Liquid Core – Silica Shell Particles

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Liquid Core / Sold Shell Particles (Microcapsules)

Applications

(1) *protection*   and/or

(2) Sustained or triggered *release* of some active ingredient:

- agrochemical (pesticides, herbicides, fungicides, fertilizers, plant growth promoters, insect pheromones).

- pharmaceutical (targeted drugs)

- food additives (e.g. flavourings)

- laundry products (perfumes, sequesterents, bleaches, enzymes, buffers)

- dyes and pigments

- lubricants

- flocculating / gelling agents / polymerisation initiators

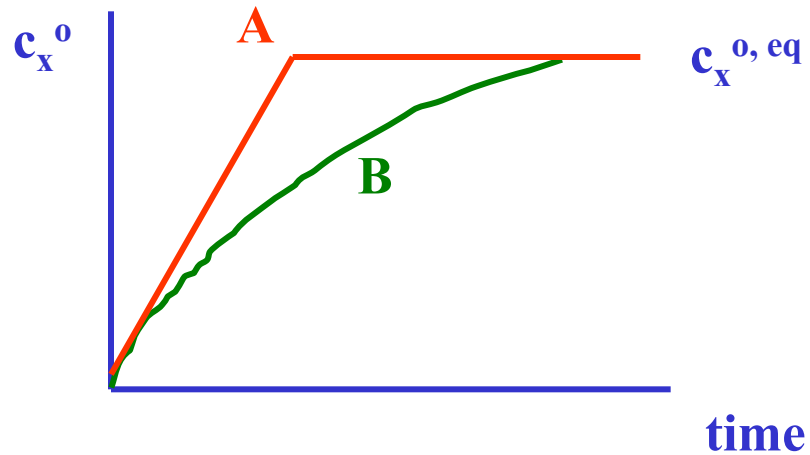The liquid core (pure or solution) may be oil- or water-based.

Sustained Release
(molecules small compared to pore size)

c_x^o

c_x^i

R^o

R^i

δ

$\delta = R^o - R^i$
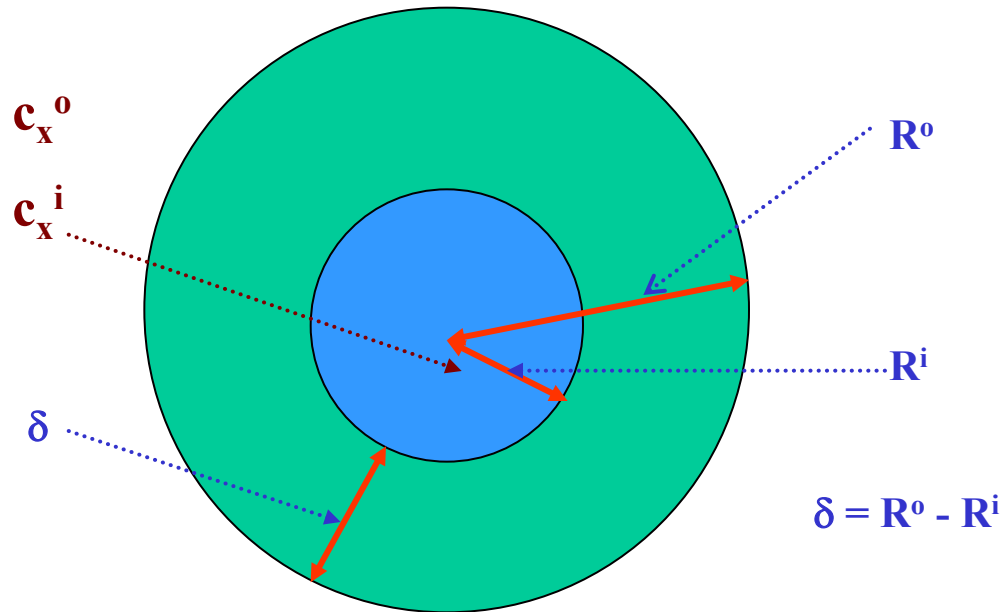
core: solution of some active (NB pure liquid difficult)

shell: porous solid (inorganic e.g. silica or polymer)

Sustained Release Profile

A = *zeroth* order : *constant* release rate (saturated solution, i.e. a colloidal dispersion of slightly soluble active)

B = *first* order (solution):
$$\frac{dc_x^0}{dt} = \frac{4\pi R^o R^i P\left(c_x^0 - c_x^i\right)}{\delta}$$

P = the permeability of the shell

Triggered Release
(active molecules *large* compared to pore size)

For triggered release the shell is usually ruptured at some point in the process (so release is "instantaneous"). Hence the solid shell needs to be brittle. Inorganic solids are often used (e.g. silica, calcium carbonate). NB the core could now be a pure liquid.

Methods of rupture:

Mechanical stress (e.g. a drill bit, a washing machine)

Osmotic: if the core liquid and exterior liquid are miscible (e.g. both aqueous), so that *inward* diffusion of solvent molecules across the solid shell can occur

NB *Double-shelled* microcapsules can offer both triggered and sustained release: outer shell brittle, inner shell permeable.

Principle Methods of Preparation of liquid core / solid shell microcapsules

1) From "Pickering" emulsions: fusion or growth of the adsorbed, solid particles

2) Template methods, e.g. using surfactant liposomes

3) Layer-by-layer adsorption of polymers / polyelectrolytes

4) Induced phase separation of polymers in the continuous phase.

5) Induced phase separation of polymers within preformed droplets.

6) Interfacial polymerisation.

Interfacial polymerisation

In this method, a polycondensation reaction between two monomers occurs at the droplet interfaces in an O/W or W/O emulsion.

Monomer 1 is oil-soluble, and monomer 2 is water-soluble, so that the interface is the only locus of polymerisation.

e.g. a diamine in the aqueous phase + a diacid chloride in the oil phase would give a nylon shell at the oil / water interface.

NB the nylon "rope trick"! (next slide)

The nylon rope trick

Silica Shells formed by interfacial Polymerisation

We have worked extensively with this method. Two types of system will be described here:

1) oil core / silica shell systems

2) water core / silica shell systems

With these systems relatively thick shells may be produced.

OIL CORE /

SILICA SHELL

PARTICLES

General Methods for preparing *Monodisperse* Emulsions

the basis for making monodisperse capsules

1) comminution methods : e.g.
   micro-fluidics (David Weiss)
   cross-flow membrane devices (Richard Williams / Leeds).

2) nucleation and growth methods (c.f. colloidal particles)
   more useful for smaller droplets (< 10 μm)

