Electronic Supplementary Information

Giant pH-Responsive Microgel Colloidosomes: Preparation, Interaction Dynamics and Stability

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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, Univar Chemicals) and potassium chloride (99.0 % purity, Fisher Scientific) were used as received. Potassium hydroxide was purchased from Chem-Supply (KOH, 99%) and used as 0.1 M aqueous solution to adjust aqueous electrolyte solutions to pH 10. Nitric acid (Univar Chemicals) or hydrochloric acid (35% in H_2O, VWR International) were used to adjust the aqueous solution pH to 3.

Aqueous emulsion polymerisation

A charge-stabilised PTBAEMA latex was prepared using surfactant-free aqueous emulsion polymerisation. Full details of the latex synthesis has been reported previously.[1] The particles were purified via dialysis to remove excess TBAEMA and APS initiator until the surface tension was close to that of pure water (71 ± 1 mN m^{-1}). The latex diameter measured by dynamic light scattering was 240 ± 50 nm. The zeta potential of the latex was -31 mV at pH 10.

Dynamic Light Scattering (DLS)

Hydrodynamic diameters were determined at 25 °C using a Malvern Zetasizer NanoZS Model ZEN 3600 instrument equipped with a 4 mW He-Ne solid-state laser operating at 633 nm. Back-scattered light was detected at 173° and the mean particle diameter was calculated from the quadratic fitting of the correlation function over thirty runs of 10 s duration. All measurements were performed three times on 0.01 w/v % aqueous latex dispersions and are shown in Figure S1. The pH of the deionised water used to dilute the latex was matched to that of the initial latex (around pH 10) and was adjusted from 10 to 3 using dilute HCl in the presence of 0.001 M KCl. Due to their hydroplasticisation it is not possible to acquire well-resolved scanning electron microscope (SEM) images of these particles.[1]

Aqueous Electrophoresis

Zeta potentials were determined using the same Malvern Zetasizer NanoZS Model ZEN 3600 instrument equipped with an autotitrator (MPT-2 multipurpose titrator, Malvern Instruments) with electrophoretic mobilities modelled via the Smoluchowski equation. The solution pH was adjusted from 10 to 3 using dilute HCl in the presence of 0.001 M KCl. The results are shown in Figure S1.

Pendant drop tensiometry

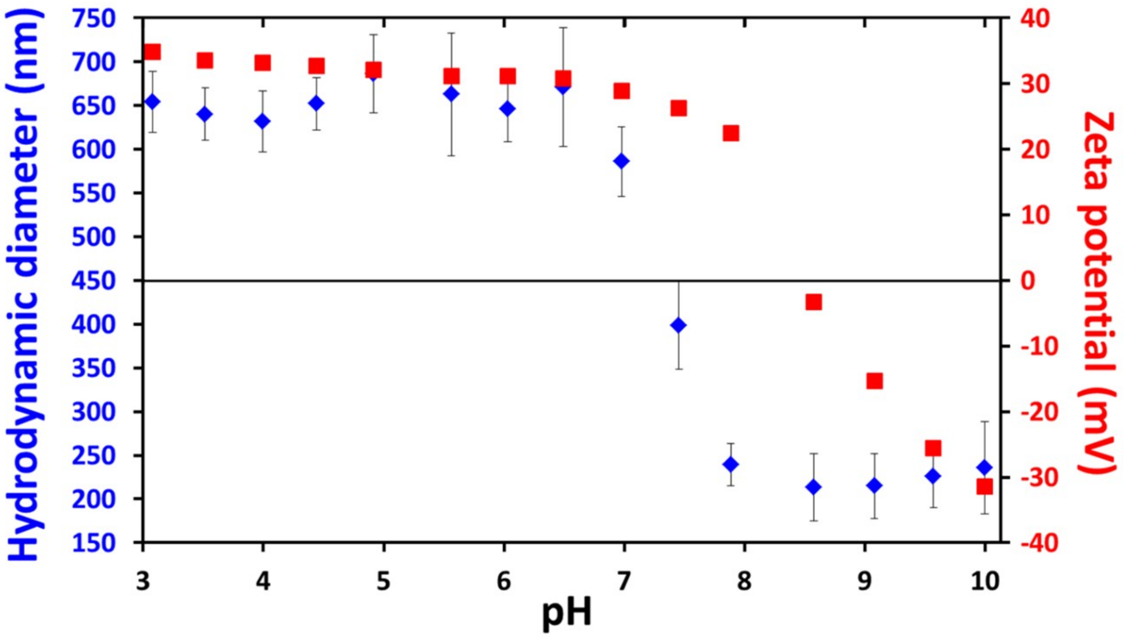
The interfacial tension of single pendant oil drops (10 μL) suspended in either water or aqueous microgel dispersions was measured using a PAT-1 tensiometer (SINTERFACE Technologies, Germany). *n*-Dodecane, isopropyl myristate and sunflower oil droplets prepared in the presence of aqueous salt (0.01 M KNO_3 for former two oils or 0.10 M KNO_3 for the latter oil) at pH 3 were investigated in the absence and presence of PPG-TDI (0.1 mg mL^{-1} for *n*-dodecane and isopropyl myristate; 1.0 mg mL^{-1} PPG-TDI for sunflower oil) 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} % w/v of the cationic PTBAEMA microgel. The profile of the droplet was monitored during a 5 min equilibration period to correlate with experiments performed using the coalescence rig. The calculated interfacial tension data represent the mean and standard deviation of five runs. Subsequently 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 elasticity and dilational viscosity. Interfacial elasticity and dilational viscosity derive from the response of the interface to changes in droplet volume. The interfacial elasticity relates to the magnitude of the change in interfacial tension; the larger the value the more the interface is affected, while a lower value indicates the interface resists the change. The dilational viscosity is a measure of how fast the interface response; low values indicate rapid response, while large values are associate with an interface that changes slowly. For the 'acid challenge' experiments, pendant isopropyl myristate drops were suspended in a latex dispersion at pH 10 and aged for 5 min prior to a rapid adjustment of the pH to 3.

