Electronic Supplementary Information

Arrested Coalescence Behavior of Giant Pickering Droplets and Colloidosomes Stabilised by Poly(*tert*-butylaminoethyl methacrylate) Latexes

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Materials and Methods

Materials

2-(*tert*-Butylamino)ethyl methacrylate (TBAEMA, 97%, Aldrich) and divinylbenzene (DVB; 80 mol % 1,4-divinyl content; Fluka, UK) were treated with basic alumina to remove any inhibitor and stored at -20 °C prior to use. Ammonium persulfate (APS; > 98 % purity), *n*-dodecane, isopropyl myristate, sunflower oil, and tolylene 2,4-diisocyanate-terminated poly(propylene glycol) [PPG-TDI] (97 % purity) were each purchased from Aldrich and used as received. Millipore Milli-Q water was used in all experiments. Potassium nitrate (KNO_3, 99.5 % purity) was purchased from Ajax Chemicals, (Australia) and used as received. Potassium hydroxide was purchased from Chem-Supply, (Australia) (KOH, 99%) and used as 0.1 M aqueous solution to adjust to pH 10.

Aqueous emulsion polymerisation

A charge-stabilised PTBAEMA latex was prepared using surfactant-free aqueous emulsion polymerisation. Full details of the latex synthesis have been reported previously.[1]{Morse, 2012 #109} The particles were purified via dialysis to remove excess TBAEMA monomer and APS initiator until the surface tension was close to that of pure water (71 ± 1 $mN{\cdot}m^{-1}$). The latex diameter measured by dynamic light scattering was 260 ± 58 nm at pH 10. The zeta potential of the latex in 0.001 M KCl was -31 mV at this pH; this is attributed to sulfate groups originating from the persulfate initiator on the surface of the latex.[1]

Pendant drop tensiometry

Interfacial tension measurements of single pendant oil drops (10 μL) suspended in water and aqueous latex dispersions were measured using a PAT-1 tensiometer (SINTERFACE Technologies, Germany). The interfaces of *n*-dodecane, isopropyl myristate and sunflower oil droplets prepared in the presence of aqueous 0.01 M KNO_3 (or 0.1 M KNO_3 for the sunflower oil experiments) at pH 10 were investigated in both the presence and absence of 0.1 mg·mL^{-1} PPG-TDI (1.0 mg·mL^{-1} PPG-TDI for sunflower oil experiments) dissolved in the oil phase. These particle-free interfaces were then compared to pendant oil drops in contact with an aqueous phase containing 3.8×10^{-2} wt % of the 260 nm PTBAEMA latex. This concentration was chosen to yield the same fraction of depleted particles as occurred in the coalescence rig experiments based on the different cell volume and total interfacial area. The profile of the droplet was monitored during a five-minute equilibration period to correlate with experiments performed using the coalescence rig. In the case of *n*-dodecane, each pendant drop was then subjected to a ± 1 μL volume oscillation with a period of 5 s for ten complete cycles in order to assess the impact of the adsorbed latexes on the interfacial viscosity and elasticity. The calculated interfacial tension data represent the mean and standard deviation of five runs.

Oil droplet zeta potential measurements

Zeta potential values for bare oil droplets were determined in the presence of 0.001 M KNO_3 electrolyte at pH 10 using a Malvern Zetasizer NanoZS Model ZEN 3600 instrument. The chosen oil (0.5 mL) was added to the aqueous electrolyte (9.5 mL). The lower electrolyte concentration was required to prevent immediate coalescence of oil droplets in these higher surface area emulsions. The mixture was then homogenised for 2 min using an IKA Ultra-Turrax T-18 homogeniser with a 10 mm dispersing tool operating at 12 000 rpm. The zeta potential of the emulsion droplets was analysed immediately before phase separation was observed which took about 10 min for *n*-dodecane and isopropyl myristate, and about 30 min for sunflower oil.

