*Macromolecules* **2006,** *39,* 8171−8177

# Environmental Responsiveness of Microgel Particles and Particle-Stabilized Emulsions

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*Received June 20, 2006; Revised Manuscript Received September 1, 2006*

ABSTRACT: Using stimulus-sensitive microgel particles as an emulsifier, we have prepared a new type of emulsion responsive to pH, ionic strength, and temperature changes. Each of these environmental changes can trigger a volume phase transition in poly(*N*-isopropylacrylamide) (PNIPAM) microgel particles containing some carboxylic groups. Depending on their hydrophobicity and charging state, such PNIPAM microgel particles can adsorb to the droplets of an octanol-in-water emulsion and provide excellent stability against coalescence and ripening. We have studied in detail the correlation between the particles' response to changes in the solution conditions and the corresponding response of particle-decorated emulsion droplets. In their swollen, hydrophilic state, the microgel particles consistently stabilize the octanol droplets, but inducing a microgel collapse usually results in a destabilization of the emulsion and eventually in phase separation. A notable exception was found at high pH where particles are highly charged: in this regime emulsions remain stable even upon a temperature-induced collapse of the microgel particles and prove sensitive only to high levels of screening ions. Microscopy studies of toluene-in-water emulsions stabilized by compact polystyrene particles of variable surface charge further suggest an intimate connection between the charge and packing density of interfacial particles and hint at a charge-induced interparticle attraction.

## Introduction

Emulsions are thermodynamically unstable and in general separate into two phases over a period of time. It is well documented that solid particles of colloidal size, just like traditional low molar mass surfactants, polymeric surfactants, or amphiphilic polymers, can self-assemble at oil−water interfaces and provide excellent long-term kinetic stability to both simple and multiple emulsions.[1−4] Such solid-stabilized emulsions, often referred to as "Pickering emulsions", were already described a century ago.[5,6] Our current understanding of the stabilization mechanism credits the particles both for providing a steric hindrance to droplet−droplet coalescence and for modifying the rheological properties of the interfacial region. At sufficiently high interfacial concentrations of the solid (typically $\geq$80% of close particle packing), the interface exhibits viscoelastic behavior, and the rate of film drainage between coalescing droplets is retarded due to the increased energy required to displace particles from the interdroplet contact region.[7,8]

Experimentally, a wide variety of solid materials has been used as stabilizers of either water-in-oil (w/o) or oil-in-water (o/w) emulsions, including silica,[9−12] clay,[13,14] and latex particles.[15−17] These inorganic and polymeric particles offer a number of potential advantages over conventional surfactants, such as reduced foaming, more robust formulations, or reduced health hazards in certain applications. Binks and co-workers have carried out a comprehensive study on the formation, stability, and structure of emulsions stabilized exclusively by solid particles.[4,9] They have shown that the inversion of emulsions can be achieved by tuning the particle hydrophobicity or varying the relative volume fraction of water and oil. Recently, Armes et al.[18−20] have used polystyrene particles with grafted copolymer containing amine groups as an emulsifier in a hexadecane−water system and shown that particle charge and hydrophobicity are important parameters in determining the emulsion type and stability. The particle hydrophobicity is linked to the contact angle $\theta$ between the particle surface and the liquid−liquid interface. Hydrophilic particles, like metal oxides, with a contact angle less than 90° (measured through the water phase) tend to stabilize o/w emulsions, while hydrophobic particles, like carbon, with a contact angle larger 90° tend to stabilize w/o emulsions.[3,4]

Recently, there has been growing interest in Pickering emulsions because of their importance in the cosmetics, food, agricultural, and paint industries.[21] In addition, Pickering emulsions have been used as templates for the formation of microcapsules. Dinsmore and co-workers[22] have coined the word "colloidosomes" for interfacial particles assembled into a shell of defined porosity, and a number of controlled-release applications have been suggested for such systems. In recent studies, advances have been made in developing environmentally responsive Pickering emulsions based on polymer microgels[23] or polymer−silica composite microgel particles.[24]

We have recently reported a novel surfactant-free octanol-in-water emulsion stabilized solely by poly(*N*-isopropylacrylamide) (PNIPAM) microgel particles.[23] These microgel particles resemble hydrophobic colloids in many respects; they can be flocculated by the addition of salt or polymers and can be readily characterized by standard techniques such as electrophoresis and dynamic light scattering. Structurally, however, microgel particles constitute a three-dimensional, covalently cross-linked network and can swell in good solvents.[25,26] One advantage of using PNIPAM microgel particles for emulsification lies in the fact that PNIPAM-based microgels exhibit an extreme response to changes in temperature, which can lead to dramatic changes in particle size, surface charge density, and water content over a small (5−10 °C) temperature change, reflecting a change of hydrophobicity of the microgels. On the other hand, the

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10.1021/ma061366k CCC: \$33.50

incorporation of some carboxylic groups introduces a similar sensitivity to the pH and ionic strength, thus providing additional triggers of the volume phase transition in PNIPAM microgels.[27] One can therefore imagine that this new kind of multivariable emulsifier provides extended emulsion control, opening up a large range of applications.

