Novel emulsions stabilized by pH and temperature sensitive microgels

To Ngai, Sven Holger Behrens* and Helmut Auweter

Surfactant-free oil-in-water emulsions prepared with temperature and pH sensitive poly(N-isopropylacrylamide) (PNIPAM) microgel particles offer unprecedented control of emulsion stability.

Emulsions are metastable systems that usually involve low molar mass surfactants, polymeric surfactants, or amphiphilic polymers.[1] It has long been known, however, that solid colloidal particles can also be very efficient emulsifiers.[2] This efficiency stems from the fact that particles of the correct wettability are adsorbed at the liquid–liquid interface, and the energy required to remove one particle from the interface can be much higher than the corresponding cost of removing a surfactant molecule in a conventional emulsion.[3] Solid-stabilized emulsions, often referred to as "Pickering emulsions", can be prepared with a wide variety of organic or mineral particles. Recently, there has been growing interest in particulate emulsifiers because they open new avenues of emulsion formulation and may potentially replace more hazardous surfactants.[3] In addition, solid-stabilized emulsions have been proposed as templates for the self-assembly of particles into solid capsules.[4] For emulsions with a water phase it has been shown that the particles' hydrophobicity determines both the emulsion type and stability. With silanized silica, particles of different hydrophobicity, *e.g.*, emulsions of either oil-in-water (o/w) or water-in-oil (w/o), can be produced.[5] For o/w-emulsions stabilized by polystyrene latex particles with ionizable amino surface groups, demulsification can be triggered by decreasing the pH.[6]

Here we introduce a new type of emulsion responsive to both pH and temperature changes. PNIPAM microgel particles containing some carboxyl groups are shown to stabilize octanol-in-water emulsions at room temperature above a solution pH of 6, but below this threshold the emulsifier activity gradually decreases with pH. On the other hand, for stable emulsions prepared at neutral pH, coarsening and destabilization occurs when the temperature is raised to 60 °C, whereas the oil droplets are stable when heated at a higher pH (>8). Hence, this novel emulsion allows for extended stability control through both pH and temperature, opening up a large range of applications.

Monodisperse PNIPAM microgels were synthesized using surfactant-free precipitation polymerization, based on N-isopropylacrylamide as a monomer, cross-linked with N,N′-methylene bisacrylamide, and 5.0 wt.% of methacrylic acid (MAA) as a comonomer.[7] The PNIPAM microgels exhibit a volume phase transition upon changes in temperature.

Fig. 1a shows that, for a given pH, the mean hydrodynamic diameter d_H, measured by dynamic light scattering, decreases when the temperature is raised. This behaviour is expected, since linear
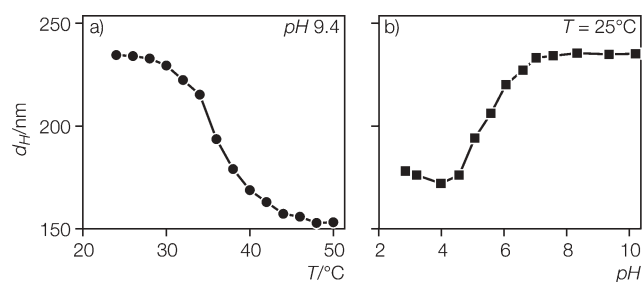
*sven-holger.behrens@basf-ag.de

Fig. 1 Temperature and pH dependence of the mean hydrodynamic diameter d_H of PNIPAM microgel particles in an aqueous dispersion (no salt added) at a microgel particle concentration of 20.5 mg L^{-1}.

PNIPAM has a lower critical solution temperature (LCST) of ~32 °C in aqueous solution,[8] at which point the polymer switches from a hydrophilic random coil at lower temperature to a hydrophobic globule at higher temperatures.

