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Membrane Emuslification and the use of Particulate Stabilisers

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  - EPSRC
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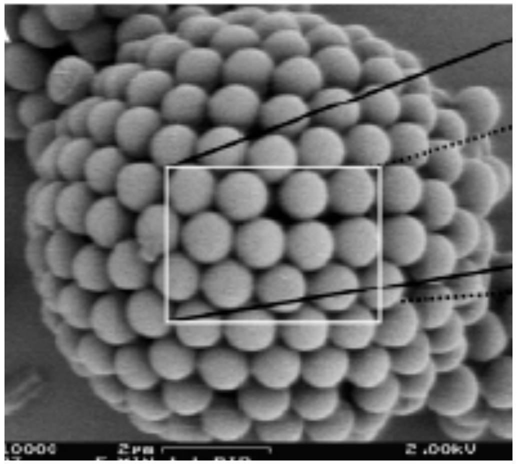
  - Prof. Steve Armes

Motivation

- Unmet technology need
  - Efficient encapsulation methods that offer:
    - Targeted delivery
    - Triggered release
    - ‘Scaleable’ manufacturing approaches
    - Cost effective solutions ...

Current approaches

- Hollow Capsules
  - Interfacial polymerisation on emulsion templates
    - e.g. Melamine formaldehyde
  - Polymer precipitation
  - Particle stabilised emulsions
    - e.g. ‘colloidosomes’
- Solid or matrix capsules
  - Latex particles
  - Spray dried agglomerates



Dinsmore et al., Science, 2002

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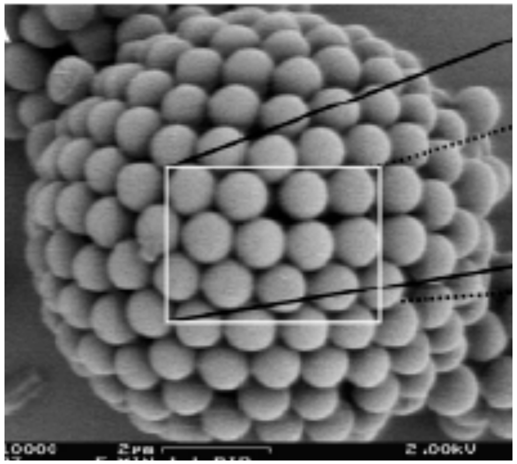
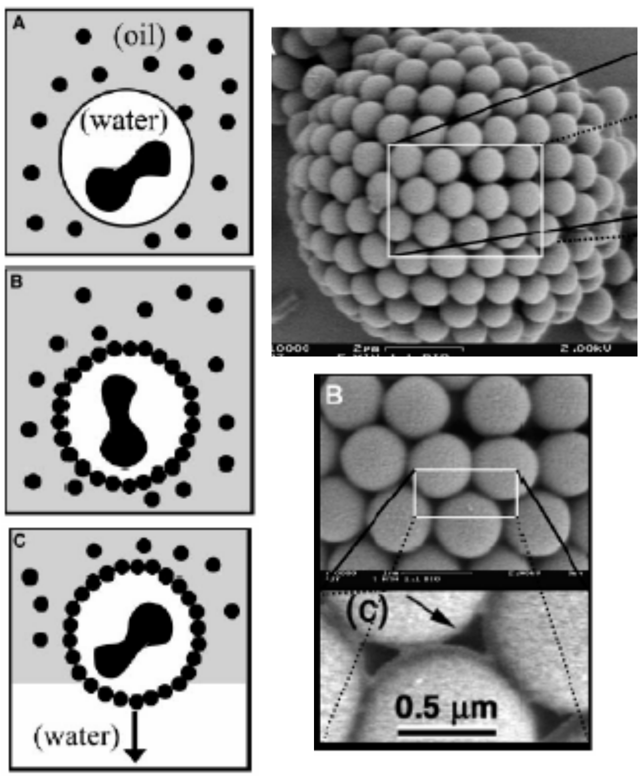


Dinsmore et al., Science, 2002

Previous work on particle stabilised systems



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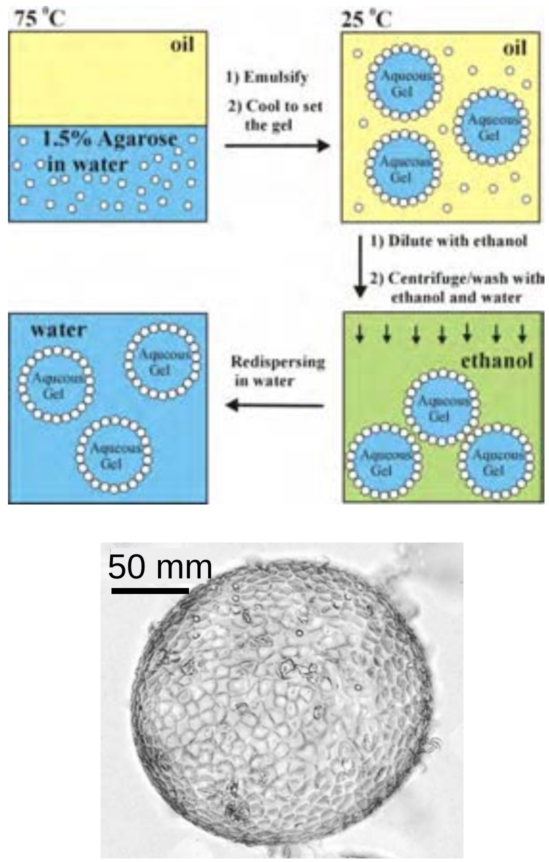
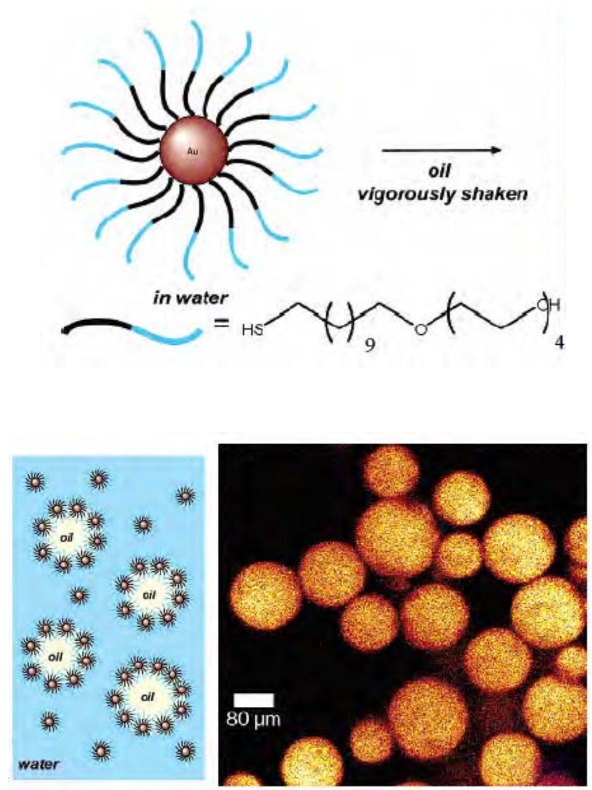