In the present study, we examine in more detail the correlation of the microgel particles' charge and hydrophobicity with their emulsification performance by varying solution pH, ionic strength, and temperature. We also extend our studies to the effects of the particle concentration, oil/water ratio, and the polarity of the oil phase on the behavior of such PNIPAM-based microgel emulsifiers during the emulsion preparation. Finally, the role of charge for compact particulate emulsifiers was examined in a parallel experiment using toluene-in-water emulsions stabilized by polystyrene particles of variable surface charge.

## Experimental Section

**Materials.** *N*-Isopropylacrylamide (NIPAM, Fluka) was recrystallized from a toluene/*n*-hexane mixture. *N*,*N*′-Methylenebis(acrylamide) (MBAA, Fluka), methacrylic acid (MAA, Merck), and the fluorescent dye methacryloxyethylthiocarbamoyl rhodamine B (MRB, Polysciences, Inc.) were used as received. Styrene monomer (BASF) was distilled under reduced pressure before use. Divinylbenzene (Fluka), potassium persulfate (KPS, Merck), commercial Pluronic F108 (BASF), and oils (octanol, toluene, and hexadecane, Fluka) were used without further purification. Deionized water was used in all the experiments.

**Microgel Preparation.** PNIPAM microgel particles were synthesized using surfactant-free precipitation polymerization.[27] Typically, 6.0 g of NIPAM, 0.18 g of MBAA, and 0.3 g of MAA were dissolved into 280 mL of deionized water in a 500 mL reactor fitted with a nitrogen bubbling inlet and outlet, a mechanical stirrer, and a reflux condenser. Then the solution mixture was adjusted to pH 10 with sodium hydroxide (NaOH). After stirring the solution for 40 min at 70 °C under a nitrogen purge, the polymerization was initiated by adding 0.065 g of KPS dissolved in 20 mL of deionized water. The reaction mixture was kept at 70 °C for 8 h, and the resulting microgel particles were used as particulate emulsifiers in the solid-stabilized emulsions. In some cases, PNIPAM microgel particles were also labeled by copolymerization with 0.1 wt % MRB for easier identification of the microgel-containing phase after emulsion breaking.

**Polystyrene Particle Preparation.** Emulsifier-free polymerization of cross-linked polystyrene latex particles with carboxylic group was conducted in the same kind of reactor. 12.0 g of styrene, 0.60 g of divinylbenzene, and 0.60 g of MAA were dissolved in 280 mL of deionized water and heated to 65 °C under a nitrogen purge for 40 min to remove dissolved oxygen. Then, 0.132 g of KPS dissolved in 20 mL of deionized water was added to start the polymerization. During polymerization, some NaOH (∼0.20 g) was added to partially ionize the carboxylic groups. The reaction was carried out continuously at 65 °C for 8 h, and the resulting polystyrene particles were used as particulate emulsifiers in some of the solid-stabilized emulsions described below.

**Emulsion Preparation.** Stock solutions of PNIPAM microgel particles or polystyrene particles at the desired solid content were prepared by dilution. The pH values of aqueous dispersions of microgel and polystyrene particles were adjusted with HCl or NaOH. Batch emulsions were prepared by mixing the microgels or polystyrene particle dispersions with the proper amount of oil (octanol, toluene, or hexadecane) and then homogenizing the mixture for 3 min using an Ultra-Turrax (Janke and Kunkel) rotor−stator mixer with an 18 mm dispersing head operating at 8000 rpm. The total emulsion volume was 20 cm$^3$. The emulsion type was determined by measuring the conductivity and by observing whether a drop of emulsion dispersed when added to a small volume of pure water or oil.

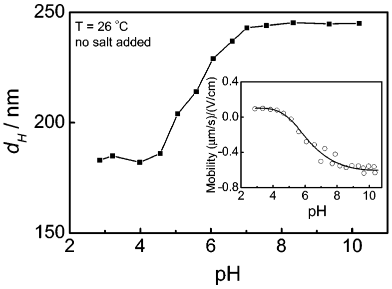

**Figure 1.** pH dependence of the mean hydrodynamic diameter $d_H$ of PNIPAM microgel particles in an aqueous dispersion at a microgel particle concentration of 20.5 mg L$^{-1}$. The inset shows the pH dependence of the electrophoretic mobility of PNIPAM microgel particles, where 10 mM KCl was added as the background electrolyte.

**Physical Measurements.** The size of microgel and polystyrene particles was measured using laser light scattering (LLS). The apparatus used for LLS measurements was an ALV-5000 goniometer setup (ALV Laser) equipped with a helium−neon laser and a digital correlator. Mean hydrodynamic particle diameters $d_H$ were obtained from a third-order cumulant fit to the measured intensity autocorrelation function.[28] The electrophoretic mobility of the microgel particles was measured using a Malvern Zetasizer 3000 HS$_A$. Emulsion drop size distributions were examined using a Malvern Mastersizer light diffraction instrument and optical microscopy just after the preparation of emulsions. For information on the structure of the assembled particle layer at the liquid−liquid interface, some of the emulsions were imaged using freeze-fracture scanning electron microscopy (SEM).

