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Emulsions

Inversion of Particle-Stabilized Emulsions to Form High-Internal-Phase Emulsions**

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High-internal-phase emulsions (HIPEs) occur as end products in a wide range of areas, including the food, cosmetic, pharmaceutical, and petroleum industries. They are commonly defined as emulsions containing an internal phase volume of 70 % or greater, which causes the internal droplets of the emulsion to be of non-uniform size or deformed. Owing to the low ratio of the continuous phase, HIPEs tend to be highly viscous, and they have also been called gel emulsions.[1,2] If the continuous phase is polymerizable, HIPEs can be used as templates to prepare porous polymeric materials, known as PolyHIPEs, which are considered for numerous applications, such as biological tissue scaffolds,[3] sensor materials,[4] supports for solid phase synthesis,[5] and for hydrogen storage.[6] Conventional HIPEs are commonly stabilized by large amounts of surfactants (5–50 wt %). Moreover, the preparation requires careful selection of surfactant, which must be only soluble in the continuous phase to prevent emulsion inversion at high internal phase fractions.[7,8] Along with surfactants, solid particles of sizes between a few nanometers to micrometers have also been used to stabilize emulsions since the early 20th century.[9,10] These emulsions are now called Pickering emulsions, although Ramsden was the first to report them. One interesting advantage of the use of solid particles as emulsifier for emulsions is that these particles can be irreversibly adsorbed at the interface of emulsion because of their high energy of attachment, which makes the final emulsions extremely stable, with shelf-life stabilities of months or even years.[11] In particle-stabilized emulsions, a key parameter controlling the type of emulsion formed is the wettability of the particle, quantified in terms of the contact angle θ (measured through water) it makes with the oil–water interface. If the particles are relatively hydrophilic ($\theta < 90°$), they will preferentially stabilize oil-in-water (o/w) emulsions. Conversely, for relatively hydrophobic particles ($\theta > 90°$), water-in-oil (w/o) emulsions are preferred. Nevertheless, it is possible to modify the wettability of solid particles to influence the type of emulsion, such as by adsorbing surfactant molecules onto the particle surfaces or by silanation.

In recent years, there has been increasing interest in the use of solid particles as sole emulsifier to stabilize the internal phase (e.g., droplets) of the HIPEs. However, one important limitation still remains. Kralchevsky et al.[12] have theoretically predicted that particle-stabilized emulsions will phase-invert above an internal-phase volume fraction of 0.5. Colver et al.[13] reported that in practice, emulsions are stabilized by sub-micrometer microgel particles with volume fractions of the dispersed phase of only 50 %. Binks and co-workers showed that particle-stabilized emulsions commonly phase-invert between volume fractions of 0.65 to 0.70.[14] Recently, Bismarck et al. reported on the successful preparation of HIPEs stabilized solely by functionalized titantia or silica particles with 90 % internal phase volume.[15,16] Most systems reported in the literature are concerned with inorganic particles, from modified silica, clay to metal; organic latex particles have only recently attracted attention as emulsifiers to form HIPEs.[17] In principle, organic latex particles should be particularly attractive for preparing stable HIPEs, as they can be readily designed. For example, by employing flexible pH- and thermo-sensitive poly(*N*-isopropylamide-*co*-methacrylic acid) (PNIPAM-*co*-MAA) microgel particles as sole emulsifier, we have recently prepared a stable HIPE with internal phase volume fraction up to 0.90.[18] This success has widened the types of particles that can be used to prepare HIPEs.

Herein we describe a new strategy to prepare HIPEs by phase inversion of an oil–water system that contains ionizable poly(styrene-*co*-methacrylic acid) (PS-*co*-MAA) particles as particulate emulsifier. Phase inversion of particle-stabilized emulsion has been extensively studied to control the type of emulsion. The inversion can be manipulated by varying the oil/water ratio,[14,19] the ratio of hydrophilic to hydrophobic particles in mixture,[19,20] the aqueous-phase pH value,[21–23] or the temperature.[24] However, most studies are concerned with equal volumes (1:1) of the two liquids. Herein, we show that phase inversion of the ionizable polystyrene-stabilized dichloromethane–water system from the ordinary o/w emulsion to the w/o emulsion at a fixed oil/water ratio (27/73) can be simply driven by either a change of pH value or salt concentration in the single system. This novel inversion directly leads to stable w/o HIPE because the majority continuous phase (namely 73 vol % water) in the original emulsion becomes the dispersed phase, and has not been observed in the corresponding systems stabilized by conventional surfactants or functionalized inorganic particles. The resultant HIPE so produced is also a way of encapsulating

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water, with the adsorbed stimulus-sensitive particle layer providing a means to control the release of the active liquid components.

