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

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The coalescence of two oil droplets grown at pH 10 in the presence of lightly cross-linked 260 nm diameter charge-stabilised poly(*tert*-butylamino)ethyl methacrylate (PTBAEMA) latexes was monitored using a high-speed video camera. Three model oils (*n*-dodecane, isopropyl myristate and sunflower oil) were investigated, each in the absence and presence of an oil-soluble cross-linker [tolylene 2,4-diisocyanate-terminated poly(propylene glycol), PPG-TDI]. In the absence of PPG-TDI, rapid coalescence was observed for giant PTBAEMA-stabilised Pickering oil droplets, which exhibited faster coalescence times compared to bare oil droplets. However, an increase in the damping coefficients for coalescing Pickering droplets (compared to those of bare oil droplets) indicated PTBAEMA latex particle adsorption. Addition of PPG-TDI cross-linker to oil droplets in the absence of latex particles led to a reduction in the interfacial tension confirming its surface-active nature. The oil-soluble PPG-TDI reacts with the secondary amine groups on the PTBAEMA latex, producing giant colloidosomes that remain stable to coalescence when brought into contact. This stability to coalescence was not observed for bare oil droplets in the presence of PPG-TDI, confirming that the cross-linked latex particles at the interface provide the additional stability. Finally, interactions between asymmetric *n*-dodecane droplets were examined. Adding oil-soluble cross-linker to only one droplet resulted in “arrested coalescence” behaviour in the presence of PTBAEMA latex particles. In this context, the droplet ageing time was found to be critical and is attributed to the slow particle adsorption kinetics. Ageing times of less than 60 s led to catastrophic droplet coalescence, whereas ageing times longer than 60 s indicated cross-linker diffusion from one droplet to the other, which produced inter-cross-linked colloidosomes. Arrested coalescence was only observed for ageing times of approximately 60 s.

Introduction

Pickering emulsions consist of colloidal particles adsorbed at the interface between two immiscible liquids (typically oil and water) thus preventing coalescence of the droplet phase.[1-3] An early report of latex-based Pickering emulsifiers was made by Velev and co-workers, with charge-stabilised polystyrene (PS) latex being utilised to stabilise 1-octanol droplets.[4] In this case, either sulphate or amidine surface groups conferred charge stabilisation. The propensity for such latex particles to self-assemble at the oil/water interface primarily depends on the particle wettability.[3] This parameter is directly related to the contact angle, θ, made by a particle when it is adsorbed at the oil/water interface. θ is always less than 90° for hydrophilic particles, which are located preferentially in the water phase; the resulting curvature favours oil-in-water emulsions. On the other hand, θ exceeds 90° for hydrophobic particles, which reside preferentially in the oil phase; this scenario inevitably leads to water-in-oil emulsions.[5, 6]

Colloidosomes are microcapsules whose shells are composed of colloidal particles that are locked in place via physical (e.g. sintering)[7-10] or chemical (e.g. cross-linking)[11-16] reinforcement, conferring additional stability to the emulsion. Pickering emulsions have been used as precursors for colloidosomes because of the close-packing of colloidal particles at the oil/water interface. The first reported case of colloidosomes was in 1996 by Velev and co-workers, who reported the adsorption of latex particles onto emulsion droplets to form hollow “supraparticles”.[4] However, the term "colloidosome" was not coined until 2002, when Dinsmore et al. sintered latexes to form permeable microcapsules made up of micrometre-sized polystyrene latex.[7] Colloidosomes have also been obtained by utilising surface functional groups on sterically-stabilised latexes to covalently cross-link the particles at the oil/water interface.[11] This method removes the need for an internal aqueous gelator,[17] and also the high temperatures required for sintering.[18] Walsh et al. recently demonstrated this concept by using a styrene-functionalised poly(ethylene imine) macromonomer for the emulsion polymerisation of styrene in order to prepare PEI-PS latexes, which in turn stabilise o/w emulsions.[19] The amine-functional stabiliser chains were subsequently cross-linked using an oil-soluble cross-linker [tolylene 2,4-diisocyanate-terminated poly(propylene glycol), PPG-TDI] to form urethane bonds and hence obtain robust colloidosomes.

The use of cross-linked poly(tert-butylamino)ethyl methacrylate (PTBAEMA) latexes as Pickering emulsifiers has also been examined.[20] The pK_a of these particles was determined to be 7.8 by acidic titration. Thus stable Pickering emulsions were only formed when homogenisation was carried out above this pK_a. PTBAEMA latex particles were found to stabilise *n*-dodecane, isopropyl myristate and sunflower oil. The only notable difference between the three oils was the higher viscosity associated with the sunflower oil, which led to longer creaming time frames (> 30 mins vs ~10 mins for *n*-dodecane and isopropyl myristate). All Pickering emulsions were found to be stable on standing at 20 °C for more than six months.

Ata has monitored the stability and coalescence of two immobilised pendant bubbles or droplets using high-speed video microscopy.[21] Initial investigations focused on model froth flotation systems. For example, the coalescence of air bubbles coated with 66 µm diameter glass beads was examined.[22] The post-coalescence dynamic oscillations were recorded at up to 3700 frames·s^{-1}, from which the projected area of the coalesced bubble was monitored and modelled as a simple harmonic function from which a damping coefficient was determined.

Single giant pendant Pickering droplets consisting of polystyrene latexes adsorbed from aqueous solution to the *n*-decane/water interface were reported by Ashby et al.[23] These particle-stabilised droplets were able to be transferred through a planar oil/water interface resulting in a pendant water-oil-water colloidosome. The oil film supporting the latex monolayer required neither sintering, nor cross-linking, being sufficiently robust itself to maintain the colloidosome intact. The interaction of two mm-sized Pickering droplets and giant colloidosomes has recently been reported by Thompson et al.[24] Here poly(glycerol monomethacrylate)-stabilised polystyrene (PGMA50-PS) latex particles were adsorbed at the *n*-dodecane/water and sunflower oil/water interface to form Pickering droplets, which could then be converted into colloidosomes by the addition of PPG-TDI to the oil phase. A previous study on the formation of conventional (as opposed to giant) colloidosomes with the same sterically-stabilised latex indicated complete coverage of the oil/water interface for both oils.[11] Thompson et al. reported that the latex particle size impacted the stability of the Pickering droplets as judged by the coalescence time, with larger particles (902 nm diameter) conferring greater stability than smaller particles (135 nm diameter). It was also evident that droplets coated with the larger latex exhibited a broader range of coalescence times. However, the particle size did not impact the post-rupture dynamics. The effect of particle size on the Pickering droplet stability is the result of interactions in the contact zone between the two droplets. The particles represent a steric barrier to thin film drainage in the contact zone and hence retard the rupture of the oil/water/oil interface; larger particles create a higher steric barrier and thus are more effective stabilisers. Longer coalescence times were also reported when using sunflower oil compared to *n*-dodecane. This is because of the higher viscosity of the former oil, which also retards the rate of thin film drainage. Coalescence was attributed to defects in the particle packing, which enables extensive local drainage of the thin film separating the two droplets.

Thompson et al. also reported the effect of addition of PPG-TDI cross-linker to the sunflower oil to create giant colloidosomes.[24] For short cross-linking times (2 – 10 min) the coalescence of interacting pairs of droplets was not prevented, although the stability of the drops was enhanced relative to the Pickering (PPG-TDI-free) droplets. When cross-linking was allowed to proceed for more than 20 min, the giant colloidosomes were rendered permanently stable, as the cross-linked network of particles at the interface was sufficiently extensive to prevent coalescence. Even in the case of an asymmetric interaction (whereby only one sunflower oil droplet contained PPG-TDI), coalescence of the two droplets in contact was still prevented. Interestingly, when these two droplets were manually separated, a filament of cross-linked particles formed a bridge between the two droplets. This filament formed in the contact zone of the two droplets, and was attributed to the transfer of PPG-TDI between the droplets through the contact zone. The complete coverage and close-packed nature of the latex particles at the oil/water interface meant that the ends of the filament remained in a fixed position as the drops were pulled apart, resulting in extension of the filament connecting the two droplets.