## Results and Discussion

**Effect of pH on Emulsion Stability.** Figure 1 shows that, for a given temperature, the size of the PNIPAM microgel particles increases continuously from pH 4.0 to pH 8.0 and plateaus at higher pH. With increasing pH, more and more carboxylic groups (−COOH) within the microgel particles are deprotonated to the anionic −COO$^-$ form so that the internal electrostatic repulsion within the microgel particles is enhanced. When the repulsion overcomes the attractive force due to hydrogen bonding or hydrophobic interaction, the microgel swells. The electrophoretic mobility shown in the inset of Figure 1 illustrates the charging of the microgel particles as more carboxyl groups are ionized.

It has been mentioned that the surface charge and hydrophobicity of the particle emulsifier are key parameters in determining emulsion type and stability.[3,4] We have therefore correlated the responsiveness of such PNIPAM microgel particles to solution pH with their suitability for stabilizing oil-in-water emulsions. At high pH, such emulsions showed no signs of coalescence or ripening. A typical freeze-fracture SEM image of an octanol-in-water emulsion prepared at pH 9.4 is shown in Figure 2. As the micrographs suggest, self-assembly of the swollen particles at the octanol−water interface under these conditions leads to a dense coverage of the octanol droplets with the stabilizing PNIPAM microgel.

Figure 3 shows the effect of solution pH on the size distribution of the octanol droplets in emulsions stabilized by 1.0 wt % of PNIPAM microgel particles. All of these emulsions were of o/w type at a 30% volume fraction of octanol, and no surfactant was added. Size distributions for emulsions prepared above pH 6.0 remain essentially unchanged even after 4 months of storage at room temperature. When the solution pH is decreased below pH 6.0, the initially stable emulsions start to coarsen. The distribution shown for pH 4.5 in fact represents a mere snapshot of a continually coarsening system, which eventually undergoes macroscopic phase separation. Further

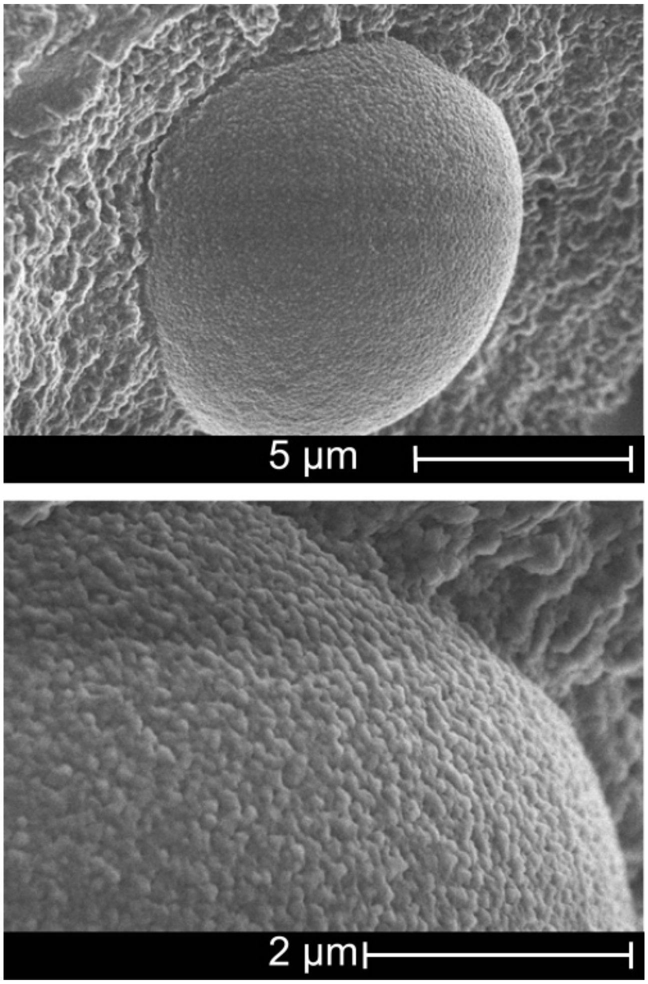

**Figure 2.** Typical freeze-fracture SEM pictures of a densely covered droplet in an emulsion prepared at pH 9.4 and 25 °C, which contains 30 vol % of octanol and 1.0 wt % PNIPAM microgel particles.

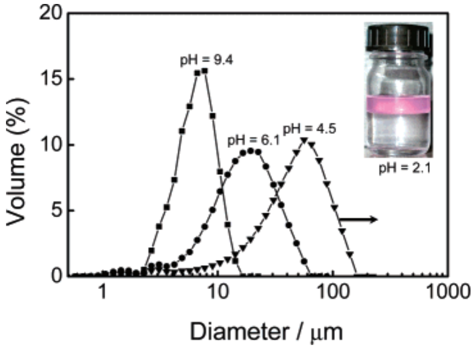

**Figure 3.** pH dependence of the size distribution of emulsion droplets stabilized by PNIPAM microgel particles at 25 °C, where emulsions contain 30% volume fraction of octanol and 1.0 wt % PNIPAM microgel particles. The distribution shown for pH 4.5 represents only a snapshot of a continually coarsening emulsion. The inset shows a photograph taken after rapid phase separation of an emulsion prepared at pH 2.1. Note that the oil phase is strongly colored by the dye-labeled microgel particles.

acidification below pH 3 leads to a rapid breaking of the emulsion. In the case of the phase-separated system shown in the inset of Figure 3, dye-labeled microgel particles were used to stabilize the original emulsion, which was broken by adjusting the pH to 2.1. From the strong coloring of the separated oil phase we infer that the dye-labeled microgel particles, which are fully protonated at this pH, are mostly driven into the oil phase.