On the other hand, the PNIPAM microgels presented in this study are also sensitive to pH and ionic strength due to the copolymerization with the ionic comonomer MAA. Fig. 1b shows that the microgel particles' size in water at 25 °C increases continuously from pH 4 to pH 8 as expected.[9] With increasing pH the carboxyl groups in the polymer are deprotonated so that the electrostatic repulsion is enhanced. When this repulsion overcomes the attractive forces such as hydrogen bonding or hydrophobic interaction, the gel network swells. Fig. 1 suggests that either by raising the solution temperature or by decreasing the pH, we can indeed increase the hydrophobicity of the microgel particles.

It has been mentioned that the hydrophobicity of particulate emulsifiers is crucial for the emulsion type and stability.[3,5] One might therefore expect that the PNIPAM microgel particles can in some conditions be used to stabilize emulsions and impart to them their twofold responsiveness to temperature and pH. This hypothesis has been verified experimentally in the present study.

Emulsions containing octanol (at an oil volume fraction of 0.30) and an aqueous dispersion of 1.0 wt.% PNIPAM microgel particles were prepared using an Ultra-Turrax homogenizer (18 mm head) operating at 8000 rpm for 3 min. The microgel particles were labelled by copolymerization with 0.1 wt.% of the fluorescent dye methacryloxyethyl thiocarbamoyl Rhodamine B to identify the phase containing the microgels. The pH of the aqueous phase was adjusted by addition of HCl or NaOH.

All emulsions are of o/w type and, although surfactant-free, they show no sign of ageing after four months if kept above pH 6. The bottom right image in Fig. 2 shows a typical example of an emulsion at pH 9.4. Its stability results from dissociation of the –COOH groups and the ensuing hydrophilicity of the microgel

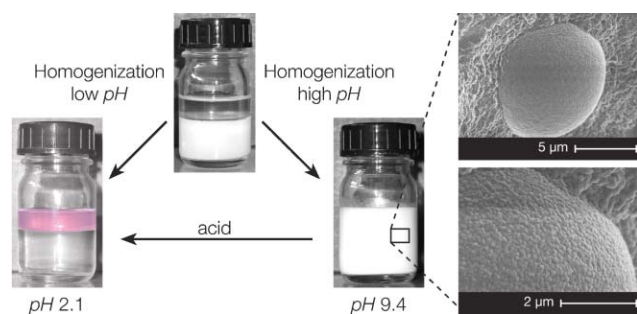**Fig. 2** Influence of the solution pH on the formation of octanol-in-water emulsions after 48 h at $T = 25$ °C. The oil phase in the leftmost photograph is strongly coloured by the dye-labelled particulate stabilizers; when distributed throughout the water phase or the stable emulsion, the particles only cause a faint tint not reproduced in the photographs. The inset shows freeze–fracture SEM pictures of a particle-covered droplet in an emulsion prepared at pH 9.4.

Fig. 3 Optical micrographs illustrating the temperature dependent stability of an octanol-in-water emulsion stabilized by microgel particles at pH 6.1 and 9.4 respectively. The scale bar is 20 μm.

Fig. 4 The stabilizing efficiency of PNIPAM microgel particles for octanol-in-water emulsions as a function of pH and temperature. ■: Stable, ●: Unstable, ◆: Phase separation. (Arrows indicate the probed transitions)

particles. A large fraction of the particle surface then resides in the water phase, where the electrostatic repulsion between particles is weaker than in the oil phase due to screening and a larger dielectric constant.[10] This reduction of interparticle repulsion supposedly leads to a good coverage of the oil droplets by microgel particles, which inhibits coalescence. The inset of Fig. 2 shows freeze–fracture SEM images of a particle-covered octanol droplet at pH 9.4, further supporting the notion that the microgel particles adsorb densely at the oil–water interface when they are highly charged.[11] Destabilization however occurs when the pH is decreased below 6. A likely explanation is that the –COO⁻ groups inside the gel network are protonated as the pH is lowered and the microgel particles become more hydrophobic. As a result, the interfacial microgel particles move deeper into the oil phase, where their electrostatic interaction is stronger.[10] We conjecture that the enhanced interparticle repulsion promotes partial desorption of particles, reducing the coverage of the oil–water interface. The emulsion droplets then ripen or coalesce, thereby shrinking the total interfacial area until sufficient coverage by the microgel particles is achieved.[12] Further acidification triggers fast macroscopic phase separation, and interestingly, the dye-labelled PNIPAM microgel particles are driven into the oil bulk, as can be inferred from the colour of the oil phase in Fig. 2 (left).