The PS-*co*-MAA latex particles used to stabilize the emulsions were prepared by surfactant-free emulsion polymerization described before (see the Supporting Information).[25] Copolymerization with MAA provides the carboxylic acid groups that allows the surface charge, that is, the wettability of the particles, to be varied by either changing the solution pH or salt concentration. For imaging with confocal microscopy, the particles were also labeled by copolymerizing with the fluorescent dye methacryloxyethyl thiocarbamoyl rhodamine B (MRB). The resultant PS-*co*-MAA particles coated with carboxylic acid groups have an average hydrodynamic diameter of about 326 nm with a solution pH of 7.5 as determined by dynamic laser light scattering and scanning electron microscopy (SEM). An SEM image (Supporting Information, Figure S1 inset) further confirms that the synthesized particles are spherical and monodispersed. The pH dependence of the zeta potential of the synthesized particles indicates that MAA are copolymerized onto the particles surface (Supporting Information, Figure S2). As the pH value of the solution increases, deprotonation of the carboxylic acid groups on the surfaces results in the surface charge or hydrophilicity of these particles increasing significantly, which are expected to preferentially stabilize o/w emulsions. In contrast, particles with predominantly unionized carboxylic acid group at the low pH value are expected to be more hydrophobic and stabilize water droplets in oil.

It has been mentioned that the surface charge and wettability of the particle emulsifier are key parameters in influencing emulsion type and stability. We have therefore correlated the responsiveness of such PS-*co*-MAA particles to solution pH with their suitability for stabilizing emulsions. Particle-stabilized emulsions were prepared by mechanically shearing a mixture containing the oil phase, dichloromethane, and an aqueous dispersion of PS-*co*-MAA particles (see the Experimental Section). At a fixed internal fraction of dichloromethane (27 vol%), mixing results in three regimes, depending on the particle hydrophilicity (Figure 1). At high pH values ($\mathrm{pH} > 8.0$), emulsions are of high conductivity, disperse in water and not oil, and are thus o/w type. Inversion to low conductivity w/o emulsions, which disperse in oil and not water, occurs just below 7.5. Note that the same phase inversion by controlling the hydrophilicity of particles was recently reported by Binks et al.[21] However, they demonstrated mixture of equal volumes (1:1) of the two liquids. Moreover, the addition of salt (1M NaCl) is needed to promote the carboxylic acid group dissociation on the particle surface; otherwise, the emulsions could not be inverted. In contrast, the phase inversion presented herein results in a transition from an ordinary o/w emulsion to a w/o high internal phase emulsion, because the majority continuous phase in the original emulsion (73 vol% water) becomes the dispersed phase after the inversion. To our knowledge, such a novel inversion approach to directly prepare HIPE has not been demonstrated in oil–water systems stabilized by conventional surfactants and solid particles. Surprisingly, when aqueous solutions of the particles were strongly acidified ($\mathrm{pH} \leq 2$), no flow of emulsion was observed even though the vial was inverted (Figure 1 a), which indicates that the formed HIPE is typical gel emulsion.

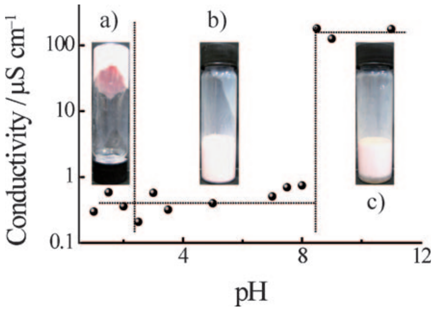

Figure 1. Conductivity of emulsions containing dichloromethane and water stabilized by 5.0 wt% of PS-*co*-MAA latex particles at different pH values. Note that no salt was added. Photographs show typical prepared emulsions in three different regimes: a) gel, b) water/oil HIPE, c) = oil/water.