The above observations indicate that the stabilizing power of our microgel particles is related to the dissociation of the $-$COOH groups and the ensuing particle charge; the detailed stabilization mechanism, however, is far from obvious. It may in fact seem counterintuitive that dense packing of the particles in the liquid interface occurs in a situation where the particles are the most charged and where the electrostatic repulsion between interfacial particles—dipolar in nature due to the asymmetry of their counterion atmosphere—should be particularly strong.[29,30] The explanation for the observed close contact between such putatively repulsive particles most likely involves the following arguments: in addition to any lateral force, charged particles in a liquid−liquid interface also experience a normal force, pushing them more deeply into the medium of higher electric permittivity,[31] in our case the water phase. This normal force is stronger for more highly charged particles and should be particularly pronounced if some of the particle charge faces the less polar liquid, i.e., if charges exist at the particle−oil interface.[31] As a result of the normal force, strongly charged particles protrude deeply into the water phase where their electrostatic interaction is weaker (high $\epsilon$) and shorter ranged due to screening. More importantly, the normal force deforms the interface and gives rise to a capillary interaction between the particles.[32] There has recently been an intense debate regarding the range[31−38] and even the sign[39,40] of the capillary force, but experimental evidence clearly suggest a strong attraction, at least for short and intermediate separations.[31,37] We suspect that it is this capillary attraction which facilitates the dense coverage of our emulsion droplets with microgel particles when the pH and particle charge are high.

Conversely, as the pH and particle charge are lowered, so are the normal force on the particles and the ensuing capillary attraction. At the same time, the particles' stronger immersion into the oil phase increases the range of the remaining electrostatic repulsion.[41,42] An important point to note here is that the microgel particles used in present study are neither classical amphiphilic emulsifiers nor compact solid particles. They are (partially) water-swollen even when particles protrude into the oil phase, which facilitates the ionization of $-$COOH groups inside the gel network. We conjecture that the strong interparticle repulsion across the oil phase promotes partial desorption of microgel particles, reducing the coverage of the oil−water interface. The incompletely covered droplets are more prone to coalescence and ripening; hence the coarsening of our emulsions below pH 6. Direct experimental evidence for a reduced packing density of interfacial particles in response to a reduction of the particle charge will be given for a different Pickering system in the last paragraph of this article.

When strongly acidified (pH 2), our microgel-stabilized emulsions undergo rapid separation into a particle-depleted water phase and particle-rich oil phase. The partitioning of particles between the two phases can be inferred from the strong coloring of the separated oil phase by the fluorescent label of the microgel particles (Figure 3); it suggests a massive transfer of particles from the liquid interface into the bulk of the oil phase as the likely cause for demulsification.

One may wonder whether the originally water-swollen particles completely expel their water load in the process or whether they carry water along into the oil. To answer this question, a drop of the oil phase was diluted with octanol and then compared with a freeze-dried sample that was redispersed in octanol. Figure 4 shows the typical size distributions $f(d_H)$ of the PNIPAM microgel in pure water (the dispersion at pH $\sim$ 2.5), in pure octanol (after freeze-drying), and in the octanol

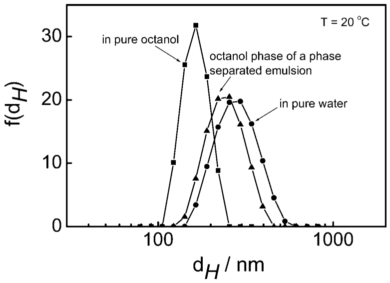

**Figure 4.** Typical hydrodynamic diameter distributions $f(d_H)$ of PNIPAM microgel particles in pure water, in pure octanol (redispersed after freeze-drying), and in the octanol phase of a phase separated emulsion.

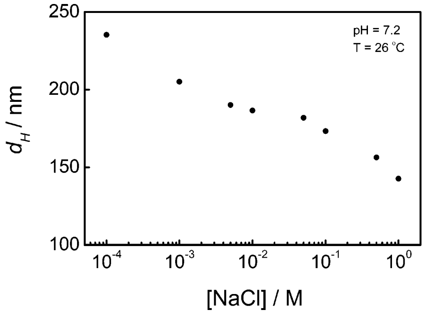

**Figure 5.** Ionic strength dependence of mean hydrodynamic diameter $d_H$ of PNIPAM microgel particles in an aqueous dispersion at pH 7.2 and 26 °C. The microgel particle concentration is 20.5 mg L$^{-1}$.

phase of a corresponding broken emulsion. Generally, the PNIPAM microgels are more swollen in water than in octanol, which can be attributed to the fact that water is a better solvent than alcohol for PNIPAM at 20 °C.[43,44] For the tested sample from the octanol phase of a broken emulsion, the size distribution resembles more closely the one of the aqueous dispersion, which reveals that the microgel particles still remain partially water-swollen, even when transferred into the octanol phase.