Arrested coalescence is an intermediate stage that occurs between complete coalescence and the stabilisation of two droplets.[25-29] This phenomenon is observed if the rheological resistance of a droplet offsets the Laplace pressure driving force for coalescence.[30] Arrested coalescence requires initial coalescence to occur, followed by stabilisation via either coalescing droplet. Pawar et al. observed arrested coalescence for a silica-stabilised *n*-hexadecane-in-water emulsion.[30] These workers found that the particle surface coverage (Φ) was the most important parameter.[30] If the *n*-hexadecane droplets had a relatively high surface coverage (Φ ~ 90 %) of silica particles, then no coalescence was observed. Conversely, if the particle surface coverage was too low (Φ ~ 30%), then complete coalescence was observed. The particle surface coverage required for arrested coalescence was determined to be when Φ1 + Φ2 (i.e. the surface coverage of the respective droplets) ranged from 1.43 to 1.81.[30]

Herein we compare the interactions of pairs of Pickering emulsion droplets and giant colloidosomes formed by the adsorption of charge-stabilised PTBAEMA-based latex at the *n*-dodecane/water, isopropyl myristate/water, and sunflower oil/water interfaces. The particles were adsorbed from aqueous solution adjusted to pH 10. Addition of PPG-TDI to the oil phase cross-links the latex particles via the secondary amine functionality of the PTBAEMA. Interfacial tension measurements were performed to confirm the adsorption of particles and an oil-soluble cross-linker at the oil/water interface, while the stability of the oil droplets and post-coalescence dynamics were monitored using high speed video microscopy. Finally, the asymmetric interaction of an *n*-dodecane Pickering droplet and a covalently cross-linked *n*-dodecane colloidosome is investigated. We report for the first time the observation of arrested coalescence using our bespoke coalescence rig.

Experimental

Materials

See ESI Materials and Methods.†

Aqueous emulsion polymerisation

See ESI Materials and Methods.†

Droplet coalescence apparatus

The apparatus used in this work was reported previously for studying the coalescence of two latex-coated air bubbles[31] or oil droplets[24] in aqueous solution. Two stainless steel capillaries (inner diameter 0.41 mm and outer diameter 0.71 mm) were inserted into a beaker containing 50 mL aqueous latex dispersion and a magnetic stirrer bar. Two microsyringe pumps (Sarasota, FL) were used to produce *n*-dodecane, isopropyl myristate or sunflower oil droplets from the tips of the capillaries. Between experiments, the glassware, syringes, capillaries and stirrer bar were thoroughly cleaned using 2-propanol or ethanol to remove any oil residue and then rinsed with Millipore Milli-Q water at least ten times to remove any residual contaminants.

Coalescence data were recorded using a high-speed video camera (Phantom 5, Vision Research, USA). Images were collected using Phantom 6.30 (Nikon) software at 512 × 256 resolution. A light source was used for back illumination of the droplets.

Sample preparation

The particle suspensions were required to be of sufficiently low turbidity to enable good quality high-speed video capture. The PTBAEMA 260 nm latex (0.20 mL of a 3.9 wt % dispersion) was added to a beaker containing 50 mL of a 0.01 M KNO_3 (or 0.1 M for the sunflower oil experiments) solution at pH 10. This led to a latex concentration of 1.6×10^{-2} wt %. The stability of pure *n*-dodecane and sunflower oil droplets in neutral aqueous solution without added electrolyte has been previously reported.[24] Added electrolyte (0.1 M KCl) was needed to promote bubble instability since the coalescence of *n*-dodecane or sunflower oil droplets in pure water rarely occurred. At pH 10 the coalescence of *n*-dodecane and isopropyl myristate droplets was promoted by the lower 0.01 M electrolyte, while sunflower oil still required 0.1 M. These concentrations were used throughout so that coalescence occurred with the minimum of added salt.

Droplet coalescence procedure and data analysis

n-Dodecane, isopropyl myristate or sunflower oil was held in the two syringes and then connected to the capillaries. All air bubbles were expelled from the capillaries. The beaker containing the aqueous PTBAEMA latex dispersion and a magnetic flea (or without the addition of particles for the bare oil droplet experiments) was placed inside a rectangular Perspex vessel containing water to prevent optical distortion arising from the cylindrical surface of the beaker. The beaker was then placed on a magnetic stirrer mounted on a lab jack beneath the capillaries. 2 mL of the oil used was injected onto the water surface once the capillaries were submerged in the solution. This was required to maintain a constant surface area of the oil throughout the experiment, as well as preventing evaporation of the aqueous phase. The syringe pump rate was set to 0.3 $mL{\cdot}h^{-1}$. Oil droplets were then grown from the capillaries until approximately 1.7-2.0 mm in diameter. After ageing the droplets for an appropriate length of time, the capillaries were moved together using a linear actuator at a speed of 0.238 $cm{\cdot}s^{-1}$ until the droplets were just touching (corresponding to a capillary separation of 1.0-1.3 mm). The droplet coalescence time was measured from the moment of droplet contact until coalescence and analysed from video footage recorded at 300 $frames{\cdot}s^{-1}$. Each coalescence experiment was conducted at least ten times and the mean and standard deviation for the coalescence time was recorded. The frame rate was also increased to 6024 $frames{\cdot}s^{-1}$ to allow more detailed analysis of the post-coalescence behaviour. The projected surface area of the droplets before and after coalescence was measured as a function of time. The droplet area in each frame was analysed using Image J software and the results were plotted as the percentage change in projected area relative to the initial area of the droplets prior to coalescence.

For these experiments, if the PTBAEMA latex particles adsorbing at this concentration were to fully coat the two oil droplets in close-packed monolayers as well as the oil on the top of the aqueous phase, the fraction of particles depleted from the aqueous phase would be approximately 3 %.

Cross-linking experiments

The same protocol was used for the production of covalently cross-linked colloidosomes. The pure oil phases used in the syringes were replaced with a solution of PPG-TDI cross-linker dissolved in oil at a concentration of 0.1 $mg{\cdot}mL^{-1}$ (1.0 $mg{\cdot}mL^{-1}$

PPG-TDI was used in the case of the sunflower oil experiments in order to increase the diffusion rate of the cross-linker in this higher viscosity oil).

Asymmetric droplet coalescence experiments

The same protocol was also used to investigate asymmetric droplet interactions between a giant Pickering emulsion droplet and a covalently cross-linked giant colloidosome. Pure *n*-dodecane was placed in the fixed left-hand (stationary) syringe, while 0.1 $mg \cdot mL^{-1}$ PPG-TDI cross-linker was added to the *n*-dodecane in the right-hand syringe, which can be moved towards (or away from) the immobile left-hand droplet.

Pendant drop tensiometry

See ESI Materials and Methods.†

Oil droplet zeta potential measurements

See ESI Materials and Methods.†

Bulk viscosity measurements

See ESI Materials and Methods.†

Results and Discussion

General remarks

It is worth briefly commenting on the nature of the PTBAEMA particles used in this study.[20] The charge-stabilised PTBAEMA latex was prepared via monomer-starved aqueous emulsion polymerisation at pH 10. Such particles had a hydrodynamic diameter of 260 nm and were found to be pH-responsive, undergoing a latex-to-microgel transition below pH 7.8 to produce swollen cationic microgels of 660 nm diameter.[20] These charge-stabilised PTBAEMA latex particles adsorb at oil/water interfaces at pH 10, acting as effective Pickering emulsifiers to stabilise oil-in-water emulsions prepared using *n*-dodecane, isopropyl myristate or sunflower oil at submonolayer coverage.[20] No such emulsions were formed when homogenisation was performed below the latex pK_a, where the PTBAEMA particles exist in their cationic protonated microgel form. The secondary amine functionality on the TBAEMA residues could be reacted with an oil-soluble cross-linker (PPG-TDI). When the particles acted as a Pickering emulsifier, cross-linking between adjacent latex particles led to the formation of stable colloidosomes that were sufficiently robust to survive demulsification via an acid challenge.[32] In the current study, our investigation is focused on the interaction and stability of giant Pickering and colloidosome droplets at pH 10.

Bare oil droplet interactions

Initially, the behaviour of the pure oil/water interfaces (at pH 10) was investigated. The dynamic interfacial tensions for oil droplets at 20 °C (as calculated from pendant drop profilometry) are shown in Fig. 1, with the mean values for droplets aged for 5 min summarised in Table 1. The occasional vertical blips in the data are attributed to a temporary loss of resolution causing anomalous results. The isopropyl myristate reached its equilibrium interfacial tension within a few seconds, while *n*-dodecane needed tens of seconds and sunflower oil required approximately 100 s to reach their equilibrium values. The interfacial tension of the *n*-dodecane/water interface aged for 5 min is approximately a factor of two greater than of the isopropyl myristate oil/water interface, which is in turn approximately twice that of the sunflower oil/water interface. In addition, the interfacial tension of each oil containing PPG-TDI was measured against aqueous KNO_3 at pH 10. The PPG-TDI is highly surface-active in *n*-dodecane since a rapid and substantial lowering of the interfacial tension is observed. Surface activity is also evident when dissolved in both isopropyl myristate and sunflower oil, for which a slower lowering of the interfacial tension occurs, see Fig. 1. However, for interfaces aged for 5 min, in the case of sunflower oil this decrease is not significant (see Table 1). Lowering of the oil/water interfacial tension on dissolving PPG-TDI in either *n*-dodecane or sunflower oil (albeit in the absence of electrolyte and without pH adjustment) has been recently reported by Thompson et al.[24]

Table 1. Influence of oil type and oil-soluble cross-linker (PPG-TDI) on the interfacial tension, coalescence time and damping coefficient of pendant oil droplets grown in aqueous electrolyte at pH 10. Oil droplets were 1.7 to 2 mm in diameter.