In order to confirm the hypothesized temperature dependence, stable emulsions were prepared at room temperature with pH 6.1 and 9.4 respectively, and heated in a water bath at 60 °C for 1 h. Before and after heating, one drop of each sample was viewed under a microscope fitted with a CCD camera. As seen in Fig. 3, oil droplets of the unheated emulsions are spherical and fairly polydisperse, with a mean diameter around 10 μm.

When the temperature is increased, coarsening is observed in emulsions prepared at pH 6.1. Heating, like pH reduction, causes shrinking and possibly partial desorption of the increasingly hydrophobic interfacial particles. Again, the oil droplets compensate for insufficient coverage by undergoing ripening or coalescence with a concomitant reduction of total interfacial area.[12] At pH 9.4, however, the emulsions are stable even at 60 °C, indicating that the highly charged, partially hydrophobic microgel particles remain in the oil–water interface and inhibit droplet coalescence. This observation is consistent with previous reports about the
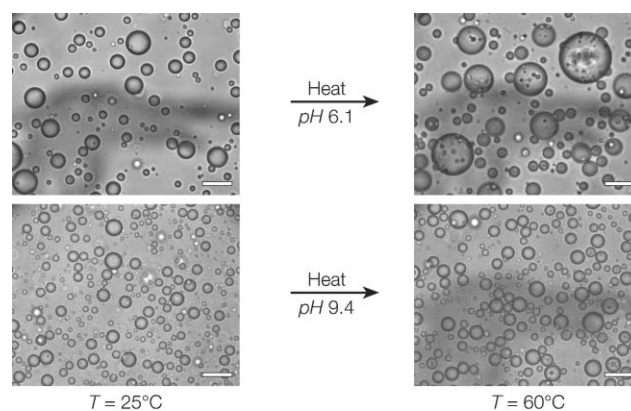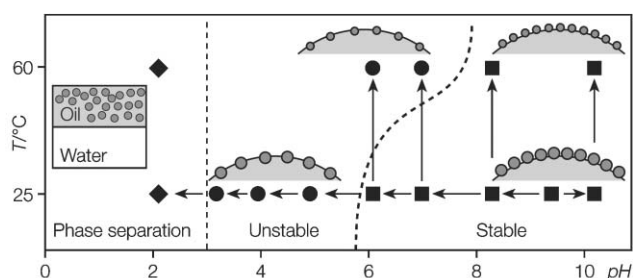
high emulsifying efficiency of weakly flocculated dispersion particles.[13]

Experimental observations regarding the stabilizing properties of our microgel particles for oil-in-water emulsions are summarized in Fig. 4. Initially stable emulsions coarsen when the pH is decreased. At very low pH rapid macroscopic phase separation occurs as the microgel particles become completely immersed in the oil phase, leaving the droplet surfaces unprotected. An alternative way to increase the hydrophobicity of the microgel is to raise the temperature. Consequently, emulsions prepared at pH 6.1 become unstable when heated up to 60 °C. Emulsions prepared above pH 8, on the other hand, remain perfectly stable, which shows that the highly charged partially hydrophobic microgel particles retain a good coverage and protection of the oil-water interface even at elevated temperatures.

We believe that such stimulus-responsive microgel particles have a great potential for applications in the field of cosmetic or pharmaceutical formulations.

To Ngai, Sven Holger Behrens* and Helmut Auweter
BASF Aktiengesellschaft, Polymer Physics, 67056, Ludwigshafen, Germany. E-mail: sven-holger.behrens@basf-ag.de; Fax: +49 621 60 72660; Tel: +49 621 60 95272

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