Oil droplet zeta potential measurements

Zeta potentials for bare oil droplets were measured in the presence of 0.001 M KNO_3 electrolyte at pH 3 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 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 results were inconclusive owing to phase separation occurring within 5 min. What can be stated is that the zeta potential was near neutral (< 10 mV).

Bulk aqueous solution behaviour of PTBAEMA particles

Figure S1. Variation of the mean hydrodynamic diameter (♦) and zeta potential (■) with solution pH for a 0.01 wt % aqueous dispersion of 0.8 mol % DVB cross-linked PTBAEMA particles.



Sunflower Oil Experiments

Added electrolyte was required to promote bubble instability, since the coalescence of oil droplets in pure water rarely occurred. Empirically, it was found that coalescence of sunflower oil droplets required 0.10 M KCl.[2] This concentration was used throughout so that coalescence occurred in the presence of the minimum level of added salt.

The data in Table S1 and Figure S2 indicates swollen microgels adsorb to the sunflower oil/water interface at pH 3 with the adsorption continuing for up to 300 s. Sunflower oil exhibited the greatest *normalised* reduction in interfacial tension relative to the bare oil interface of the three oils studied. Together with the higher electrolyte concentration used here, this is expected to facilitate stronger microgel adsorption for this particular oil. It can be noted that the reduction in interfacial tension observed here was less than when PTBAEMA latex particles adsorb at pH 10.[2]

The coalescence times when the droplets were not allowed to age are lower in the presence of adsorbed microgel particles. However, the stability of the sunflower oil droplets increased substantially when these droplets were allowed to age for 60 s prior to being brought into contact; this is consistent with additional microgel adsorption, as indicated by Figure S2. If the sunflower oil droplets carry significantly higher cationic charge owing to stronger microgel adsorption facilitated by the higher electrolyte concentration, this enhanced stability should be electrosteric in origin.

The damping coefficients shown in Table 1 and Table S1 primarily reflect the oil viscosities; sunflower oil is significantly more viscous than the other two oils and shows a slight increase in damping coefficient for droplets aged for 60 s prior to being brought into contact, which is most likely because of the presence of fatty acids.[2, 3] In the case of sunflower oil, the presence of the PPG-TDI cross-linker was sufficient to damp the coalescence dynamics to such an extent (see Figure S3) that it could not be modelled by a simple harmonic oscillator function.