Interface	Interfacial tension after 5 min equilibration ($mN \cdot m^{-1}$)	Coalescence time (s)	Damping coefficient (ms^{-1})
n-Dodecane/aqueous 0.01 M KNO_3	39.7 ± 0.1	7.0 ± 3.2	0.0414 ± 0.002
(*n*-Dodecane + PPG-TDI)/aqueous 0.01 M KNO_3	13.6 ± 0.7	8.0 ± 4.7	0.0757 ± 0.008
Isopropyl myristate/aqueous 0.01 M KNO_3	18.2 ± 0.2	8.2 ± 4.8	0.0400 ± 0.003
(Isopropyl myristate + PPG-TDI)/aqueous 0.01 M KNO_3	13.9 ± 0.8	15.8 ± 3.3	0.0424 ± 0.002
Sunflower oil/aqueous 0.1 M KNO_3	7.4 ± 0.4	26.6 ± 2.5	N/A
(Sunflower oil + PPG-TDI)/aqueous 0.1 M KNO_3	7.3 ± 0.1	30.1 ± 3.8	N/A

The addition of electrolyte is required to overcome the build-up of negative charge on the oil surface via the adsorption of hydroxide ions from solution,[33, 34] leading to the formation of relatively stable anionic droplets. For example, the zeta potential of bare *n*-dodecane droplets in water has been reported to be -58 ± 7 mV.[35] Significantly higher zeta potential values of bare oil droplets were measured at pH 10: -90 ± 10 mV (*n*-dodecane), -92 ± 6 mV (isopropyl myristate) and -102 ± 4 mV (sunflower oil). Therefore, in the current work background electrolyte was added to promote coalescence of bare oil droplets. The droplet coalescence times were determined as shown in Table 1 and can be correlated with both

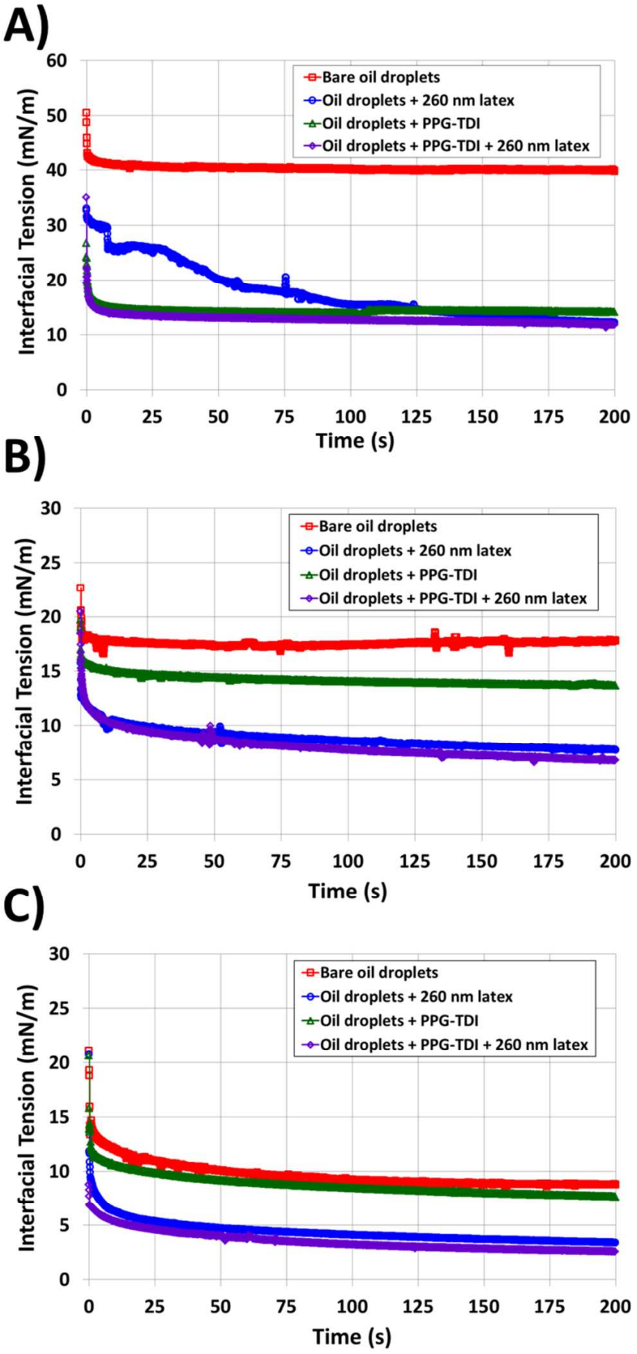

Fig. 1. Dynamic interfacial tension of (A) *n*-dodecane (0.01 M KNO_3 background electrolyte), (B) isopropyl myristate (0.01 M KNO_3 background electrolyte) and (C) sunflower oil (0.1 M KNO_3 background electrolyte) in the absence (□) and presence (○) of a 3.8×10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex 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 latex particles and PPG-TDI (◊). The aqueous phase was at pH 10 in each case.

interfacial tension and surface charge (as measured by zeta potential). Lower interfacial tension necessarily means the droplet has less energy per unit area and hence a weaker tendency to undergo coalescence, while the higher surface charge provides a greater electrostatic barrier to coalescence; both effects lead to longer coalescence times. As far as we are aware, this is the first report of the high speed video analysis of isopropyl myristate droplets in aqueous solution. Thus images of the coalescence behaviour of pure isopropyl myristate droplets (at pH 10) are shown in Fig. S1 in the ESI.†

Droplet coalescence for all three oils was observed in the presence of electrolyte, with the resulting single droplet undergoing dynamic oscillations until the excess energy is dissipated into the aqueous phase. Analysis of the oscillatory behaviour for these bare oil droplets was achieved by a frame-by-frame examination of the video footage and recording the change in the projected surface area as a function of time, see □, Fig. 2. When present, the oscillatory behaviour was fitted to a damped simple harmonic oscillator with a damping coefficient.[22] The damping coefficients of the two oil droplet coalescence events were calculated to be 0.0414 and 0.0400 ms^{-1} for the *n*-dodecane and isopropyl myristate interfaces, respectively. The damping coefficient for *n*-dodecane is similar to that reported by Thompson et al. in the presence of 0.1 M KCl at neutral pH.[24] The coalescence dynamics of the sunflower oil shown in Fig. 2C exhibit significantly higher damping than reported by Thompson et al., and is attributed to the higher pH used in the current investigation (pH 10). Here, the data for sunflower oil could not be accurately modelled by a simple harmonic oscillator function. Sunflower oil contains a mixture of fatty acids, including palmitic, stearic, oleic and linoleic acids, all of which have pK_a values lying in the range 8 – 10.[36] At pH 10, these fatty acids are likely to be surface-active and hence adsorb at the oil/water interface, as suggested by slow equilibration and the low interfacial tension of the sunflower oil/water interface in Fig. 1. For reference, the interfacial tension of sunflower oil in neutral water was reported to be 21.3 ± 1.6 mN·m^{-1}.[24] A recent study using the same experimental set-up was reported by Bournival et al., who demonstrated that surfactant adsorption at the air bubble/water interface led to enhanced damping of the post-coalescence dynamics.[37] For comparison, the droplet coalescence dynamics at pH 10 and pH 3 for each oil are shown in Fig. S2 in the ESI.†

The addition of PPG-TDI increased the coalescence time in all three oils, indicating adsorption of this cross-linker and concomitant enhanced droplet stability (see Table 1). The presence of PPG-TDI also has an effect on the oscillatory behaviour of the coalescing oil droplets, see Δ, Fig. 2. The calculated damping coefficients for the PPG-TDI/oil solutions are 0.0757 and 0.0424 ms^{-1} for the *n*-dodecane and isopropyl myristate interfaces, respectively (see Table 1). The large increase in damping coefficient observed for the coalescing *n*-dodecane droplets is attributed to PPG-TDI adsorption, as reported for adsorbed surfactant on coalescing air bubbles in water.[37] In comparison, the increase in damping coefficient for isopropyl myristate is significantly lower. Combined with the interfacial tension data obtained in the absence and presence of PPG-TDI (see Fig. 1 and Table 1), this indicates that PPG-TDI adsorbs more readily to the *n*-dodecane interface. Once again, the highly damped coalescence dynamics of the sunflower oil in the presence of PPG-TDI is not consistent with a simple harmonic oscillator model.