Bulk viscosity measurements

The viscosities of the *n*-dodecane, isopropyl myristate and sunflower oil were measured using an AR-G2 rheometer (TA Instruments) operating at a shear rate of 3.568 to 285.4 s^{-1} using a 40 mm 2° steel cone and plate geometry at 20 °C. Viscosities were determined to be 1.4±0.4

mPa·s for *n*-dodecane, 5.8±0.4 mPa·s for isopropyl myristate and 69±0.4 mPa·s for sunflower oil. In the presence of 0.1 mg·mL^{-1} PPG-TDI, *n*-dodecane had a viscosity of 1.6±0.4 mPa·s, isopropyl myristate had a viscosity of 5.8±0.5 mPa·s and sunflower oil containing 1.0 mg·mL^{-1} PPG-TDI had a viscosity of 71±0.4 mPa·s. Thus for the relevant quantities of added cross-linker there was no detectable effect on the viscosity of *n*-dodecane or isopropyl myristate, but a slight increase in the viscosity of sunflower oil.

References

1. A. J. Morse, D. Dupin, K. L. Thompson, S. P. Armes, K. Ouzineb, P. Mills and R. Swart, *Langmuir*, 2012, **28**, 11733-11744.

Figure S1. Sequence of images (every fiftieth frame) recorded for bare coalescing isopropyl myristate droplets at pH 10 in 0.01 M KNO_3. The outer diameter of the capillaries is 0.71 mm which acts as an appropriate scale bar.