**Effect of Ionic Strength on Emulsion Stability.** The introduction of carboxyl groups via the free radical copolymerization of methacrylic acid (MAA) also makes the PNIPAM microgels presented in this study responsive to changes in the ionic strength. Figure 5 shows that the addition of sodium chloride to an aqueous dispersion of PNIPAM microgel particles reduces their size. In the absence of added electrolyte, PNIPAM microgels are almost fully swollen at 26 °C when the solution pH is greater than 7.2 (Figure 1). As the concentration of sodium chloride increases, the electrostatic repulsion within the microgel particles is screened, resulting in the observed dramatic shrinking of the particles.

Figure 6 shows the dependence of emulsion stability on ionic strength. Different amounts of NaCl were added to stable emulsions prepared at pH 9.4 using equal volumes of octanol and a 1.0 wt % aqueous dispersion of PNIPAM microgel particles. These emulsions were found to be of the o/w type both by conductivity measurements and by the “drop test”, which infers the emulsion type from a comparison of the emulsion’s miscibility with either of the pure liquids.

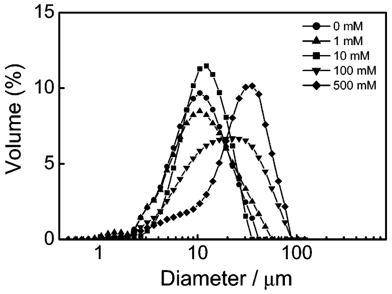

**Figure 6.** Ionic strength dependence of the size distribution of emulsion droplets stabilized by PNIPAM microgel particles at pH 9.4 and 25 °C, where emulsions contain 50 vol % of octanol and 1.0 wt % PNIPAM microgel particles. The ionic strength is adjusted by adding NaCl to the emulsion. The distributions shown for 100 mM NaCl and above are highly unstable.

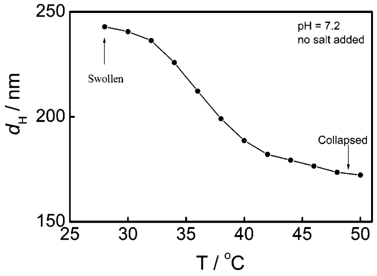

**Figure 7.** Temperature dependence of the mean hydrodynamic diameter $d_H$ of PNIPAM microgel particles in an aqueous dispersion at pH 7.2 with a microgel particle concentration of 20.5 mg L$^{-1}$. The same qualitative behavior has been observed for this type of particle at pH 9.4.[23]

At high pH, the PNIPAM microgel particles are deprotonated and hence behave like conventional polyelectrolytes. The added salt screens the interchain and interparticle electrostatic repulsion and renders the microgel particles more hydrophobic, as suggested by Figure 5.[27] Coarsening and destabilization occur when the concentration of salt is progressively increased. Above 100 mM NaCl, the emulsion droplets are larger and with a very broad size distribution that evolves fast toward a phase separation. These observations indicate that under conditions of high salt concentration the activity of microgel particles at the interface is substantially reduced, leaving the oil droplets unprotected.

**Effect of Temperature on Emulsion Stability.** Figure 7 shows the temperature dependence of the mean hydrodynamic diameter $d_H$ for the PNIPAM microgel particles in water at a constant pH of 7.2. Qualitatively similar results were obtained at pH 9.4 on another batch of microgel particles.[23] The microgel particles gradually shrink into an increasingly collapsed state when the temperature is raised to 50 °C. The swelling and shrinking of a polymeric gel network can be generally attributed to a balance between the repulsion and attraction among functional groups attached to the gel network. When attractive forces such as hydrogen bonding or hydrophobic interaction overcome the repulsive force, usually electrostatic in nature, the gel network shrinks. The decrease of $d_H$ shown in Figure 7 is expected since the increase of temperature weakens the hydration and the PNIPAM chain gradually becomes more hydrophobic, leading to the collapse of the microgel particles.[25]

Given the particles’ response to temperature changes, one might expect their emulsifying properties to be a function of temperature, too. We have therefore investigated the influence of temperature on the stability of microgel-stabilized emulsions. Stable o/w emulsions were prepared at room temperature with pH = 6.1 and 9.4 and then heated in a water bath at 60 °C for 1 h. Before and after heating, one drop of each sample was characterized by light microscopy. Figure 8 shows that heating leads to the coarsening of emulsions prepared at pH 6.1. We relate this effect to the increased hydrophobicity of the collapsed particles. In this hydrophobic state, the interfacial particles are again expected to move deeper into the oil phase and possibly some desorption takes place. The insufficiently covered emul-

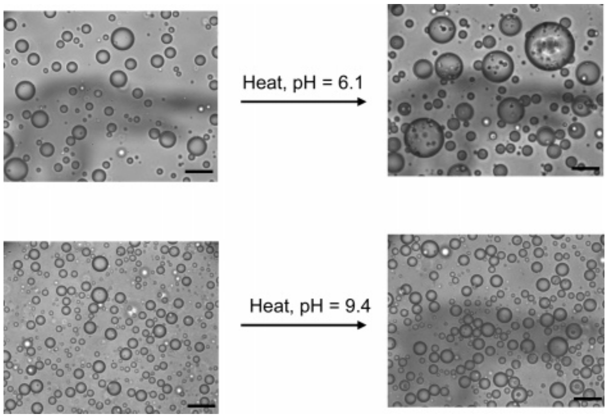

**Figure 8.** Optical micrograph illustrating the temperature-dependent stability of an octanol-in-water emulsion prepared with PNIPAM microgel particles at pH 6.1 and 9.4. The scale bar corresponds to 20 $\mu$m.