The data in Figure 1 and Figure S2 indicate that, on the minimum 10-15 s timescale required for a coalescence experiment, the interfacial tension of the aqueous microgel solution/*n*-dodecane interface is close to the equilibrium value; only minimal further reduction is observed up to 60 s. Conversely, the interfacial tension of the aqueous microgel solution/sunflower oil interface decreases substantially over the 60 s ageing period. This enhanced microgel adsorption leads to the observed reduction in damping coefficient for aged sunflower oil droplets brought into contact.

Table S1. Influence of presence of 655 nm charge-stabilised PTBAEMA microgels and/or oil-soluble cross-linker (PPG-TDI) on the interfacial tension, coalescence time and damping coefficient of pendant sunflower oil droplets grown at pH 3 in 0.1 M KNO_3 background electrolyte. Oil droplets were 1.8 to 2.0 mm in diameter.

Interface	**Interfacial Tension After 5 min Equilibration (mN m^{-1})**	**Coalescence Time (s)**	**Damping Coefficient (ms^{-1})**
Sunflower oil/aqueous solution	18.2 ± 0.2	0 s ageing: 6.2 ± 2.8 60 s ageing: 7.7 ± 1.7	0.0614 ± 0.003 0.0638 ± 0.004
(Sunflower oil + **PPG-TDI**)/aqueous solution	10.5 ± 0.2	0 s ageing: 14.5 ± 2.6 60 s ageing: 16.4 ± 3.7	N/A
Sunflower oil/aqueous **PTBAEMA microgel** solution	10.7 ± 0.7	0 s ageing: 3.4 ± 0.7 60 s ageing: 45 ± 6	0.0706 ± 0.008 0.0535 ± 0.008
(Sunflower oil + **PPG-TDI**)/ aqueous **PTBAEMA microgel** solution	7.7 ± 0.1	0 s ageing: 12.6 ± 2.4 60 s ageing: No coalescence	0.0591 ± 0.008 No coalescence

Table S2. Dynamic interfacial rheological parameters of pendant sunflower oil droplets grown in both the absence and presence of 655 nm charge-stabilised PTBAEMA microgels after ageing for 5 min. The aqueous phase was pH 3 and 0.1 M KNO_3 background electrolyte in each case.

Interface	**Interfacial Elasticity (mN m^{-1})**	**Dilational Viscosity (mN s m^{-1})**	**Interfacial Elasticity (mN m^{-1}) + PTBAEMA microgel particles**	**Dilational Viscosity (mN s m^{-1}) + PTBAEMA microgel particles**
Sunflower oil/aqueous solution	8.7 ± 2.4	5.5 ± 1.9	18.6 ± 1.3	3.7 ± 0.7
(Sunflower oil + **PPG-TDI**)/aqueous solution	6.9 ± 0.5	4.1 ± 0.4	4.7 ± 0.3	0.4 ± 0.3

Figure S2. Dynamic interfacial tension of sunflower oil in the absence (□) and presence (○) of a 3.8×10^{-2} % w/v aqueous dispersion of charge-stabilised PTBAEMA microgel particles, as well as bare oil droplets in the presence of an oil-soluble cross-linker, PPG-TDI (Δ) and oil droplets prepared in the presence of both PTBAEMA microgel particles and PPG-TDI (◊). The aqueous phase was pH 3 and 0.1 M KNO_3 background electrolyte in each case.