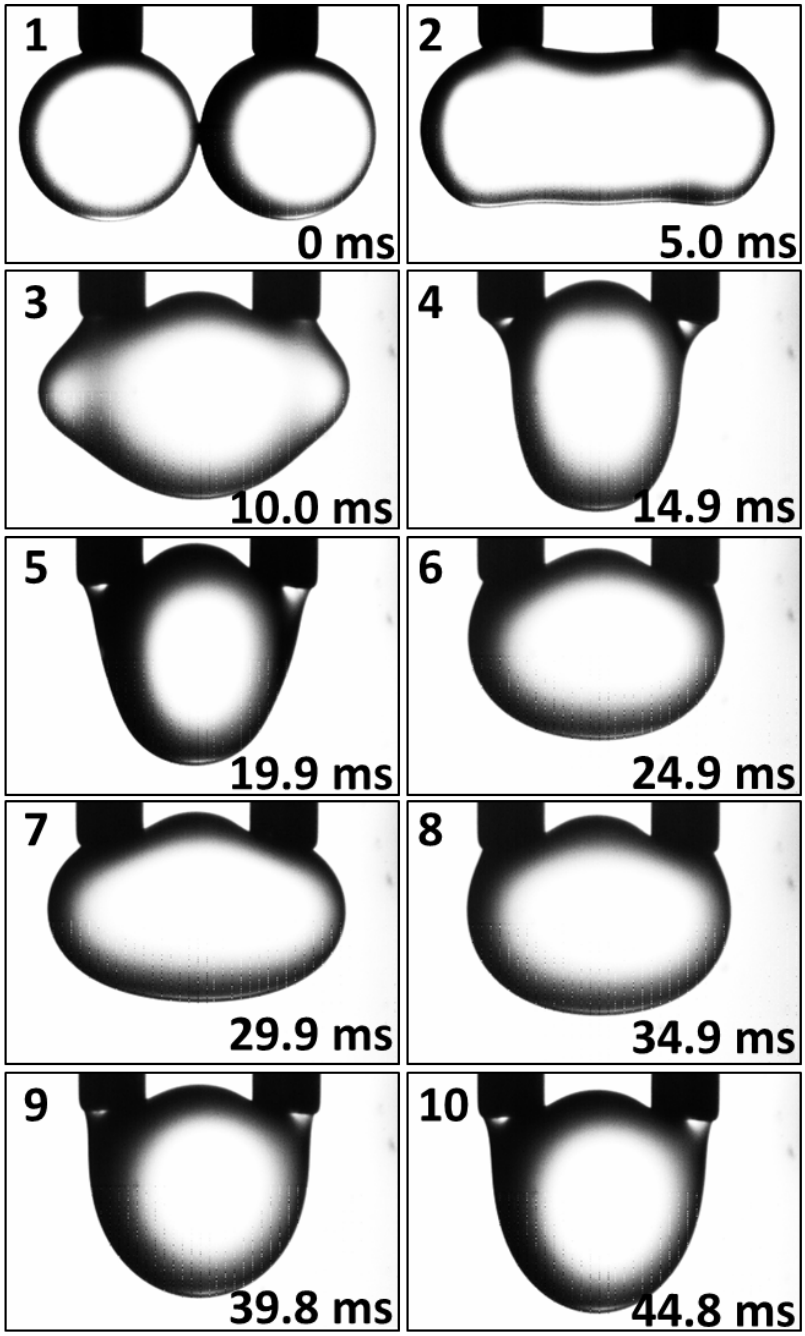

Figure S2. Comparison of the coalescence dynamics of pairs of (A) *n*-dodecane (0.01 M KNO_3 background electrolyte), (B) isopropyl myristate (0.01 M KNO_3 background electrolyte) and (C) sunflower oil (0.1 M KNO_3 background electrolyte) droplets at pH 10 (□) and pH 3 (○).