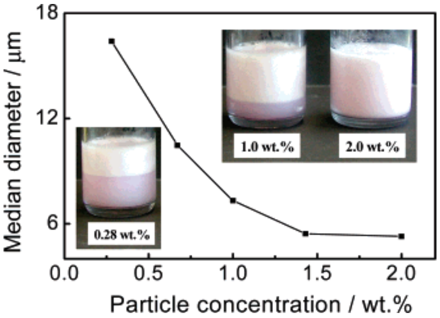

**Figure 9.** Effect of particle concentration on the median drop diameter of emulsions stabilized by PNIPAM microgel particles at pH 9.4 and 25 °C, where emulsions contain 30% volume fraction of octanol. Optical micrographs in the inset illustrate the concentration-dependent stability of emulsions against creaming.

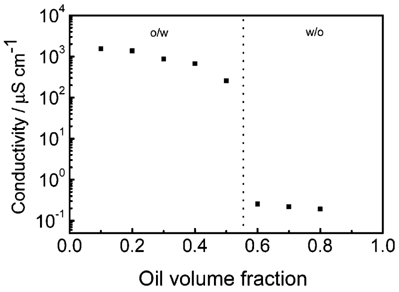

**Figure 10.** Conductivity of octanol-in-water emulsions for different compositions as an indication of the emulsion type. The emulsions were prepared at pH 9.4 and 25 °C, with 1.0 wt % PNIPAM microgel particles.

sion droplets will undergo ripening or coalescence, with a concomitant reduction in total interfacial area between oil and water, until a sufficient coverage of the interface by the microgel particles is achieved.[45] At pH = 9.4, however, the emulsions are stable even at 60 °C, indicating that the high particle charge at this pH promotes a dense coverage of the emulsion droplets by particles even in the collapsed particle state. Any free liquid–liquid interface opening up through the temperature-triggered shrinkage of adsorbed particles seems to get covered fast by the adsorption of additional particles from the bulk water phase. Again, we conjecture that charge-induced capillary forces are responsible for the intimate contact between interfacial particles and refer to the last paragraph for an experimental correlation between the particles' charge and their packing density on emulsion droplets.

**Effect of Microgel Particle Concentration on Emulsion Stability.** Figure 9 shows the effect of particle concentration on the average size and stability of droplets obtained by emulsifying octanol in water with PNIPAM microgel particles at pH 9.4. The size of the droplets falls by a factor of ~3 for increasing the microgel particle concentration up to 2.0 wt %. Our findings suggest that the lower microgel particle concentrations used do not allow for an immediate coverage of the liquid–liquid interfacial area produced by the forceful mixing process. When the agitation is stopped, partially unprotected droplets coalesce, thereby raising the average droplet size but reducing the total the interfacial area until this area is fully covered by adsorbed particles. From this point on all emulsions are stable against further coalescence, but as shown in the inset, the stability against creaming decreases progressively with decreasing particle concentration. One advantage of using relatively high concentration of microgel particles is that excess particles may form a weak gel in the continuous phase, which in turn can inhibit creaming of the oil droplets.[9] Such emulsions therefore have a longer shelf life and better fulfill aesthetic requirements.

**Effect of Oil/Water Ratio on Emulsion Stability.** Figure 10 shows that phase inversion of emulsions, from o/w to w/o, can be achieved in PNIPAM microgel particle-stabilized systems by changing the oil–water volume ratio on rehomogenizing the system. Up to an octanol volume fraction of 0.5, emulsions are of high conductivity and dispersible in water by the drop test, identifying them as o/w emulsions. Inversion to weakly conducting w/o emulsions occurs as the oil volume fraction increases above of 0.6. It is worth pointing out that this kind of inversion, known as catastrophic phase inversion, does not occur in emulsions stabilized by one single type of surfactant or by most conventional solid particles. Instead, a highly viscous emulsion is usually formed if one keeps increasing the volume fraction of dispersed phase.[3,4] The ability to make both types of emulsion with the same PNIPAM microgel particles represents a significant advantage of this new type of emulsifier.

**Effect of Oil Type on Emulsion Stability.** In recent studies, Binks and co-workers have suggested that the nature of the oil phase also plays an important role in solid-stabilized emulsions.[19,46] The effectiveness of particles in stabilizing the emulsions is often rationalized in terms of the particle attachment energy $E$. This is the energy required to expel a particle from the interface into one of the bulk phases, which can be expressed as[3,4]

$$E = \pi(d/2)^2\gamma_{\mathrm{ow}}(1 \pm \cos\theta)^2 \qquad (1)$$

where $d$ is the particle diameter, $\gamma_{\mathrm{ow}}$ is the tension of the oil–water interface, and $\theta$ is the contact angle between the particle surface and the liquid–liquid interface measured through the water phase. The sign inside the parentheses is negative for transfer of a particle from the interface into the water phase and positive for transfer into the oil phase. It is obvious from this equation that the values of both $\gamma_{\mathrm{ow}}$ and $\theta$ are important in determining the strength of particle adsorption to the interface, which in turn plays a role in stabilizing emulsions. We have therefore prepared three oil-in-water emulsions with different polarities of the oil phase and dielectric constants ranging from $\epsilon = 1.991$ for a hydrocarbon (hexadecane) to $\epsilon = 10.3$ for an alcohol (octanol). The photograph in Figure 11 shows that, by using dye-labeled PNIPAM microgel particles as emulsifier, weaker coloring of the continuous phase was found in the octanol-in-water emulsions in comparison with hexadecane-in-