PDMS O/W Emulsion Synthesis by Nucleation & Growth

Novel Monodisperse Silicone Oil/Water Emulsions
Obey and Vincent
J. Colloid and Interface Science, 1994 **163** 454
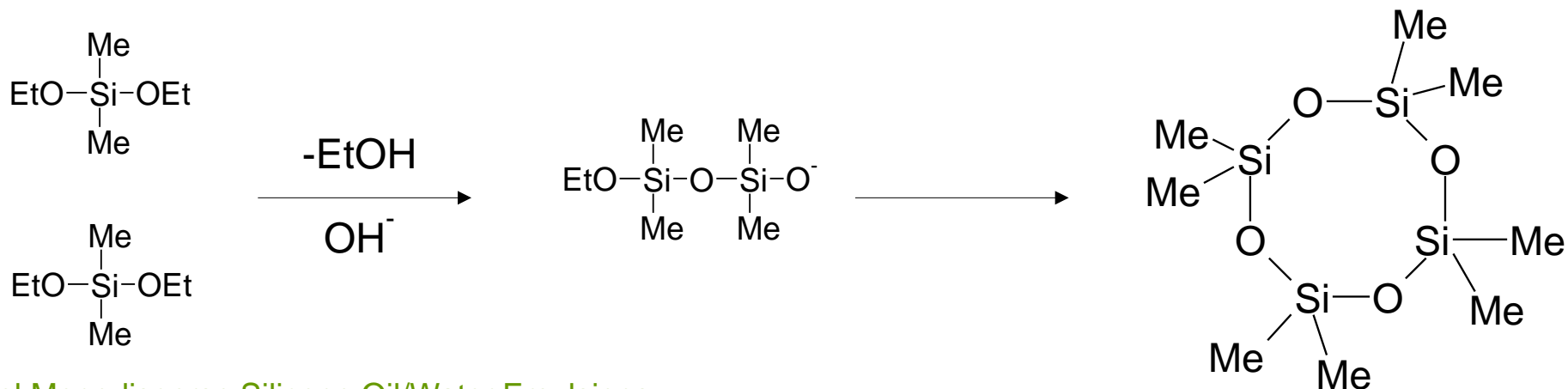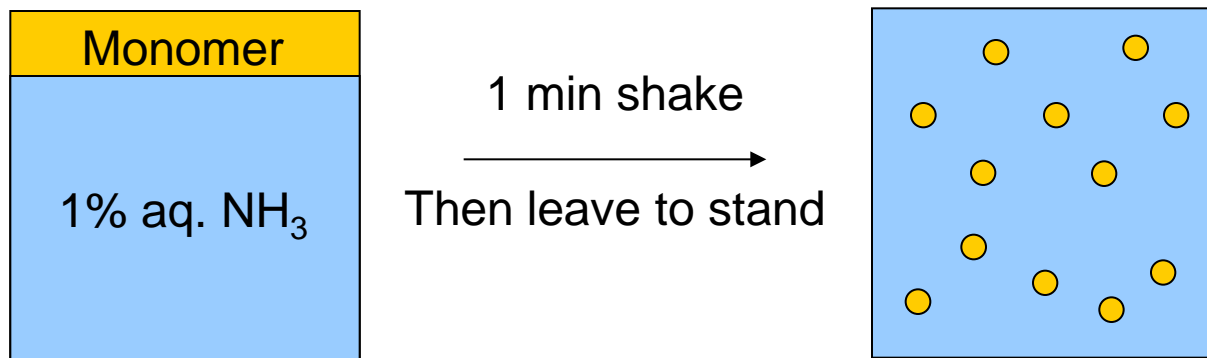
PDMS Oligomers
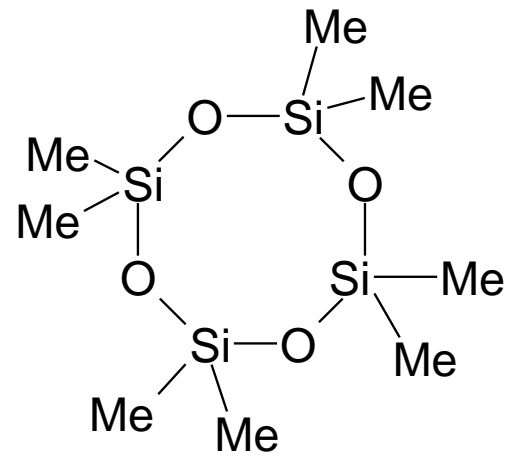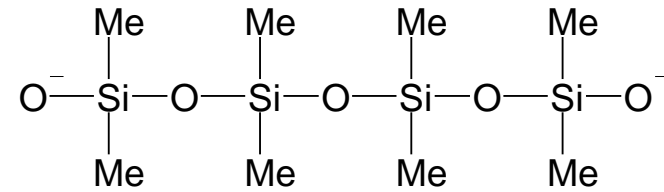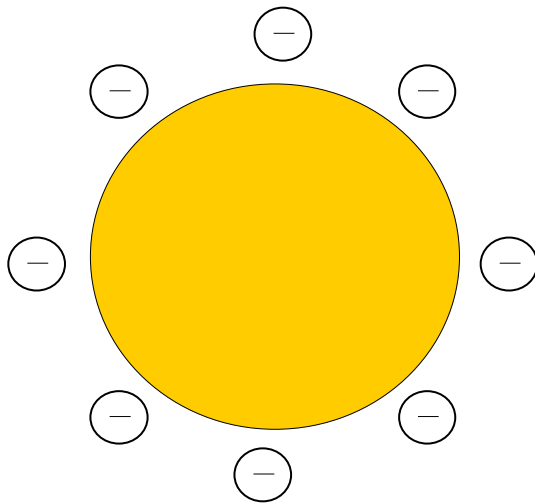
optical micrographs of PDMS droplets

monodisperse and

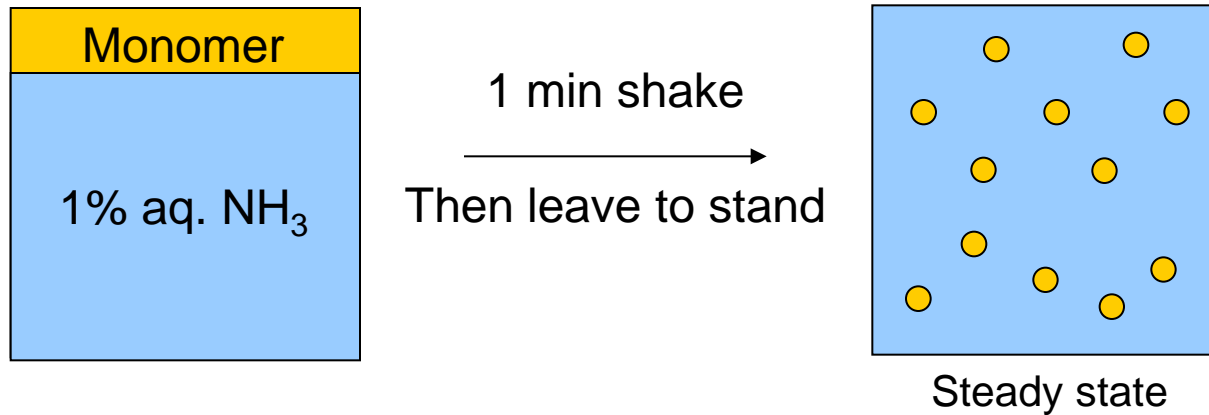*charge-stabilsed*

(no surfactant added)
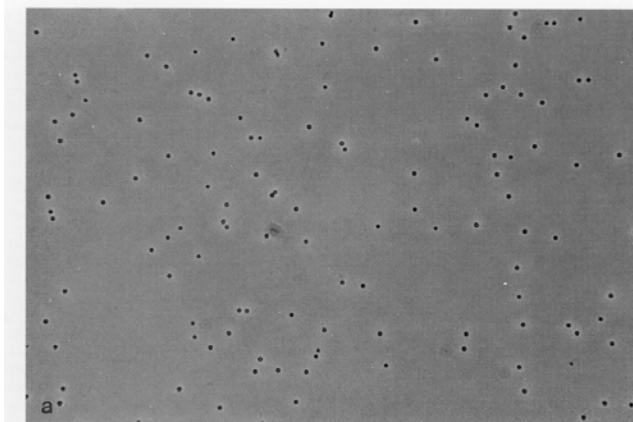
average diameter 1.5 μm
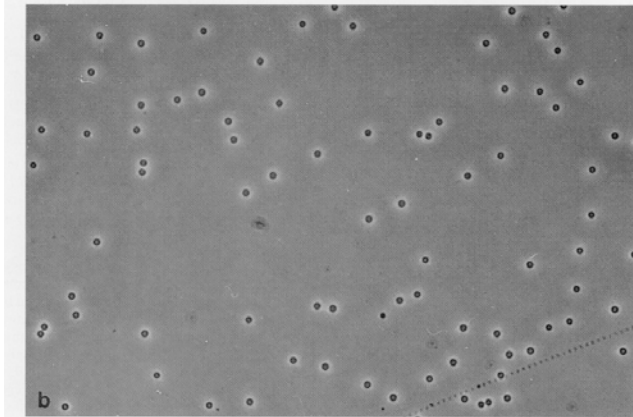
average diameter 2.5 μm