Cayre et al., J.Mater.Chem., 2004



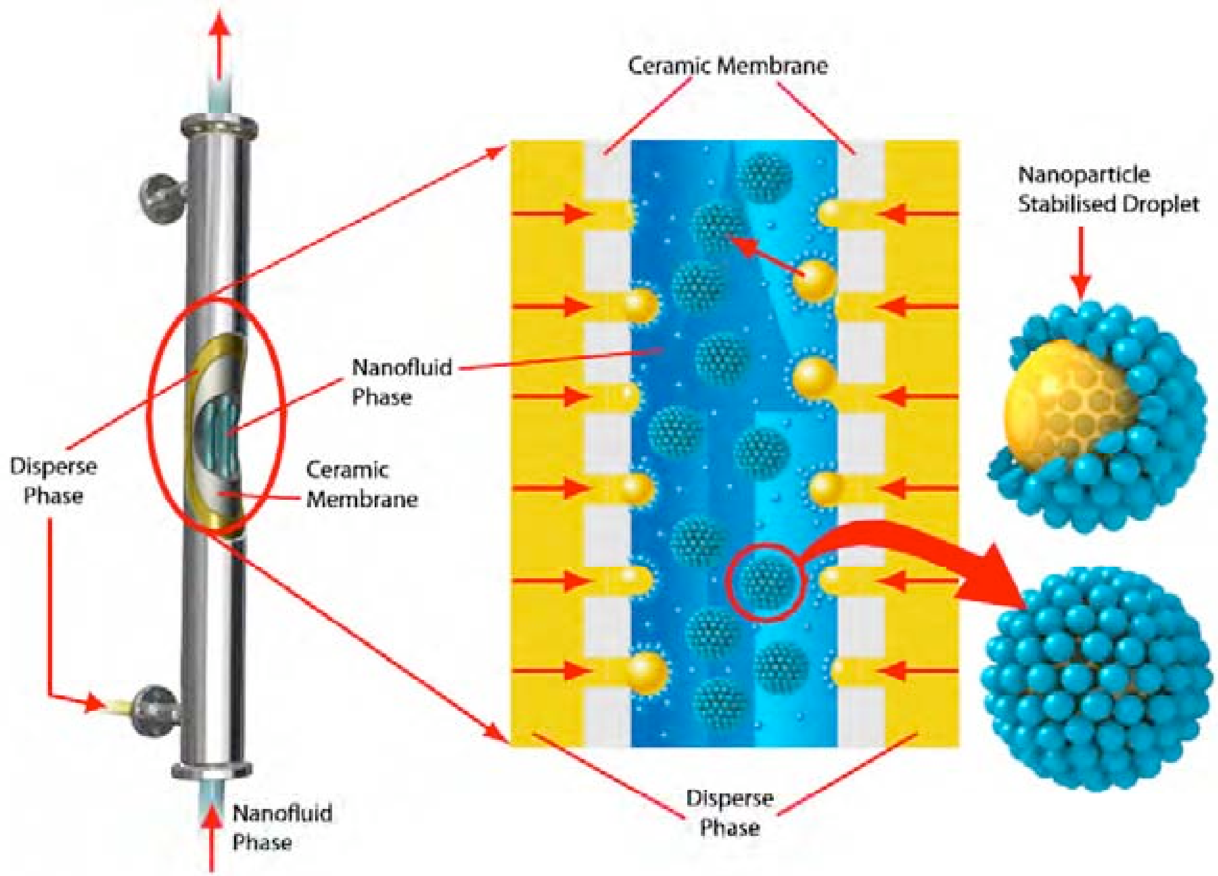
Glogowski et al., NanoLett., 2007

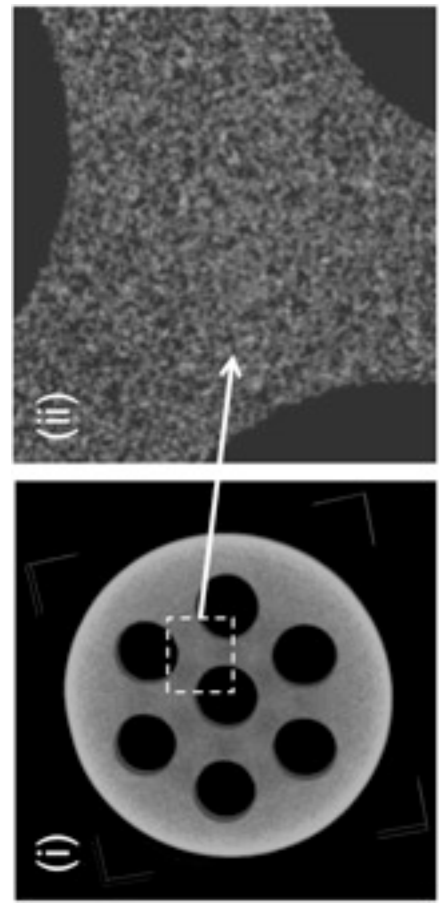
Advantages and challenges

- Advantages
  - defined and easily ‘varied’ physical/chemical properties
  - controlled wall thickness
  - ability to post- or pre-modify particles
- Challenges
  - reliable manufacturing at scale
  - locking of particles into a permanent shell
  - control of porosity

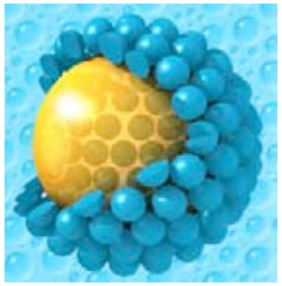
Manufacturing

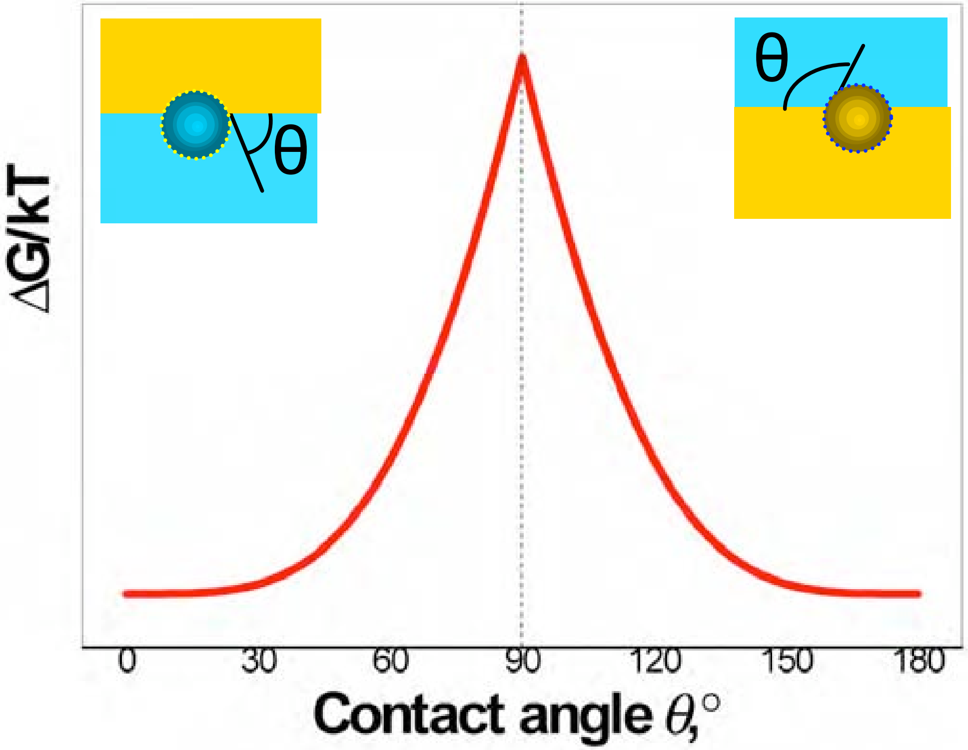
- Membrane emulsification

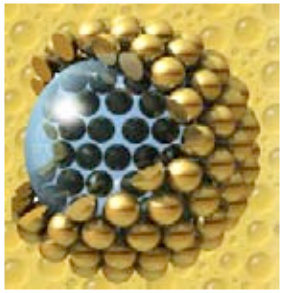




Contact angles

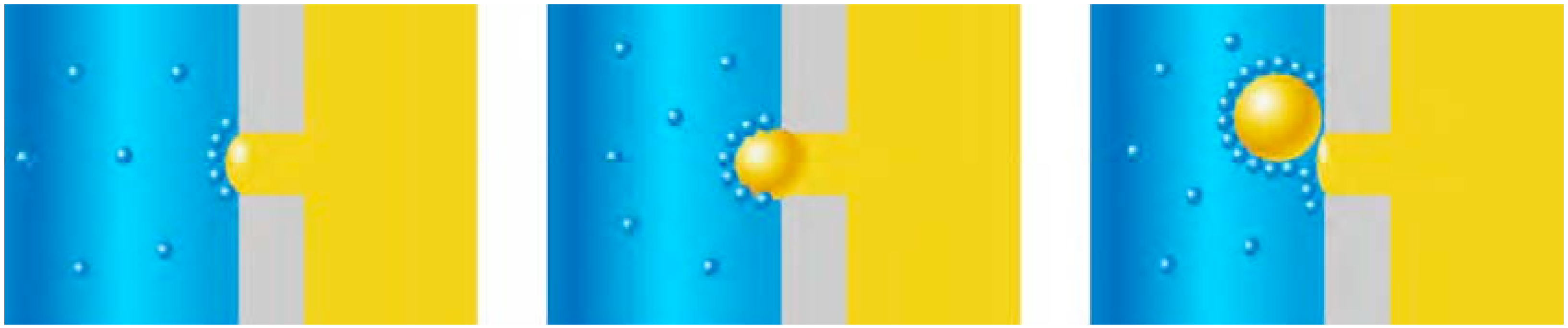




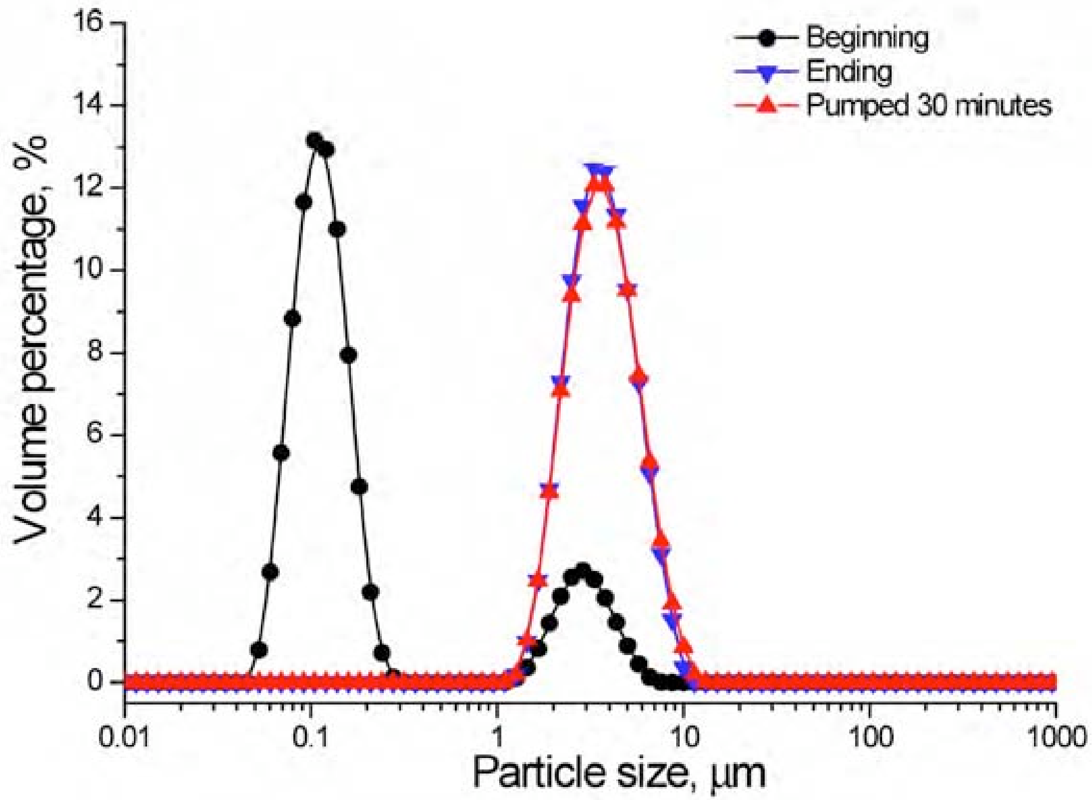


Manufacturing challenges

- Particle contact angle control
  - Need sufficient affinity for the interface
- Adsorption kinetics
  - Stabilise single droplets as they form

