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Use of sterically-stabilised polystyrene latex particles as a pH-responsive particulate emulsifier to prepare surfactant-free oil-in-water emulsions†

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A pH-responsive, sterically-stabilised polystyrene latex is used as a particulate emulsifier for oil-in-water emulsions; demulsification occurs rapidly on lowering the solution pH and the original emulsion can be reformed on pH cycling.

The emulsifying properties of fine particles have been recognised for exactly one century.[1] For example, oil-in-water (o/w) emulsions can be readily prepared using hydrophilic nano-sized silica sols[2] and submicrometre-sized charged latex particles can likewise be employed for water-in-oil emulsions.[3] The surface hydrophobicity of the particle emulsifier is a key parameter in determining stabiliser efficiency and emulsion type and stability.[4] Paunov *et al*.[5] have recently proposed a thermodynamic model to describe the adsorption isotherms for charged particles at fluid–fluid interfaces. Very recently, Dinsmore *et al*. have coined the phrase 'colloidosome' to describe the micrometre-sized particle aggregates that can be prepared by sintering the particulate emulsifiers around the droplet phase, and a number of controlled-release applications have been suggested for such systems.[6]

Herein we show that a pH-responsive sterically-stabilised polystyrene latex acts as an efficient particulate emulsifier for oil-in-water emulsions at around neutral pH but exhibits no emulsifier activity at low pH. Thus demulsification can be reversibly induced simply by varying the solution pH (see Fig. 1).

The latex was prepared by dispersion polymerisation using a poly[2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate] [PDMA-PMMA] diblock copolymer as described previously.[7] This steric stabiliser was prepared by group transfer polymerisation,[8] and had a number-average molecular weight of 38 400 g mol^{-1} and a polydispersity of 1.14, as judged by gel permeation chromatography (THF eluent, poly(methyl methacrylate) standards, refractive index detector). ^{1}H NMR spectroscopy studies indicated a DMA content of 80 mol%. The PMMA block is designed to adsorb onto the latex surface and the solvated PDMA block acts as the steric stabiliser, thus ensuring good colloid stability. Serum replacement (ultrafiltration) was used to remove excess steric stabilizer (and trace monomer, initiator) and hence purify the latex particles. Ultrafiltration was performed using a Molecular/Por® stirred Spectrum® cell by replacing the serum with water. The weight-average particle diameter of the latex particles was determined to be 162 ± 20 nm by disc centrifuge photosedimentometry (Brookhaven BI-DCP instrument). Scanning electron microscopy studies of the dried latex particles indicated particle diameters in the range 150–180 nm (see ESI†). An ^{1}H NMR spectrum ($CDCl_3$) of the dissolved polystyrene latex enabled the signals due to the DMA and MMA residues of the stabiliser to be identified at δ 4.2 and d 3.6, respectively. Comparison of these integrated peaks with those due to the polystyrene indicated a stabiliser content of around 8% by mass (see ESI).

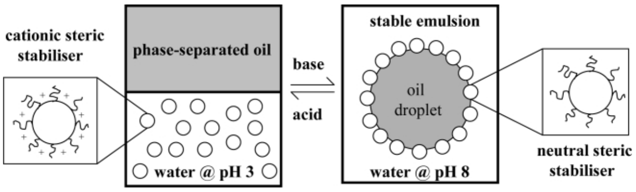

Fig. 1 Schematic representation of the formation of an oil-in-water emulsion using pH-responsive latex particles.

The hydrophilic character of the PDMA-PMMA stabiliser can be adjusted by controlling the solution pH. Above pH 8, the DMA residues are in their neutral, non-protonated form and are only weakly hydrophilic (PDMA homopolymer exhibits inverse temperature solubility behaviour at around 35–45 °C, depending on its degree of polymerisation[9]). In acidic solution the DMA residues are fully protonated at pH 4.[10] Neutral PDMA homopolymer is soluble in a wide range of non-polar solvents, including toluene and (hot) *n*-hexane, whereas protonated PDMA homopolymer is only soluble in aqueous solution. Thus adsorption of the sterically-stabilised latex particles at the oil–water interface is expected to be pH-dependent. This proved to be the case. Emulsions of equal volumes of *n*-hexadecane and aqueous latex dispersion containing 2 wt% of particles were prepared using an Ultra Turrax (IKA) rotor-stator homogeniser operating at 11 000 rpm for 2 min. The emulsion type was determined *via* conductivity measurements and using the drop test. Emulsion stability at 25 °C was assessed in graduated vessels by monitoring the movement of the oil–emulsion and emulsion–water interfaces with time. The pH of the aqueous phase was lowered progressively from its initial value of 8.1 by addition of conc. HCl. All emulsions were of the oil-in-water (o/w) type. Between pH 8.1 and 5.6, the emulsions were completely stable to coalescence but creamed slowly with time. The neutral/weakly charged PDMA-based stabiliser enables the latex particles to adsorb strongly at the oil–water interface, leading to the formation of stable emulsions. Most of the oil droplets are spherical and fairly polydisperse, with a median diameter of approx. 60 µm. On lowering the pH of the aqueous continuous phase from 5.6 to 2.2, the PDMA-based stabiliser chains become fully protonated, increasingly hydrophilic and hence insoluble in the oil phase. This leads to progressive desorption of the sterically-stabilised latex particles from the oil–water interface, which in turn destabilises the emulsion, see Fig. 2. Coalescence of the oil droplets occurs, followed by macroscopic phase separation. This observation of demulsification is