1 % PDMS Droplet Growth with Time
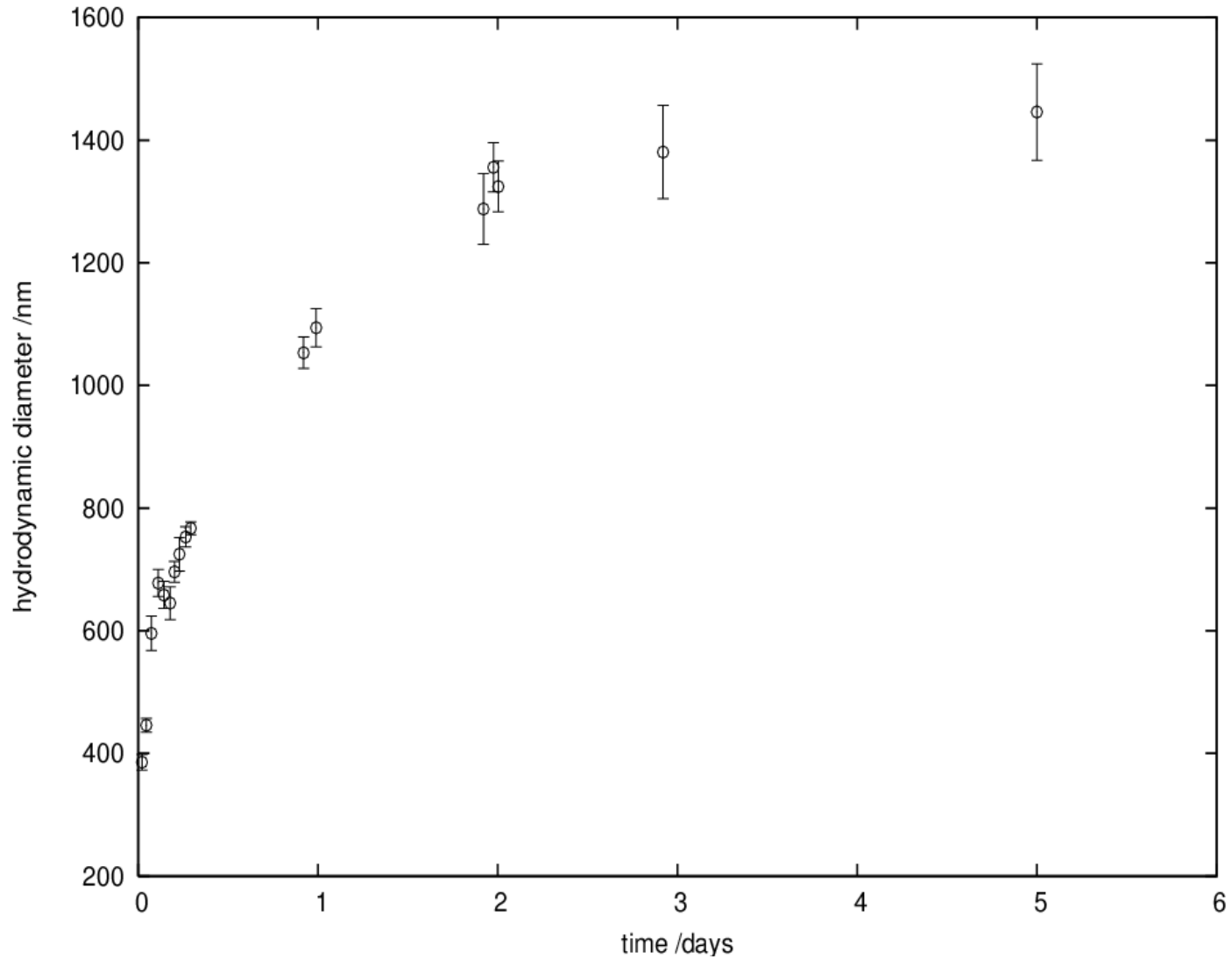
PDMS Microgel Synthesis
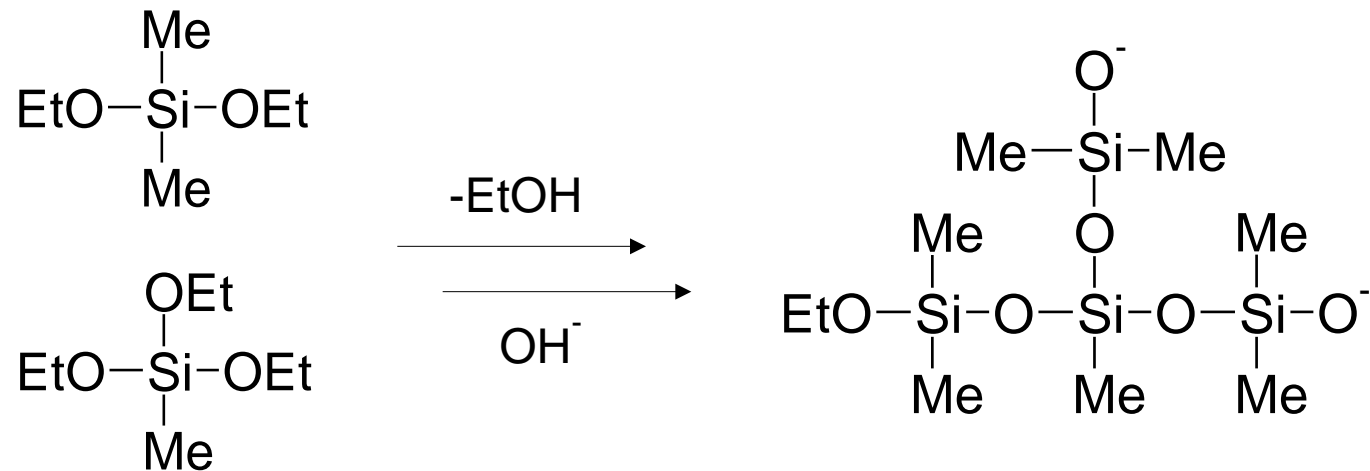
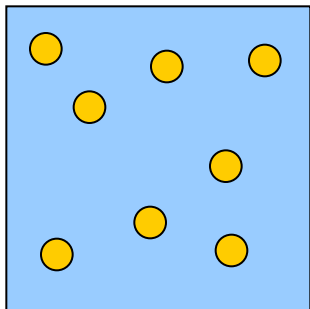# cross-linked PDMS microgel particles:

swelling with n-heptane
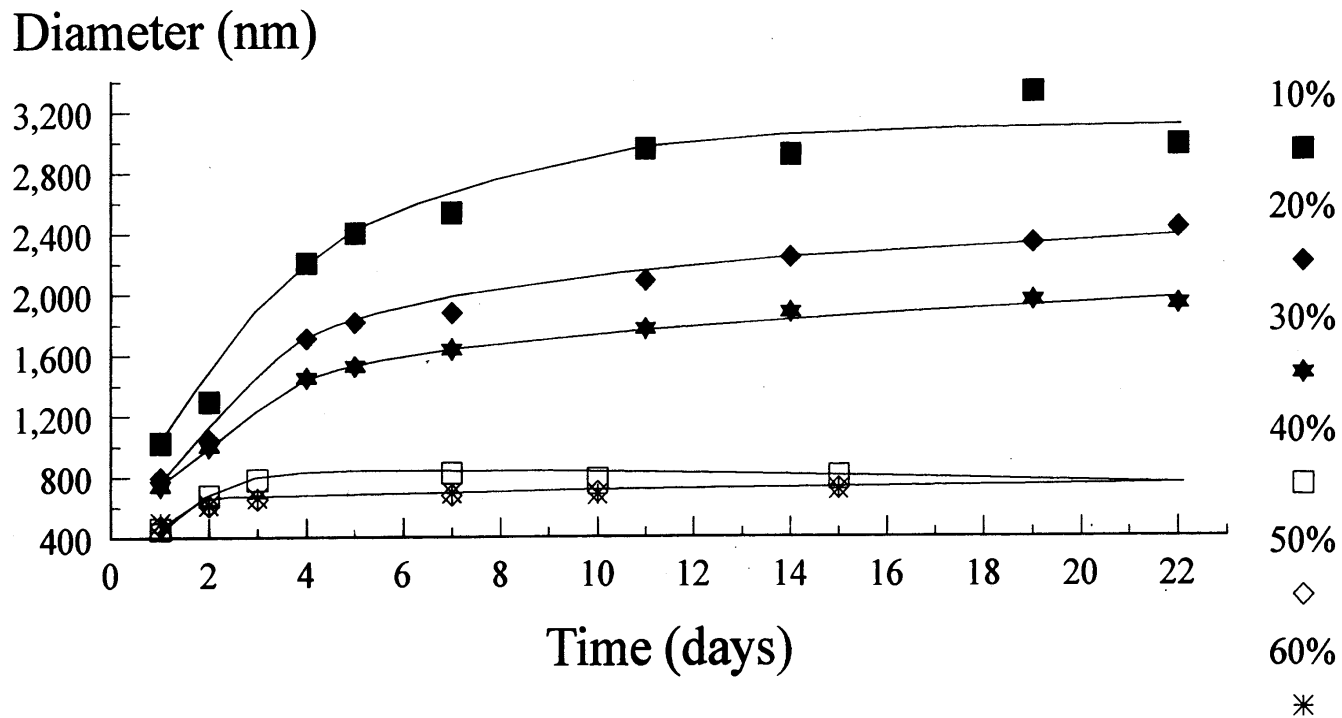
Shell Formation:

Silica Precipitation onto PDMS Droplets / Microgel Particles

Route 1 (1998): because TEOS is soluble in PDMS, we originally thought we would need a two-stage route:

• **stage 1 :** PDMS droplets are first encapsulated in a thin coating of silica by precipitation and deposition from aqueous sodium silicate solution. However, one cannot form *thick* layers this way.