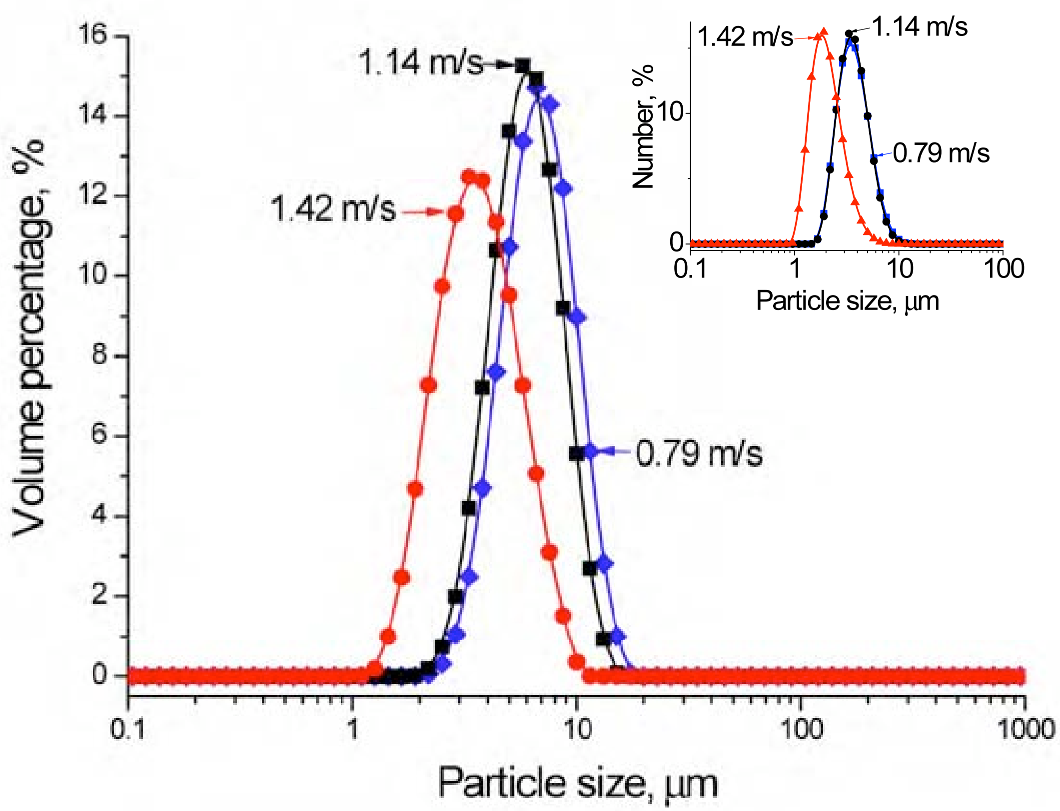


Membrane emulsification: particle stabilisation



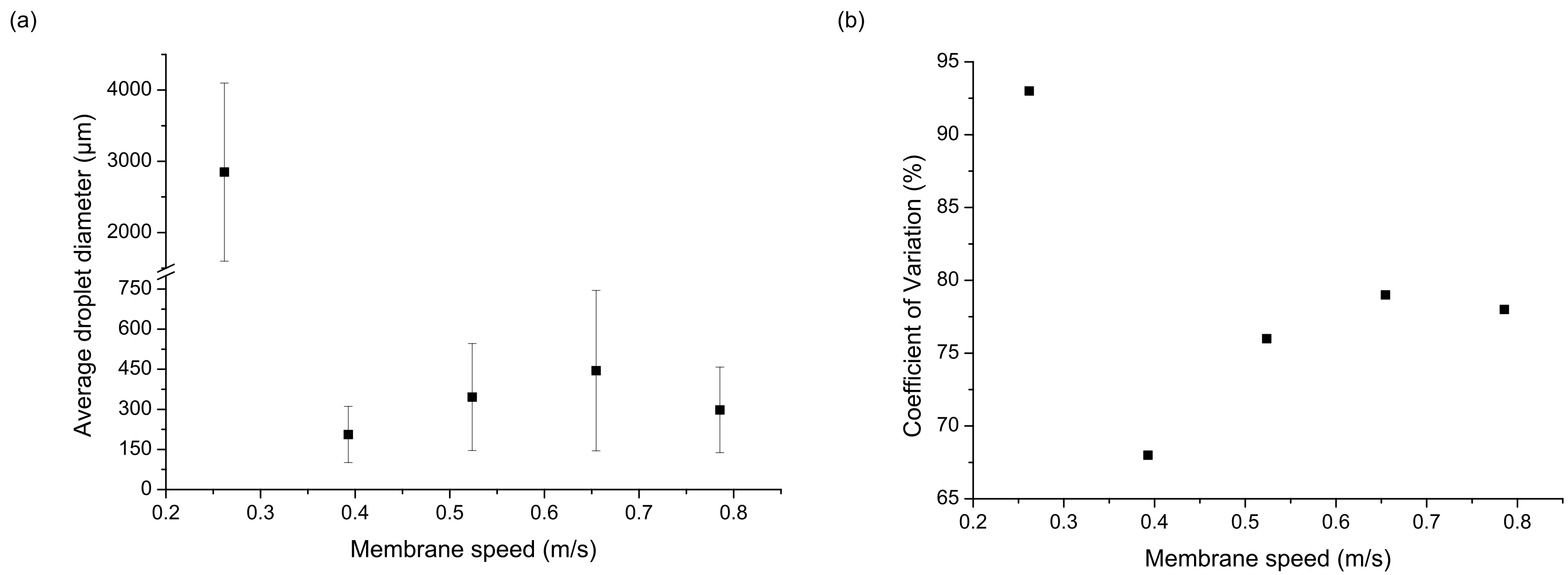
- 100 nm silica @ 15 vol%
- Aqueous phase (pH < 7; density 1.36)
- Oil (n = 12 mPa.s; density = 0.95)

Membrane emulsification: size control



- 100 nm silica @ 15 vol%
- Aqueous phase (pH < 7; density 1.36)
- Oil (n = 12 mPa.s; density = 0.95)

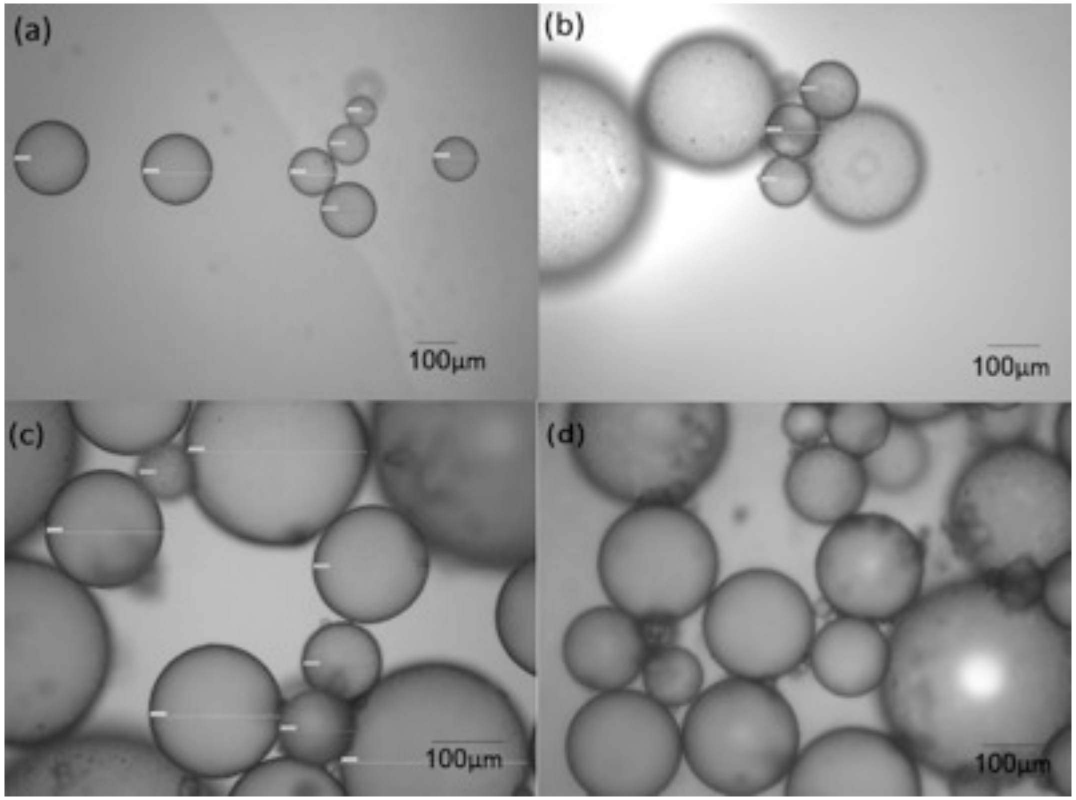
Effect of shear field on droplet stability



- Key issue is rate of particle absorption into interface
  - attachment rate
  - wetting of particle