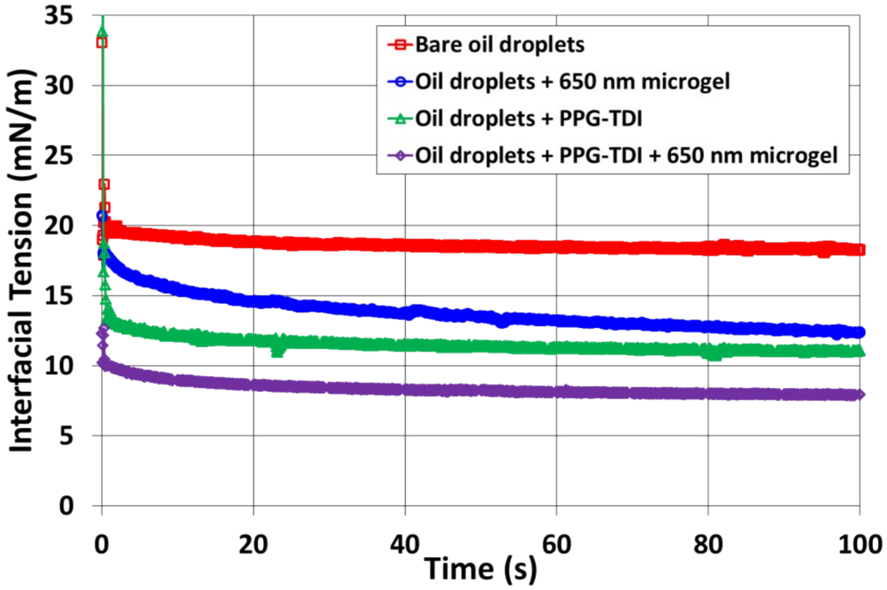
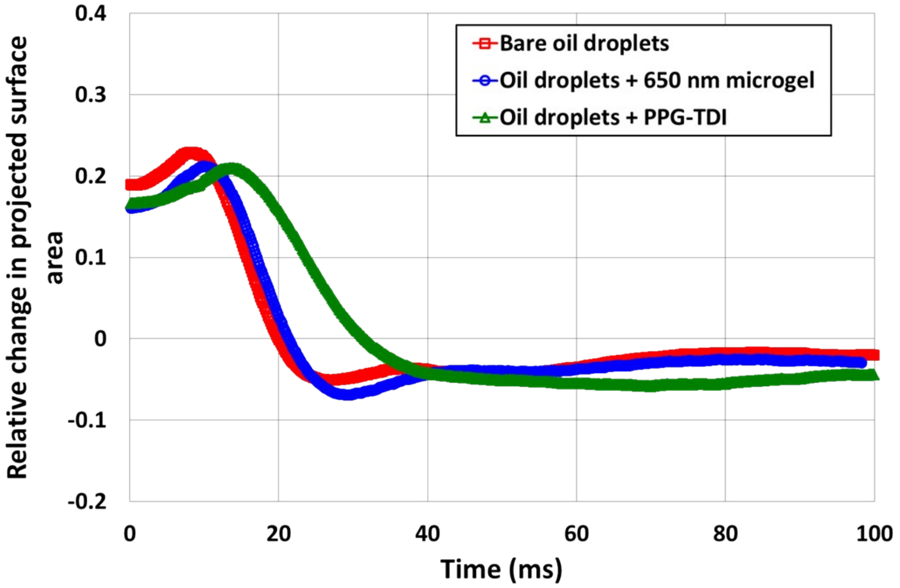
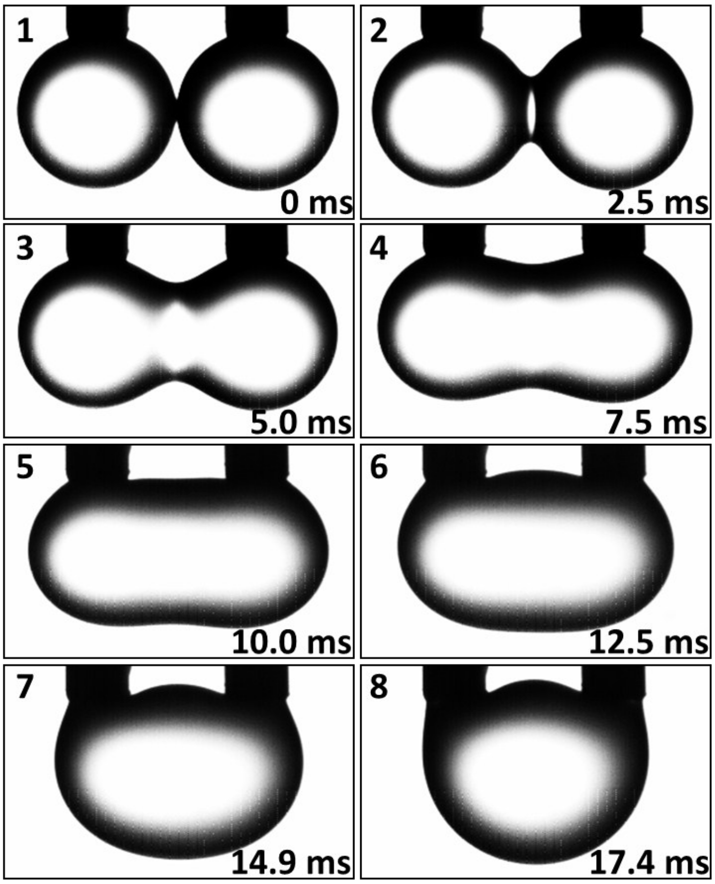


