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Novel Pickering Emulsifiers based on pH-Responsive

Poly(*tert*-butylaminoethyl methacrylate) Latexes

A. J. Morse^a, D. Dupin^{a§}, K. L. Thompson^a, S. P. Armes^{a*}, K. Ouzineb^b, P. Mills^b, R. Swart^b

a. Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK.

b. Cytec Surface Specialities S.A./N.V., Anderlechstraat, 33, 1620 Drogenbos, Belgium.

Abstract

Emulsion copolymerization of 2-(*tert*-butylamino)ethyl methacrylate in the presence of divinylbenzene (DVB) cross-linker and monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) macromonomer at 70 °C afforded sterically-stabilized latexes at approximately 10% solids at pH 9. Dynamic light scattering (DLS) and scanning electron microscopy (SEM) confirmed that relatively narrow size distributions were obtained. SEM confirmed the formation of spherical particles in the absence of any DVB cross-linker using a simple batch protocol, but in the presence of DVB it was necessary to use seeded emulsion polymerization under monomer-starved conditions to prevent the formation of latexes with ill-defined non-spherical morphologies. Lightly cross-linked latexes acquired cationic microgel character upon lowering the solution pH, as expected. Increasing the degree of cross-linking led to a progressively lower effective pK_a of the copolymer chains from 8.0 to 7.3, which implies a gradual reduction in their basicity. Poly(*tert*-butylamino)ethyl methacrylate latex proved to be an effective Pickering emulsifier at pH 10, forming stable oil-in-water emulsions when homogenized with either *n*-dodecane or sunflower oil at 12 000 rpm for 2 min. These Pickering emulsions exhibited pH-responsive behavior: lowering the solution pH to pH 3 resulted in immediate demulsification due to spontaneous desorption of the cationic microgels from the oil/water interface. With subsequent rehomogenization at high pH, four successive demulsification/emulsification pH cycles could be achieved without discernible loss in performance. However, no demulsification occurred on acidification of the fifth cycle.

* *Author to whom correspondence should be addressed.*

§ *Present address: CIDITEK IK4, Parque Tecnológico de San Sebastián- p^o Miramón, 196, 20009 Donostia, San Sebastian, Spain.*

Introduction

Pickering emulsions involve the self-assembly of colloidal particles at the interface between two immiscible liquids (typically oil and water) to prevent coalescence of the droplet phase.^{1, 2, 3} In principle, Pickering emulsifiers offer a number of advantages over conventional surfactants such as (i) more robust and reproducible formulations, (ii) reduced foaming problems and (iii) lower toxicity (at least compared to certain surfactants). There are many literature examples describing the use of inorganic particles such as silica,^{4, 5} barium sulfate⁶ or calcium carbonate⁷ as Pickering emulsifiers. Recently, considerable attention has been devoted to the use of organic (e.g. polymer latex) particles as emulsifiers. Velev and co-workers were the first to report latex-based Pickering emulsifiers, with charge-stabilized polystyrene latex being utilized to stabilize 1-octanol droplets.⁸ In this case, either sulfate or amidine surface groups conferred charge stabilization. Other groups have also investigated the interfacial packing of charge-stabilized latexes. For example, Aveyard et al. reported the formation of ordered monolayers using sulfate-functionalized polystyrene latexes ranging from 0.2 to 2.6 μm diameter at both the air/water and oil/water interface.⁹ The propensity for solid 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 favors 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.^{10, 11} We are aware of some literature describing the use of pH-sensitive inorganic particles. e.g. silica.^{5, 12, 13} However, polymer latexes have become widely used as Pickering emulsifiers due to the ability to tailor their surface properties during their synthesis. It is also worth mentioning the work by Dai's group, who reported the production of stable Pickering emulsions at substantially below monolayer coverage using micrometer-sized polystyrene latex particles. This phenomenon appears to be due to strong lateral repulsion between the adsorbed charged particles.¹⁴ Various types of pH-sensitive organic Pickering emulsifiers are also known. For example, poly[2-(dimethylamino)ethyl methacrylate-*block*-methyl methacrylate] [PDMA-PMMA] has been used as a steric stabilizer for the synthesis of polystyrene latexes.¹⁵⁻¹⁸ If *n*-dodecane is used as the oil phase and the solution pH is 2-3 (i.e. below the pK_a of the PDMA stabilizer), then these latex particles do not stabilize Pickering emulsions since the protonated PDMA chains are too hydrophilic to wet the oil droplets.

However, if the PDMA chains are deprotonated and homogenization is conducted above their pK_a of ~ 7.0 , then stable Pickering emulsions can be obtained using the same oil. These were described as *pH-dependent* emulsifiers, since the solution pH is critical in dictating whether a Pickering emulsion is formed.^{17, 18} The first genuine example of a *pH-responsive* Pickering emulsifier was reported by Fujii et al., who used poly(4-vinylpyridine)/silica (P4VP/SiO₂) nanocomposite microgels to stabilize *n*-dodecane, methyl myristate or 1-undecanol droplets.¹⁹ These emulsions were readily broken on lowering the solution pH below the pK_a of the P4VP chains,^{19, 20} since the protonated microgel particles spontaneously desorbed from the emulsion droplet interface.^{21, 22} More recently, Dupin et al. found that pH-responsive sterically-stabilized latexes based on 2-vinylpyridine (2VP) could be synthesized using a PDMA-based macromonomer.²³ The poly(2-vinylpyridine) (P2VP) core and the PDMA stabilizer have differing pK_a values (4.1 and 7.0, respectively), thus these particles can exist in three different states (protonated microgel at low pH, cationic stable latex at intermediate pH or flocculated latex above pH 8). Depending on the conditions, this PDMA-P2VP latex could act as either a *pH-dependent* or a *pH-responsive* Pickering emulsifier for water droplets dispersed in 1-undecanol.²³

There are many reports describing the synthesis of well-defined block copolymers based on either primary or tertiary amine methacrylates.²⁴⁻²⁷ Moreover, there are also several examples of tertiary amine methacrylate-based latexes prepared via aqueous emulsion polymerization.^{28, 29} However, as far as we are aware, there are relatively few literature reports concerning *secondary* amine methacrylates such as 2-*tert*-butylaminoethyl methacrylate (TBAEMA). In our experience, primary amine-based methacrylates undergo facile intermolecular rearrangement to form the corresponding methacrylamide.³⁰ Smith et al. also reported that the hydrolysis of such amine-functional methacrylates was greatly diminished after their polymerization.³¹ In principle, secondary amine methacrylates are also susceptible to this undesirable side reaction. However, in the case of TBAEMA its *t*-butyl substituent provides sufficient steric congestion to confer stability.^{31, 32} Creutz et al. used anionic polymerization to synthesize a series of well-defined TBAEMA-based homopolymers and diblock copolymers in THF at -78 °C.³² Later, de Paz B  n  ez et al. reported using oxyanion-initiated polymerization at room temperature to produce both TBAEMA homopolymers and also diblock copolymers with other tertiary amine methacrylates.³³ The preparation of PTBAEMA brushes using living radical polymerization

has also been reported.³⁴ However, to the best of our knowledge, there have been no studies of the synthesis of PTBAEMA latexes via aqueous emulsion polymerization.

In the present work we explore the synthesis of novel PTBAEMA latexes prepared by emulsion polymerization using varying amounts of divinylbenzene (DVB) cross-linker in the presence or absence of a commercial monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) macromonomer. The aqueous solution behavior of these pH-sensitive latexes was studied using DLS and aqueous electrophoresis. Finally, we examined whether such latexes could act as pH-responsive Pickering emulsifiers for a range of model oils. In this context, it was interesting to consider whether the presence of the PEGMA stabilizer affected the particle wettability at the oil /water interface.

Experimental Section

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. The PEGMA macromonomer (kindly donated by Cognis Performance Chemicals, Hythe, UK) had a mean degree of polymerization (DP) of 45 and an M_w/M_n of 1.10. Ammonium persulfate (APS; > 98%), *n*-dodecane, isopropyl myristate and sunflower oil were each purchased from Aldrich and used as received. Deionized water was obtained using an Elga Elgastat Option 3 system. NMR solvents ($CDCl_3$) and ethanol were purchased from Fisher Scientific. Dialysis tubing (molecular weight cut-off of 100 kDaltons) was purchased from Fisher Scientific and stored in a moist environment at 4 °C until use.

Aqueous Emulsion Polymerization. The appropriate amount of PEGMA (0.50-1.00 g) was weighed into a 100 mL two-neck round-bottomed flask equipped with a magnetic flea. Deionized water (40.0 g) was added, followed by TBAEMA “head monomer” (0.50 g) and the initial solution pH was recorded. This emulsion was purged with nitrogen gas for 15 minutes using a cannula, then heated to 70 °C with the aid of an oil bath and stirred at 250 rpm using a magnetic stirrer. After 10 minutes, the appropriate amount of APS initiator (1.0-2.0 wt % based on TBAEMA) dissolved in deionized water (5.0 g) was injected into the reaction vessel to commence the first-stage polymerization. After 1 h, further TBAEMA monomer (4.25–4.50 g) together with the appropriate amount of DVB (0-0.25 g) was added

dropwise (3.0 ml h^{-1}) using a syringe pump. The reaction solution gradually turned milky-white within 30 minutes and was stirred for a total of 24 h at $70 \text{ }^{\circ}\text{C}$. Charge-stabilized PTBAEMA latex was also prepared using the same protocol, but without the addition of PEGMA. In addition, a ‘one-shot’ batch polymerization of TBAEMA was conducted using 10 wt. % PEGMA stabilizer, 0.8 mol % DVB cross-linker and 2.0 wt. % APS initiator at $70 \text{ }^{\circ}\text{C}$ for 24 h.