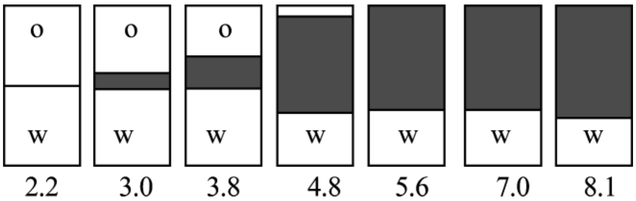

Fig. 2 Effect of varying the solution pH on the appearance of the emulsion after standing for 24 h at 25 °C. Residual stable emulsion is shaded.

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† Electronic supplementary information (ESI) available: SEM and NMR spectrum of the polystyrene latex particles. See http://www.rsc.org/suppdata/cc/b3/b304967a/

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consistent with earlier work by Binks and Clint, which shows that particles with very hydrophilic surfaces are poor emulsion stabilisers.[4] The effect of varying the solution pH on the stability of the *n*-hexadecane–water emulsions prepared using the polystyrene latex is summarised in Table 1.

An air–water surface tension *vs.* pH curve obtained for a 6.7 w/v% aqueous dispersion of the sterically-stabilised polystyrene particles is shown in Fig. 3. Clearly, latex adsorption at the air–water interface is pH-dependent. At high pH, the PDMA-based stabiliser chains are non-ionic and are moderately surface-active (the surface tension is around 50 mN m^{-1} at pH 9). On lowering the pH using HCl, the surface activity is reduced markedly[11] as the DMA residues become protonated at around pH 6. Under these conditions the PDMA-based stabiliser is highly cationic and, like conventional linear polyelectrolytes, its adsorption at the air–water interface is minimal, leading to relatively high surface tension values (72 mN m^{-1}). This pH-modulated surface activity is fully reversible and the adsorption/desorption of the latex particles at the air–water interface reflects their behavior at the oil–water interface in the emulsions.

Table 1 Conductivity (κ) and stability of 1 : 1 *n*-hexadecane-in-water emulsions stabilised by polystyrene latex at different pH at 25 °C (κ = 145 μS cm^{-1} for 2% aqueous latex at pH 8.1; κ = 0.01 μS cm^{-1} for *n*-hexadecane)

Aqueous pH	κ/μS cm^{-1}	Emulsion stability after 24 h
2.2	1470	100% coalescence
3.0	367	90% coalescence; cream
3.8	163	64% coalescence; cream
4.8	154	12% coalescence; cream
5.6	135	Creaming only
7.0	132	Creaming only
8.1	121	Creaming only

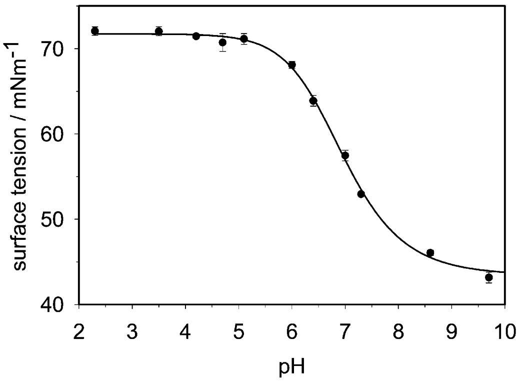

Fig. 3 Air–water surface tension *vs.* pH curve for a 6.7% w/w dispersion of latex particles at 20 °C.

In summary, we report the first example of pH-responsive latexes for the preparation of oil-in-water emulsions. Lowering the pH increases the hydrophilicity of the particles *in situ*; this leads to their desorption from the oil–water interface and results in rapid demulsification. Moreover, this effect is reversible: adjusting the solution pH from 3.8 to 8.4 allows the original emulsion to be reformed on re-homogenisation; thus the latex emulsifier can be re-used.

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