• **stage 2 :** the silica layer is then built-up on these coated droplets, by hydrolysis of TEOS added to the bulk aqueous /ethanolic ammonia solution. The silica particles form at / deposit on the surface of the encapsulated oil droplets.
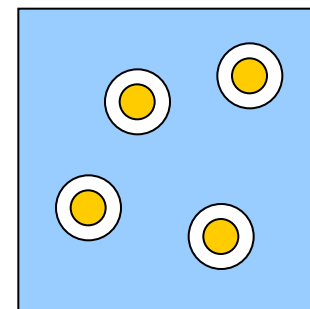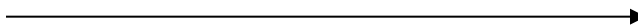
M.I. Goller, B. Vincent, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 1998 **142** 281

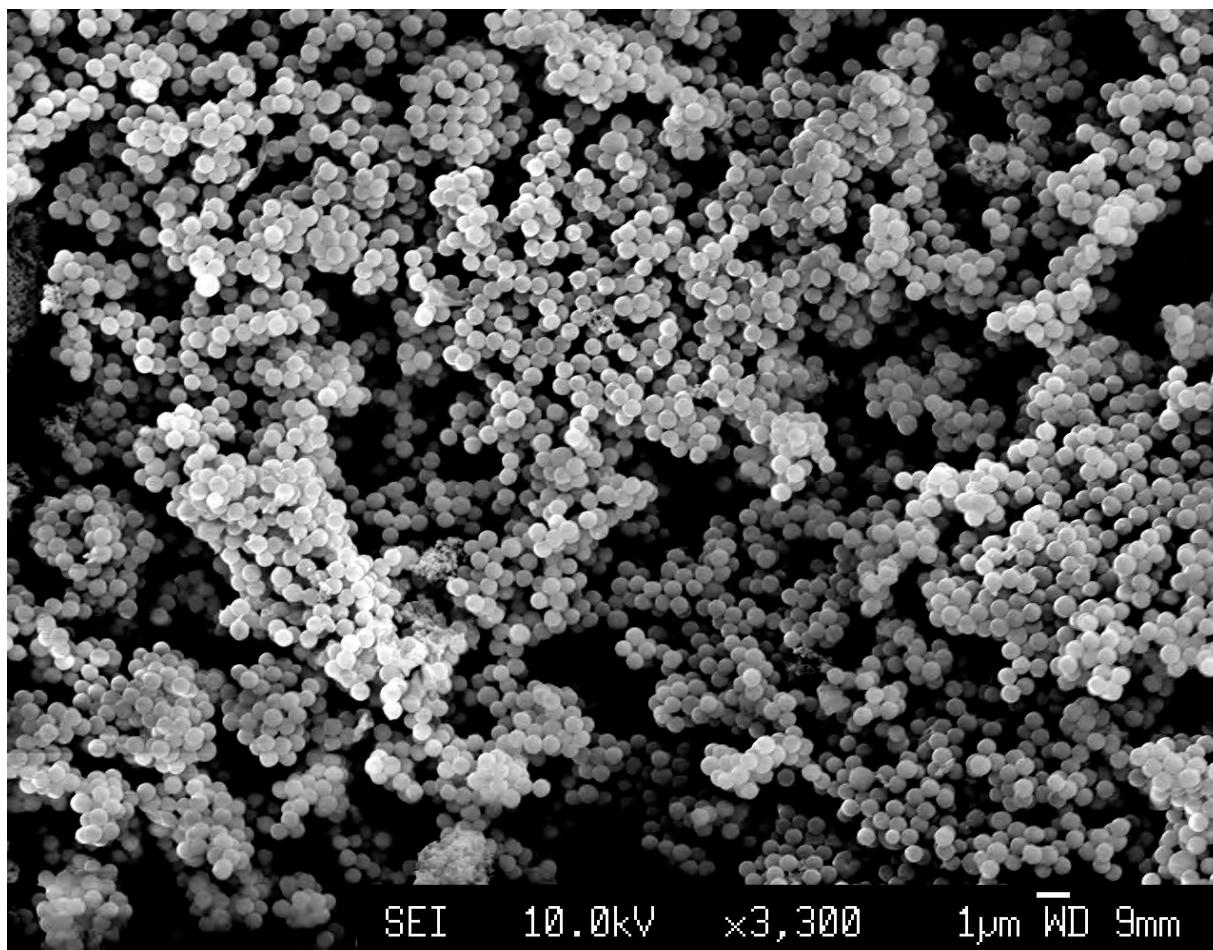# Silica Shells on PDMS Droplets & Microgel Particles

Precipitation from sodium silicate
to form a silica skin around PDMS
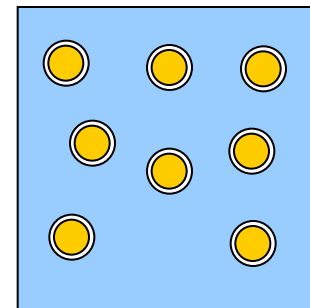
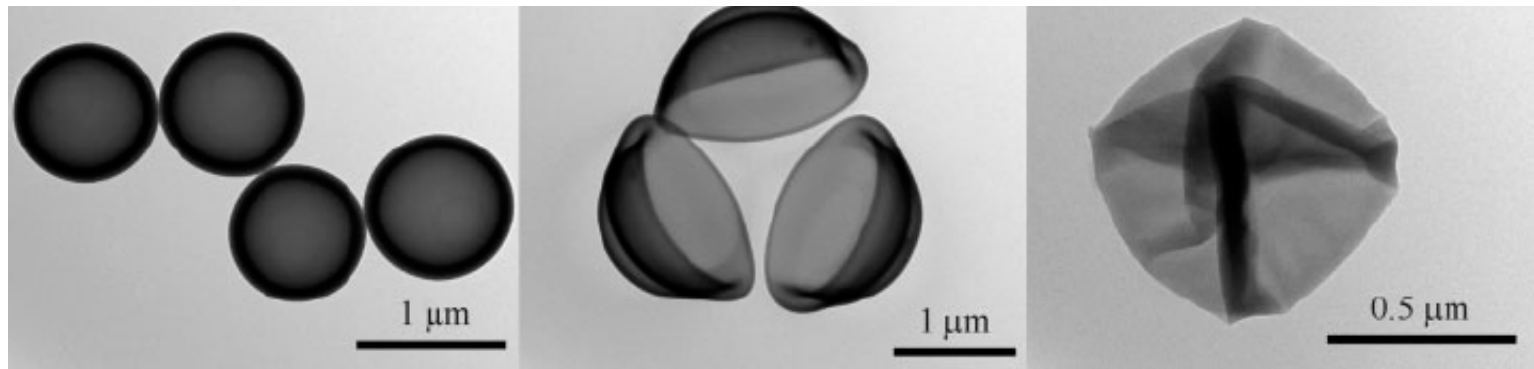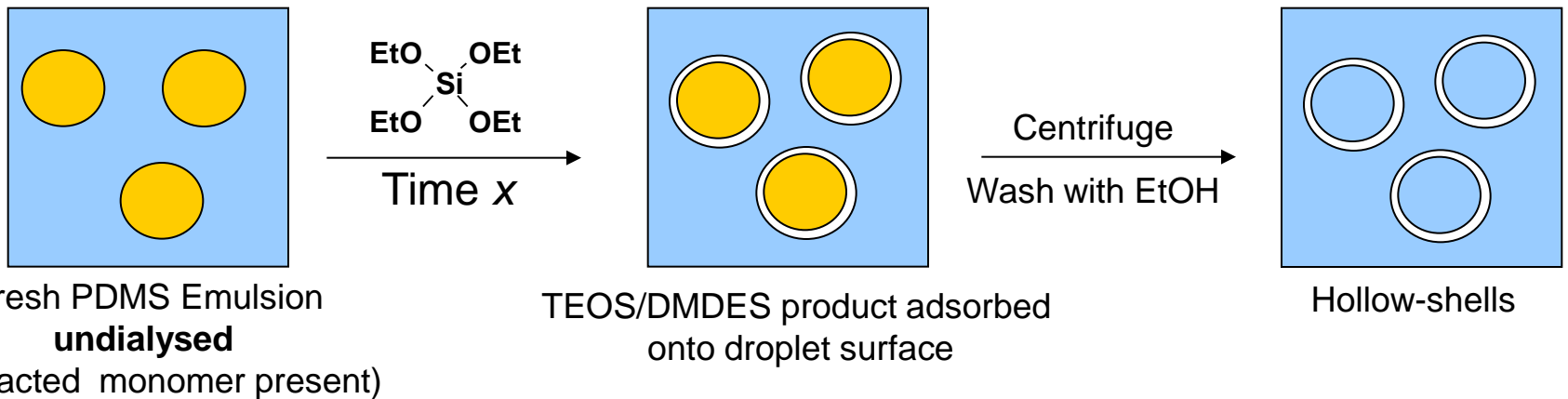Shell growth in NH$_3$/EtOH
with slow addition of TEOS

