation method	DLS Diameter (nm)	SEM Diameter (nm)	PGMA content (%)	Γ / mg m^{-2}	XPS surface coverage (%)
Emulsion	120	85	9.4	1.8	44
Dispersion	1100	950	0.7	1.16	53

Table S1. Summary of PGMA$_{50}$-PS latex characterization data. Particle diameters as determined by dynamic light scattering and scanning electron microscopy. Macromonomer contents as determined by ^{1}H NMR. XPS surface coverages were estimated from the intensity of the O1s signals due to the PGMA$_{50}$ stabiliser chains on the latex surface normalized to that of the PGMA$_{50}$ macromonomer alone.

Oil Type	Emulsion Type[a]	Droplet Diameter (μm)[b]		
		120 nm latex		1100 nm latex
		Ultra-Turrax	Silverson	Ultra-Turrax
n-Dodecane	oil-in-water	145 ± 96	58 ± 31	100 ± 75
Sunflower oil	oil-in-water	64 ± 26	39 ± 13	85 ± 75
Paraffin	oil-in-water	204 ± 89	65 ± 33	73 ± 36
1-Undecanol	oil-in-water	100 ± 48	65± 24	71 ± 67

(a) As determined by the 'drop test' and confirmed by a conductivity measurement of > 1 μS cm^{-1},
(b) As determined by laser diffraction (Malvern Mastersizer) measurements.

Table S2. Pickering emulsions formed when using 5.0 ml of PGMA$_{50}$-PS latex particles (1.0 wt. % for 120 nm latex or 5.0 wt. % for 1100 nm latex) with 5.0 ml oil homogenised for 2 minutes at either 12,000 rpm (UltraTurrax) or 9,000 rpm (Silverson stirrer).


Non cross-linked dodecane/water emulsions

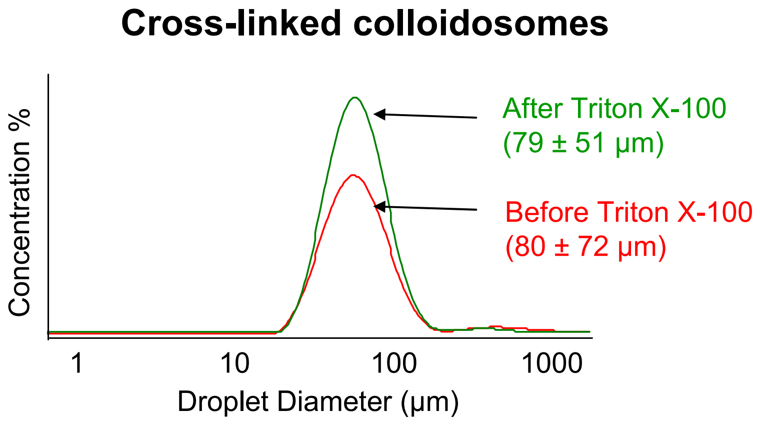

Cross-linked colloidosomes

Fig S3. Laser diffraction (Malvern Mastersizer) particle size distribution curves obtained for both non-crosslinked (top) and crosslinked (bottom) 120 nm PGMA$_{50}$-PS latex-stabilised *n*-dodecane-in-water emulsions, before and after addition of Triton X-100 surfactant. A Triton X-100-stabilised *n*-dodecane-in-water emulsion is provided as a reference.