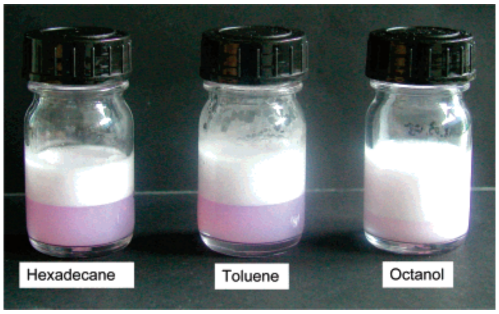

**Figure 11.** Influence of the polarity of oils on the formation of oil-in-water emulsions after 24 h at 25 °C. The aqueous phase in the hexadecane and toluene-in-water emulsions is strongly colored by the dye-labeled microgel particles.

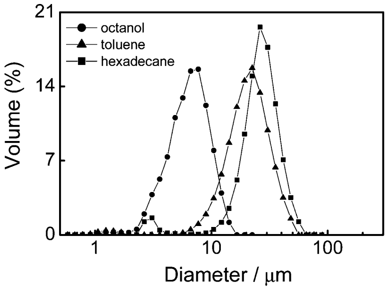

**Figure 12.** Influence of the polarity of oils on the size distribution of emulsion droplets stabilized by PNIPAM microgel particles at pH 9.4 and 25 °C, where emulsions contain a 30% volume fraction of oil and 1.0 wt % PNIPAM microgel particles.

water and toluene-in-water emulsions. This reveals that the absorption of the water-swollen microgel particles to the oil−water interface is substantially reduced when the polarity of the oil is decreased. We also found that creaming occurs faster in both hexadecane- and toluene-in-water emulsions, which is in line with the increase in average droplet size of the corresponding emulsions shown in Figure 12. Note that the size distribution of the nonpolar oil droplets is relatively narrow. This can be related to fact that the particles do not, at first, provide a sufficient coverage of the emulsion droplets created by the agitation. The homogenization step is then followed by limited coalescence, a process known to yield narrow droplet size distributions.[46,47]

**Correlation of Particle Charge and Droplet Coverage: Toluene-in-Water Emulsions Stabilized with Carboxylate Polystyrene Particles.** In previous sections discussing the pH-dependent stability of the microgel-stabilized emulsions and their insensitivity to temperature changes at high pH, we repeatedly invoked the idea that highly charged particles in liquid−liquid interfaces form dense layers, possibly due to charge-induced capillary attraction, whereas weakly charged particles favor larger interparticle separations. While the dense coverage provided by highly charged microgel particles could be seen directly in cryo-SEM pictures (Figure 2), the hypothesized low coverage at low charge is more difficult to observe because the emulsions are unstable in this regime. We found that the correlation of particle charge and droplet coverage can be studied more easily in toluene-in-water emulsions stabilized by polystyrene particles with carboxylic acid surface groups and adsorbed amphiphilic copolymers.

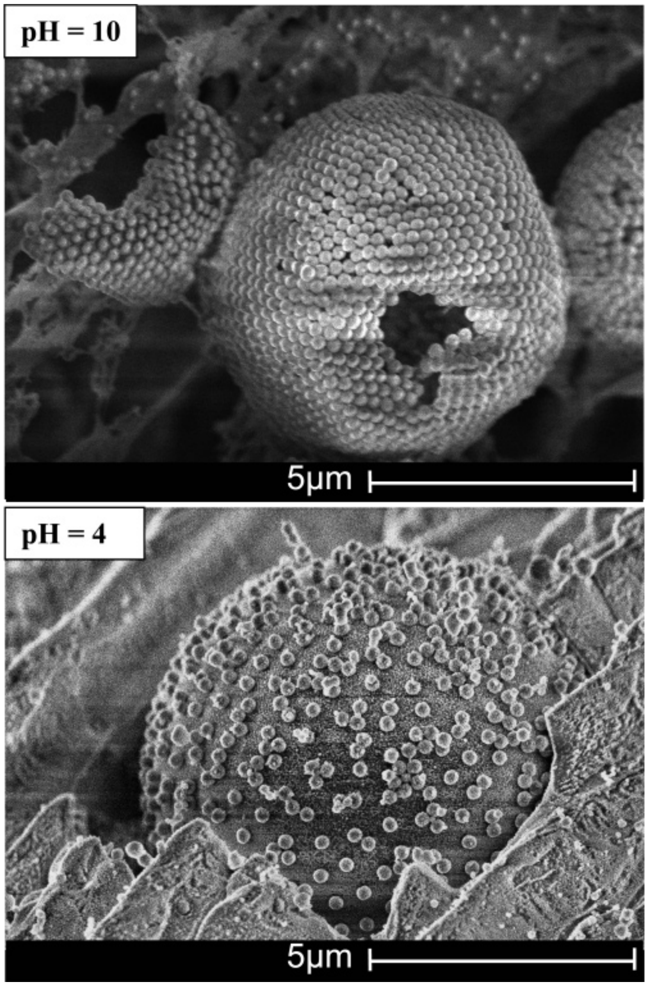

**Figure 13.** Typical freeze-fracture SEM pictures illustrating the pH-dependent packing polystyrene particles around toluene droplets.