Shelled PDMS Microgel Particles

SEI   10.0kV   ×3,300   1μm WD 9mm

Route 2: Zoldesi (2005) *one-shot* method

Synthesis of Monodisperse Colloidal Spheres, Capsules, and Microballoons by Emulsion Templating , Carmen I Zoldesi and Arnout Imhof, *Adv. Mater.* **17,** 924-928, 2005
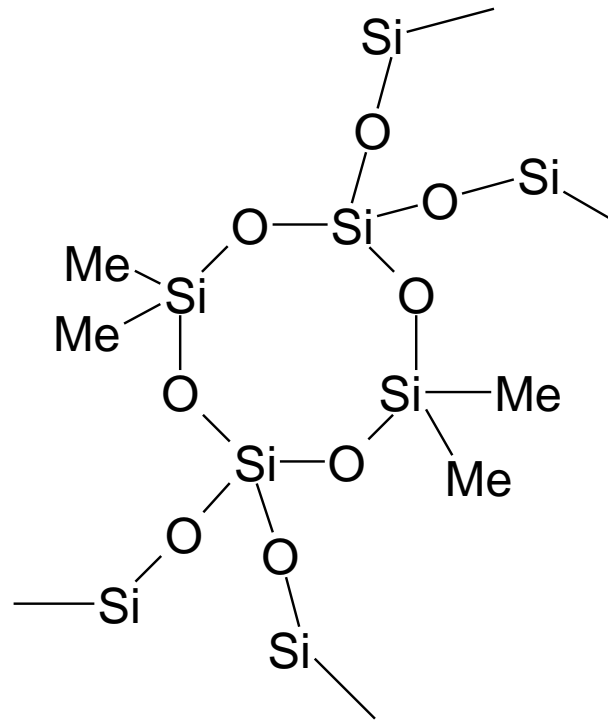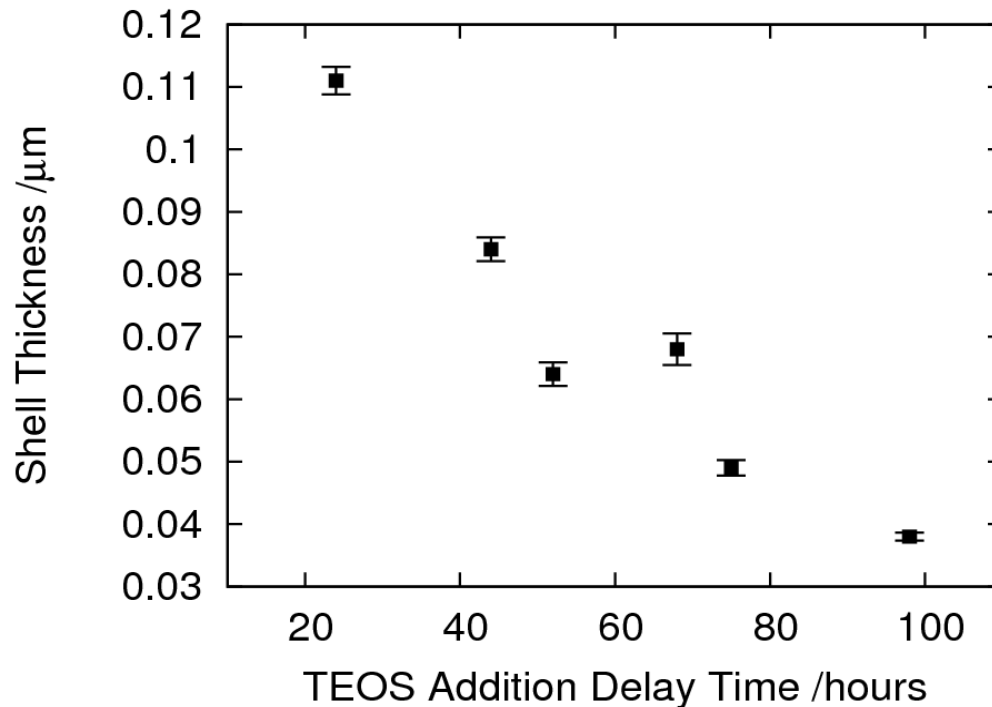

EtO   OEt
   Si
EtO   OEt

Time *x*

Centrifuge
Wash with EtOH

Fresh PDMS Emulsion
undialysed
(unreacted monomer present)

TEOS/DMDES product adsorbed
onto droplet surface

Hollow-shells

Time *x* =   24 hours   48 hours   72 hours

Shell Material

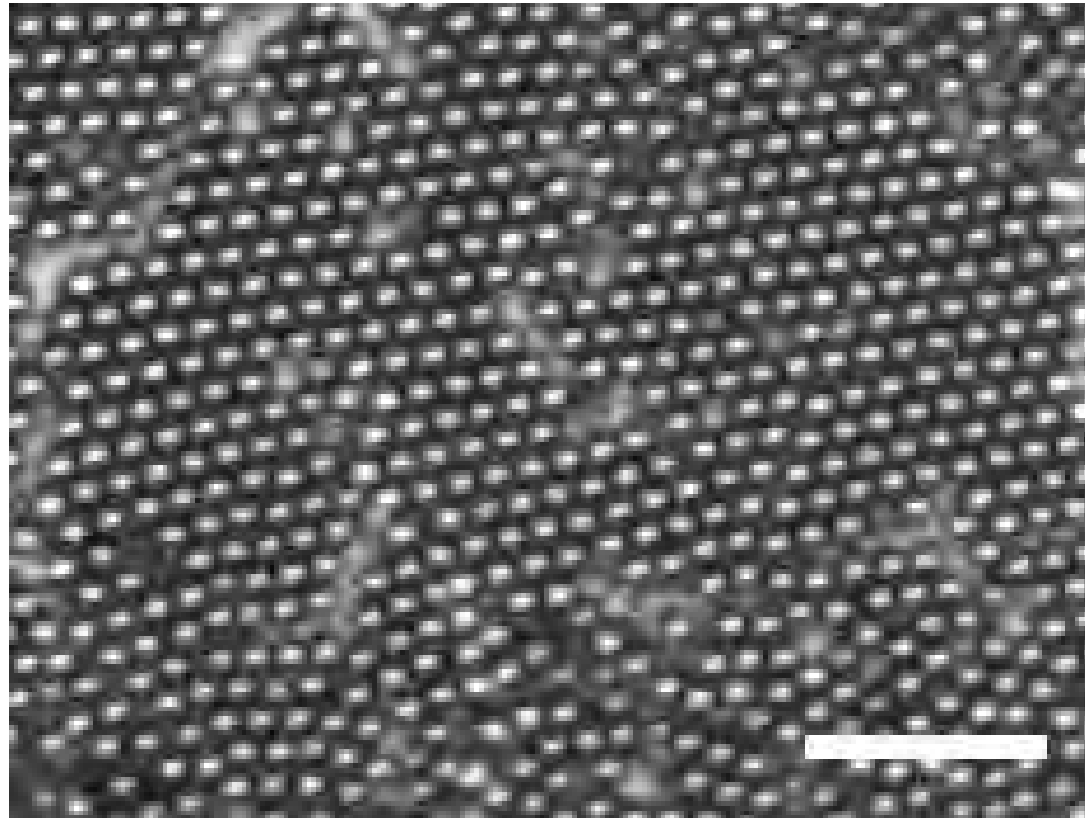# Shell thickness as a function of delay time
(Zoldesi method)