Purification. The PEGMA-stabilized latexes were purified by centrifugation at 20 000 rpm for 2 h, followed by careful decantation of the supernatant and replacement with fresh deionized water at pH 9.5. The sedimented particles were redispersed in each case with the aid of an ultrasonic bath. This protocol was repeated for a further nine centrifugation/redispersion cycles to remove any unreacted TBAEMA, APS initiator and non-grafted PEGMA macromonomer. Purification was continued until the surface tension of the supernatant was close to that of pure water ($70 \pm 2 \text{ mN m}^{-1}$). Charge-stabilized latexes were purified via dialysis to remove excess TBAEMA and APS initiator until the surface tension was close to that of pure water ($71 \pm 1 \text{ mN m}^{-1}$).

Pickering Emulsion Preparation. The redispersed PTBAEMA latex was adjusted to approximately 1.1 % solids using deionized water (assessed by gravimetry using a moisture analyzer) and the latex dispersion was adjusted to approximately pH 10.5 using either 0.1 M HCl or 0.1 M NaOH as appropriate. The PTBAEMA latex (4.0 mL) was then added to a 14 mL vial, to which the same volume of oil (e.g. *n*-dodecane or sunflower oil) was added. This oil/water mixture was then homogenized for 2 minutes using an IKA Ultra-Turrax T-18 homogenizer with a 10 mm dispersing tool operating at 12 000 rpm. The resulting Pickering emulsion was allowed to stand at $20 \text{ }^{\circ}\text{C}$ for 30 minutes.

Latex Characterisation

^1H NMR spectroscopy. All ^1H NMR spectra were recorded in CDCl_3 using a 400 MHz Bruker Avance-400 spectrometer.

Dynamic Light Scattering (DLS). Hydrodynamic diameters were measured at $25 \text{ }^{\circ}\text{C}$ 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 ten seconds duration. All measurements were performed three times on 0.01

w/v % aqueous latex solutions. The pH of the deionized water used to dilute the latex was matched to that of the latex (typically around pH 10) and was ultra-filtered through a 0.20 μm membrane so as to remove any dust.

Scanning Electron Microscopy (SEM). SEM studies were performed using a FEI Sirion field mission gun scanning electron microscope using a beam current of 244 μA and a typical operating voltage of 20 kV. Latexes were dried directly onto carbon tape and allowed to dry overnight before being sputter-coated with a thin layer of gold prior to examination so as to prevent sample charging.

Aqueous Electrophoresis. Zeta potentials were determined in the presence of 1 mM KCl using the same Malvern Zetasizer NanoZS Model ZEN 3600 instrument equipped with an autotitrator (MPT-2 multipurpose titrator, Malvern instruments). The solution pH was lowered from 10 to 3 using dilute HCl.

Pickering Emulsion Characterization

Conductivity Measurements. The conductivity of the continuous phase was measured using a digital conductivity meter (Hanna model Primo 5). Conductivities well above 10 $\mu\text{S cm}^{-1}$ indicated that water was the continuous phase (i.e. an o/w emulsion). In contrast, conductivities below 10 $\mu\text{S cm}^{-1}$ indicated that oil was the continuous phase (i.e. a w/o emulsion).

Drop Test. This test was used to confirm the continuous phase indicated by the conductivity measurement. An emulsion droplet was placed into either deionized water or oil. When dropped into the same liquid as the continuous phase, the droplet disperses rapidly. If dropped into the liquid of the internal droplet phase, the droplet remains intact, with little or no dispersion.

Laser Diffraction. A Malvern Mastersizer 2000 instrument equipped with a small volume Hydro 2000SM sample dispersion unit (ca. 50 mL), a HeNe laser operating at 633 nm, and a solid-state blue laser operating at 466 nm was used to size the emulsion droplets at pH 10. The stirring rate was adjusted to 1000 rpm in order to avoid creaming of the emulsion during analysis. The mean droplet diameter was taken to be the volume mean diameter ($D_{4/3}$), which is mathematically expressed as $D_{4/3} = \Sigma D_i^4 N_i / \Sigma D_i^3 N_i$. The standard deviation for each diameter provides an indication of the width of the size distribution. After each measurement, the cell was rinsed once with ethanol, followed by three rinses using water. The glass walls of

the cell were carefully wiped with lens cleaning tissue to avoid cross-contamination, and the laser was aligned centrally on the detector. This set-up allowed continuous measurements to be made after the sample chamber pH had been adjusted from 10 to 3. This allowed droplet stability to be examined with regard to any changes in pH.

Acid Challenge. The Pickering emulsion (1.0 mL) was added to a 1.5 mL vial to which sufficient HCl was added to lower the solution pH to around 3. This protocol allows visual confirmation of demulsification.

Optical Microscopy. A drop of the diluted emulsion was placed on a microscope slide and viewed using an optical microscope (James Swift MP3502, Prior Scientific Instruments Ltd.) connected to a PC laptop to record images. This technique was used to estimate the mean droplet diameter. The response of the o/w emulsion droplets following *in situ* acidification of the aqueous phase was also assessed using this equipment.

Results and Discussion

General remarks

It is worth briefly comparing the physical properties of PTBAEMA with that of poly(2-(diethylamino)ethyl methacrylate) (PDEA), which has already been prepared in latex form.²⁸ Acid titration (see Figure S1 in the Supporting Information) indicates that linear PTBAEMA latex has a pK_a of 8.0, which is slightly higher than the literature value of 6.8-7.2 for linear PDEA latex.^{24, 28} The glass transition temperature (T_g) of PTBAEMA latex was determined to be 38.5 °C by differential scanning calorimetry (see Figure S2 in the Supporting Information), whereas the literature value is around 16 to 24 °C³⁵ for PDEA homopolymer and -5 °C³⁶ for PDEA latex, respectively. In principle, this should make electron microscopy studies of the former latex less problematic than that of the latter, for which partial film formation has been observed.²⁸ However, in the light of recent work by Tsavalas and co-workers it seems likely that the N-H bonds on the TBAEMA residues may promote hydroplasticization, which would lower the effective T_g of the aqueous latex dispersion.³⁷ Finally, it is noted that these secondary amine groups could be potentially utilized for cross-linking the PTBAEMA chains. This possibility is not explored in the present study but will be examined in future work.

Latex Preparation and Characterization

The two main classes of acid-swellaible latexes reported in the literature are based on poly(2-vinylpyridine)^{23, 38, 39} and PDEA.^{28, 29} The synthetic route for the preparation of a new class of acid-swellaible latex based on lightly cross-linked PTBAEMA particles is outlined in Figure 1. The steric stabilization shown in Figure 1 is supported by freeze-thaw experiments, which confirm that PEGMA-PTBAEMA latex has much better colloidal stability than the charge-stabilized PTBAEMA latex, as expected (see Figure S3 in the Supporting Information). More specifically, PEGMA-PTBAEMA latex (entry 4, Table 1) survived three freeze-thaw cycles, whereas charge-stabilized PTBAEMA latex (entry 10, Table 1) flocculated upon thawing, as confirmed by DLS studies. However, we cannot rule out the possibility that some fraction of the PEGMA chains may be located within the latex particles. These syntheses were typically conducted via aqueous emulsion copolymerization at approximately 10 % solids under monomer-starved conditions at 70 °C; relevant synthesis parameters are summarized in Table 1. Under mildly alkaline conditions (initially around pH 10) monomer conversions of at least 90 % were routinely obtained, see Table 1. After polymerization, the final pH is around pH 9.5, which is still well above the pK_a for the PTBAEMA chains. This pH drift is associated with the choice of initiator. Nevertheless, the final pH is sufficiently high to ensure that the PTBAEMA is obtained in its non-protonated latex form, rather than as a soluble cationic polyelectrolyte. The ‘one-shot’ batch synthesis of PTBAEMA particles using 10 wt % PEGMA macromonomer and 0.8 mol % DVB cross-linker produced a relatively polydisperse latex with a hydrodynamic diameter of 540 nm (see entry 1, Table 1). Inspection of these particles by SEM indicated an ill-defined, non-spherical morphology, see Figure 2a. There is some literature evidence to suggest that this non-spherical morphology might be related to cross-linking. For example, Song et al. had reported similar observations for the alcoholic dispersion polymerization of styrene using the same DVB cross-linker.⁴⁰⁻⁴² Therefore the ‘one-shot’ batch formulation was repeated in the absence of any cross-linker (see entry 8, Table 1). DLS studies reported an intensity-average diameter of 430 nm for the resulting linear latex, while SEM indicated the formation of well-defined spherical particles, see Figure 2b. This linear latex dissolves molecularly at low pH and ultimately proved to be a useful reference material for ¹H NMR spectroscopy studies. However, the main aim of the present work was to develop a new class of acid-swellaible latexes that exhibit a reversible latex-to-microgel transition. Thus omission of the DVB cross-linker was not desirable, since cross-linking is essential to prevent latex dissolution at low

pH. Instead, an alternative seeded emulsion polymerization formulation under monomer-starved conditions was examined, which fortunately produced reasonably spherical latex particles even in the presence of DVB cross-linker, see Figures 2c and 2d. In each case near-monodisperse cross-linked PTBAEMA latexes ranging from 150 nm to 200 nm diameter were obtained in high yield, see entries 2-7 in Table 1. There is some evidence that cross-linking leads to smaller particles (compare entries 2 and 8 and also entries 3 and 4 in Table 1). In addition, a linear PEGMA-stabilized PTBAEMA latex was prepared in the absence of any DVB cross-linker using a monomer-starved protocol (see entry 9 in Table 1). A charge-stabilized DVB cross-linked PTBAEMA latex was also prepared in the absence of any PEGMA steric stabilizer (entry 10 in Table 1). DLS studies of this charge-stabilized latex indicated a relatively narrow particle size distribution and an intensity-average diameter of 220 nm, which is only slightly larger than that achieved in the presence of the PEGMA stabilizer. The charge-stabilized nature of this 220 nm latex is most likely due to the use of a persulfate initiator and was confirmed by three freeze-thaw cycles (see Figure S3 in the Supporting Information). However, it should be emphasized that the latex showed no signs of sedimentation or flocculation over long periods of time (months).