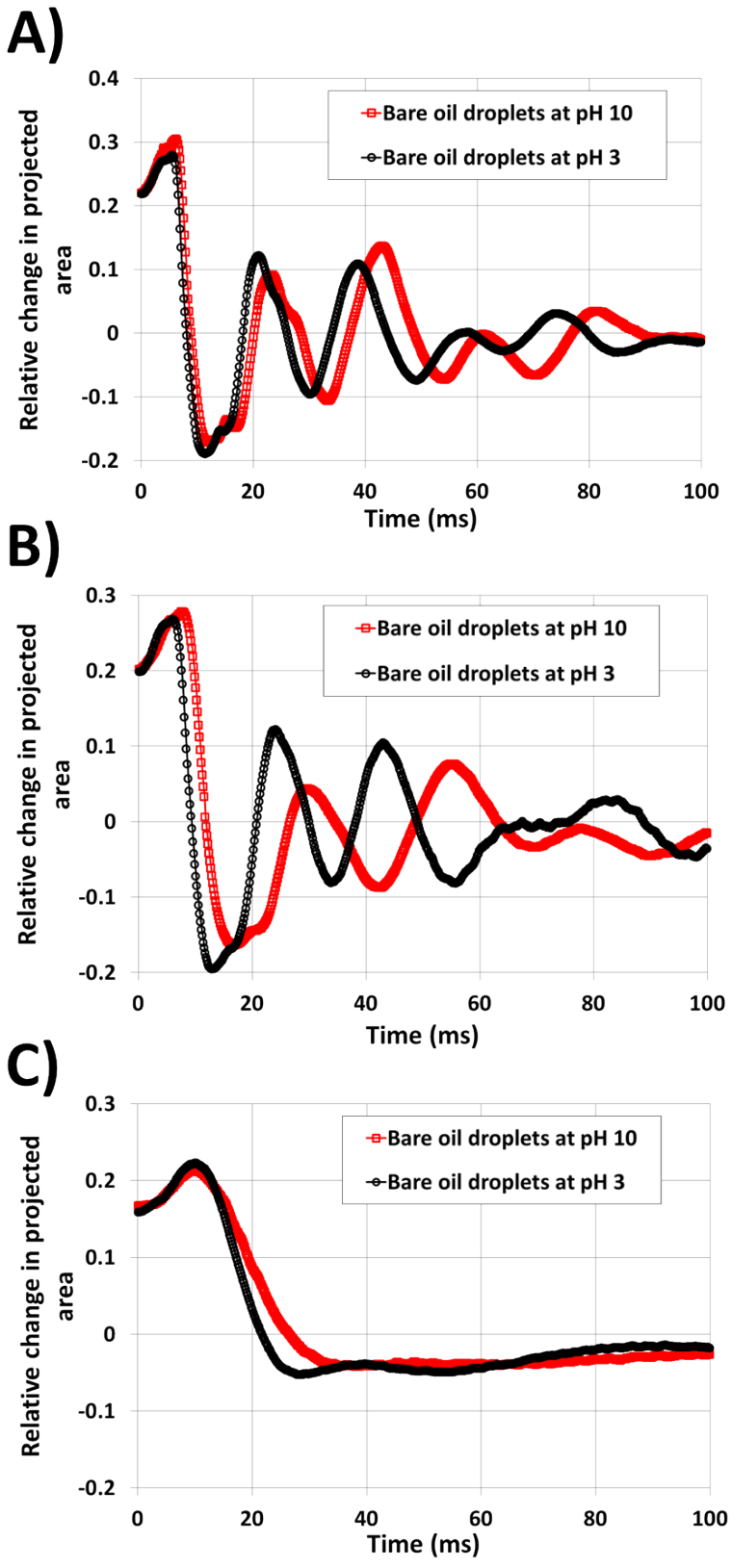

Figure S3. Schematic representation of the estimated increase in the contour length following inter-colloidosome cross-linking and capillary separation. Digital images of two colloidosomes formed are shown when *n*-dodecane oil droplets containing PPG-TDI cross-linker (0.1 mg·mL^{-1}) were exposed to a 1.6 × 10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles (0.01 M KNO_3 background electrolyte). The droplets were aged in isolation for 60 s before being moved into contact (top image). After 5 min in contact the droplets were moved apart stepwise using a linear actuator with a step size of 0.15 mm (bottom image).