Figure 2 a shows the appearance of emulsions formed by varying the pH values of particles in the initial dispersion after 12 h preparation. As fluorescent PS-*co*-MAA particles were used as emulsifier, some emulsions were selected and examined by confocal microscopy. All the emulsions showed no sign of coalescence as long as they were prepared. For relatively hydrophilic particles, $\mathrm{pH} \geq 8.0$, stable o/w emulsions are obtained as confirmed by the confocal image (Figure 2d). Most of the oil droplets (the green color arises from the dissolved pyrene excited by laser with wavelength

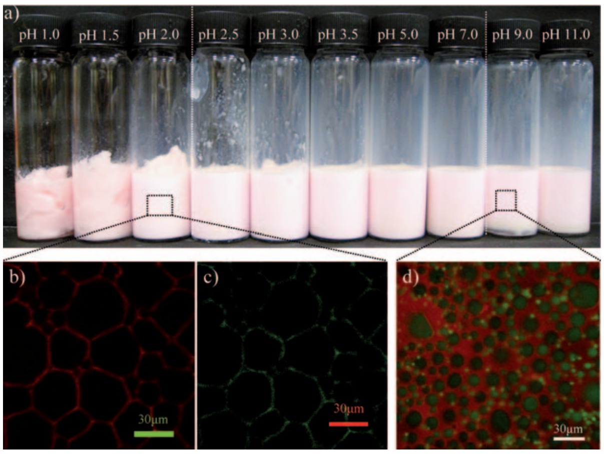

Figure 2. a) Photograph of prepared emulsions as a function of the pH value at room temperature. Samples contain dichloromethane and water and are stabilized by 5.0 wt% PS-*co*-MAA latex particles. Emulsions are o/w at $\mathrm{pH} \geq 8$ (left), w/o HIPEs at $2.5 \leq \mathrm{pH} \leq 7.5$ (middle), and w/o gel emulsions at $\mathrm{pH} \leq 2$ (right). b,c) Confocal images of the same emulsion with 73 vol% water stabilized by 5 wt% PS-*co*-MAA particles excited by lasers with wavelengths 408 nm and 543 nm, respectively. Fluorescent PS-*co*-MAA particles: red; oil with dissolved pyrene: green. d) Confocal image of emulsion with 27 vol% dichloromethane stabilized by 5 wt% PS-*co*-MAA particles simultaneously excited by lasers with wavelengths 408 nm and 543 nm.

408 nm) are spherical, and the fluorescent PS-*co*-MAA particles are clearly seen to be adsorbed at the interface, acting as a barrier against oil-droplet coalescence. For particles of intermediate hydrophobicity ($2.5 \leq \mathrm{pH} \leq 7.5$), stable w/o emulsions form with an internal fraction of water of 73 vol%, and are therefore typical HIPEs. However, no clear water droplets are observed under the confocal microscopy (Supporting Information, Figure S3). For very hydrophobic particles ($\mathrm{pH} \leq 2.0$), stable w/o gel emulsions are obtained that are stable against both coalescence and sedimentation. We observed that the PS-*co*-MAA particles in the aqueous dispersions before emulsification were strongly flocculated at such low pH values because of the absence of repulsion between uncharged carboxylic acid groups on the surface (Supporting Information, Figure S4). These particle aggregates are thereby preferentially wetted by oil and lead to w/o emulsions when the aqueous dispersions are strongly acidified. Figure 2c indicates that dichloromethane with dissolved pyrene is the continuous phase. One the other hand, Figure 2b shows that most of the water droplets are non-spherical, because shape relaxation after deformation is prevented by an armored particle layer. Furthermore, it reveals that particles are located at the oil phase, and excess particles aggregates in oil are probably contiguous with these adsorbed, thus serving to bind the water droplets together into a three-dimensional network, in turn inhibiting the gravity-induced separation. This effect can be of practical importance when excellent HIPE stabilizion is required.

Charged PS-*co*-MAA particles are not only responsive to pH but they are also are sensitive to the presence of electrolyte.[17,21,26] We therefore investigated the influence of salt concentration on a relatively hydrophilic particle system that forms an initial o/w emulsion. The emulsion was prepared by shearing dichloromethane (1.5 mL) and an aqueous dispersion of PS-*co*-MAA particles at a pH value of 9. The internal phase of the oil was also kept at 27 vol%. We discover that the same phase inversion occurs from o/w at low salt concentration to w/o HIPE at high salt concentration (Figure 3a). At salt concentrations below 0.004 M, the conductivity is relatively high, which indicates that the emulsions are dispersed in water and not oil, and therefore water is the continuous phase. The confocal image (Figure 3b) agrees well with the conductivity measurement because it clearly shows that oil droplets are dispersed in water and stabilized by the adsorbed particles. Furthermore, at such a low ionic strength, the particles are relatively hydrophilic and do not aggregate. At intermediate salt concentrations ($0.004\,\mathrm{M} < [\mathrm{NaCl}] < 0.5\,\mathrm{M}$), the emulsions exhibit low conductivities, disperse in oil rather than in water, and are therefore oil-continuous. Again, this inversion directly leads to a HIPE in which water is encapsulated. However, the particles are located in the oil phase and they formed a partially connected network to trap the water droplets (Figure 3c). At higher salt concentrations, ($[\mathrm{NaCl}] \geq 1\,\mathrm{M}$), gel emulsions result (see photographs in Figure 3c). The strongly flocculated particles in the aqueous dispersions before emulsification was also observed at the high salt concentration because the added salt screens the electrostatic repulsion between the charged carboxylic acid groups and renders the particles more hydrophobic (Supporting Information, Figure S5).[27] Therefore, these particles become preferentially wetted by oil and stabilize water droplet in the oil. Figure 3d reveals the excess particles (or particle aggregates); those adsorbed also form a three-dimensional network to trap water droplets inside the gel matrix, which abruptly increase the viscoelastic properties of the emulsions. Importantly, the salt-induced phase inversion most likely leads to a more uniform and smaller water droplet encapsulated in the gel network.