Vincent – O'Sullivan Modification of Zoldesi Method: *post-addition* of a mixture of DEODMS + TEOS

1) Let the emulsion growth reaction go to completion first (5days)

    i.e. *no* un-reacted DEODMS left in the PDMS droplets

2) Add a *mixture* of DEODMS + TEOS (rather than just TEOS) in various ratios. DEODMS partitions inside the droplets.

3) For the example shown here the TEOS conc. was fixed at 0.018 mol dm^{-3} . The DEODMS conc. was varied between 0.005 and 0.035 mol dm^{-3}.

AIM: better *predictive* control over the shell thickness

O'Sullivan, Zhang, Vincent Langmuir 2009 **25** *7962*
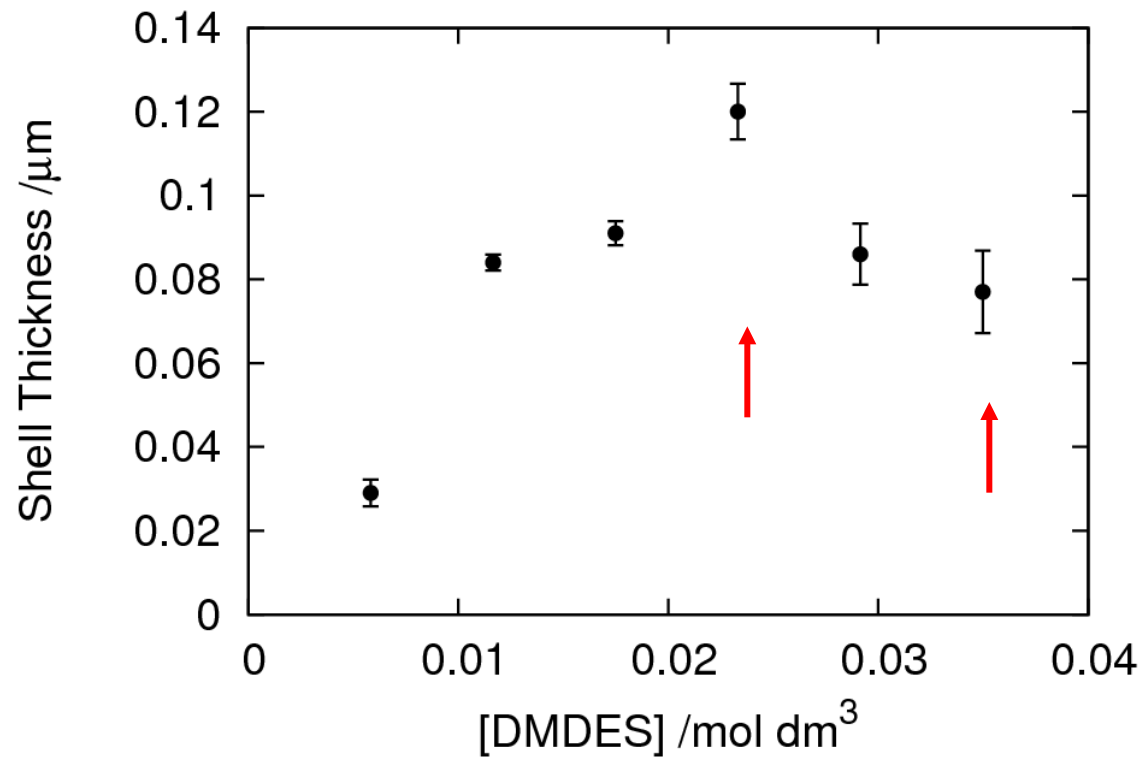
.

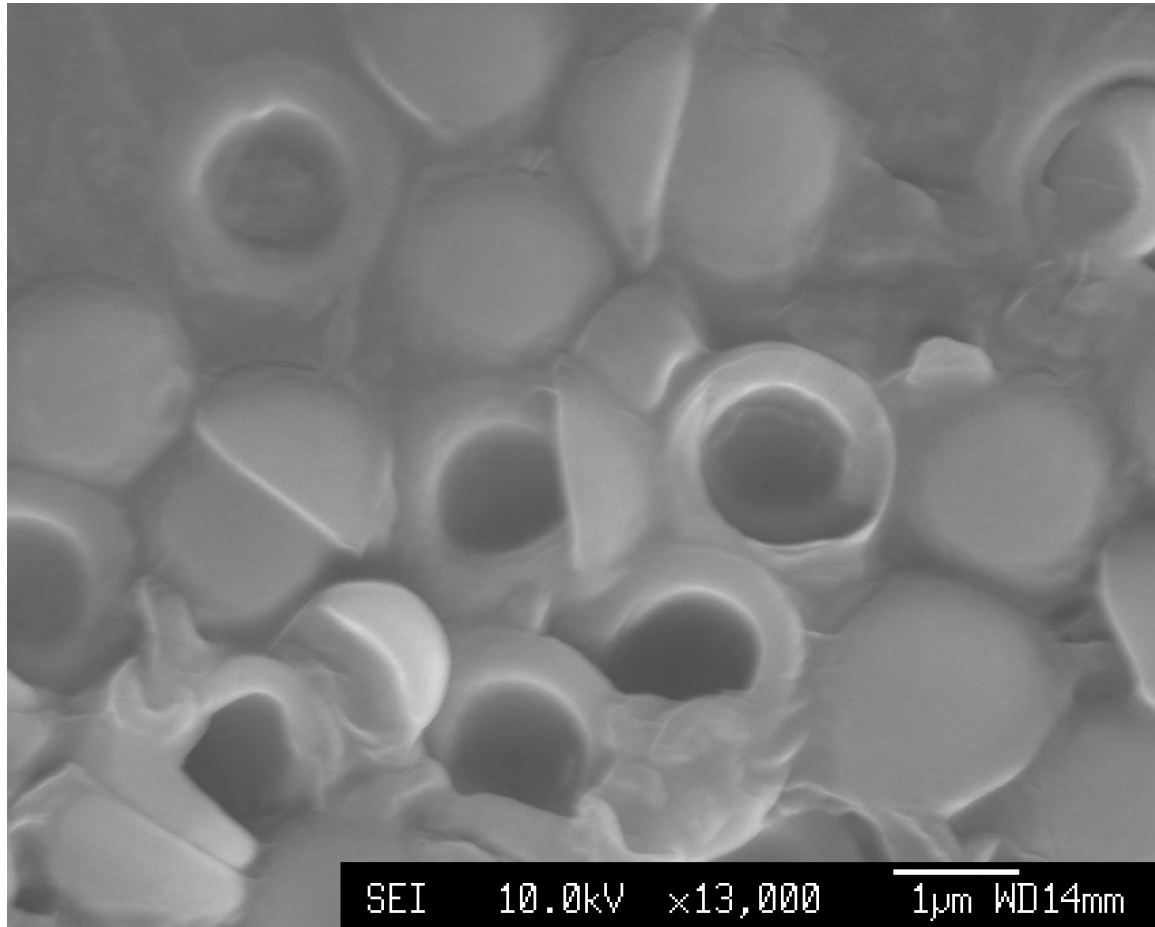# Core-shell particles prepared by the *post–addition* method