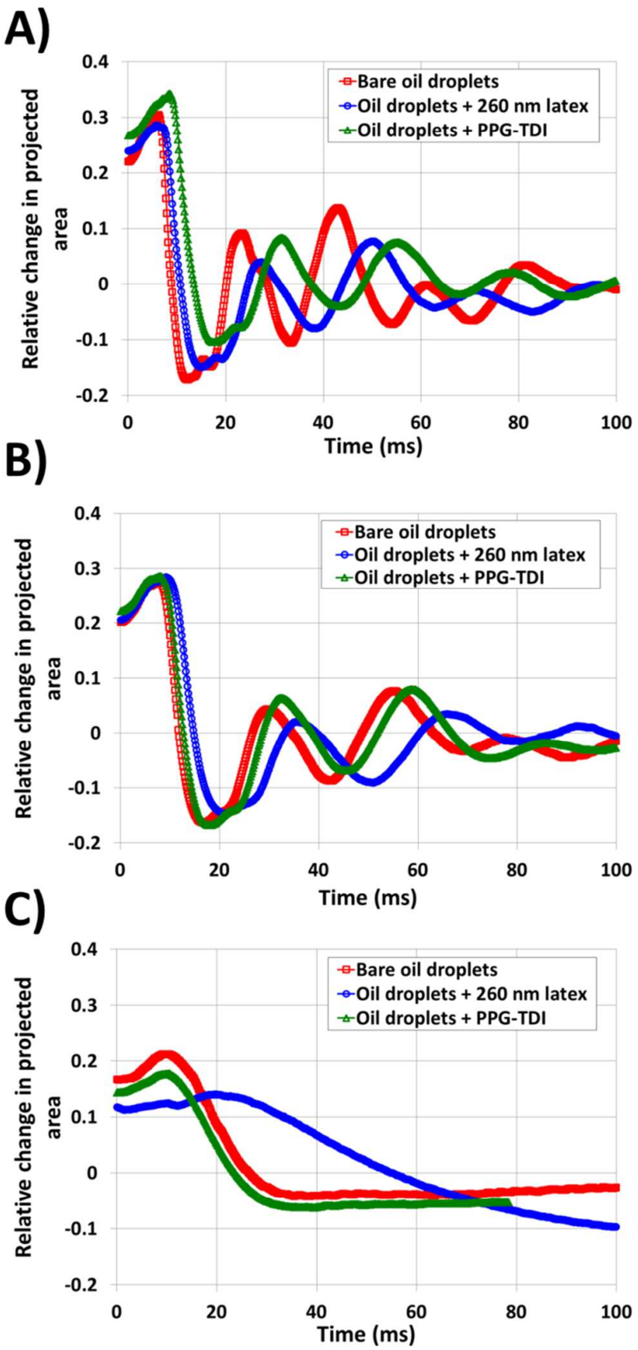

Fig. 2. Comparison of the coalescence dynamics of pairs of (A) *n*-dodecane (0.01 M KNO_3 background electrolyte), (B) isopropyl myristate (0.01 M KNO_3 background electrolyte) and (C) sunflower oil (0.1 M KNO_3 background electrolyte) droplets in the absence (□) and presence (○) of a 1.6 × 10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles, as well as bare oil-droplets in the presence of an oil-soluble cross-linker, PPG-TDI (△). All were conducted at pH 10.

Pickering droplet interactions

Following investigation of the bare oil/aqueous solution interfaces, PTBAEMA latex particles were added to the aqueous electrolyte solution at pH 10. As stated previously, analogous latexes have been previously shown to be efficient Pickering emulsifiers for each of the oils used in this study.[20] The latex concentration used produced a sufficiently low turbidity to allow clear visualisation of the oil droplets. Dynamic interfacial tension data for the three oils in the presence of PTBAEMA latex particles are presented in Fig. 1 with the mean values for Pickering droplets aged for 5 min summarised in Table 2.

Table 2. Influence of oil type and oil-soluble cross-linker (PPG-TDI) on the interfacial tension, coalescence time and damping coefficient of pendant oil droplets grown in the presence 260 nm charge-stabilised PTBAEMA in aqueous electrolyte at pH 10. Oil droplets were 1.8 to 2 mm in diameter.

Interface	Interfacial tension after 5 min equilibration ($mN{\cdot}m^{-1}$)	Coalescence time (s)	Damping coefficient (ms^{-1})
n-Dodecane/aqueous 0.01 M KNO_3	12.2 ± 0.1.1	2.5 ± 0.7	0.0529
(*n*-Dodecane + PPG-TDI)/aqueous 0.01 M KNO_3	10.2 ± 0.7	No coalescence	No coalescence
Isopropyl myristate/aqueous 0.01 M KNO_3	7.3 ± 0.1	1.6 ± 0.3	0.0506
(Isopropyl myristate + PPG-TDI)/aqueous 0.01 M KNO_3	6.3 ± 0.1	No coalescence	No coalescence
Sunflower oil/aqueous 0.1 M KNO_3	2.7 ± 0.6	3.9 ± 0.7	N/A
(Sunflower oil + PPG-TDI)/aqueous 0.1 M KNO_3	2.9 ± 0.5	No coalescence	No coalescence

The true physical meaning of such interfacial tension data is somewhat controversial,[38, 39] but it is clear that the oil droplet profiles change significantly in the presence of a gently stirred dispersion of the latex particles: this is attributed to particle adsorption at the oil/water interface. These observations are particularly evident for the *n*-dodecane droplets, where both particle adsorption and interfacial rearrangements could be responsible for the substantial reduction in interfacial tension and slow equilibration (which required at least 200 s). In the case of the other two oils, the magnitude of the reduction in interfacial tension is less which may indicate that fewer particles are adsorbed, although the total equilibration times were similar, which suggests relatively slow particle adsorption kinetics in all three oils.

Coalescence of giant PTBAEMA latex-stabilised Pickering droplets brought into contact in pH 10 aqueous electrolyte was observed for all three oils. A schematic representation of the coalescence of Pickering droplets is shown in Route A, Fig. 3. Interestingly, the coalescence times for each of the three oils were significantly shorter in the presence of the latex than for the bare oil droplets, see Table 2. We attribute this reduction in oil droplet coalescence time to the surface-active PTBAEMA latex particles acting as a film-draining agent by bridging the two oil droplets when these are brought into contact.[24] Previous work has demonstrated that PTBAEMA latex stabilises

Pickering emulsions even at sub-monolayer coverage, and that a significant proportion of the particles do not adsorb even when utilising latex concentrations much lower than that required for monolayer coverage.[20] We believe that the PTBAEMA latex particles do not adsorb onto the pendant oil drops in a close-packed arrangement, as observed previously for the PGMA50-PS latex particle.[11] Consequently, the adsorbed layer of PTBAEMA latex will inevitably contain packing defects,[40] enabling rapid thin film drainage and driving coalescence.[24] This is supported by the relatively slow adsorption kinetics indicated by the dynamic interfacial tension data shown in Fig. 1. The data in Table 2 indicate that, on average, the more viscous sunflower oil droplets take slightly longer to coalesce than the other two oils. This is believed to be the result of the hindered particle rearrangement, leading to overall slower film drainage and the reduced probability of film rupture.[24] The reason why the PTBAEMA latex particles are able to stabilise conventional Pickering emulsions prepared with these oils in bulk solution but do not prevent coalescence in the present study can be explained by the geometry of the interaction. In the case of bulk Pickering emulsions, droplet diameters are less than 150 µm. As such, the contact zone between droplets is highly curved and a substantial Laplace pressure (~1/r) prevents coalescence. Additionally, adsorption of charged particles to an oil/water interface enhances the effect of the electrical double layer, increasing repulsion between the interfaces.[41] For the ~2 mm droplets used in the coalescence rig, which are mechanically forced into contact (overcoming any electrostatic repulsion), the contact zone is almost planar, so the Laplace pressure is substantially reduced.[24]