Polystyrene particles were prepared by surfactant-free polymerization. Copolymerized methacrylic acid again provides the carboxylic groups that allow to vary the surface charge by changing the solution pH. To prevent the polystyrene particles from dissolving in toluene, the cross-linker divinylbenzene was added during the polymerization. The resulting polystyrene particles were roughly spherical and monodispersed with a mean diameter around 270 nm, which is similar to the size of PNIPAM microgel particles used in the present study.

According to the literature, the use of bare, charge-stabilized polystyrene as particulate emulsifiers always leads to the formation of w/o emulsions.[22,48] Grafted copolymers or adsorbed surfactants, however, can modify the particles' hydrophobicity and make them suitable for stabilizing o/w emulsion.[18,49] In our case, polystyrene particles were mixed with Pluronic F108 copolymer (0.5 wt %) at room temperature 24 h before using them to emulsify toluene in water. The Pluronic F108 is a triblock poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), or PEO−PPO−PEO, copolymer with a molecular weight of 14 600 g/mol and a PEO/PPO/PEO monomeric ratio of 129/56/129.[50] It is expected that the Pluronic F108 triblock copolymers physisorb onto the polystyrene surface through the hydrophobic interactions between the polystyrene and the central PPO block, which acts as an anchor, while the more hydrophilic PEO chains extend into the aqueous solution.[51]

Toluene-in-water emulsions (30% oil volume fraction) with pH 4 and 10 were prepared by with such pH-responsive, Pluronic-coated polystyrene particles (1.0 wt %) as emulsifiers. Typical freeze-fracture SEM pictures of particle decorated droplets are shown in Figure 13. At pH 10 (top of figure) the oil droplets appear completely covered with the polystyrene particles, reflecting the dense adsorption of particles at the oil−

water interface under conditions where the particles are highly charged. The hole in a shell of particles visible in the top of Figure 13 confirms the notion of a hollow capsule formed by a monolayer of particles. When the emulsions were prepared at pH 4.0 (bottom of Figure 13), the packing density of polystyrene particles adsorbed to the toluene−water interface was found to vary quite a bit, but typically a less complete coverage of the oil droplets was observed.

Regardless of the pH and interparticle spacing the emulsions appeared perfectly stable over several months. The fact that even weakly covered emulsion droplets did not undergo coalescence hints at a stabilizing role for the excess Pluronics, which might well adsorb to the free droplet surface. It is worth noting that a similar work performed with confocal microscopy has concluded that close packing is not necessary to stabilized emulsions.[17] On the other hand, to examine the particular contribution of the free Pluronic F108 or polystyrene latex particles alone to the emulsification, we have prepared additional samples (not shown here) with toluene-in-water emulsion, but in place of the F108-coated polystyrene particles, we substituted the supernatant of a centrifuged F108-coated polystyrene suspension or polystyrene latexes alone as the aqueous emulsifier solution. The samples produced no emulsion phase. Neither the use of Pluronics alone nor of polystyrene particles alone would produce stable toluene-in-water emulsion. Thus, the primary effect of the Pluronics in this system seems to be the surface modification of the polystyrene particles that promotes their adsorption to the fluid interface. Since the Pluronics generally do not exhibit any pH sensitivity, we do not give them any credit for the observed differences in interparticle spacing for different pH, but take this observation as a further indication for a charge-induced particle−particle attraction, most likely involving capillary forces.

## Conclusions

We have prepared a novel type of surfactant-free o/w emulsions stabilized by stimulus responsive PNIPAM microgel particles. The hydrophobicity, charge, and electrostatic screening of the microgel particles, which can be tuned by varying temperature, solution pH, or ionic strength, have been found key factors in determining the stabilizer efficiency. Demulsification can be triggered by lowering the solution pH or by raising the solution temperature or the ionic strength. Therefore, this new kind of multivariable emulsifier provides extended emulsion stability control and may prove very useful for applications in the field of cosmetic or pharmaceutical formulations. A surprising robustness of microgel-stabilized emulsions at high pH as well as microscopic studies of emulsions stabilized by polystyrene particles with pH-dependent surface charge suggest an unanticipated correlation between the charge and packing density of particles in oil−water interfaces.

**Acknowledgment.** We thank F. Mongitore, F. Spindler, and Dr. T. Frechen for help with the SEM pictures and Dr. Y. Liu and U. Benkert for the help with electrophoretic mobility measurement. Dr. T. Ngai gratefully acknowledges a fellowship by the Croucher Foundation, Hong Kong and DAAD, Germany, to support his research in BASF.

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MA061366K