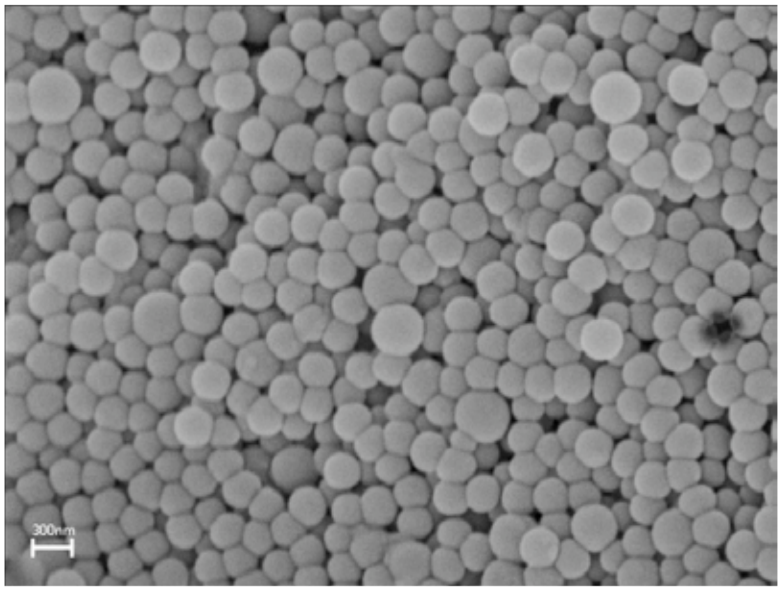
Membrane emulsification

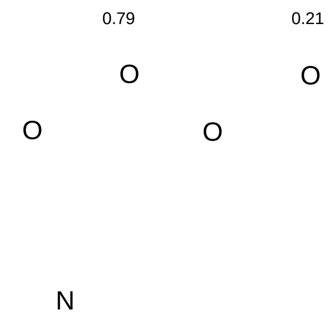
- Summary
  - Ability to produce size controlled particle stabilised systems proven
  - Possible to ensure full uptake of stabiliser particles
  - Matching of oil and aqueous phase properties is a key component
  - Can be a relatively gentle process