In principle, the PEGMA content of the sterically-stabilized latexes can be determined by ^1H NMR spectroscopy. In practice, this proved problematic for latexes prepared using 0.8 mol % DVB cross-linker since they become highly viscous in their swollen microgel form, which leads to significant line-broadening and hence overlapping NMR signals.³⁸ The linear PTBAEMA latexes prepared under the same reaction conditions in the absence of DVB proved useful, since their molecular dissolution in CDCl_3 led to well-resolved ^1H NMR spectra. Figure 3 shows the ^1H NMR spectra recorded in CDCl_3 for a purified PEGMA-stabilized linear PTBAEMA latex (entry 9 in Table 1; spectrum A) and a charge-stabilized linear PTBAEMA latex (entry 11 in Table 1; spectrum B). The additional signal observed at δ 3.7 ppm in the former case is assigned to the oxyethylene protons due to the PEGMA chains;^{38, 43} comparison of this peak integral with that signal at δ 4.05 ppm due to the oxymethylene protons adjacent to the ester group of the PTBAEMA residues indicated a PEGMA content of approximately 1.8 mol %. Given the comparable particle diameters obtained for the cross-linked and linear PTBAEMA particles (see Table 1), the former latexes should contain similar amounts of PEGMA stabilizer to the latter. However, this assumes that introducing the DVB cross-linker does not affect the grafting efficiency of the PEGMA stabilizer. If the PEGMA chains are located exclusively at the particle surface, an adsorbed

amount of PEGMA, or Γ (in mg m^{-2}), can be estimated. Γ was calculated to be 2.3 mg m^{-2} for the linear PTBAEMA latex, which is consistent with values reported by Dupin et al.³⁸ for a PEGMA-stabilized P2VP latex and by Amalvy et al.¹⁶ for poly(tertiary amine methacrylate) latexes.

The PEGMA content of DVB cross-linked PTBAEMA latexes was also assessed. Thus selected latexes (initially at pH 10) were centrifuged at 13 000 rpm for 1 h (Heraeus Biofuge Pico microcentrifuge) and the sedimented particles were redispersed into D_2O . However, the resulting ^1H NMR spectra were only very poorly resolved (see Figure S3 in the Supporting Information). The appearance of signals attributable to the PTBAEMA chains after protonation using DCI was anticipated, since acidification induces a latex-to-microgel transition. In addition, the relatively sharp signal at ~ 3.7 ppm observed in spectra (a) and (b) (see Figure S3; entry 4 in Table 1) can be assigned to the oxyethylene protons of the grafted PEGMA stabilizer.^{35,40} As expected, this signal is not present in spectra (c) and (d) recorded for the charge-stabilized microgel (see Figure S3; entry 10 in Table 1). However, due to significant line broadening and overlapping NMR signals in the protonated microgel spectra, *linear* PTBAEMA latexes of similar diameter were used in order to estimate the extent of PEGMA incorporation (see above).

The pK_a values for a *linear* PTBAEMA latex (prepared by aqueous emulsion polymerization in the absence of DVB cross-linker, entry 9, Table 1) were calculated by acid titration and compared to the pK_a values calculated for a series of cross-linked PTBAEMA latexes, see Figure 4. Targeting higher degrees of cross-linking clearly leads to a systematic reduction in pK_a , which indicates a reduction in basicity for the non-protonated PTBAEMA chains. Similar observations were made by Dupin et al.³⁸ for cross-linked poly(2-vinylpyridine) latexes. In both cases an approximately linear relationship is observed, with a systematic lowering of the pK_a by more than half a pH unit as the degree of cross-linking is increased. The rationale here is that it is more difficult to protonate cross-linked polybase chains because they have less scope to reduce the build-up of cationic charge density via intra-chain expansion compared to linear chains. Acid titrations were always conducted starting at low pH, so the initial physical state is molecular dissolution in both cases.

Acid-induced swelling of selected PEGMA-PTBAEMA latexes (entries 3-5, Table 1) was monitored using DLS. Latex-to-microgel transitions are observed at around pH 8 for PEGMA-stabilized PTBAEMA prepared with either 0.8 or 1.6 mol. % DVB (see Figure 5a).

This is close to the pK_a values of these particles, which suggests that a degree of protonation of approximately 50% is sufficient to induce the latex-to-microgel transition. This is similar to observations reported by Dupin et al. for cross-linked P2VP microgels, who reported that cross-linked P2VP latexes exhibit a latex-to-microgel transition between pH 4.0 and 4.5 (the corresponding pK_a of these latexes was around 4.1).³⁸ The highly swollen cationic PTBAEMA microgels formed below pH 8 possess hydrodynamic diameters of 600-700 nm, which corresponds to a volumetric expansion of more than 27. However, increasing the DVB cross-linker content to 2.4 mol % reduces the swollen microgel diameter significantly (to less than 300 nm) and the critical pH for the latex-to-microgel transition shifts from 7.9 to approximately 7.5. This correlates with the reduction in pK_a observed for higher degrees of cross-linking, as discussed earlier. There also appears to be relatively little difference in swelling behavior between charge-stabilized and PEGMA-stabilized PTBAEMA latexes prepared using the same target degree of DVB cross-linker (entry 10, Table 1). The former particles also exhibited a latex-to-microgel transition upon lowering the pH, as confirmed by DLS. Particle swelling occurred at the same pH as that observed for 0.8 mol % DVB cross-linked PEGMA-stabilized particles (see Figure 5a). The charge-stabilized swollen microgel had a hydrodynamic diameter of 625 nm upon full protonation of its secondary amine groups.

Aqueous electrophoresis measurements were conducted on three cross-linked PEGMA-stabilized PTBAEMA latexes (see Figure 5b). The zeta potential is a shear plane measurement that is sensitive to the nature of the stabilizer chains, as well as the particle cores. Given that the PEGMA chains are non-ionic, changes in zeta potential are dominated by the PTBAEMA chains (and possibly also surface sulfate groups derived from APS initiator fragments). All latexes exhibited an isoelectric point (IEP) of approximately pH 8.9. No flocculation occurred at this pH as judged by DLS due to steric stabilization conferred by the surface-grafted PEGMA stabilizer. As expected, protonation of the secondary amine groups led to cationic character below pH 8.9, with zeta potentials ranging from +28 to +44 mV. The charge-stabilized latex was also subjected to aqueous electrophoresis studies as a function of pH. The PEGMA stabilizer chains appeared to have little shielding effect on the overall surface charge of the particles. Surprisingly, no flocculation was observed for the charge-stabilized PTBAEMA particles, even at their IEP of pH 8.9 (see Figure 5b). This may be because around 10 % of the secondary amine groups are protonated under these conditions. Considering the DLS and zeta potential data together, three distinct physical states for these PTBAEMA particles could be identified. Highly cationic swollen microgels

are formed below pH 8, weakly cationic latexes are obtained at pH 8 to 8.9 and anionic latexes are produced above pH 8.9. Compared to the PEGMA-stabilized P2VP latexes prepared by Dupin et al.,³⁸ these PEGMA-stabilized PTBAEMA latexes are significantly more anionic in alkaline solution. This difference is attributed to the cationic initiator used to prepare the P2VP latexes, as opposed to the anionic initiator (APS) used in the present work.