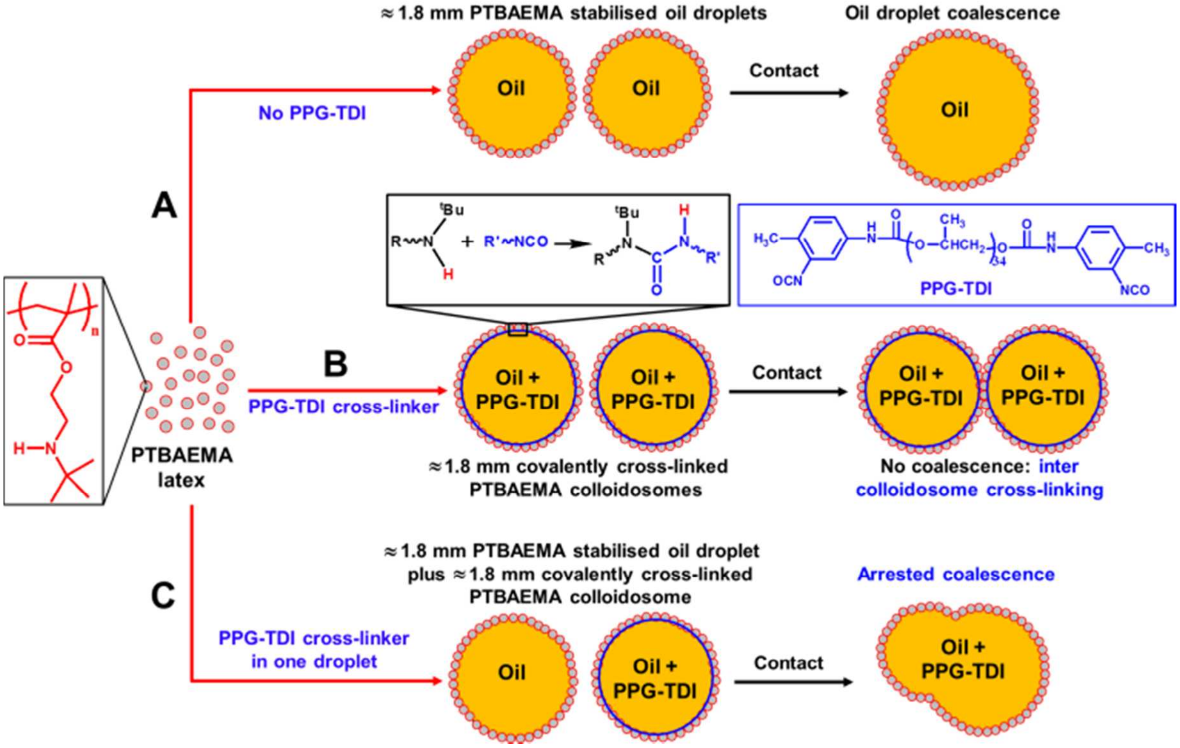

Fig. 3. Reaction scheme for the formation of: (A) Pickering emulsion droplets and their subsequent coalescence upon contact (oil = *n*-dodecane, isopropyl myristate or sunflower oil); (B) covalently cross-linked colloidosomes obtained using an oil-soluble PPG-TDI cross-linker and their subsequent inter-colloidosome cross-linking upon contact. (oil = *n*-dodecane, isopropyl myristate or sunflower oil); (C) a Pickering emulsion droplet and a covalently cross-linked colloidosome and their subsequent arrested coalescence upon contact (oil = *n*-dodecane). All droplets were coated with charge-stabilised PTBAEMA latex particles adsorbed from aqueous solution at pH 10. *Note: For simplicity, this Schematic shows monolayer coverage of the oil droplets by the PTBAEMA latex particles. It is not known whether full coverage is actually achieved in practice after extended droplet ageing, nor whether the same particle coverage is achieved on the three different oil interfaces. The surface coverage may be different from that achieved previously in the bulk emulsion study.*[20]

Sequences of images showing the coalescence of two *n*-dodecane, isopropyl myristate and sunflower oil droplets in the presence of 260 nm charge-stabilised PTBAEMA latex particles are shown in Fig. 4. Comparison of the oscillatory behaviour shown in images 2-10 highlights the difference in post-rupture motion between sunflower oil and the other two oils. For example, the coalescing *n*-dodecane and isopropyl myristate droplets deform to produce regions of high curvature (Fig. 4A and B, Image 3), with subsequent substantial deformation in the vertical direction (Fig. 4A and B, Image 5 and 6). On the other hand, it is clear that the two sunflower droplets coalesce to a single drop with minimal deformation. Additionally, examination of the time scales indicated in Fig. 4 confirms that the coalescence event is much slower for sunflower oil. This behaviour is attributed to the greater viscosity of this oil, and a frame-by-frame analysis of the video footage allows the corresponding coalescence dynamics to be assessed (see ○, Fig. 2C). This figure confirms significant

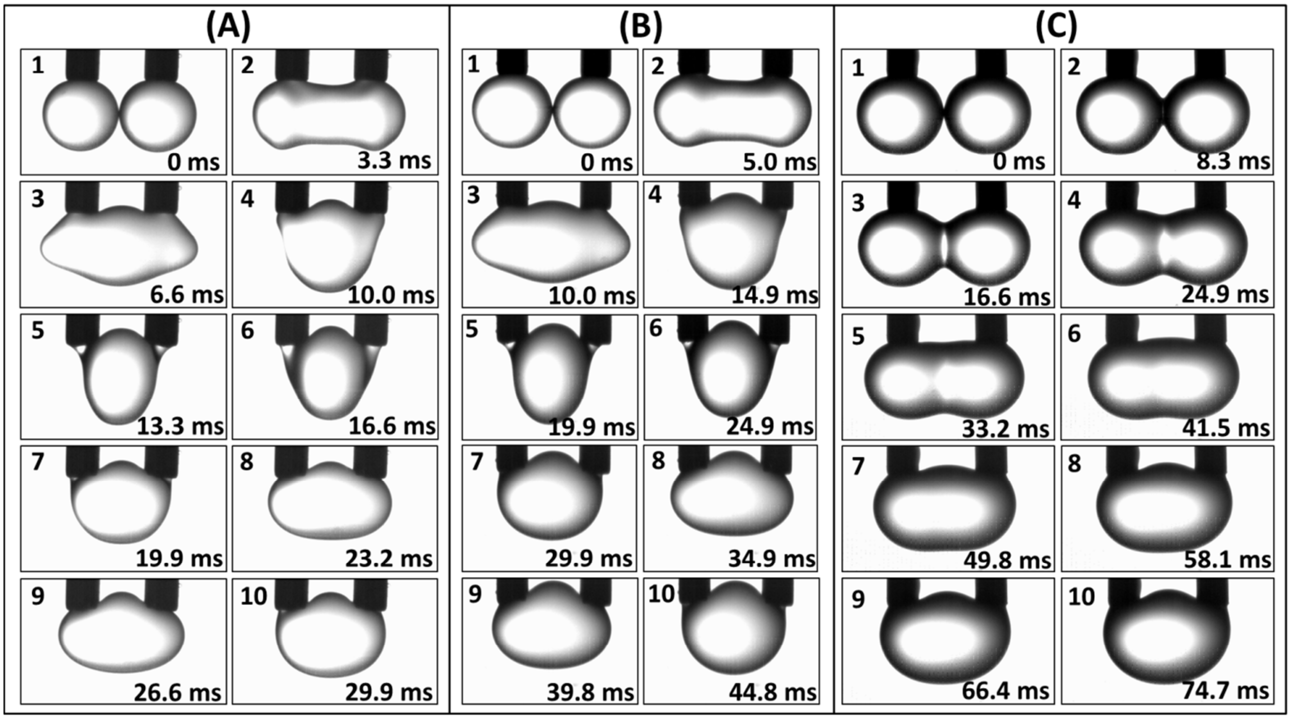

Fig. 4. Sequence of images recorded for coalescing; (A) *n*-dodecane (images shown for every twentieth frame), (B) isopropyl myristate (images shown for every thirtieth frame) and (C) sunflower oil (images shown for every fiftieth frame) in the presence of a 1.6×10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 (0.01 M KNO_3 background electrolyte for *n*-dodecane and isopropyl myristate, 0.1 M for sunflower oil). The outer diameter of the capillaries is 0.71, mm which acts as an appropriate scale bar.

damping of the coalescence dynamics in the presence of PTBAEMA latex particles when compared to bare sunflower oil. A notable change in the coalescence dynamics is also observed for *n*-dodecane and isopropyl myristate (see ○, Fig. 2A and 2B). This confirms adsorption of the latex at the respective oil/water interfaces.

Furthermore, when the oscillatory data for coalescing *n*-dodecane and isopropyl myristate Pickering droplets are fitted to a damped simple harmonic oscillator function, the damping coefficients increased relative to bare droplets (0.0529 ms^{-1} and 0.0506 ms^{-1} for *n*-dodecane and isopropyl myristate droplets, respectively). Thus the adsorbed particles exhibit similar behaviour to that associated with adsorbed surfactant, i.e. reduced interfacial tension and greater damping of post-rupture oscillations. While the coalescence dynamics for sunflower oil exhibited immediate damping in the presence of latex, a simple harmonic model could not be applied to this data set owing to the absence of any oscillation in the projected area during coalescence (see Fig. 2C). This is in contrast to observations made by Thompson et al., who reported that the higher viscosity of sunflower oil masked the effect (if any) of sterically-stabilised polystyrene latex adsorbed from neutral aqueous electrolyte.[24] However, in the current study, the adsorption of PTBAEMA latex from aqueous electrolyte at pH 10 causes discernible damping of the coalescence dynamics of all three oils investigated.