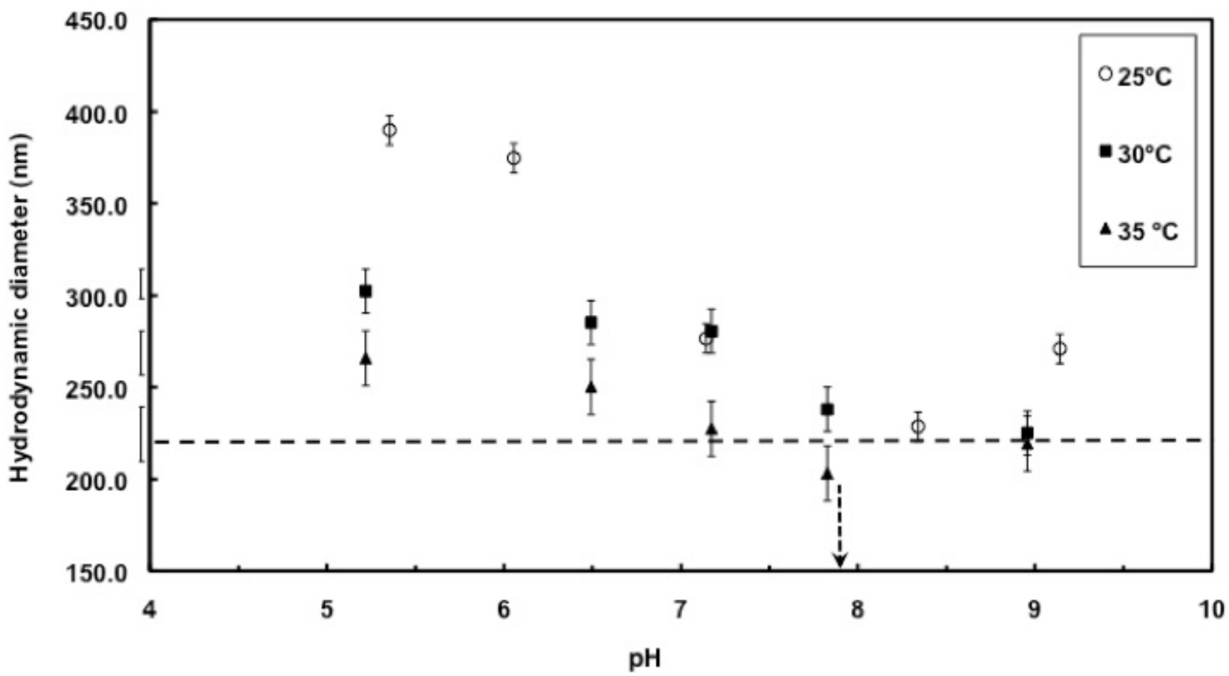
Responsive Microcapsules

- Example system: sterically stabilised latex



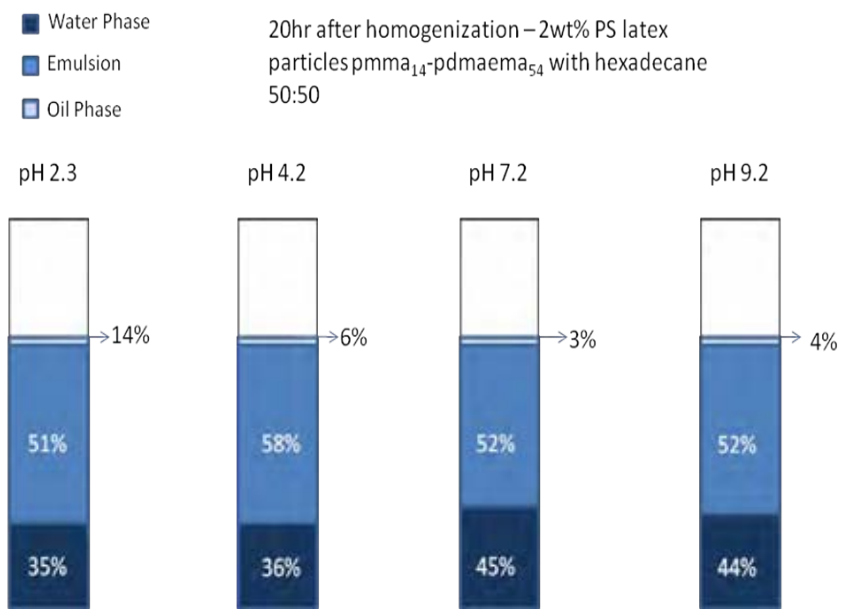


Latex Characterisation

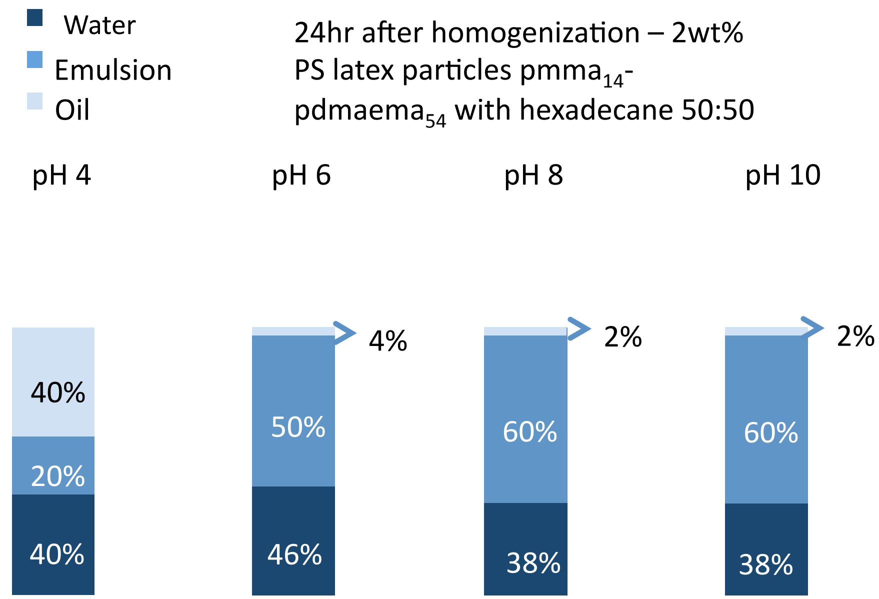


- Dual responsive system
- Contact angle variation with pH

Emulsion stabilisation



0.1M KNO_3



No added electrolyte

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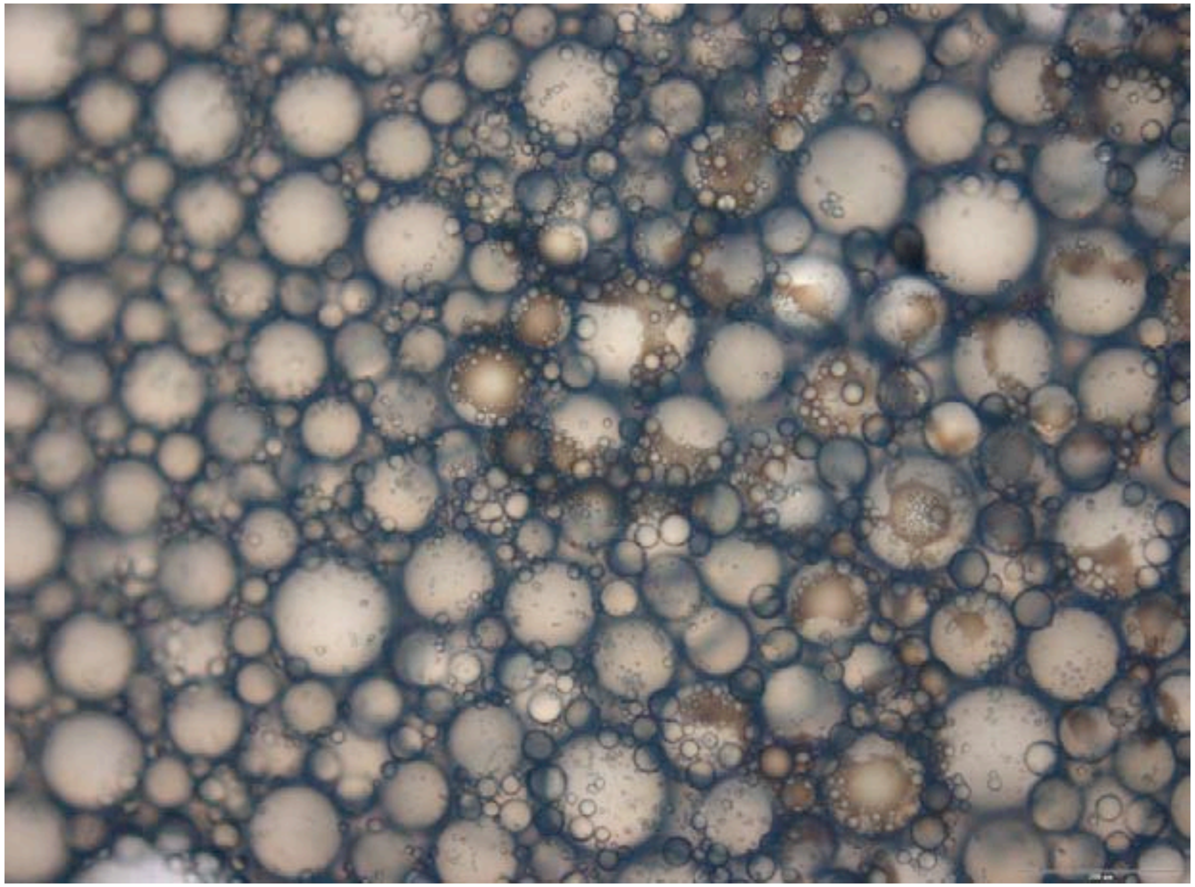
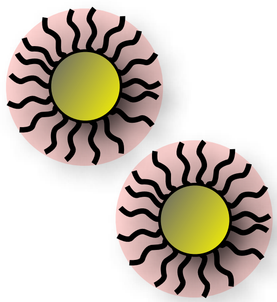
Stable droplets

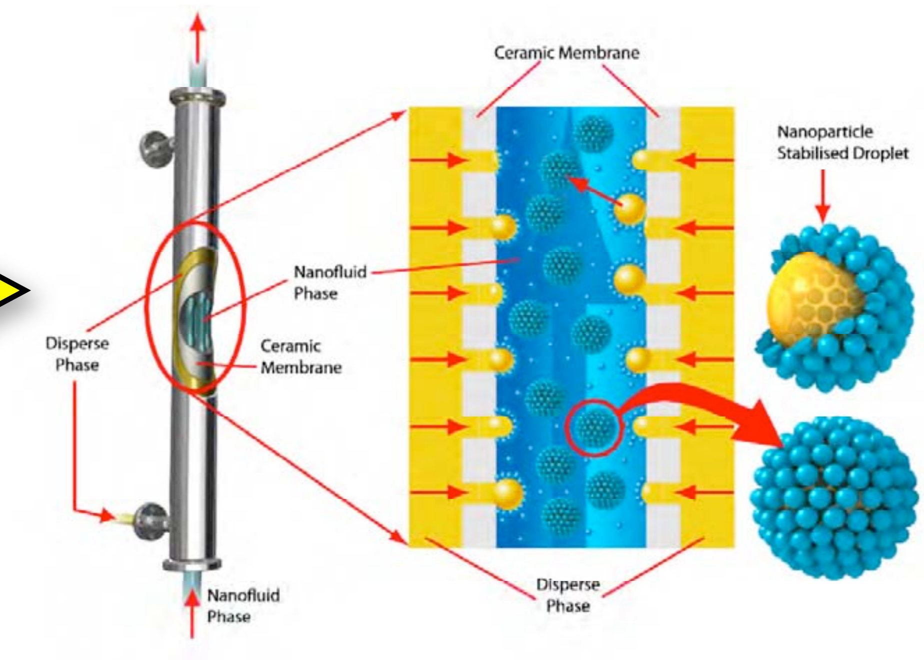


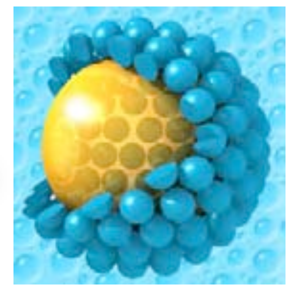
- Responsive latex stabilised emulsion
- Prepared using homogeniser
- Stable over long periods