Pickering emulsifier performance of PTBAEMA latexes

It is well-known that Pickering emulsifiers require appropriate surface wettability for strong adsorption onto emulsion droplets.^{4, 21, 44-46} PEGMA-PTBAEMA latexes proved to be excellent Pickering emulsifiers when homogenized at pH 10 at 12 000 rpm for 2 minutes using either *n*-dodecane or sunflower oil. In each case very stable emulsions were obtained when a 50:50 oil/aqueous latex volume ratio was employed. The aqueous latex concentration was adjusted to approximately 1.1 wt % (determined by gravimetry) to provide a total latex surface area of 1.13 m² for 4.0 mL of latex (assuming a PTBAEMA latex density of 1.17 g cm⁻³). It is worth emphasizing that Pickering emulsions were not obtained if the aqueous dispersion was adjusted to pH 3 to produce cationic PTBAEMA microgels. Presumably, the contact angle made by these highly hydrophilic particles at the o/w interface is simply too low for the particles to be efficiently adsorbed. The particles can therefore be classified as being pH-dependent in terms of their Pickering emulsifier performance.^{17, 18, 23} Oil-in-water Pickering emulsions were confirmed by both conductivity measurements and the 'drop test'. After allowing the emulsions formed at pH 10 to cream on standing, visual inspection confirmed that the lower aqueous phase always contained some non-adsorbed latex, regardless of the initial latex concentration (see Figure 6). This is in contrast to the unusually efficient sterically-stabilized latex-based Pickering emulsifiers reported previously by Thompson et al., where a transparent lower aqueous phase indicated no excess latex below a certain critical latex concentration.⁴⁷ In the present work, optical microscopy studies confirmed the polydisperse nature of these droplets, which ranged in size from 15 to 100 μm (see Figure 6b). Relatively high polydispersities are typical for Pickering emulsions prepared via high shear homogenization. However, it has been recently shown that more uniform Pickering emulsions can be produced using other methods such as membrane emulsification.^{48, 49} The mean droplet diameter was determined to be 50 ± 38 μm as judged by laser diffraction. In this context, the very poor Pickering emulsifier performance of PEGMA-P2VP latexes prepared by Dupin et al. is noteworthy.²³ No stable Pickering emulsions could be formed at either pH 3 or 10 using PEGMA-P2VP (or charged-stabilized

P2VP) latex after homogenization with a range of oils, including *n*-dodecane, methyl myristate and 1-undecanol. We have no satisfactory explanation for the dramatically improved Pickering emulsifier performance exhibited by the PEGMA-PTBAEMA latexes in the present work and merely note that these striking differences clearly illustrate our incomplete understanding of this field. In view of this situation, a charge-stabilized PTBAEMA latex (entry 10, Table 1) was also examined as a Pickering emulsifier in order to investigate the influence of the PEGMA chains in determining surface wettability. Perhaps surprisingly, this charge-stabilized latex was found to be an efficient oil-in-water Pickering emulsifier when homogenized with either *n*-dodecane or sunflower oil. In fact, somewhat finer (and less polydisperse) oil droplets of $42 \pm 17 \mu\text{m}$ diameter were obtained when using *n*-dodecane (data not shown). One advantage of using such a charge-stabilized PTBAEMA latex is its relative ease of purification: extensive dialysis was sufficient to remove unreacted small molecule impurities, which is more feasible than centrifugation on an industrial scale. Although both PEGMA-stabilized and charge-stabilized PTBAEMA latexes proved to be efficient Pickering emulsifiers, the rest of this article is focused exclusively on the performance of the charge-stabilized PTBAEMA particles.

According to Thompson et al., reducing the initial latex concentration should produce larger oil droplets.^{47,50} Moreover, if all the latex particles are adsorbed onto the oil droplets, the (lower) aqueous continuous phase obtained after creaming should become clear. Charge-stabilized PTBAEMA particles were homogenized with *n*-dodecane at various latex concentrations (0.20 to 2.90 wt %). Digital images confirm complete emulsification of *n*-dodecane could be achieved even when using latex concentrations as low as 0.20 wt % (see digital photographs a and b in Figure 7). However, inspection of the aqueous phase obtained after creaming (see photograph c in Figure 7) indicated appreciable turbidity, which suggested that even this relatively low latex concentration was insufficient to achieve full adsorption of particles. This preliminary conclusion was confirmed by carefully removing a portion of this aqueous continuous phase and calculating its solids content. The final latex concentration was typically only 10-20 % less than the original concentration. Similar results were recently reported by Walsh et al. for polyamine-stabilized latexes: efficient adsorption of the particles at the interface was not achieved even when lowering their concentration to as little as 0.3 wt %.⁵¹ In contrast, the poly(glycerol monomethacrylate)-stabilized polystyrene particles evaluated by Thompson et al. adsorbed efficiently onto oil droplets, forming close-packed latex monolayers as judged by fluorescence microscopy studies.⁴⁷

The relationship between the mean *n*-dodecane droplet diameter (reported by laser diffraction) and initial PTBAEMA latex concentration is shown in Figure 8, with selected optical micrographs shown as insets. These images confirm the change in mean droplet diameter and also serve to illustrate the polydisperse nature of these emulsions. As the latex concentration is reduced below approximately 1.0 wt %, larger oil droplets are formed. Oil droplets of around 120 μm diameter were obtained when using 0.20 wt % latex. However, it is important to mention that the packing efficiency of these particles is well below that required for monolayer coverage. Similar observations have been reported previously by Dai's group, who observed the production of stable Pickering emulsions at substantially below monolayer coverage using micrometer-sized polystyrene latex particles.¹⁴ It is thought that the strong lateral repulsion between the charge-stabilized PTBAEMA latex particles used in the present study is sufficient to stabilize oil-in-water Pickering emulsions at unusually low concentrations (and surface coverages).

DLS studies had already confirmed the pH-responsive nature of the charge-stabilized PTBAEMA latex in aqueous solution, with a latex-to-microgel swelling transition being observed (see above). An obvious question is whether this leads to pH-responsive Pickering emulsifier behavior. Accordingly, approximately five drops of 0.10 M HCl was added to the stable Pickering emulsion. This acidification led to rapid phase separation (see digital photograph d in Figure 7). On protonation, the swollen microgel particles desorb spontaneously from the oil/water interface, leaving bare oil droplets that undergo immediate coalescence. Similarly efficient demulsification was also achieved using sunflower oil and isopropyl myristate. However, sunflower oil-based emulsions demulsified slower than those prepared using either *n*-dodecane or isopropyl myristate. Presumably, this is simply due to the increased viscosity associated with the former oil. Similar pH-responsive emulsion behavior was also observed for PEGMA-PTBAEMA latexes (data not shown) when using *n*-dodecane, sunflower oil or isopropyl myristate as the droplet phase. Thus, both types of PTBAEMA latexes act as generic pH-responsive Pickering emulsifiers.

A Pickering emulsion with a mean droplet diameter of 72 μm (prepared using 2.0 mL of 0.80 wt. % charge-stabilized PTBAEMA latex and 2.0 mL *n*-dodecane) was subjected to an acid challenge, which led to its immediate demulsification. The two-phase solution was treated with base to induce the microgel-to-latex transition and re-homogenized once more at pH 10 (12 000 rpm for 2 min). This second Pickering emulsion was also of the oil-in-water type, and its mean diameter was comparable to the first emulsion within experimental error. Four

further demulsification/emulsification cycles were conducted, after which no demulsification occurred on addition of excess acid. This is most likely due to the build-up of background salt preventing efficient swelling of the adsorbed latex particles. To examine whether this hypothesis is correct, the same original Pickering emulsion was prepared at pH 10 in the presence of 0.01 M NaCl. In contrast, acidification of this emulsion did not lead to its destabilization, which suggests that the background salt effectively suppressed microgel swelling so that no interfacial desorption occurs. Similar results were also obtained for pH cycling experiments conducted in the absence of background salt with either sunflower oil or isopropyl myristate. It is perhaps worth noting that Pickering emulsions prepared using linear PTBAEMA latexes also demulsified. However, in the absence of any cross-linker the soluble PTBAEMA chains were unable to “remember” their original latex form, and simply produced a white precipitate within the aqueous phase on neutralization with NaOH.

Demulsification of diluted Pickering emulsions was also monitored using a Malvern Mastersizer instrument fitted with a small volume Hydro 2000SM sample dispersion unit. The solution pH was adjusted to pH 10 prior to the addition of the oil-in-water emulsion. Five measurements were recorded over 15 min to confirm the stability of the oil droplets prior to the solution pH being lowered (see Figure 9a). Acid (0.1 M HCl) was then added directly to the sample chamber so that the change in oil droplet diameter could be monitored *in situ* at approximately pH 3. However, over the following 45 min the oil droplet concentration decreased significantly and there was also a discernible shift to smaller droplets (see Figure 9b). The longer time scale required for demulsification in this experiment compared to the experiments conducted with sample vials simply reflects the much lower oil droplet concentration: droplet coalescence can only occur when bare droplets collide with each other. In this context it is worth emphasizing that, when the solution pH is maintained at around pH 10, both the oil droplet concentration and mean droplet diameter remain relatively constant for the duration of the experiment (i.e. for at least 1 h at ambient temperature). Thus emulsion destabilization is solely due to the latex-to-microgel transition that occurs on lowering the solution pH. Overall, these studies provide convincing evidence that the charge-stabilized PTBAEMA latex acts as an efficient recyclable pH-responsive Pickering emulsifier.

Conclusions

Novel PEGMA-stabilized and charge-stabilized PTBAEMA latexes have been synthesized by seeded emulsion polymerization with hydrodynamic diameters ranging from 150 to 220 nm. Unlike the poly(2-(diethylamino)ethyl methacrylate latexes reported earlier, the glass transition temperature of these PTBAEMA latexes is sufficiently high to allow SEM imaging at ambient temperature, although some deformation due to hydroplasticization³⁷ is evident. The pK_a of these PTBAEMA particles ranges from 8.0 to 7.3, with lower values being obtained at higher degrees of cross-linking as expected. Linear PTBAEMA latexes dissolved in dilute acidic solution due to protonation of the secondary amine groups on the PTBAEMA chains. In contrast, cross-linked PTBAEMA latexes undergo a reversible latex-to-microgel swelling transition, which was characterized by DLS studies and aqueous electrophoresis. Microgel/latex swelling ratios of up to 3.3 were observed at DVB contents of 0.8 mol %.