bar = 20 μm

Optical micrograph of particles dried on a microscope slide

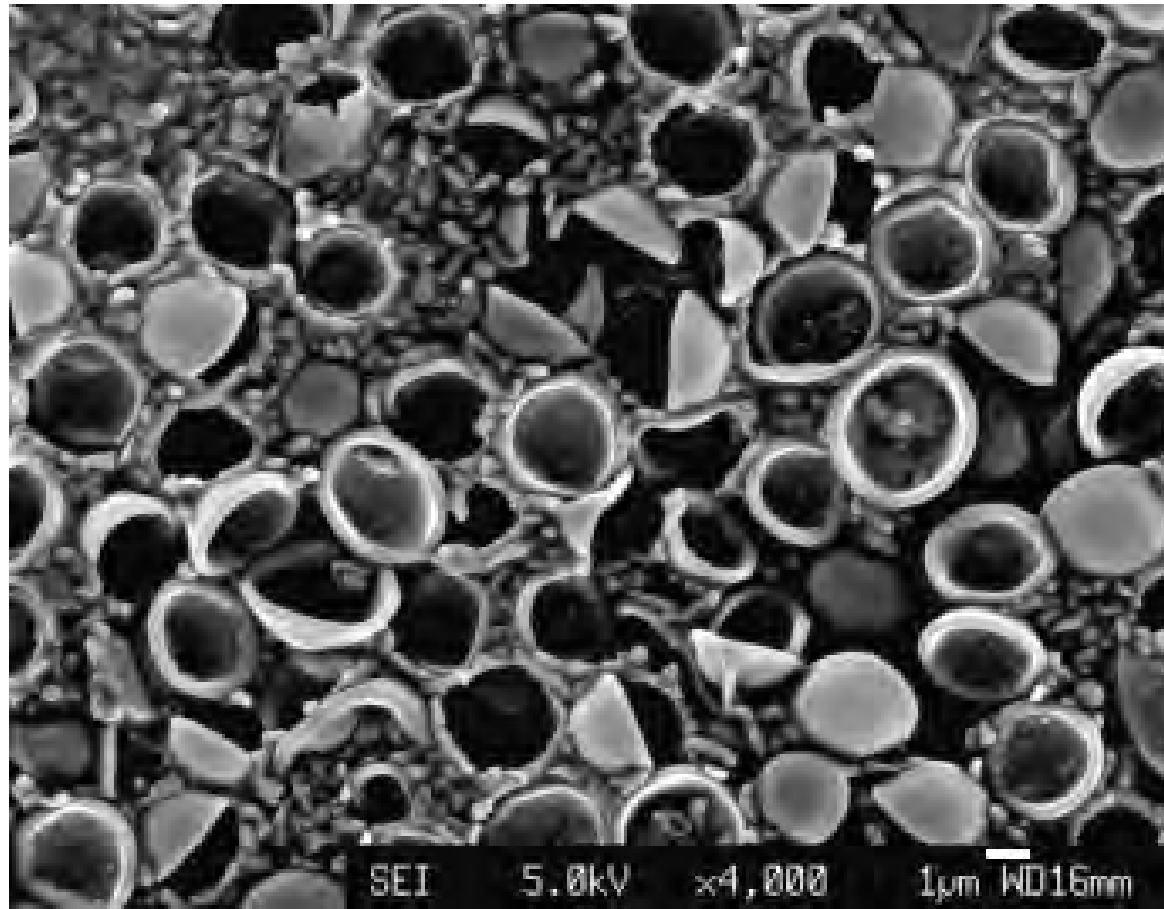# Shell thickness as a function of DEODMS conc.
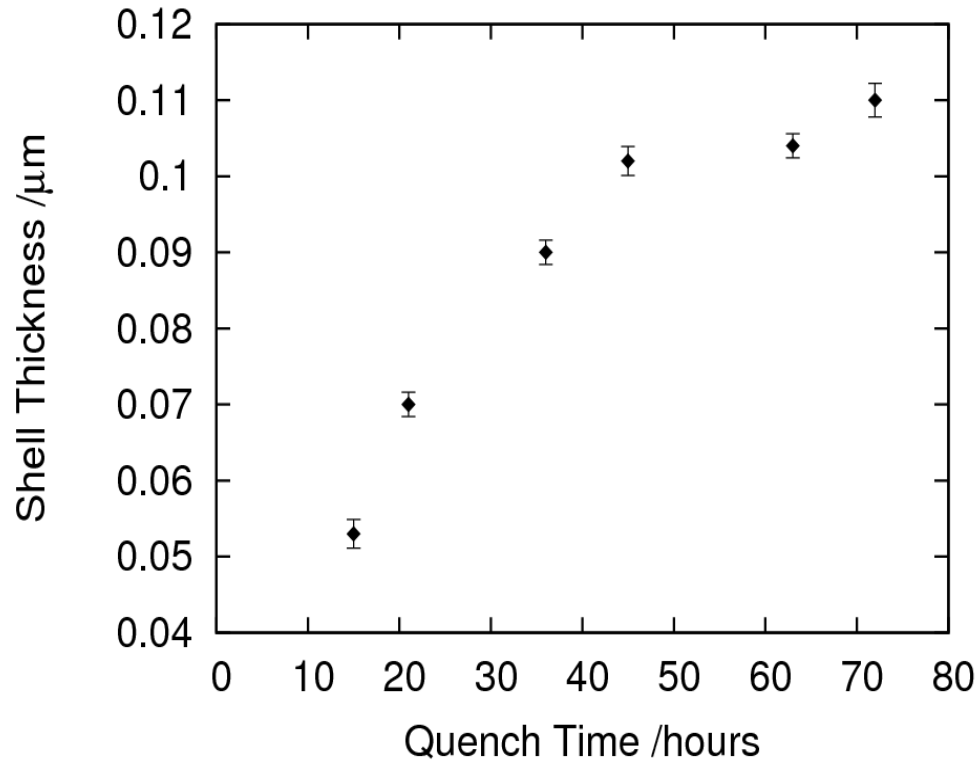

TEOS conc. fixed at 0.018 mol dm^{-3}

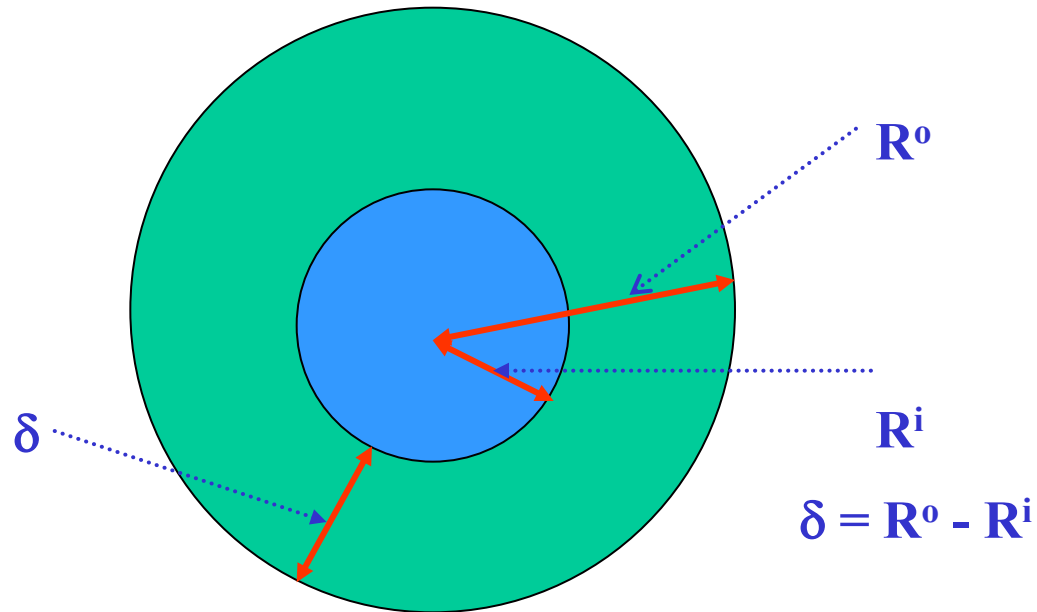# SEM: DEODMS conc. = 0.023 mol dm^{-3}

SEM: DEODMS conc. = 0.035 mol dm^{-3}

Control of shell thickness by varying the reaction *quench time*

DEODMS conc. = 0.023 mol dm^{-3}; TEOS conc. = 0.018 mol dm^{-3}

Measurement of Shell Thickness, δ

R^o

R^i

δ

$\delta = R^o - R^i$

(1) Directly from SEM images of broken capsules (as here)