Capsule formation

- Strategy







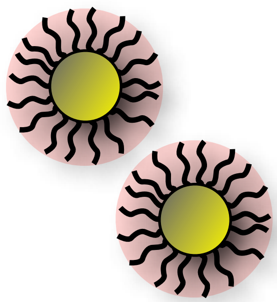
Optimise latex emulsion system

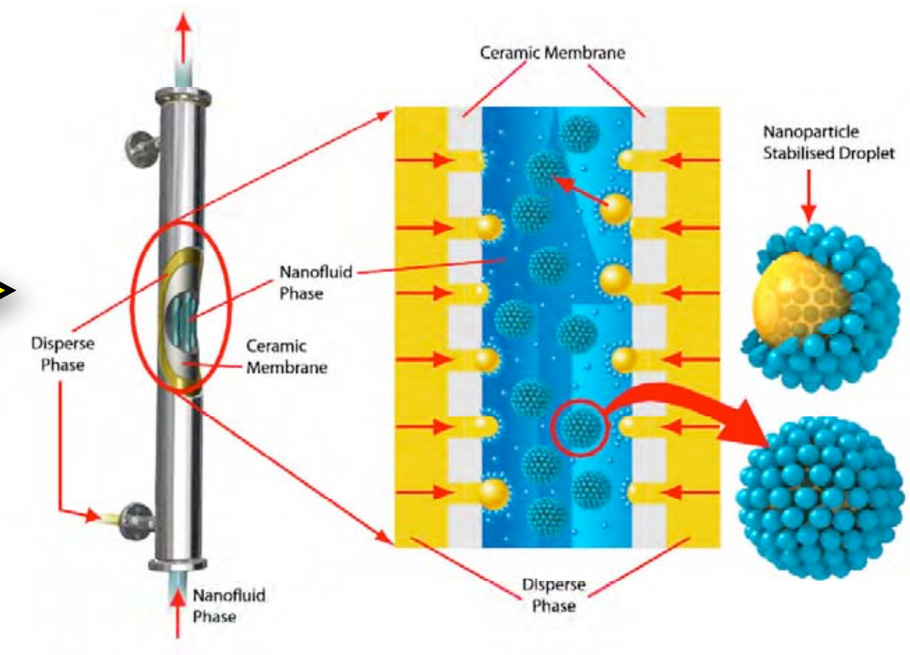
Produce stable emulsion

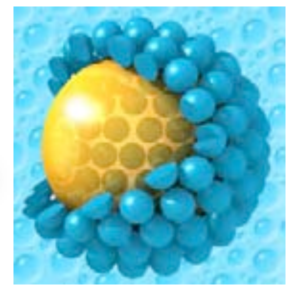
Cross link stabilisers from oil phase

Capsule formation

- Strategy







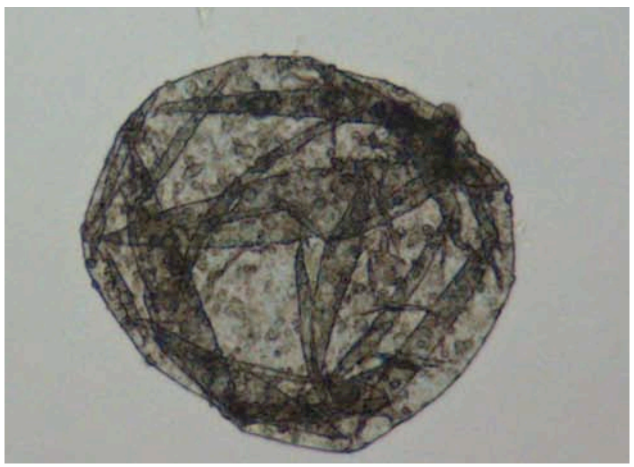
Optimise latex emulsion system

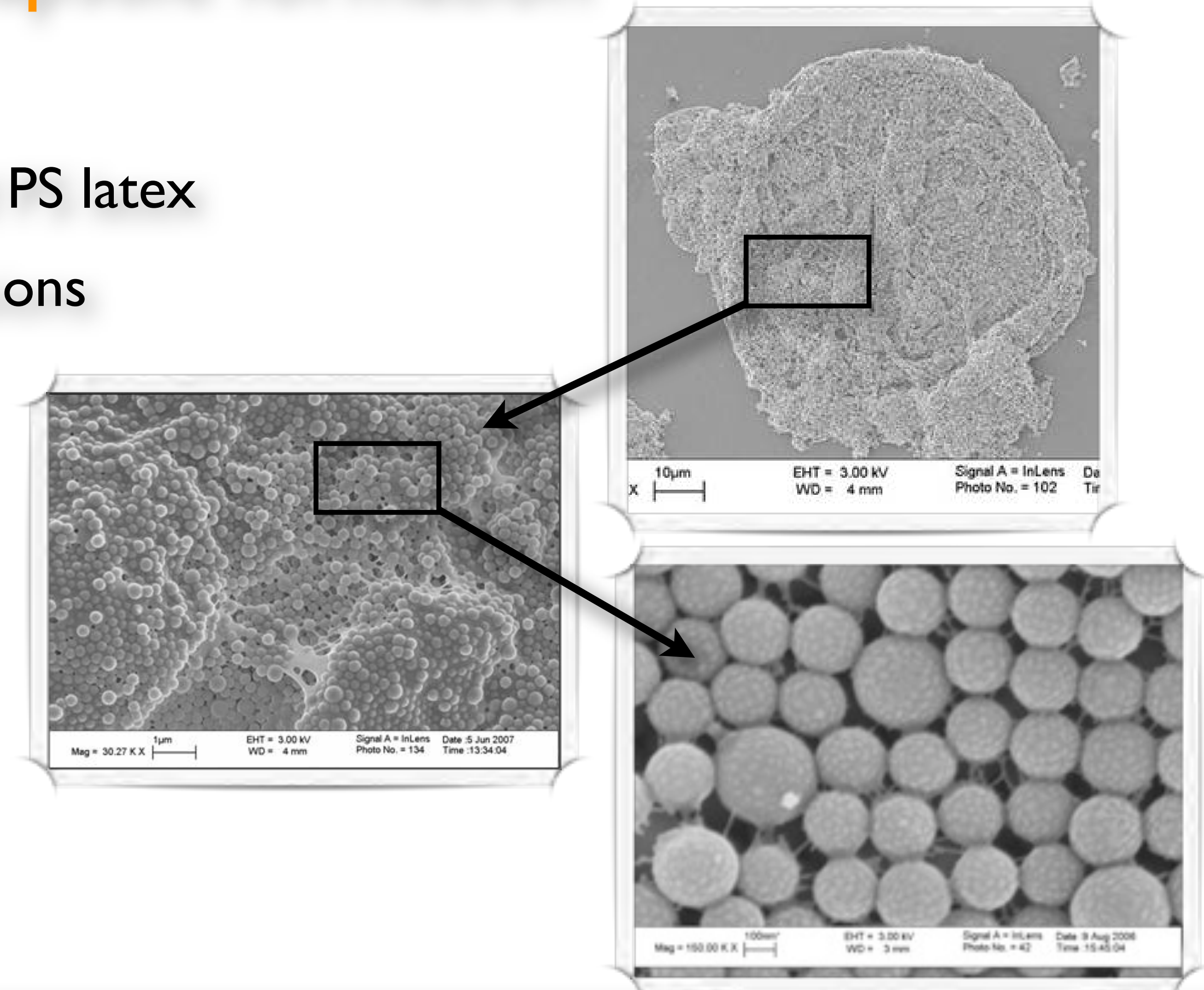
Produce stable emulsion

Cross link stabilisers from oil phase

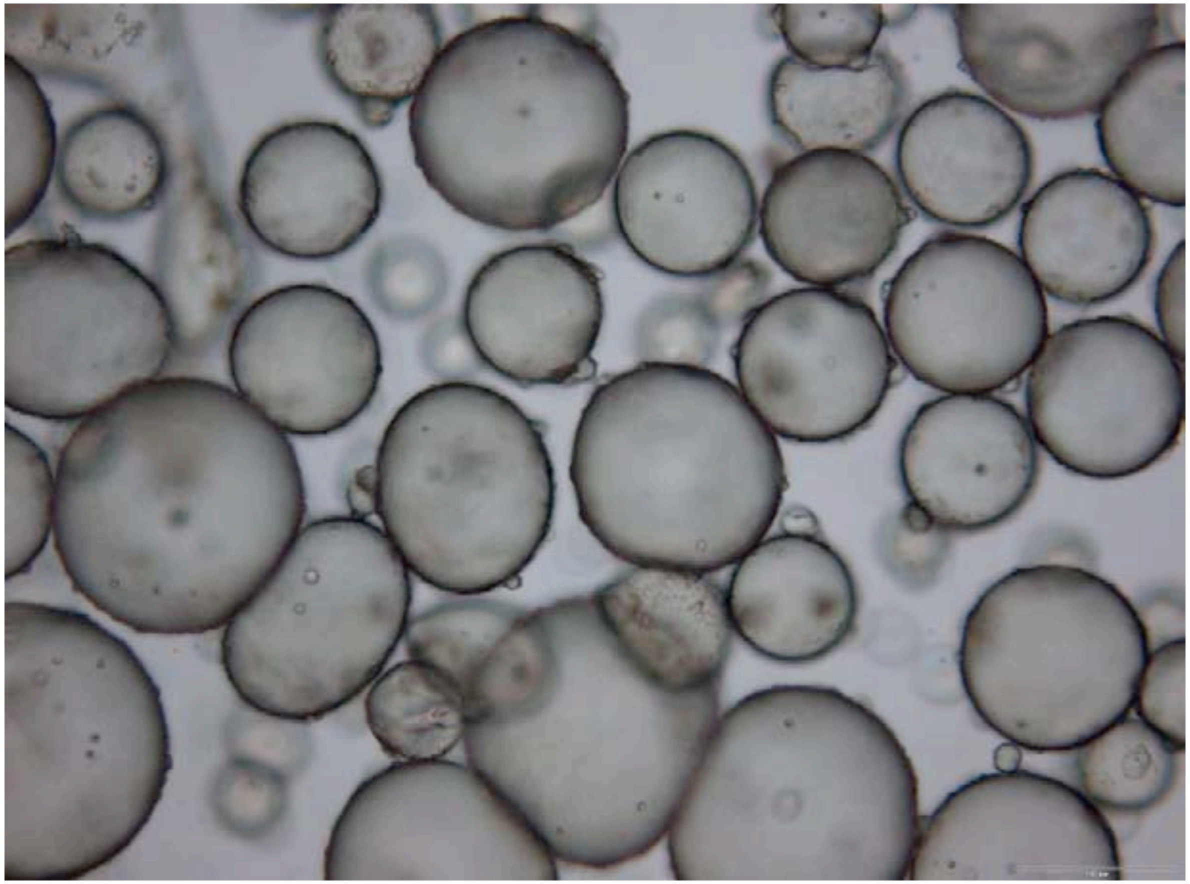
Capsule formation

- System
  - PDMAEMA stabilised PS latex
  - Dodecane o/w emulsions
  - BIEE cross linker





Dispersed Capsules



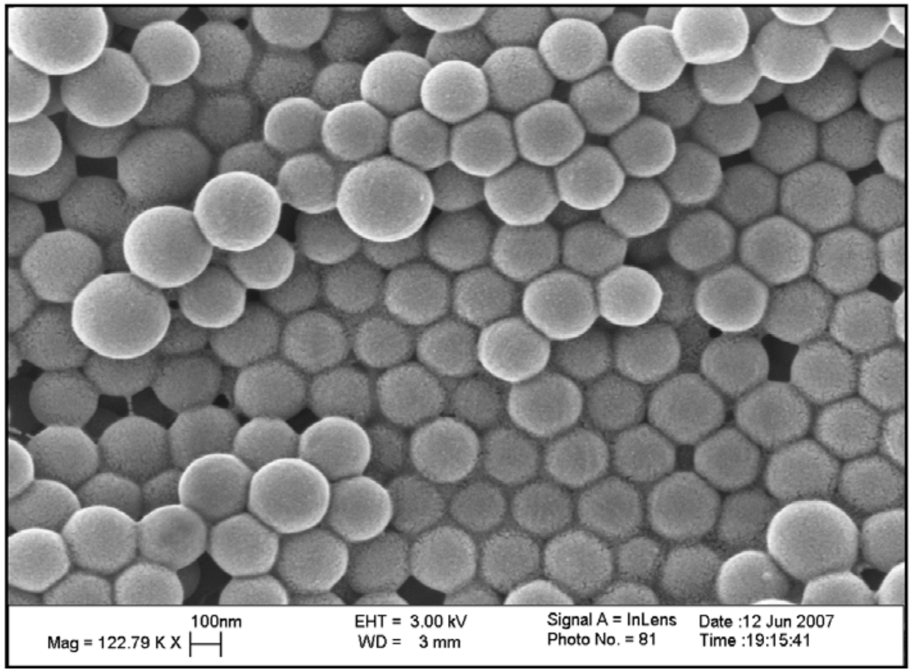
Emulsion made from sunflower oil and aqueous suspension of latex coated with PDMAEMA-PMMA

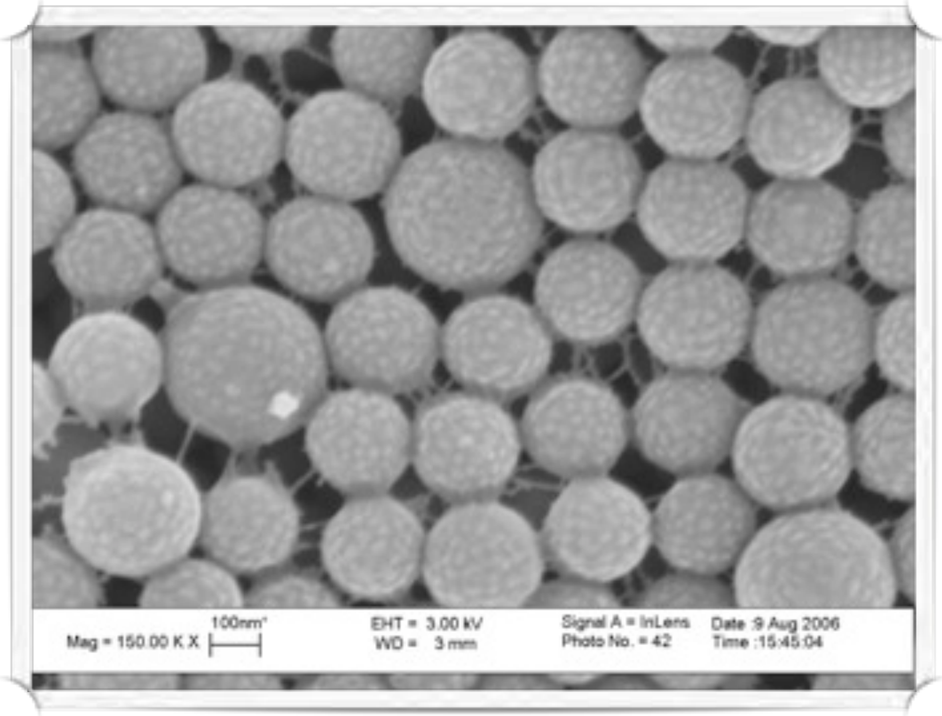
Polymer cross-linked with 3wt% BIEE and oil core removed by washing with ethanol.