Colloidosome vs colloidosome interactions

Cross-linking of PTBAEMA latex particles occurs via the secondary amine group on the TBAEMA residues, which reacts with the terminal isocyanate groups of the oil-soluble PPG-TDI cross-linker.[32] When the particles are adsorbed at the oil/water interface, this covalent cross-linking confers additional stability to the Pickering emulsion, locks the latex particles together at the oil/water interface and results in covalently cross-linked colloidosomes (see Route B, Fig. 3).[32] Such PTBAEMA-stabilised colloidosomes have been shown to withstand demulsification following an acid or ethanol challenge, confirming their greater stability relative to PTBAEMA-stabilised Pickering emulsions prepared in the absence of PPG-TDI. In contrast, Pickering emulsions rapidly demulsified under the same acidic conditions.[20] However, reaction between the secondary amine group and the isocyanate was extremely fast, requiring high-shear homogenisation (in order to form Pickering emulsions) to be conducted at around 0 °C (with the aid of an ice bath).[42] Such low temperatures were not accessible in the current study. Initial experiments conducted using the same cross-linker concentration as the previous bulk studies (1.0 $\text{mg}\cdot\text{mL}^{-1}$ PPG-TDI in *n*-dodecane) rapidly produced giant, non-spherical colloidosomes during droplet growth. Therefore the lower concentration of 0.1 $\text{mg}\cdot\text{mL}^{-1}$ PPG-TDI was chosen, which produced 1.7-2.0 mm spherical colloidosomes that proved suitable for investigation of droplet coalescence behavior when brought into contact. This lower PPG-TDI concentration was also used for cross-linking the isopropyl myristate Pickering droplets. However, the greater viscosity of the sunflower oil meant that the higher PPG-TDI concentration of 1.0 mg·mL^{-1} was required in order to increase the rate of diffusion of the cross-linker to the oil/water interface and ensure effective colloidosome formation.

Droplets of oil containing dissolved PPG-TDI grown in the presence of charge-stabilised PTBAEMA latex particles at pH 10 and immediately brought into contact did not coalesce. Furthermore, no droplet coalescence occurred even after being held in contact for greater than 10 min. This behaviour was observed for all three oils, and is in stark contrast to the behaviour of the oil droplets in the presence of solely latex particles or PPG-TDI, where coalescence was always observed. This resistance to coalescence suggests that the interfacial reaction between the PTBAEMA and the cross-linker is sufficient to produce a robust latex shell in the contact zone between the two impinging droplets. Aqueous film drainage can still occur between the droplets and indeed may promote particle rearrangement, but coalescence is prevented by the presence of both the cross-linked adsorbed particles and the adsorbed PPG-TDI, providing stability for any packing defects present within the contact zone. It should be emphasised that no droplet ageing was required prior to contact (apart from the 10-15 s required to grow and then move the droplets into contact) to produce robust colloidosomes that resist coalescence. The dynamic interfacial tension data shown in Fig. 1 confirms the dominant effect of PPG-TDI adsorption in the 15 s following droplet formation. The lack of droplet coalescence thus confirms the relatively fast reaction between adsorbed PTBAEMA latex particles and PPG-TDI cross-linker at the oil-aqueous solution interface. This is in striking contrast to analogous experiments conducted using PGMA50-PS latex particles by Thompson et al., where ageing times of more than 20 min were required before the sunflower oil droplets became sufficiently robust to withstand coalescence.[24] It should be noted that the *n*-dodecane colloidosomes could subsequently be moved apart without colloidosome fusion. However, the isopropyl myristate and sunflower oil droplets underwent some colloidosome fusion even with this short lifetime. This difference in the interfacial behaviour of *n*-dodecane compared to the other two oils is consistent with stronger PPG-TDI adsorption and the qualitatively different approach to equilibrium for the particle-coated *n*-dodecane interface shown in Fig. 1.

Interestingly, the behaviour of droplets coated with cross-linked PTBAEMA latex exhibit a strikingly different dependence on ageing time than the PS-based colloidosomes described by Thompson et al.[24] In the current study, when the oil droplets were first aged (> 60 s) in isolation, followed by colloidosome contact for at least 30 s, an independent increase in the area of contact between the two colloidosomes was observed. This was apparent for all three oils (see images 1-3, Fig. 5A-C). This increase in contact area is also manifested by a decrease in the contour length between the two capillaries; that is, the distance from the left capillary tip to the right capillary tip, via the top of the contact area on the oil droplets, see Fig. 6 and Fig. S3 in the ESI.† As the droplets have not deformed, this decrease in contour length at fixed capillary separation must be a consequence of an increased contact area. This increase in contact area suggests that inter-colloidosome adhesion and possibly, fusion has occurred.[24] Images 4-10 in Fig. 5A-C show that the contact area becomes cross-linked during the 5 min contact period, and stretches as the colloidosomes are moved further apart to produce a distinctive neck between the two initial droplets. This suggests that the oil (and thus the cross-linker) can penetrate the contact zone and cross-link the latex particles at the surface of the adjacent droplet. The longer ageing time allows further adsorption of PTBAEMA latex particles prior to colloidosome contact, as supported by the relatively slow dynamic interfacial tension kinetics shown in Fig. 1. Coupled with the rapid rate of the cross-linking reaction, it is likely that the interface of each colloidosome contains a large number of extensively cross-linked latex particles within the contact zone. The relatively low glass transition temperature (T_g) of the PTBAEMA latex which promotes film formation enhances inter-droplet fusion within the contact zone. Prior attempts to obtain high-quality SEM images of the colloidosome shell structure concluded that a combination of the low T_g (38.5 °C),[20] and hydroplasticisation resulted in film formation of the cross-linked latexes at the oil/water interface.[32]

The neck connecting the two aged *n*-dodecane-based colloidosomes was not broken when the capillaries were moved to a separation distance nearly three times their original position, Fig. 5A Image 10. Instead, as the capillaries are separated, the contour length increased with inter-capillary separation (see ■, Fig. 6). This may indicate sub-monolayer coverage of the relatively soft latex particles combined with plasticisation of the PTBAEMA latex particles, which cannot offer robust structural integrity. In addition, this film-forming shell allows the spherical droplet to undergo deformation when separated. In comparison, the cross-linked connecting filament observed for the PGMA$_{50}$-PS latex/sunflower oil system did not move on the interface due to the close-packed nature of the cross-linked high T_g latex shell.[11] Interestingly, as the capillaries are separated even further, the neck between the *n*-dodecane-based colloidosomes does not rupture. Rather, one colloidosome becomes detached from its capillary (the left-hand stationary colloidosome detaches as the right-hand capillary is moved further apart).

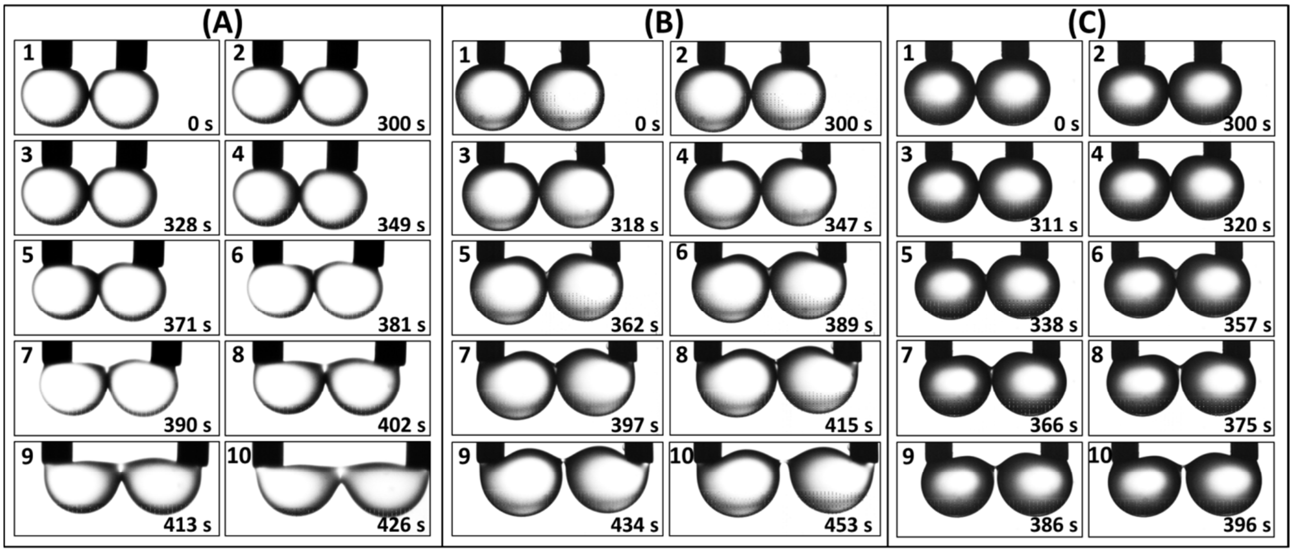

Fig. 5. Sequence of images of two pendant colloidosomes on moving apart. The colloidosomes were formed when (A) *n*-dodecane, (B) isopropyl myristate or (C) sunflower oil droplets containing PPG-TDI cross-linker (0.1 mg·mL^{-1} for *n*-dodecane and isopropyl myristate, 1.0 mg·mL^{-1} for sunflower oil) 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 for *n*-dodecane and isopropyl myristate, 0.1 M for sunflower oil). The 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 (Images 3-10). In (B) and (C), the neck joining the two colloidosomes broke upon further moving the needles apart.

