

## Stimulus-responsive Particulate Emulsifiers

Prof. S. P. Armes

*Department of Chemistry, Dainton Building, The University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK.*

We describe the synthesis and evaluation of three new classes of stimulus-responsive ‘Pickering’ type emulsifiers<sup>1</sup> based on organic polymer particles. These particles have been used to prepare polydisperse oil-in-water emulsions of 10-120  $\mu\text{m}$  diameter on emulsification with oils such as *n*-dodecane, methyl myristate or 1-undecanol. We differentiate between *pH-dependent* sterically-stabilised polystyrene latex<sup>2-4</sup> and *pH-responsive* poly(4-vinylpyridine)-silica nanocomposite microgels<sup>5,6</sup> and shell cross-linked micelles.<sup>7</sup> In the former case, stable oil-in-water emulsions are formed at pH 8 but not at pH 3. However, switching the solution pH of a latex-stabilised emulsion prepared at pH 8 does not lead to demulsification (droplet coalescence). In contrast, both the nanocomposite microgel particles and the shell cross-linked micelles allow rapid destabilisation of emulsion droplets by lowering the solution pH *in situ*. This ability to control the emulsion stability may have commercial applications

The particle size distributions of the emulsions were assessed using optical microscopy and a Malvern Mastersizer and the emulsion type (either oil-in-water or water-in-oil) was determined by conductivity measurements.<sup>3</sup> We have also examined critical point drying (CPD) in the context of our scanning electron microscopy (SEM) studies.<sup>4</sup> This sample preparation technique, which has been used by biologists for more than fifty years, allows the latex superstructure that surrounds the oil droplets to be preserved as the oil and water phases are gradually removed. SEM studies confirm that latex monolayers are obtained, as expected. Moreover, examination of ruptured latex superstructures confirm that these are hollow and that the latex particles are only adsorbed as a single monolayer. These findings are also consistent with our confocal laser microscopy studies of emulsions prepared using fluorescently labelled sterically-stabilised latex particles: the characteristic fluorescent halo that is observed around the emulsion droplets clearly indicates the presence of the adsorbed latex particles.<sup>4</sup>

We believe the spontaneous detachment of the nanocomposite microgel particles and shell cross-linked micelles from the oil droplet surface that occurs at low pH is caused by changes in the surface hydrophilicity of these particles, leading to their efficient dewetting. A tentative hypothesis explaining why pH-induced demulsification does not occur in the case of the sterically-stabilised polystyrene latex will be outlined.

### References

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