Capsules are suspended in Ethanol

Porosity control?

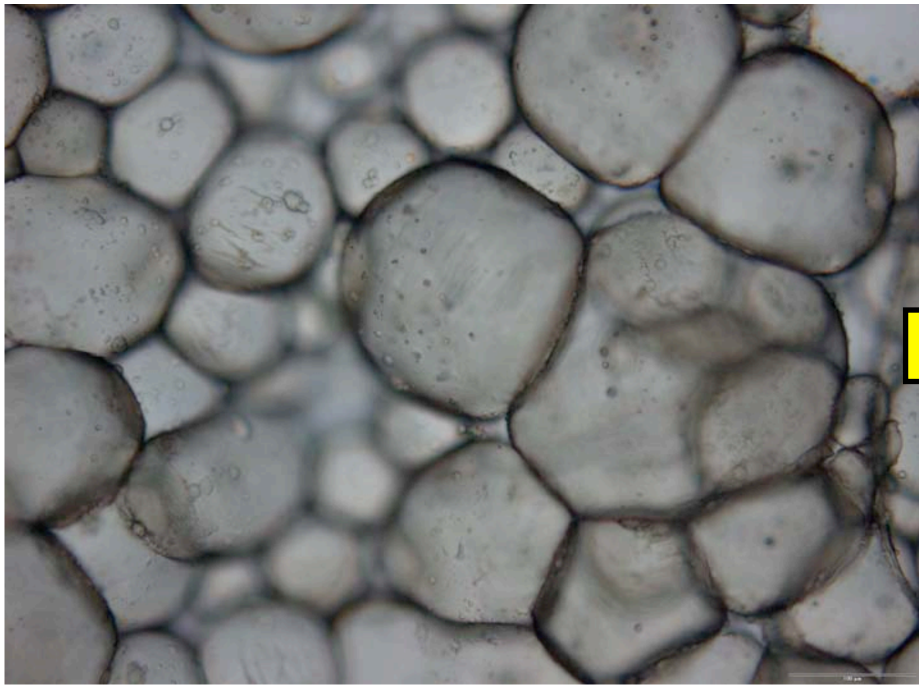
- Vary cross-linker concentration





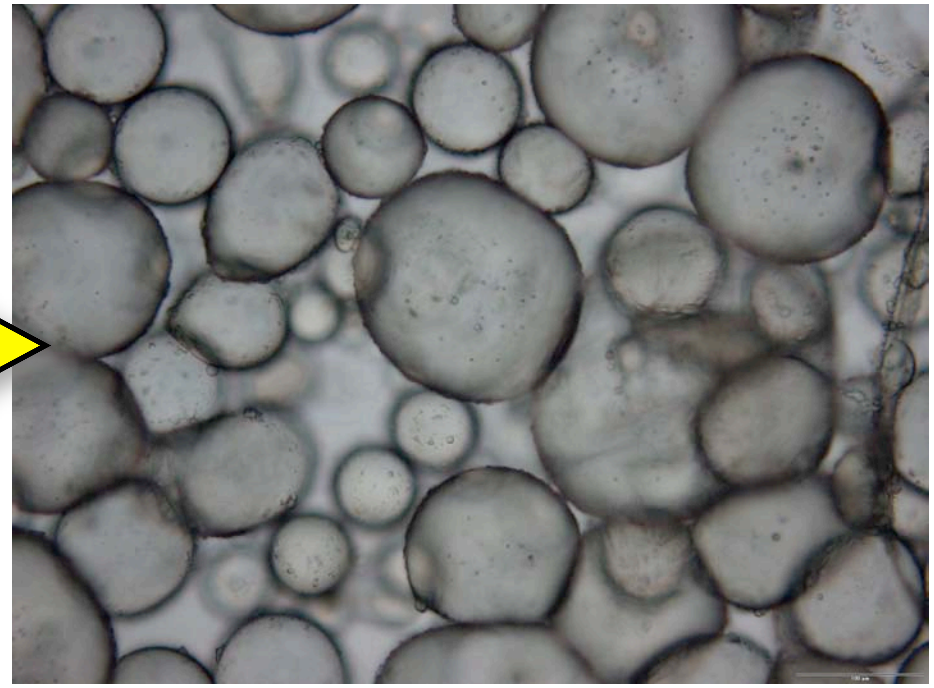
Robust capsules?

Emulsion made from sunflower oil and aqueous suspension of latex coated with PDMAEMA-PMMA



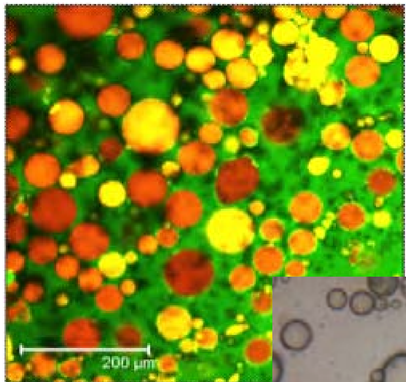
Swelling when ethanol is added - diffuses into capsules rapidly

Polymer cross-linked with 3wt% BIEE

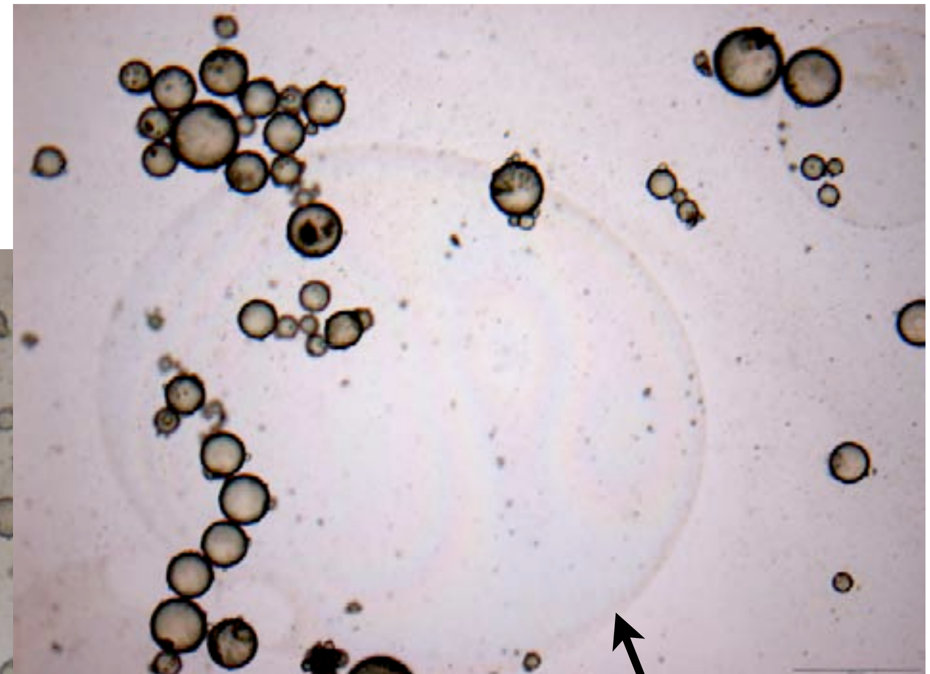


Relaxes over time as system equilibrates

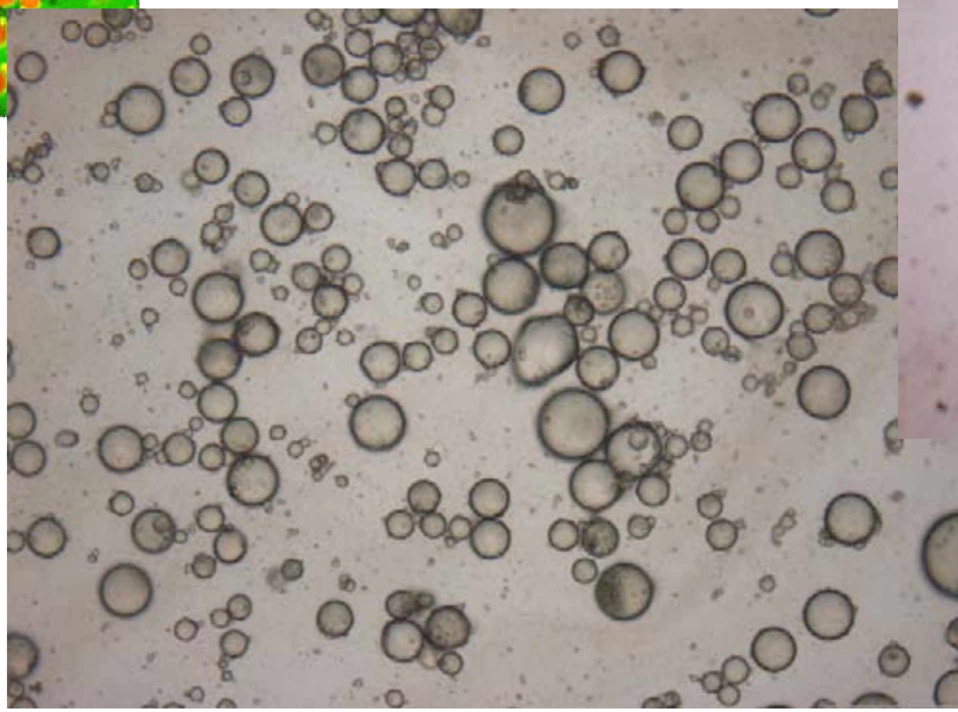
Responsive?