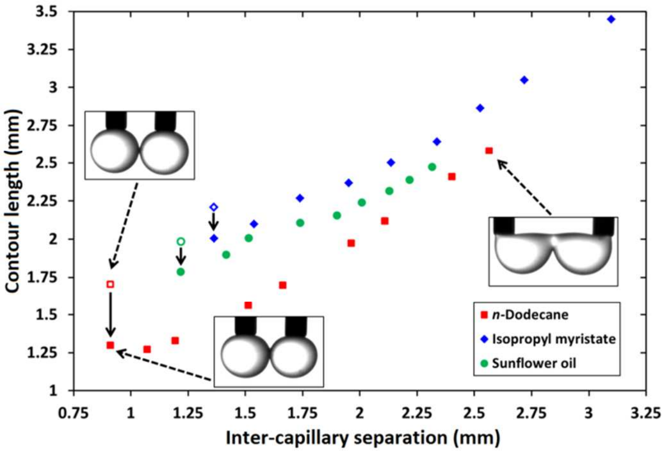

Fig. 6. Correlation of the colloidosome contour length (measured between capillary tips via the contact area) for *n*-dodecane (■), isopropyl myristate (◆, both 0.01 M KNO_3 background electrolyte) and sunflower oil (●, 0.1 M KNO_3 background electrolyte) with inter-capillary separation as the droplets were moved apart following cross-linking. The solid arrows from the first hollow points (t = 0 s) to the second points (t = 300 s) show a decrease in the contour length with no increase in the inter-capillary separation. Inset: digital images for *n*-dodecane following inter-capillary separation (dashed arrows to indicate specific points).

Similar neck formation between giant colloidosomes was observed when isopropyl myristate or sunflower oil was used as the oil phase. Fig. 5B shows a sequence of images recorded for two colloidosomes prepared using isopropyl myristate as the oil phase. The colloidosomes were aged for 60 s before being brought into contact. Like *n*-dodecane, no coalescence was observed when the colloidosomes were in contact for 5 min (see images 1 and 2, Fig. 5B). Again, colloidosome fusion connecting the two pendant colloidosomes can be observed as the capillaries are separated (see images 3-5, Fig. 5B). A neck connecting the two colloidosomes can be seen (images 6-10, Fig. 5B), which extends as the capillaries are separated. As the distance between the capillaries was increased, the neck between the isopropyl myristate droplets elongates further, and the contour length increases (see ♦, Fig. 6). Unlike *n*-dodecane, no colloidosome detachment from either capillary was observed. Instead the neck connecting the two pendant colloidosomes snapped upon further separation of the needles.

Fig. 5C shows the behaviour of sunflower oil-based colloidosomes. As with the previous two oils, these colloidosomes were aged for 60 s before contact. No coalescence is observed when the colloidosomes were left in contact for 5 min. As for *n*-dodecane and isopropyl myristate, the contour length decreases over this time period, suggesting that some adhesion has occurred as the colloidosome contact area has increased. Neck formation is observed following separation of the capillaries (see images 3-10, Fig. 5C). As the capillaries are separated, the neck between the colloidosomes extends, and the contour length increases (see ●, Fig. 6). However, the sunflower oil neck is readily broken on moving the capillaries further apart, which is similar to the behaviour observed by Thompson et al. for PGMA50-PS latex-stabilised colloidosomes prepared with sunflower oil.[24]

The similarity in the behavior of the neck formed between isopropyl myristate and sunflower oil colloidosomes, and their difference compared to *n*-dodecane, is attributed to the extent of PPG-TDI adsorption at the respective oil/water interfaces. Both the interfacial tensions (Fig. 1) and damping coefficients (Table 1) suggest that PPG-TDI has a greater affinity for the *n*-dodecane/water interface compared to the other two oil/water interfaces. This means that the rate of cross-linking is likely to be faster for the *n*-dodecane-based colloidosomes. Thus the

PTBAEMA latex particles form relatively fewer, but more extensively cross-linked, 'rafts' when using *n*-dodecane, as compared to either isopropyl myristate or sunflower oil. This means that the inter-droplet fusion must occur across a large number of adsorbed particles. Indeed, it is clear from Fig. 5A that the diameter of the neck between the colloidosomes is comparable to the size of the original contact area (compare, for example, images 3 and 10 in Fig. 5A). In the case of isopropyl myristate and sunflower oil, the slower rate of cross-linking means that the 'rafts' of cross-linked, fused latex particles are smaller. This produces a thinner, structurally weaker neck between colloidosomes prepared using these two oils.

Asymmetric droplet interactions

Asymmetric coalescence experiments were conducted to investigate how a PTBAEMA-stabilised giant Pickering emulsion droplet interacts with a PTBAEMA-based giant colloidosome as shown schematically in Route C of Fig. 3. The interactions of bare *n*-dodecane droplets (one droplet prepared in the absence (left) and one droplet prepared in the presence (right) of 0.1 mg·mL^{-1} PPG-TDI cross-linker) at pH 10 were examined prior to the addition of PTBAEMA latex particles. The asymmetric coalescence of these bare droplets can be observed in Fig. 7B. The energy of the post-coalescence dynamics deforms the PPG-TDI-loaded right-hand droplet significantly more than the non-cross-linked left-hand droplet, see Images 2 and 3 in Fig. 7B. This can be attributed to the substantially lower interfacial tension of the right-hand droplet resulting from the adsorption of the surface-active PPG-TDI at the *n*-dodecane/aqueous interface (see Fig. 1A and Table 1). In addition, the dilational viscosity of isolated pendant droplets increased two-fold from 0.8 to 1.6 mN·m^{-1} when PPG-TDI was added to the *n*-dodecane. The dilational viscosity is derived from the phase lag in the oscillated single droplet and can be related to the rate of exchange of matter between the interface and the bulk.[43] The large deformation of the right-hand droplet supports the rapid exchange of PPG-TDI between the interface and the bulk of this droplet. The mean coalescence time for these bare *n*-dodecane droplets was determined to be 1.8 ± 0.3 s. This reduced stability relative to either of the symmetric systems is attributed to the fast diffusion of PPG-TDI from the right-hand to the left-hand droplet upon contact, which is consistent with the rapid reduction in interfacial tension resulting from the high interfacial activity of PPG-TDI in *n*-dodecane as shown in Fig. 1A. The oscillatory behaviour (see □, Fig. 7A) was fitted to a damped simple harmonic oscillator model (as described above) and the damping coefficient was calculated to be 0.049 ms^{-1}. This is intermediate between that determined for the two interacting bare *n*-dodecane droplets and that calculated for the two PPG-TDI-loaded *n*-dodecane droplets (see Table 1).

When the PTBAEMA latex particles were added to the system at pH 10, complete coalescence was observed provided that the droplets were not subjected to any ageing (other than the 10-15 s required to grow the oil droplets) prior to being brought into contact. The images obtained during coalescence were similarly asymmetric in nature to those obtained for the asymmetric coalescence of the bare *n*-dodecane droplets, see Fig. 7C and support a low population of adsorbed particles as supported by the slow kinetics of particle adsorption implied by Fig. 1A. The mean coalescence time without any ageing was 4.8±0.8 s in the presence of the PTBAEMA latex particles. As expected this is greater than the 2.5 s measured for the interaction of two Pickering droplets (see Table 2) and indicates the onset of interfacial particle cross-linking. The oscillatory behaviour (see ○, Fig. 7A) was again fitted to a damped simple harmonic oscillator and the damping coefficient was calculated to be 0.0482 ms^{-1}, or equal to the asymmetric case without adsorbed latex particles.