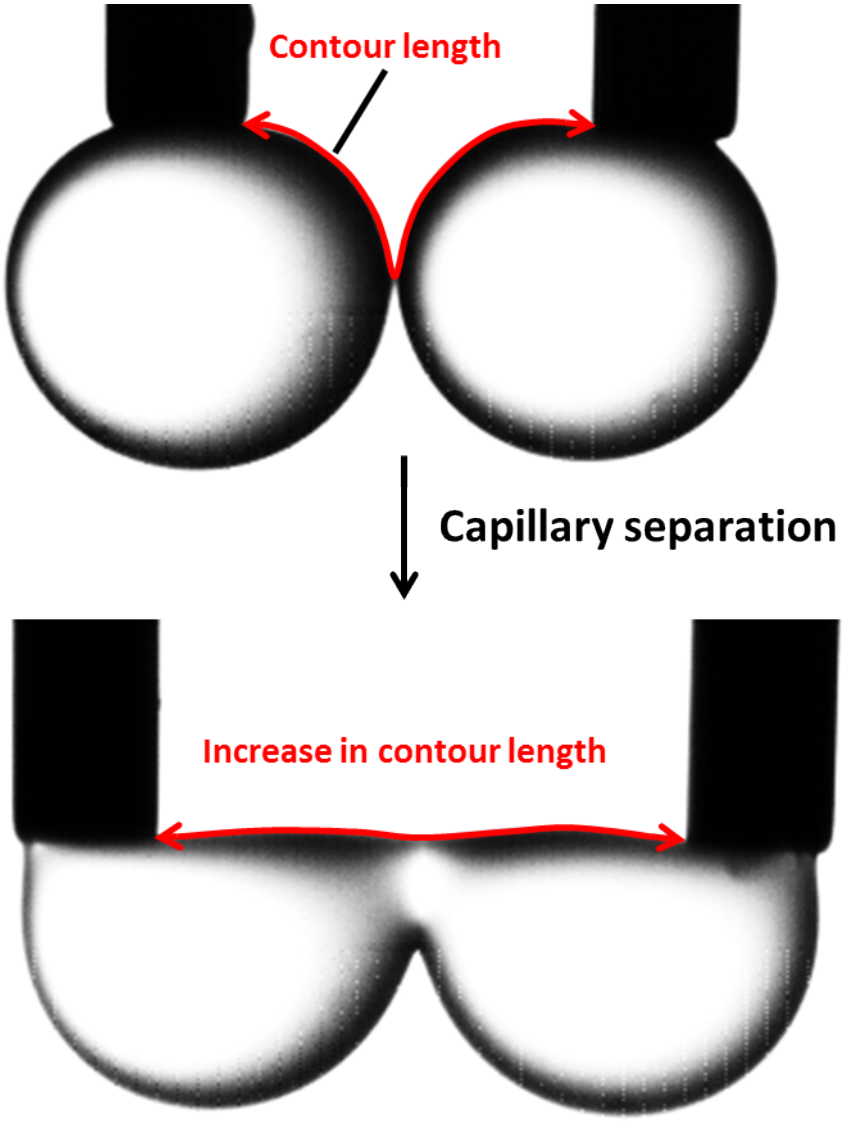

Figure S4. Repeat of experiment shown in Figure 8 to confirm reproducibility. Sequence of images recorded during asymmetric droplet experiments using two *n*-dodecane droplets grown in the presence of a 1.6×10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 in the presence of 0.01 M KNO_3. Droplets were aged in isolation for 60 s before being moved into contact (Image 1). After 5 min in contact (Image 2), the droplets were moved apart stepwise using a linear actuator with a step size of 0.15 mm (Image 3). Once arrested coalescence was observed (Image 4), droplet separation was halted and mass transport of *n*-dodecane from the left-hand droplet to the right-hand droplet was observed (Images 4-5).

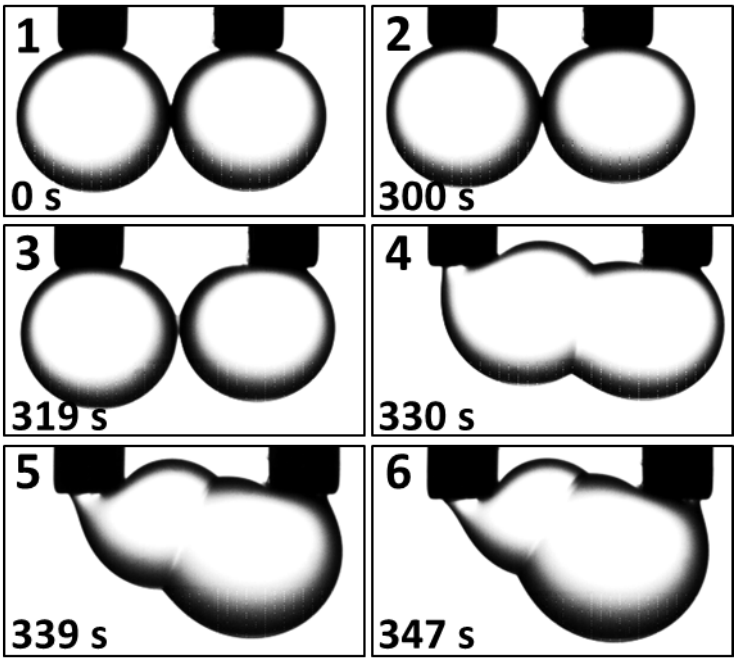

Figure S5. Sequence of images recorded during asymmetric droplet experiments using two *n*-dodecane droplets grown in the presence of a 1.6×10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 in the presence of 0.01 M KNO_3. Droplets were aged in isolation for 5 min before being moved into contact (Image 1). After 5 min in contact (Image 2), the droplets were moved apart stepwise using a linear actuator with a step size of 0.15 mm (Images 3-6).