pH 9



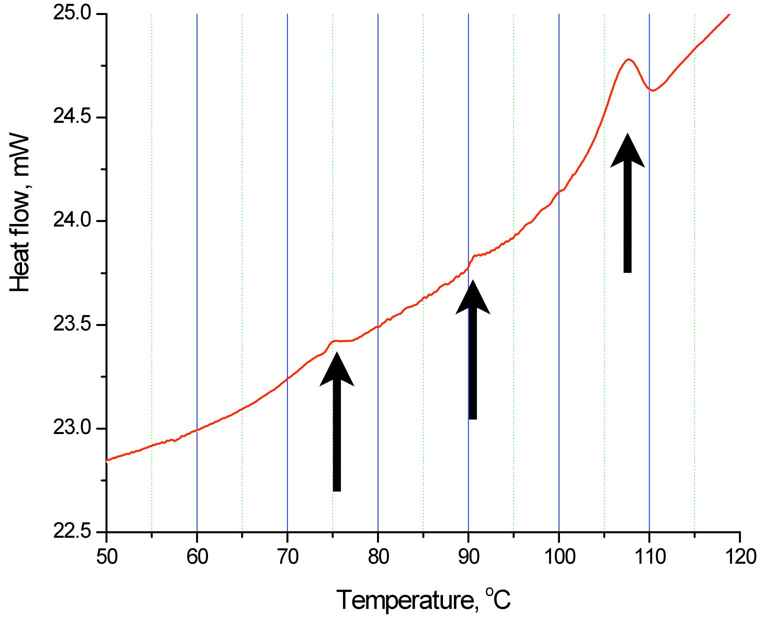
pH 5



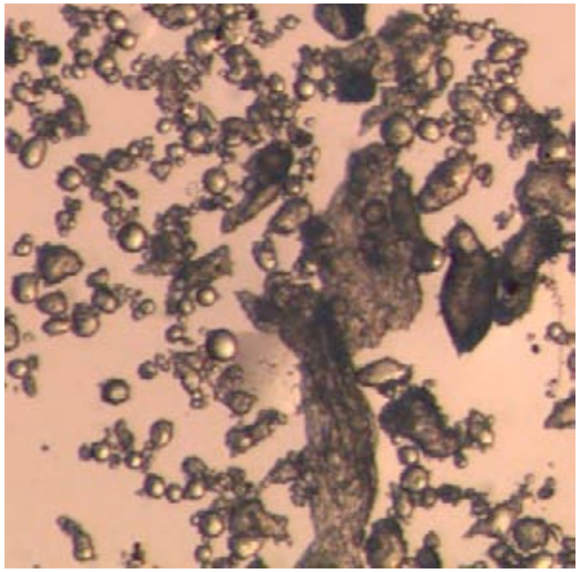
oil pool

Alternative ‘locking’ mechanism

- Heat treat latex stabilised emulsion



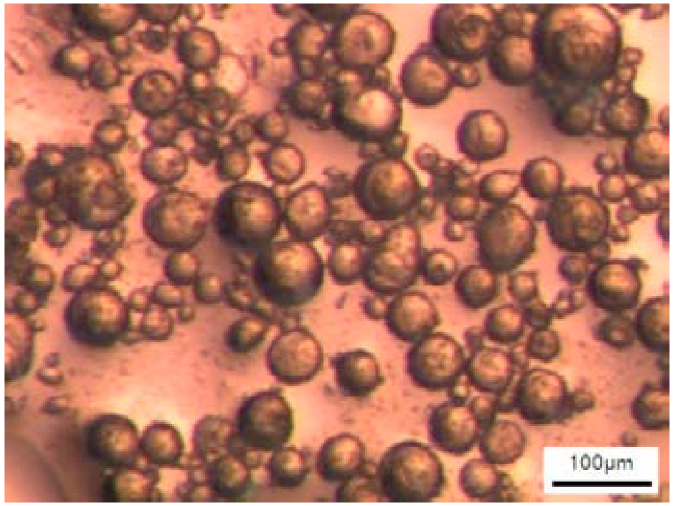
DSC trace for latex particles



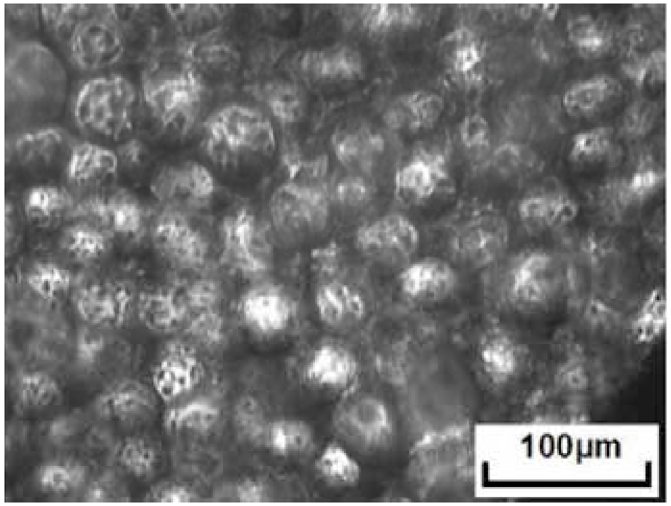
System annealed at 92°C shows considerable instability and irreversible aggregation

Images of capsules

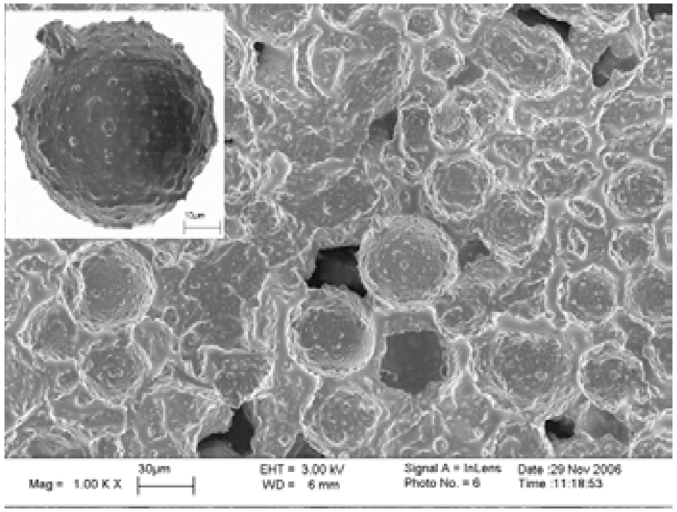
System annealed at 86°C



Optical micrograph in water



Optical micrograph dried



SEM image

Current work

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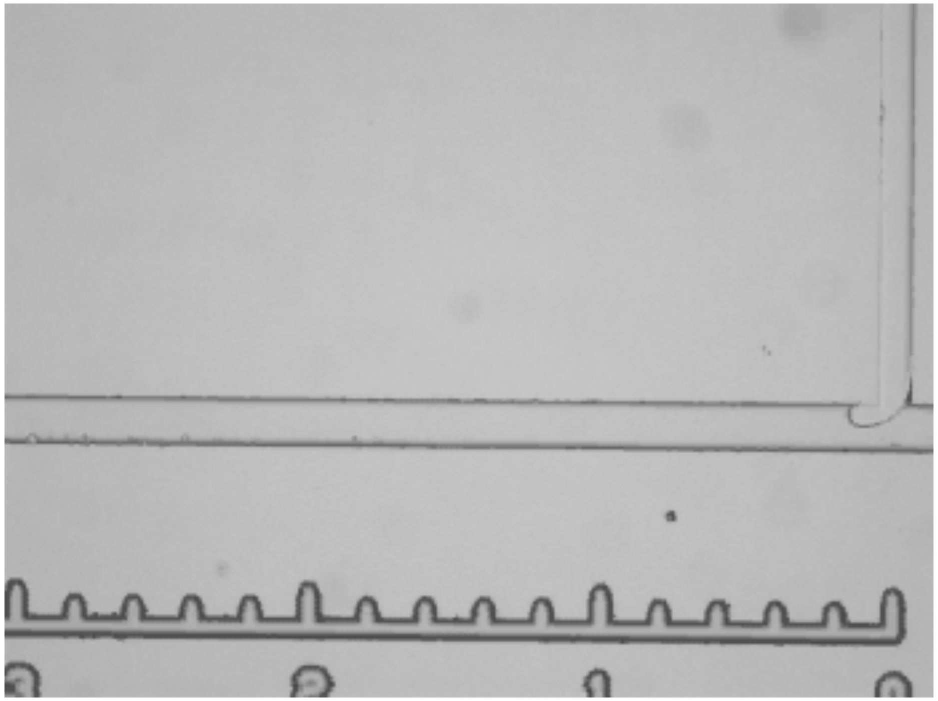

Summary

- Capability of producing microcapsules at scale demonstrated
  - Size control possible
- Novel responsive capsule architecture based on sterically stabilised latex
  - Cross-linking provides opportunity to control responsiveness
  - Can produce in concentrated emulsion systems
- Alternative annealing possibility shown