PTBAEMA latexes act as effective Pickering emulsifiers when homogenized with either *n*-dodecane, sunflower oil or isopropyl myristate, producing stable oil-in-water emulsions. However, stable emulsions were only obtained if homogenization was conducted above the latex pK_a (i.e. at around pH 10). Perhaps surprisingly, the presence of chemically-grafted PEGMA chains at the latex surface appeared to have little or no effect on its Pickering emulsifier performance: stable emulsions could be obtained using both charge-stabilized and sterically-stabilized PTBAEMA latexes. Larger oil droplets were obtained at lower latex concentrations, as expected. However, excess non-adsorbed latex was always observed over the entire concentration range investigated.

These Pickering emulsions proved to be pH-responsive on lowering the pH: protonation of the secondary amine groups leads to spontaneous desorption of cationic microgels from the surface of the emulsion droplets, which subsequently undergo coalescence within seconds. Demulsification was monitored using both optical microscopy and laser diffraction. Four successive demulsification/emulsification pH cycles could be achieved without discernible loss in performance (with homogenization being required at high pH to reform the emulsion after each cycle). However, after five cycles the resulting emulsion remained stable after acidification. Presumably, this is simply due to the build-up of background salt.

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Supporting Information Available: Acid titration curves for selected PTBAEMA latexes; DSC curve for a cross-linked PEGMA-stabilized PTBAEMA latex (0.8 mol % DVB); DLS size distributions obtained after three freeze-thaw cycles for PEGMA-stabilized PTBAEMA and charge-stabilized PTBAEMA latexes; ¹H NMR spectra recorded (in both DCI/D₂O and D₂O) for a cross-linked PEGMA-stabilized PTBAEMA latex and a cross-linked charge-stabilized PTBAEMA latex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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List of Tables

Table 1. Effect of variation of the synthesis parameters on the mean diameters of poly(2-tert-butylamino)ethyl methacrylate) latexes prepared using PEGMA stabilizer, DVB cross-linker and APS initiator at 70 °C. The wt % values in columns 2 and 4 are for DVB/TBAEMA comonomer mixtures. All latexes were prepared by emulsion copolymerization at pH 10 under monomer-starved conditions at 10 % solids, unless otherwise stated.

Entry no.	PEGMA stabilizer (wt %)	DVB cross-linker (mol %)	APS initiator (wt %)	Conversion (%) ^a	Intensity-average diameter (nm) ^b	Polydispersity index ^b
1 ^c	10.0	0.8	2.0	99	540	0.11
2	10.0	0.8	2.0	95	200	0.02
3	5.0	0.8	2.0	91	200	0.02
4	5.0	1.6	2.0	99	160	0.01
5	5.0	2.4	2.0	96	155	0.01
6	5.0	3.2	1.0	94	150	0.02
7	5.0	4.0	1.0	95	160	0.01
8 ^c	10.0	0	2.0	99	430	0.05
9	5.0	0	1.0	97	175	0.05
10 ^d	0	0.8	1.0	98	220	0.04
11 ^{c,d}	0	0	1.0	87	350	0.24

a. Determined using gravimetry.

b. Determined by dynamic light scattering at 20 °C.

c. Prepared using one-shot batch copolymerization.

d. Prepared by surfactant-free emulsion copolymerization.

Table 1

List of Figures

Figure 1. Schematic representation of the synthesis of PEGMA-PTBAEMA latex particles via emulsion polymerization at 70 °C and their subsequent acid-induced swelling behavior in aqueous solution at 20 °C to form cationic microgels.

Figure 2. Scanning electron microscopy images obtained for (A) 540 nm non-spherical 0.8 mol % DVB cross-linked PTBAEMA latex (entry 1, Table 1), (B) 430 nm non-cross-linked spherical PTBAEMA latex (entry 8, Table 1), (C) 200 nm spherical 0.8 mol % DVB cross-linked PTBAEMA latex (entry 2, Table 1), (D) 200 nm spherical 0.8 mol % DVB cross-linked PTBAEMA latex (entry 3, Table 1).

Figure 3. ^1H NMR spectra (CDCl_3) recorded for *linear* PTBAEMA latexes prepared by emulsion polymerization: (a) in the presence of PEGMA macromonomer (entry 9 in Table 1) and (b) in the absence of PEGMA macromonomer (entry 11 in Table 1).

Figure 4. Influence of the degree of DVB cross-linker of the pK_a of PEGMA-PTBAEMA latexes as determined by acid titration studies. In each case, the degree of cross-linking has been corrected to allow for the 80 mol % purity of the DVB cross-linker. The linear PEGMA-PTBAEMA latex is entry 9 in Table 1.

Figure 5. Variation of the hydrodynamic diameter (a) and zeta potential (b) with solution pH for (♦) 0.8 mol % cross-linked PEGMA-PTBAEMA (entry 3, Table 1), (■) 1.6 mol % cross-linked PEGMA-PTBAEMA (entry 4, Table 1), (▲) 2.4 mol % cross-linked PEGMA-PTBAEMA (entry 5, Table 1) and (●) charge-stabilized PTBAEMA (entry 10, Table 1).

Figure 6. Digital photographs of: (left) the initial PEGMA-PTBAEMA latex (1.1 % solids) with the dyed *n*-dodecane oil added directly to the vial, (middle) the subsequent *n*-dodecane-in-water emulsion stabilized by this PEGMA-PTBAEMA latex and (right) creaming of the less dense oil droplets and the underlying excess latex. (a) Optical microscope image and (b) Mastersizer size distribution for *n*-dodecane-in-water droplets stabilized using 200 nm PEGMA-PTBAEMA latex.

Figure 7. Digital photographs of: (a) charge-stabilized PTBAEMA latex (pH 10.5, 4 mL) plus *n*-dodecane (4 mL) for varying latex solids before homogenization, (b) PTBAEMA stabilized *n*-dodecane-in-water emulsion after homogenization at 12,000 rpm for 2 mins, (c) subsequent creaming of the less dense oil droplets 2 h after homogenization, (d) demulsification of the Pickering emulsion after treatment with 2 drops of conc. HCl. Effective latex solids in each photograph as determined by gravimetry: (1) 2.9 wt % (2) 2.0 wt % (3) 1.20 wt % (4) 0.80 wt % (5) 0.60 wt % (6) 0.30 wt % (7) 0.20 wt %.

Figure 8. Relationship between mean oil droplet diameter and latex concentration for Pickering emulsions prepared using 220 nm surfactant-free PTBAEMA (entry 10, Table 1) with *n*-dodecane as the oil phase. Latex dispersions were adjusted to pH 10.5 using 0.1 M KOH and homogenized at 12,000 rpm for 2 minutes. Optical microscopy (OM) images for selected entries are shown for the corresponding Pickering emulsions. Scale bars in all OM images are 100 μm .

Figure 9. Volume-average droplet diameter distribution curves obtained by laser diffraction for (a) PTBAEMA stabilized *n*-dodecane-in-water emulsions (1.0 % solids) at pH 10 and (b) the resulting reduction in concentration after inverting the pH to 3.05. Measurements were taken every 3 minutes for 60 minutes with the acid being added after the first 5 measurements.

Figure 1. Schematic representation of the synthesis of PEGMA-PTBAEMA latex particles via emulsion polymerization at 70 °C and their subsequent acid-induced swelling behavior in aqueous solution at 20 °C to form cationic microgels.

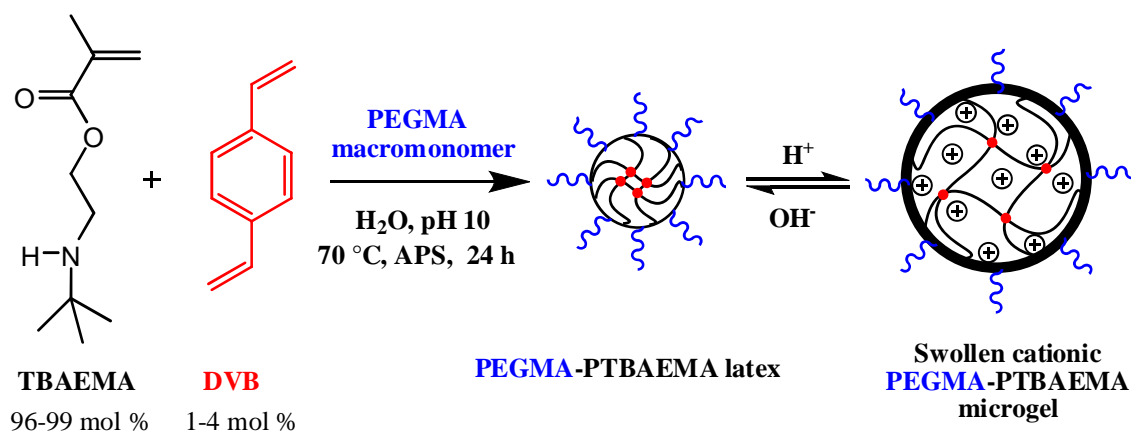


Figure 2. Scanning electron microscopy images obtained for (A) 540 nm 0.8 mol % DVB cross-linked PTBAEMA latex (entry 1, Table 1), (B) 430 nm non-cross-linked PTBAEMA latex (entry 8, Table 1), (C) 200 nm 0.8 mol % DVB cross-linked PTBAEMA latex (entry 2, Table 1), (D) 200 nm 0.8 mol % DVB cross-linked PTBAEMA latex (entry 3, Table 1).