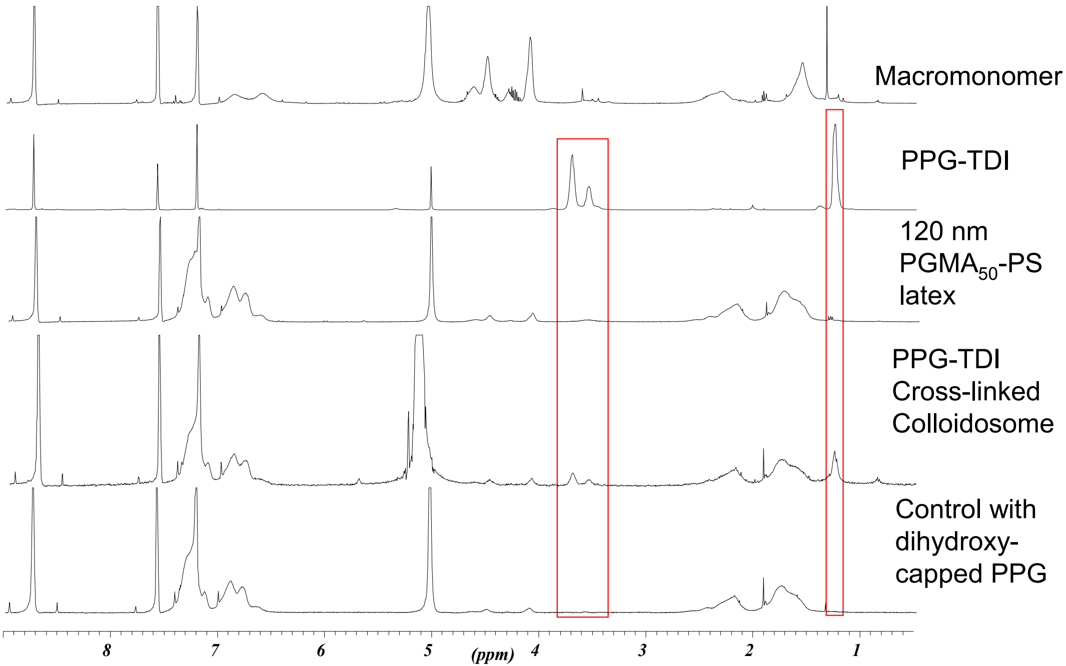


Fig S4. ^{1}H NMR spectra recorded in d$_5$-pyridine for PGMA$_{50}$ macromonomer, PPG-TDI cross-linker, 120 nm PGMA$_{50}$-PS latex particles and cross-linked colloidosomes after repeatedly washing with ethanol to remove excess cross-linker. Peaks due to the PPG chains are clearly visible in the latter spectrum, confirming the presence of the PPG-TDI cross-linker. A control experiment in which non-cross-linkable dihydroxy PPG was added to the oil phase demonstrates that this non-reactive PPG is efficiently removed by the ethanol wash process. Thus the NMR peaks attributed to the PPG-TDI are due to chemically reacted (cross-linked) PPG-TDI, rather than merely physically occluded PPG-TDI.

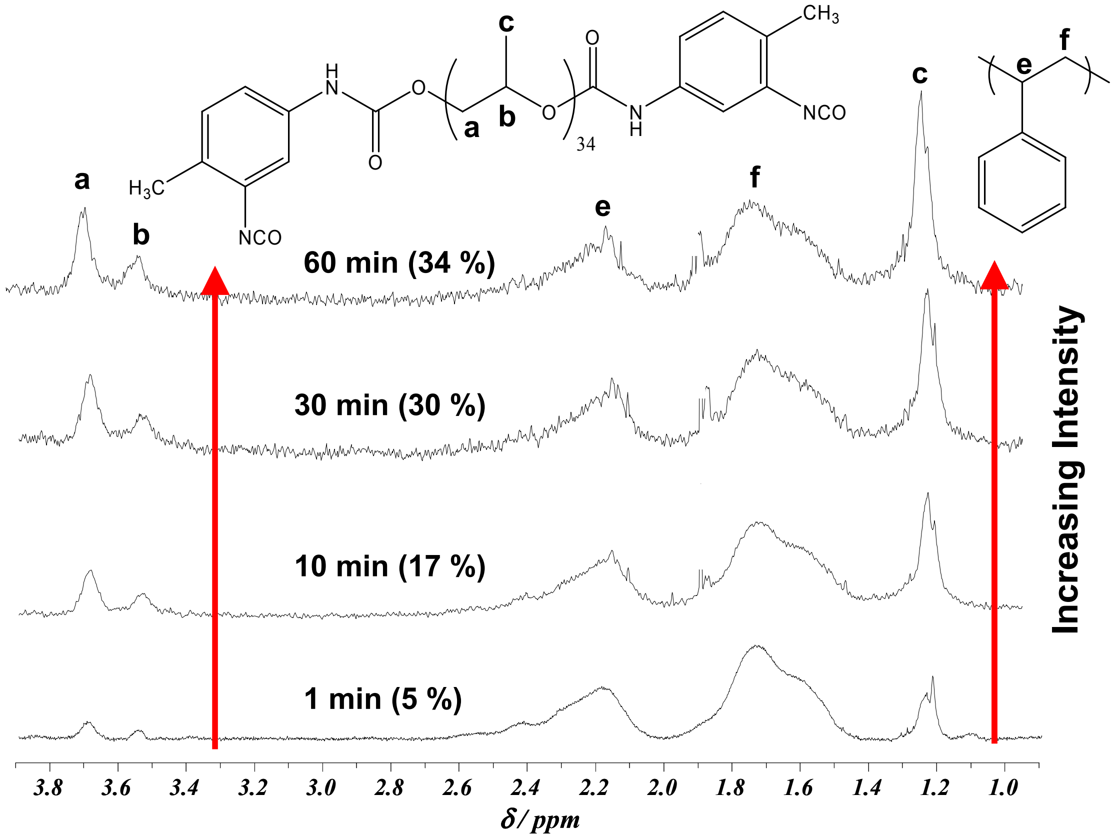


Fig S5. ^{1}H NMR spectra recorded for cross-linked colloidosomes sampled 1, 10, 30 and 60 minutes after homogenisation. Notice the increase in signal intensities at both 1.27 and 3.5-3.8 ppm due to the PPG-TDI cross-linker relative to the polystyrene backbone. For quantification purposes, the signals at 3.5-3.7 ppm were preferred since these were better resolved relative to the baseline.