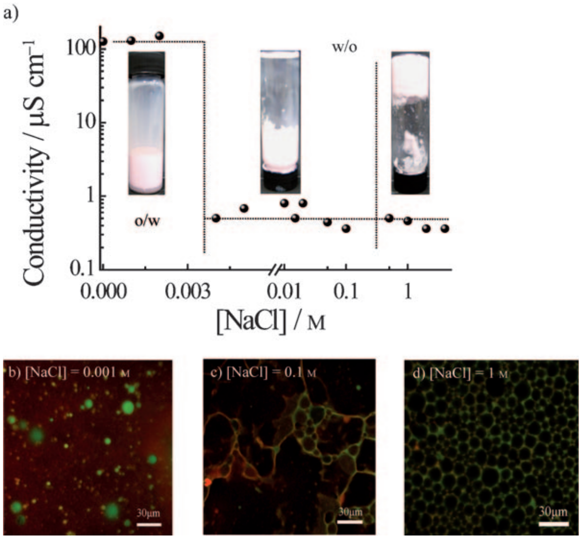

Figure 3. a) Conductivity of emulsions containing dichloromethane and water stabilized by 5.0 wt% of PS-*co*-MAA latex particles at different salt concentration. The pH value of the PS-*co*-MAA particles in the initial dispersion was 9. Photographs show prepared emulsions in three different salt concentration regimes. b–d) Confocal images of emulsion containing dichloromethane and water stabilized by 5 wt% PS-*co*-MAA particles simultaneously excited by lasers with wavelengths 408 nm and 543 nm at salt concentrations of a) 0.001 M, b) 0.1 M, and c) 1 M.

In conclusion, we have shown that stable w/o HIPEs with an internal phase of 73% can be prepared by novel inversion from a particle-stabilized ordinary emulsion. The inversion from o/w to w/o at a fixed oil/water ratio can be simply triggered by decreasing the pH value or increasing salt concentration in a single system. The reason for this change is that the hydrophilicity of the PS-*co*-MAA particles can be tuned by a progressive changing not only with pH value but also the salt concentration. At relatively low pH values or high salt concentrations, the particles are not only adsorbed at the interface to prevent the water droplets coalescence, but the excess particles also are contiguous with those adsorbed, thus serving to bind the water droplets together into a three-dimensional network, which in turn abruptly increases the sedimentation stability of the emulsion. The resultant HIPEs, in which water become encapsulated, have great potential applications in the food, pharmaceutical, and cosmetics industries.

Experimental Section

The synthesis and characterization of the PS-*co*-MAA particles is described in the Supporting Information. The pH values of aqueous dispersions of PS-*co*-MAA were adjusted with HCl or NaOH before emulsification. NaCl was directly added to vary the concentration of salt in the aqueous dispersions of PS-*co*-MAA particles. Particle-stabilized emulsions were prepared by mechanically shearing a mixture containing the dispersed phase, dichloromethane (1.5 mL), and an aqueous dispersion of particles (4 mL, 5 wt% particle concentration) for 60 s with Ultra Turrax T25 homogenizer (10 mm head) operating at 17500 rpm. The emulsion type was determined by measuring the conductivity (Jenway). The confocal microscopy pictures were taken on a Nikon Eclipse Ti inverted microscope (Nikon, Japan). Lasers with wavelengths of 543 nm and 408 nm were used to excite the fluorescently PS-*co*-MAA particles and pyrene, respectively, and an oil immersion objective (60×, NA = 1.49) was used. The emulsions were placed on the cover glass and a series of *x*/*y* layers was scanned.

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