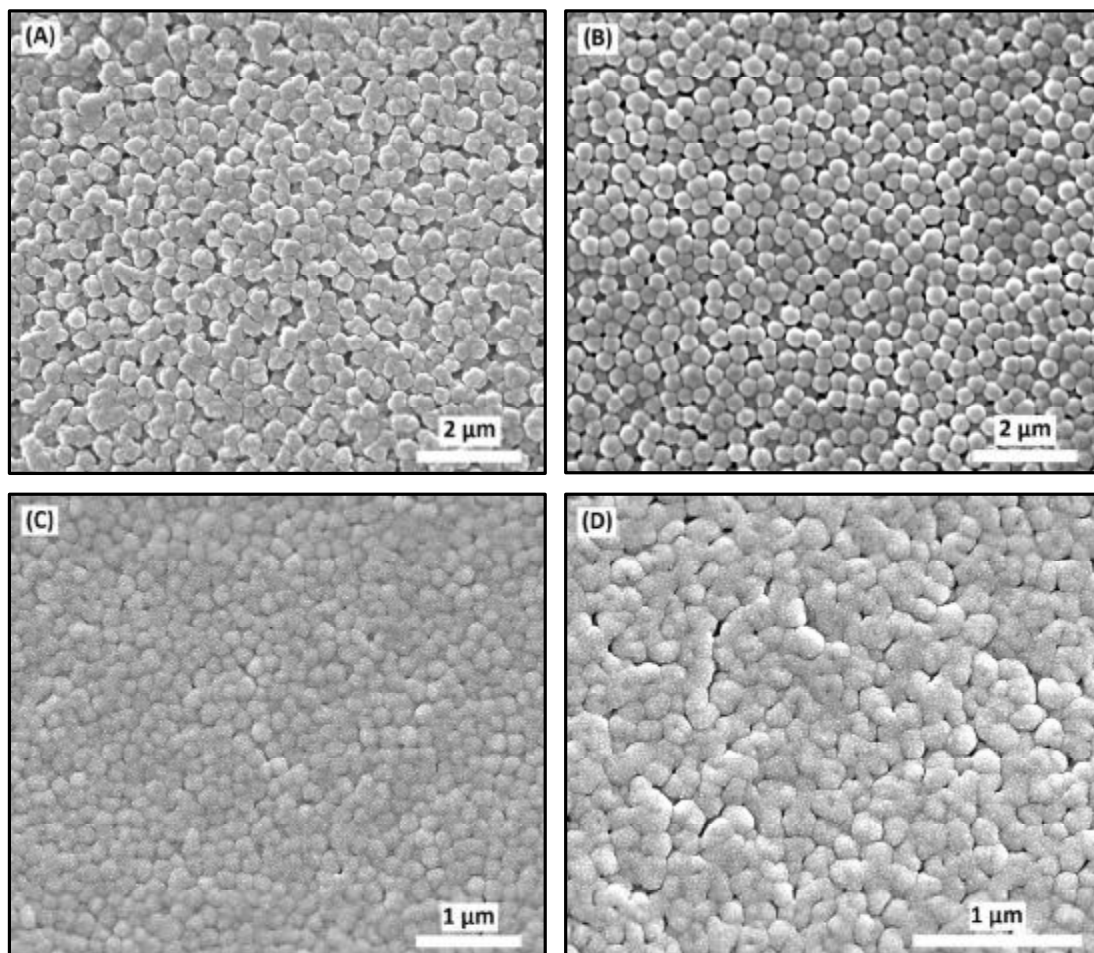


Figure 3. ^1H NMR spectra (CDCl_3) recorded for *linear* PTBAEMA latexes prepared by emulsion polymerization: (a) in the presence of PEGMA macromonomer (entry 9 in Table 1) and (b) in the absence of PEGMA macromonomer (entry 11 in Table 1).

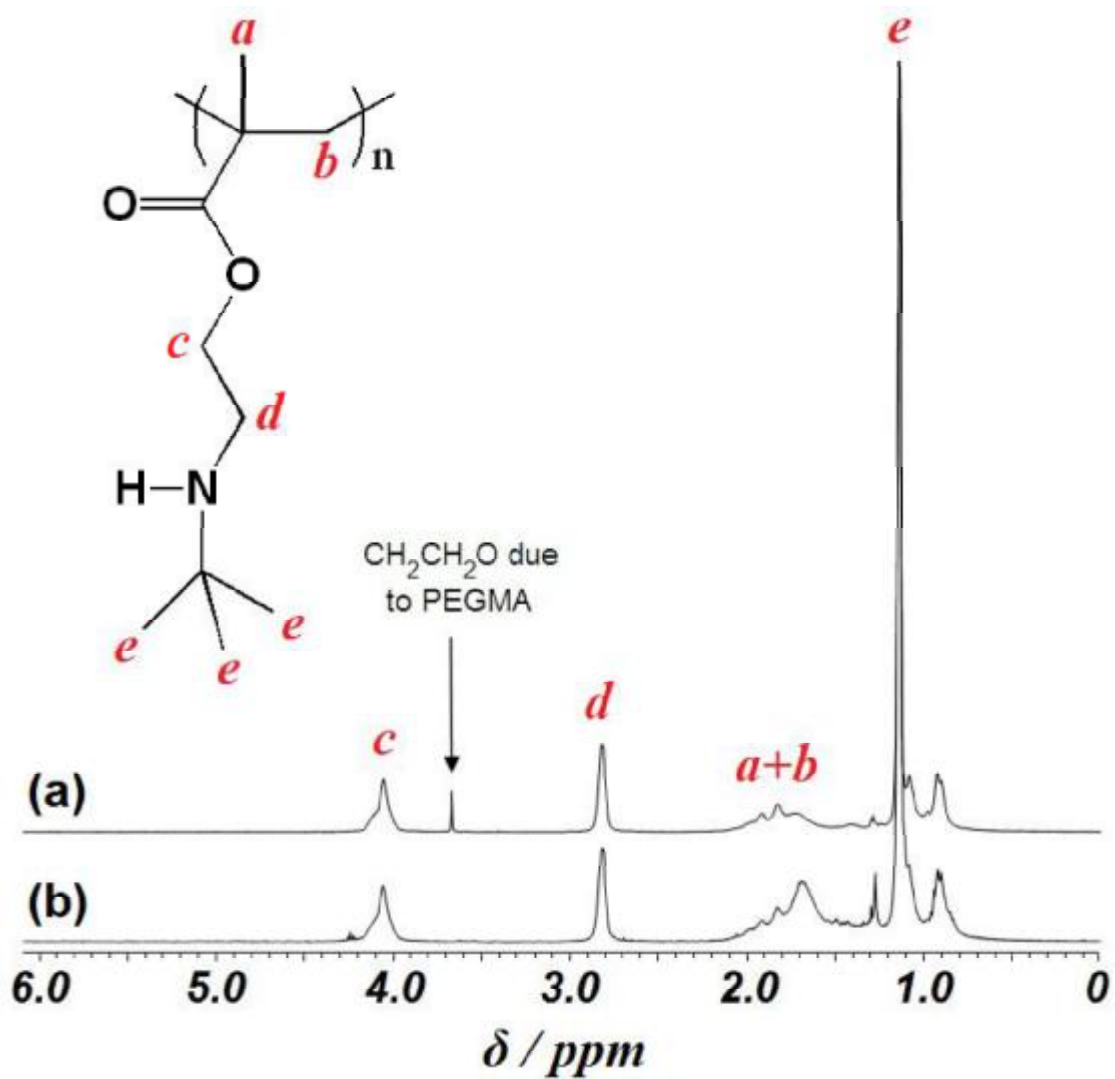


Figure 4. Influence of the degree of DVB cross-linker of the pK_a of PEGMA-PTBAEMA latexes as determined by acid titration studies. In each case, the degree of cross-linking has been corrected to allow for the 80 mol % purity of the DVB cross-linker. The linear PEGMA-PTBAEMA latex is entry 9 in Table 1.

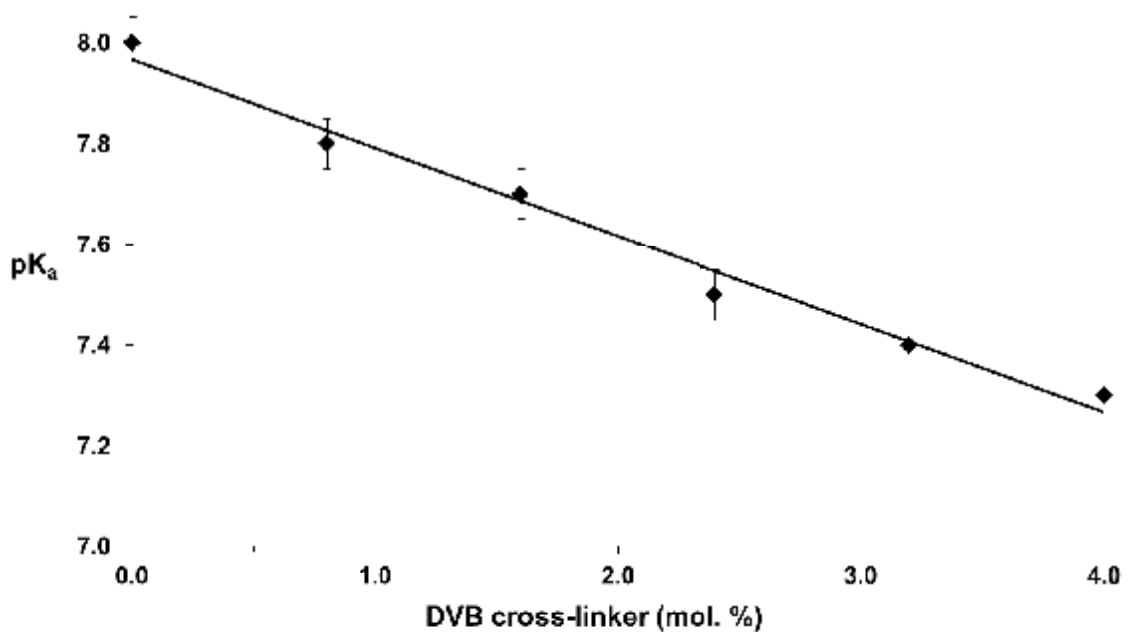


Figure 5. Variation of the hydrodynamic diameter (a) and zeta potential (b) with solution pH for (♦) 0.8 mol % cross-linked PEGMA-PTBAEMA (entry 3, Table 1), (■) 1.6 mol % cross-linked PEGMA-PTBAEMA (entry 4, Table 1), (▲) 2.4 mol % cross-linked PEGMA-PTBAEMA (entry 5, Table 1) and (●) charge-stabilized PTBAEMA (entry 10, Table 1).