Figure S3. Comparison of the coalescence dynamics of pairs of sunflower oil droplets in the absence (□) and presence (○) of a 1.6×10^{-2} wt% aqueous dispersion of 655 nm PTBAEMA microgel particles, as well as bare oil droplets in the presence of an oil-soluble cross-linker, PPG-TDI (Δ). All experiments were conducted at pH 3 and 0.1 M KNO_3 background electrolyte.



Pickering droplet interactions at pH 3

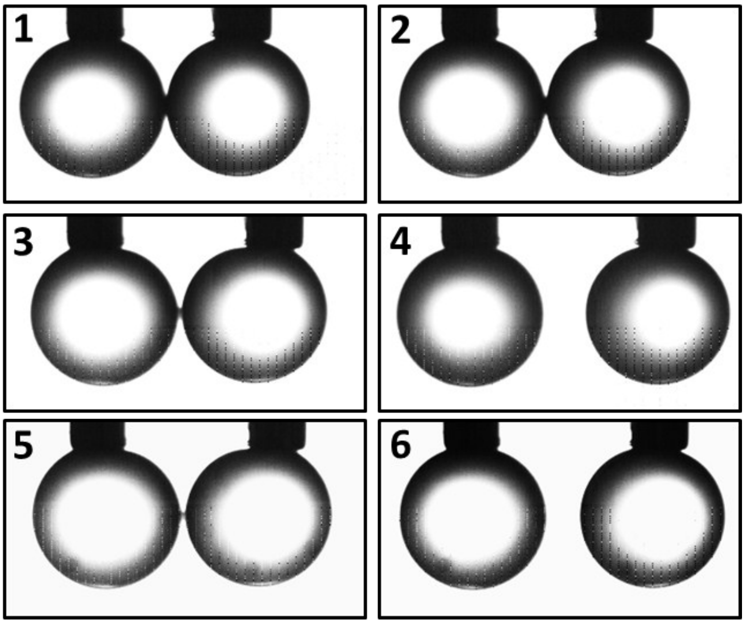
Figure S4. Sequence of video images for two coalescing sunflower oil Pickering droplets in the presence of a 1.6×10^{-2} wt % aqueous dispersion of 655 nm charge-stabilised PTBAEMA microgel particles at pH 3 and 0.1 M KNO_3 background electrolyte. The outer diameter of the capillaries is 0.71 mm, which acts as an appropriate scale bar. Images are shown for every fifteenth frame recorded.