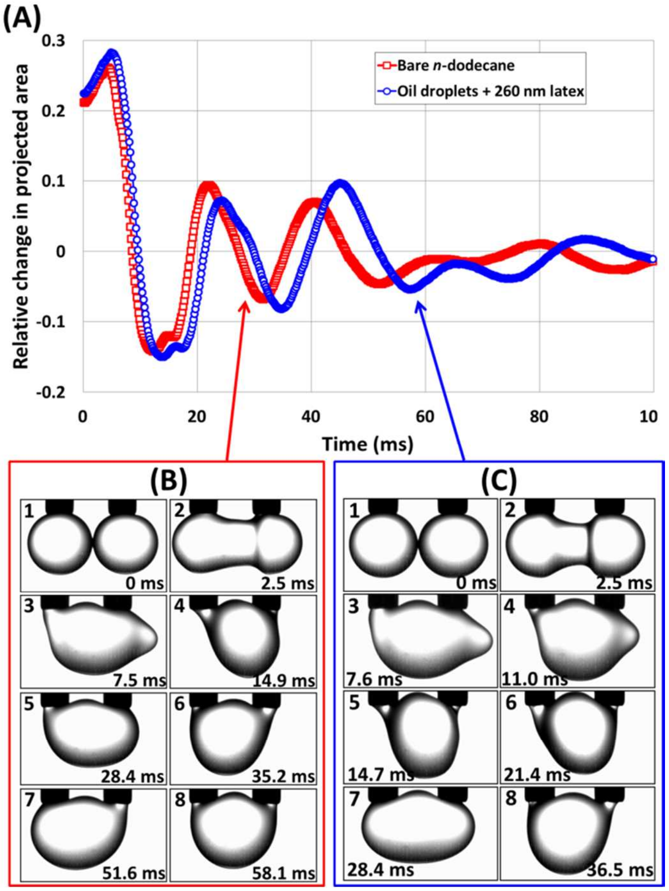

Fig. 7. Coalescence dynamics (A) for bare asymmetric *n*-dodecane droplets prepared in the absence (□) and presence (○) of a 1.6 × 10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 in the presence of 0.01 M KNO$_3$. In both cases 0.1 mg·mL^{-1} PPG-TDI cross-linker is present in the right hand droplet only. The outer diameter of each capillary is 0.71 mm, which acts as an appropriate scale bar. Below are sequences of images recorded for each pair of coalescing droplets (B+C).

Interestingly, with slightly longer ageing times the interactions between these asymmetric particle-laden drops exhibited behaviour previously unseen using this coalescence rig. No coalescence upon initial contact was observed on increasing the ageing time up to 60 s (see Image 1-2, Fig. 8). Following 5 min in contact, the *n*-dodecane droplets were initially separated, but remained connected via a neck (see

Image 3, Fig. 8), which is similar to the observations made for the separated symmetric giant colloidosomes (see Fig. 5A). This suggests that some fraction of PPG-TDI diffused from the right-hand droplet into the left-hand droplet during contact as reported previously.[24] However, unlike the study of symmetric PTBAEMA colloidosomes described above, further separation unexpectedly led to arrested coalescence, see Images 4-6 in Fig. 8. Following the initial coalescence event, net transfer of *n*-dodecane from the left-hand droplet to the right-hand droplet then occurs, leading to an increase in size of the latter droplet. This arrested coalescence experiment proved to be reproducible, although sometimes a greater capillary separation was required to induce the arrested coalescence (see Fig. S4). As reported by Pawar et al., the observed arrested coalescence is an intermediate case between that of complete coalescence and zero coalescence and occurs at a particle surface coverage below the close-packing limit.[29, 30] The interfacial elasticity of isolated pendant droplets was reduced from 12.9 to 9.8 mN·m^{-1} when PPG-TDI was added to the *n*-dodecane. Thus the oil transfer observed in Fig. 8 can be explained by the greater interfacial resistance of the cross-linked right-hand droplet being balanced by the Laplace pressure across the more highly curved left-hand droplet interface.[30] That is, the presence of a cross-linkable interface gives rise to a novel mechanism for arrested coalescence compared to previous reports, which were attributed solely to jamming of the particles at the interface. In this case, coalescence is enabled by the incomplete initial adsorption of particles at the interface of the two oil droplets that are brought into contact (as supported by Fig. 1A). However, the observation of arrested coalescence can be explained by the additional adsorption that occurs at the rest of the *n*-dodecane/water interface during the 5 min that the droplets are in contact. When the droplets were moved apart, the disturbance of the interface induced mass transport of the adsorbed particles and/or cross-linked ‘rafts’ of particles allowing complete drainage of the intervening thin film and promoting coalescence. It is possible that coalescence could have eventually occurred in the absence of any capillary movement, although this was not observed on the timescale of the experiments here.

The droplet ageing time prior to contact was subsequently increased up to 5 min, and coalescence was no longer observed under these conditions, see Fig. S5.† This markedly improved resistance to (arrested) coalescence is attributed to the further adsorption and additionally in the case of the right-hand droplet, cross-linking of PTBAEMA latex particles on this longer time scale as supported by the interfacial tension measurements given in Fig. 1A, producing a much more stable droplet contact zone.

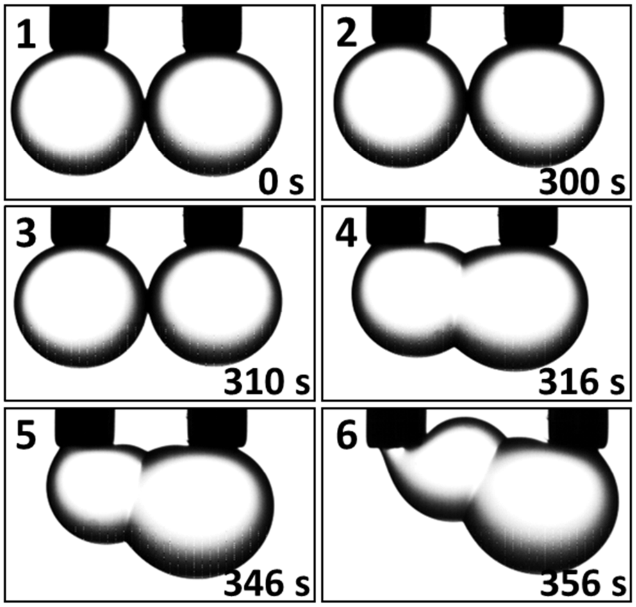

Fig. 8. Sequence of images recorded during asymmetric droplet experiments using two *n*-dodecane droplets grown in the presence of a 1.6 × 10^{-2} wt % aqueous dispersion of 260 nm charge-stabilised PTBAEMA latex particles at pH 10 in the presence of 0.01 M KNO$_3$. Droplets were aged in isolation for 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).

Conclusions

We have described coalescence interactions for *n*-dodecane, isopropyl myristate and sunflower oil droplets in the absence and presence of 260 nm PTBAEMA latex particles at pH 10. Bare *n*-dodecane and sunflower oil droplets exhibit different harmonic oscillations under these conditions compared to those reported previously by Thompson et al.,[24] who worked at approximately neutral pH. Giant Pickering oil droplets stabilised by PTBAEMA latex particles exhibited lower stability when compared to bare oil droplets, as coalescence times were significantly shorter for all three oils. However, the calculated damping coefficients are significantly greater for the *n*-dodecane/water and isopropyl myristate/water interfaces; this suggests that particle adsorption had occurred, as is supported by the dynamic interfacial tension data. Damping coefficients for the bare sunflower oil/water and Pickering droplet interfaces were not calculated owing to minimal oscillations for this more viscous oil. The presence of an oil-soluble cross-linker (PPG-TDI) significantly reduced the interfacial tension of *n*-dodecane compared to isopropyl myristate and sunflower oil.

Coalescence of all three oils was prevented when PPG-TDI was added to the oil phase and droplets were grown in the presence of PTBAEMA latex particles at pH 10. Droplet ageing times as short as 10-15 s was sufficient to prevent droplet coalescence, compared to ageing times of > 20 min for the PGMA-PS latex-based colloidosomes reported previously.[24]

When the colloidosomes were brought into contact, inter-colloidosome fusion was observed as the contact area between the two pendant colloidosomes became larger. This resulted in a reduction in the contour length for all three oil droplets. This effect was most notable with *n*-dodecane droplets, presumably because of its lower viscosity compared to the other two oils. Separation of the two pendant colloidosomes led to stretching of the contact area and formation of a bridging neck between the colloidosomes. This neck became extended between the colloidosomes upon capillary separation for all three oils.

Finally, experiments with asymmetric *n*-dodecane droplets resulted in arrested coalescence, providing that the droplet ageing time prior to contact was approximately 60 s. Shorter ageing times resulted in complete droplet coalescence, while longer ageing times produced stable cross-linked colloidosomes.

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Notes and references

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Table of Contents Graphic for manuscript:

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

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Coalescence of latex particle covered oil droplets is controlled by the presence of oil-soluble cross-linker in one or both droplets.