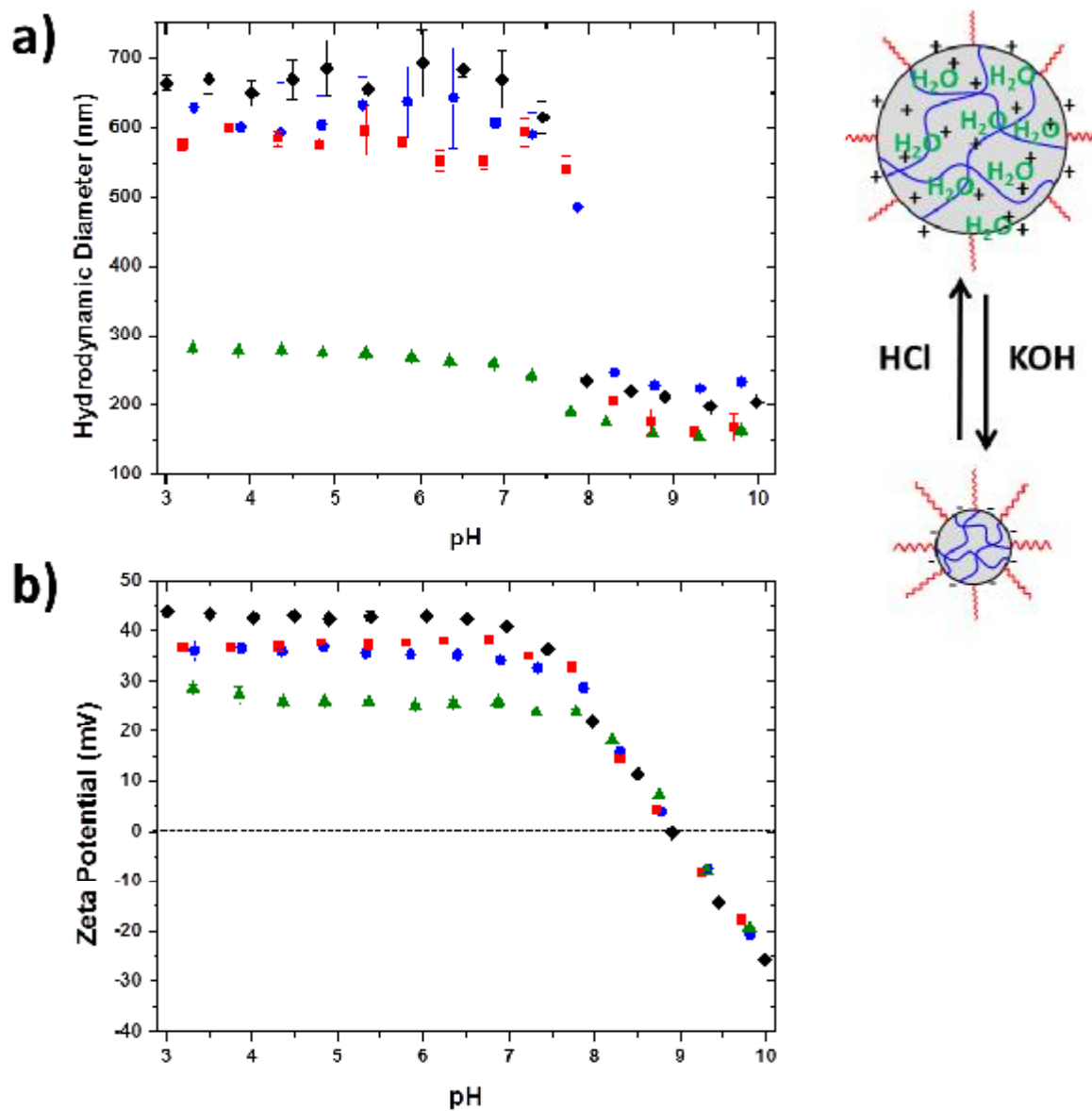


Figure 6. Digital photographs of: (left) the initial PEGMA-PTBAEMA latex (1.1 % solids) with *n*-dodecane oil (dyed with Sudan Red G for clarity) added directly to the vial, (middle) the subsequent *n*-dodecane-in-water emulsion stabilized by this PEGMA-PTBAEMA latex and (right) creaming of the less dense oil droplets and the underlying excess latex. (a) Optical microscope image and (b) Mastersizer size distribution for *n*-dodecane-in-water droplets stabilized using 200 nm PEGMA-PTBAEMA latex.

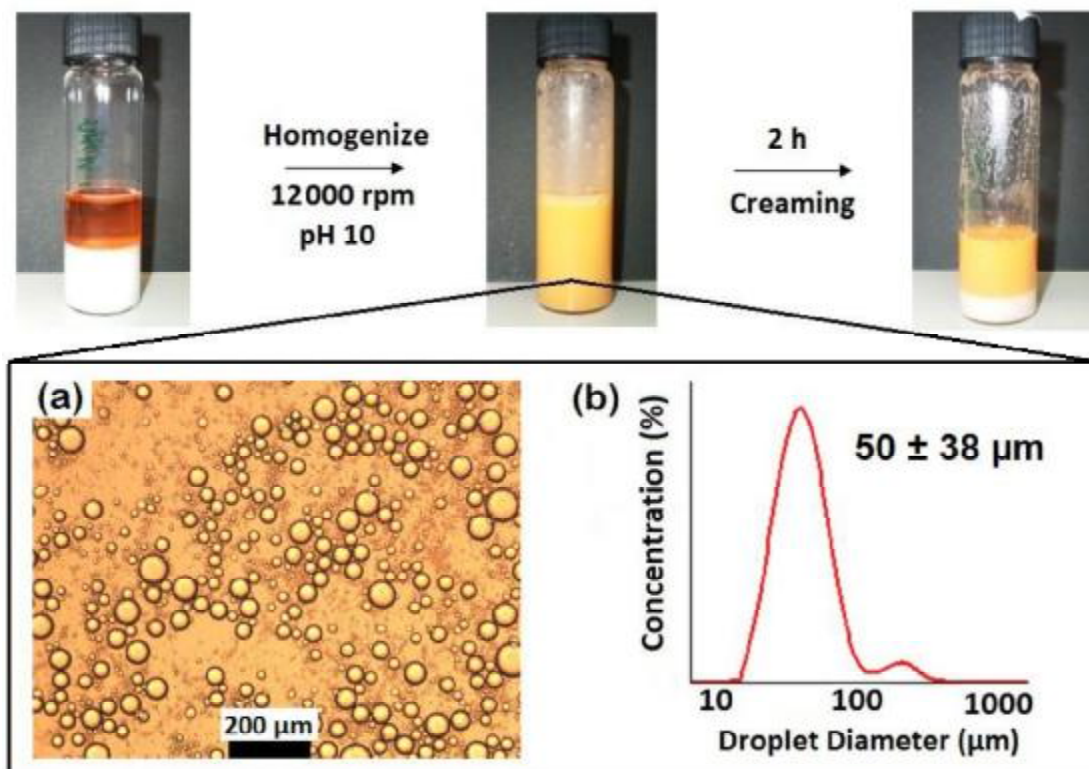


Figure 7. Digital photographs of: (a) charge-stabilized PTBAEMA latex (pH 10.5, 4 mL) plus *n*-dodecane (4 mL) for varying latex solids before homogenization, (b) PTBAEMA stabilized *n*-dodecane-in-water emulsion after homogenization at 12,000 rpm for 2 mins, (c) subsequent creaming of the less dense oil droplets 2 h after homogenization, (d) demulsification of the Pickering emulsion after treatment with 2 drops of conc. HCl. Effective latex solids in each photograph as determined by gravimetry: (1) 2.9 wt % (2) 2.0 wt % (3) 1.20 wt % (4) 0.80 wt % (5) 0.60 wt % (6) 0.30 wt % (7) 0.20 wt %.