Colloidosome vs colloidosome interactions at pH 3

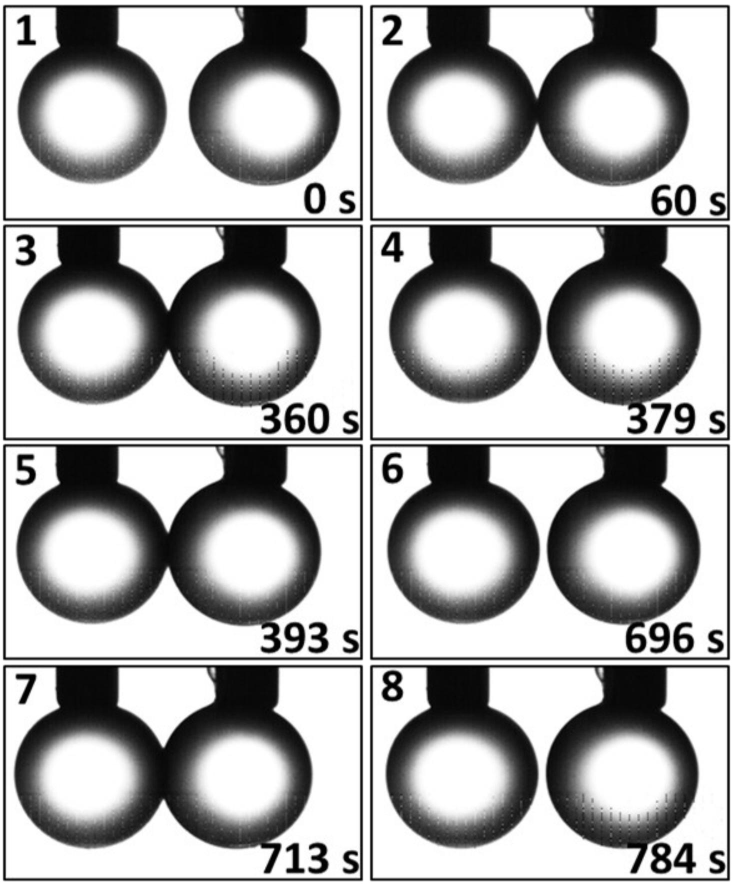
The interactions of two giant colloidosomes formed from sunflower oil were conducted using 1.0 mg mL^{-1} PPG-TDI in order to enhance the diffusion of this cross-linker in this high-viscosity oil. While this may have reduced the equilibration time required for the interfacial tension, it is clear from Figure S2 that synergistic adsorption of PPG-TDI and the microgel particles also occurred at these interfaces. As for isopropyl myristate, droplet pairs proved to be unstable if subjected to no ageing (apart from the minimum 10-15 s required to move the droplets into contact, see Table S1). The longer coalescence times compared to the Pickering droplet interaction provide good evidence for interfacial cross-linking of adsorbed microgel particles. An ageing time of 60 s was sufficient to prevent coalescence in the case of sunflower oil, as shown in Figure S5. While there was some evidence for the formation of a 'neck' between the two microgel colloidosomes when in contact (Figure S5, Image 5), this feature did not survive the subsequent increase in colloidosome separation distance.

Figure S5. Sequence of images for two pendant microgel colloidosomes at pH 3 showing contact and separation. The colloidosomes were formed sunflower oil droplets containing PPG-TDI cross-linker (1.0 mg mL^{-1}) were exposed to a 1.6×10^{-2} wt% aqueous dispersion of 655 nm charge-stabilised PTBAEMA microgel particles with 0.1 M KNO_3 background electrolyte. The droplets were aged in isolation for 60 s before being moved into contact (Image 1). After 5 min contact, the droplets were moved apart stepwise using a linear actuator with a step size of 0.15 mm (Images 2-4). The droplets were brought back into contact following separation (Image 5) and could be separated again (Image 6).



Colloidosome vs colloidosome interactions when aged in isolation at pH 10 prior to a pH jump to pH 3

Figure S6. Sequence of images obtained for two pendant colloidosomes showing contact and separation with no inter-colloidosome cross-linking. The colloidosomes were formed when sunflower oil droplets containing PPG-TDI (1.0 mg mL^{-1}) cross-linker were exposed to a 1.6×10^{-2} wt% aqueous dispersion of charge-stabilised PTBAEMA latex with 0.1 M KNO_3 background electrolyte. Droplets were aged in isolation at pH 10 for 60 s before the pH was adjusted to 3 (Image 1) and the microgel colloidosomes were brought into contact (Image 2). After 5 mins in contact (Image 3) the droplets were moved apart step-wise using a linear actuator with a step size of 0.15 mm (Image 4). No inter-colloidosome cross-linking or coalescence was observed. The microgel colloidosomes were then brought into contact again (Image 5) for a further 5 mins before being separated (Image 6). The colloidosomes were then forced into close proximity (Image 7) for 60 s more to increase their contact area, before being separated (Image 8).



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.
2. A. J. Morse, S. Y. Tan, E. C. Giakoumatos, G. B. Webber, S. P. Armes, S. Ata and E. J. Wanless, *Soft Matter*, 2014, **10**, 5669-5681.
3. K. L. Thompson, E. C. Giakoumatos, S. Ata, G. B. Webber, S. P. Armes and E. J. Wanless, *Langmuir*, 2012, **28**, 16501-16511.