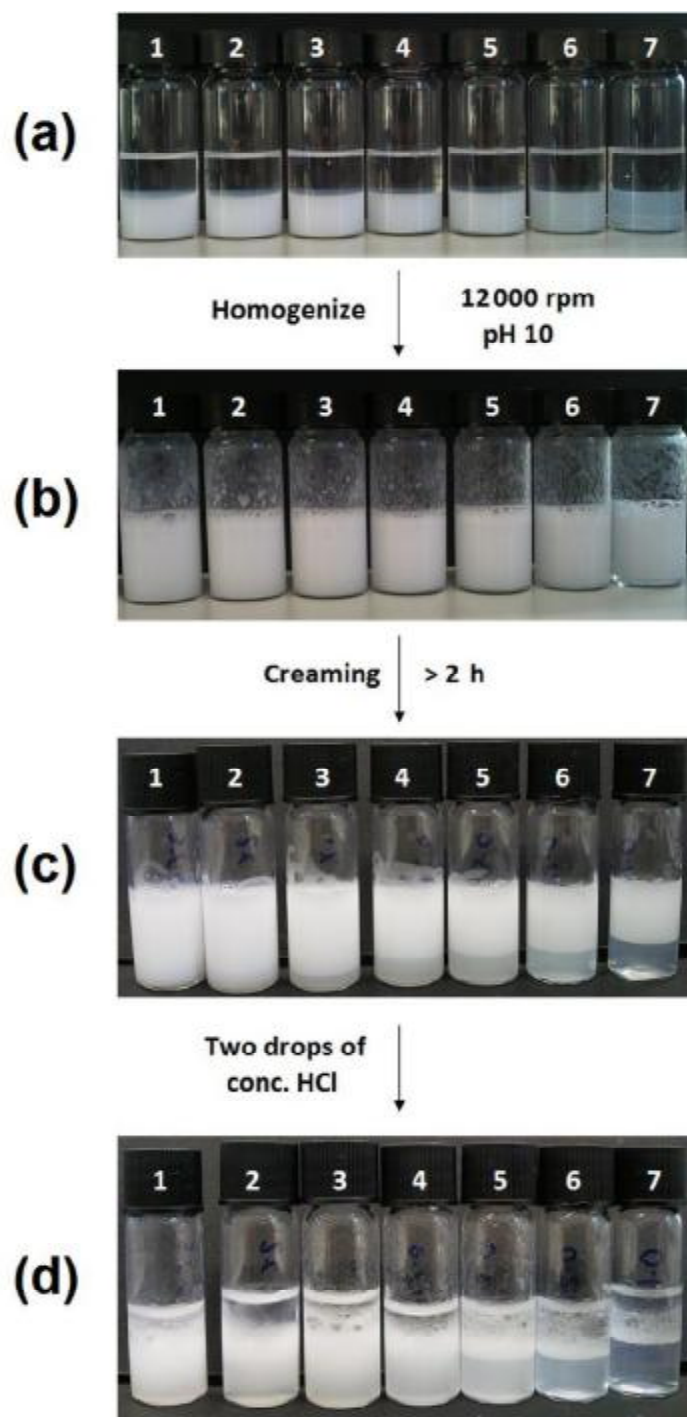


Figure 8. Relationship between mean oil droplet diameter and latex concentration for Pickering emulsions prepared using 220 nm surfactant-free PTBAEMA (entry 10, Table 1) with *n*-dodecane as the oil phase. Latex dispersions were adjusted to pH 10.5 using 0.1 M KOH and homogenized at 12,000 rpm for 2 minutes. Optical microscopy (OM) images for selected entries are shown for the corresponding Pickering emulsions. Scale bars in all OM images are 200 μm .

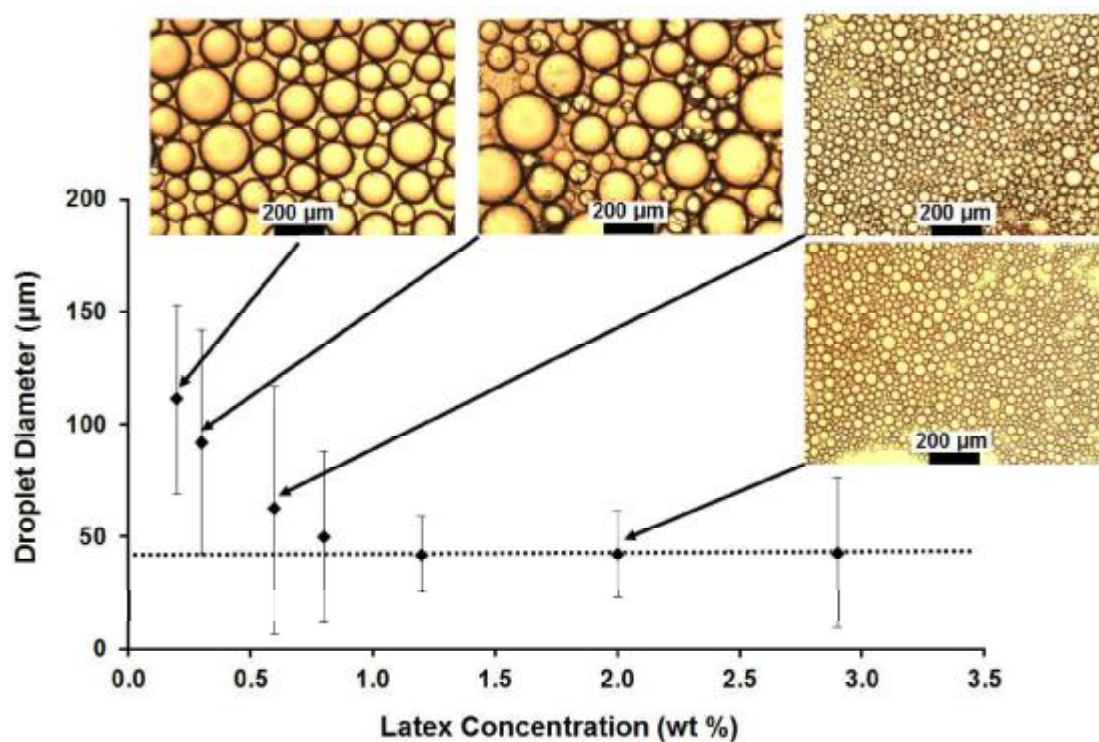


Figure 9. Volume-average droplet diameter distribution curves obtained by laser diffraction for (a) PTBAEMA stabilized *n*-dodecane-in-water emulsions (1.1 % solids) at pH 10 and (b) the resulting reduction in concentration after inverting the pH to 3.05. Measurements were taken every 3 minutes for 60 minutes with the acid being added after the first 5 measurements.

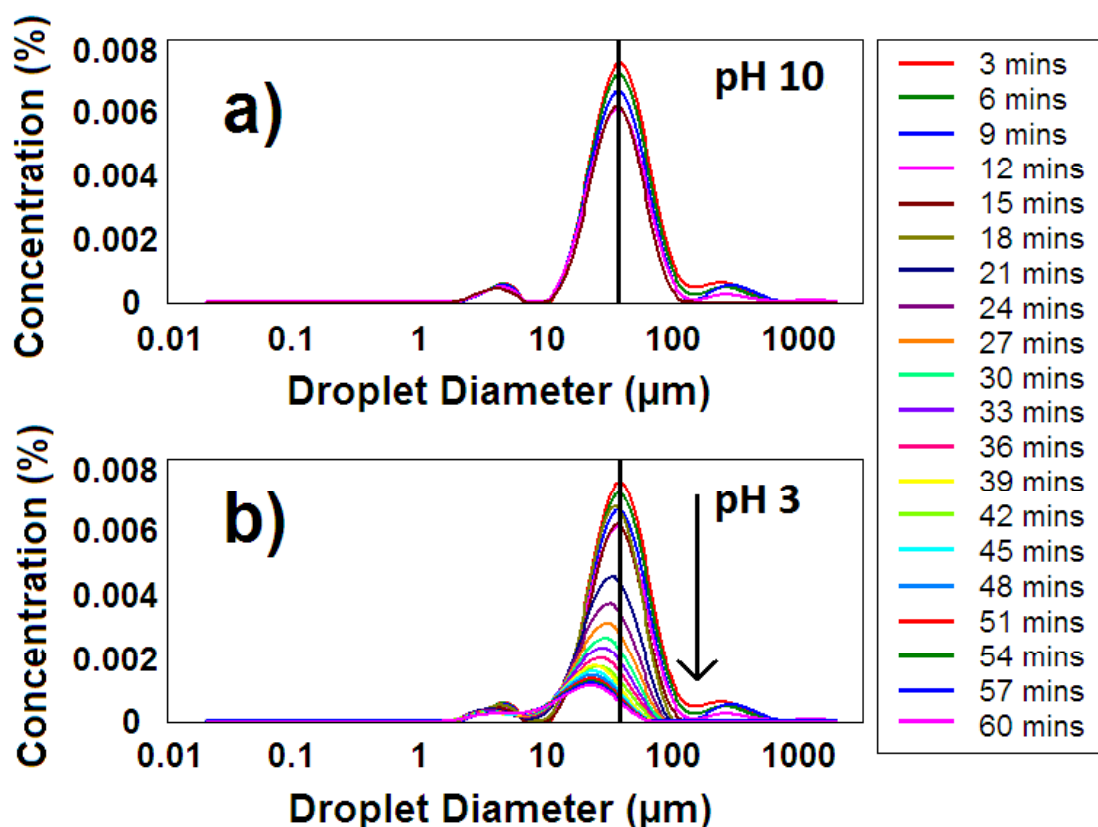


Table of Contents Graphic for Langmuir manuscript:

Novel Pickering Emulsifiers based on pH-Responsive

Poly(*tert*-butylaminoethyl methacrylate) Latexes

A. J. Morse^a, D. Dupin^{a§}, K.L. Thompson^a, S. P. Armes^{a}, K. Ouzineb^b, P. Mills^b, R. Swart^b*

a. Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK.

b. Cytec Surface Specialities S.A./N.V., Anderlechstraat, 33, 1620 Drogenbos, Belgium.