(2) *Without breaking open*: from measurement of R^o and R^i.
R^o from microscopy
R^i from NMR diffusion: *Wassenius, Nyden & Vincent,*
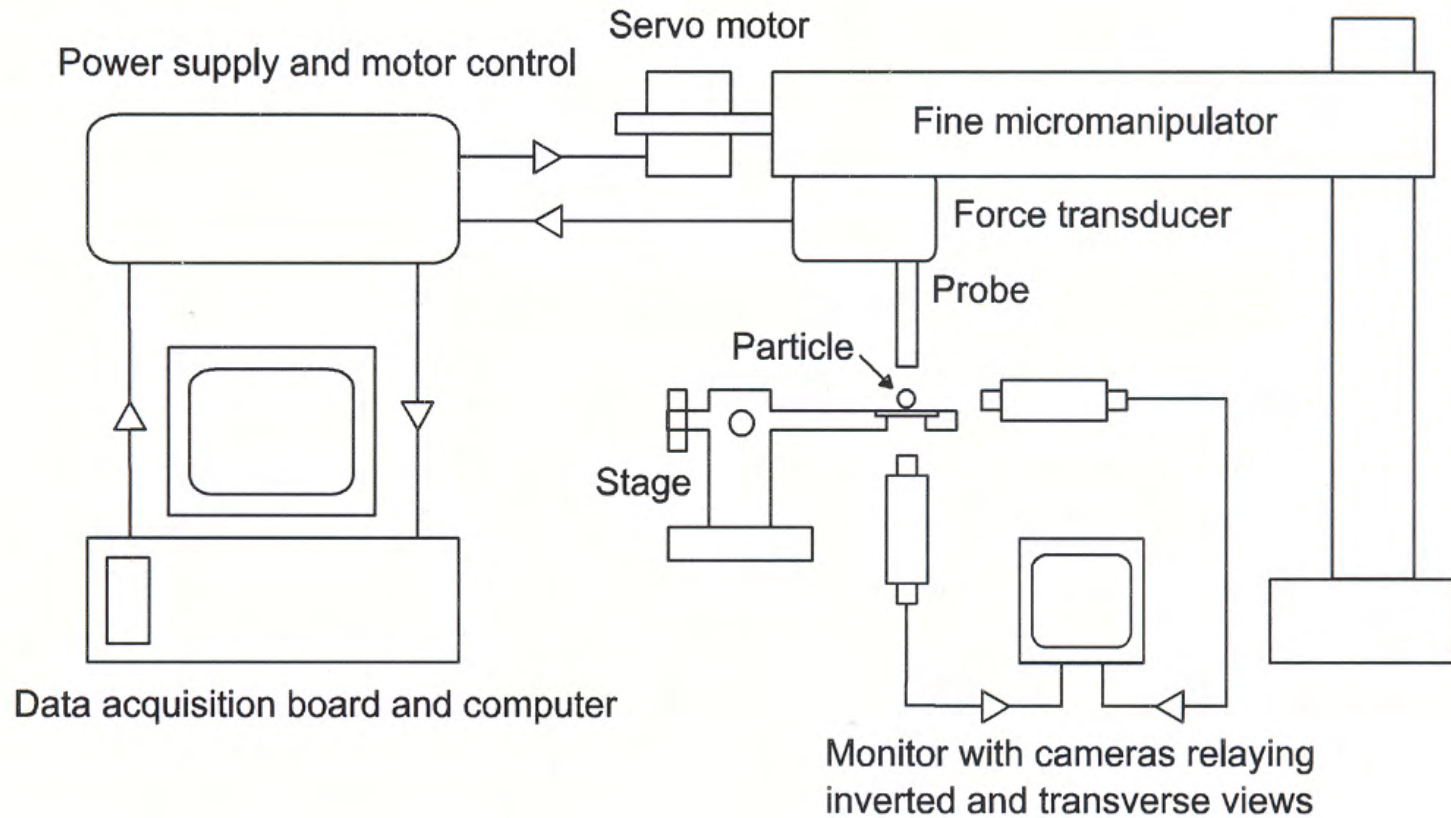*J.Colloid Interface Sci, 2003 264 538*

Mechanical Strength

- Micromanipulator (+ Z. Zhang)

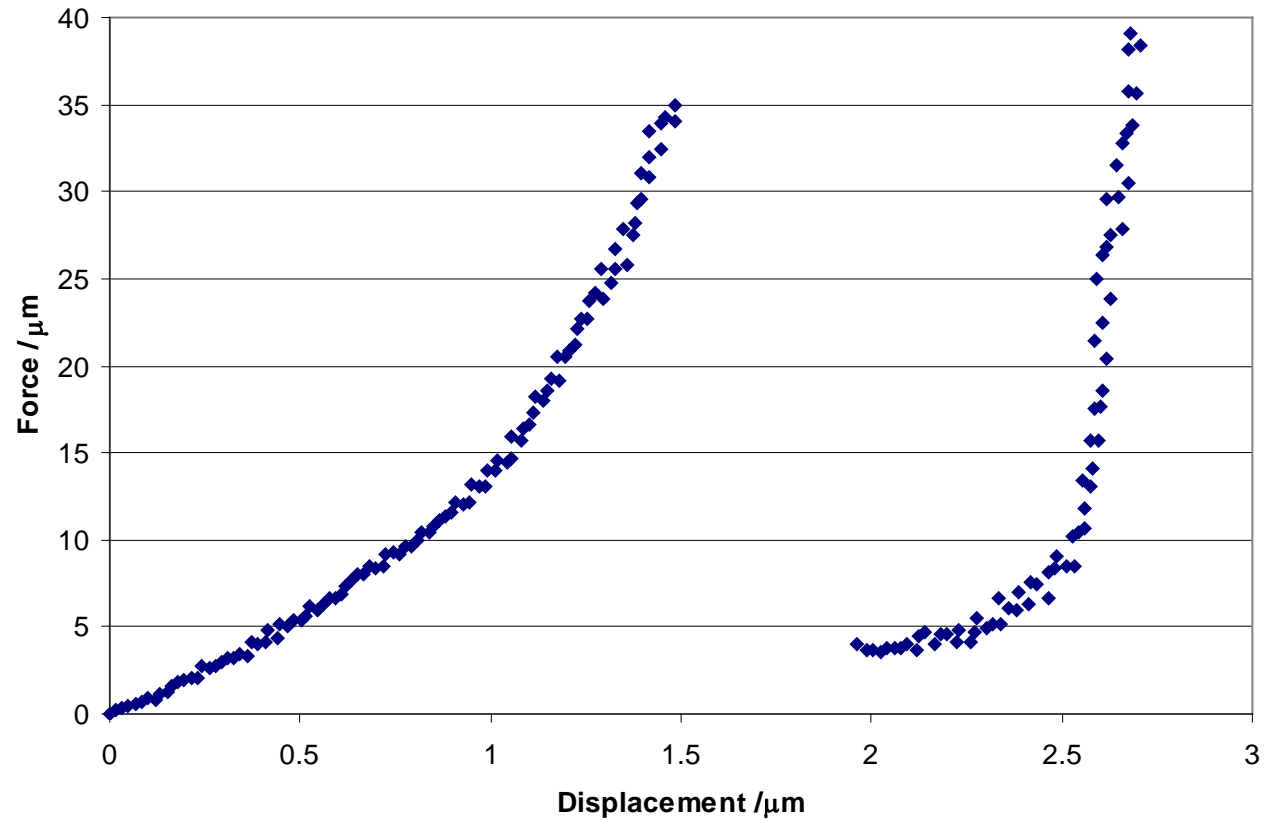- Need particles large enough to be viewed under an optical microscope

Mechanical Strength of Microcapsules Made of Different Wall Materials, G Sun and Z Zhang, *International Journal of Pharmaceutics*, **242**, 307-311, 2002
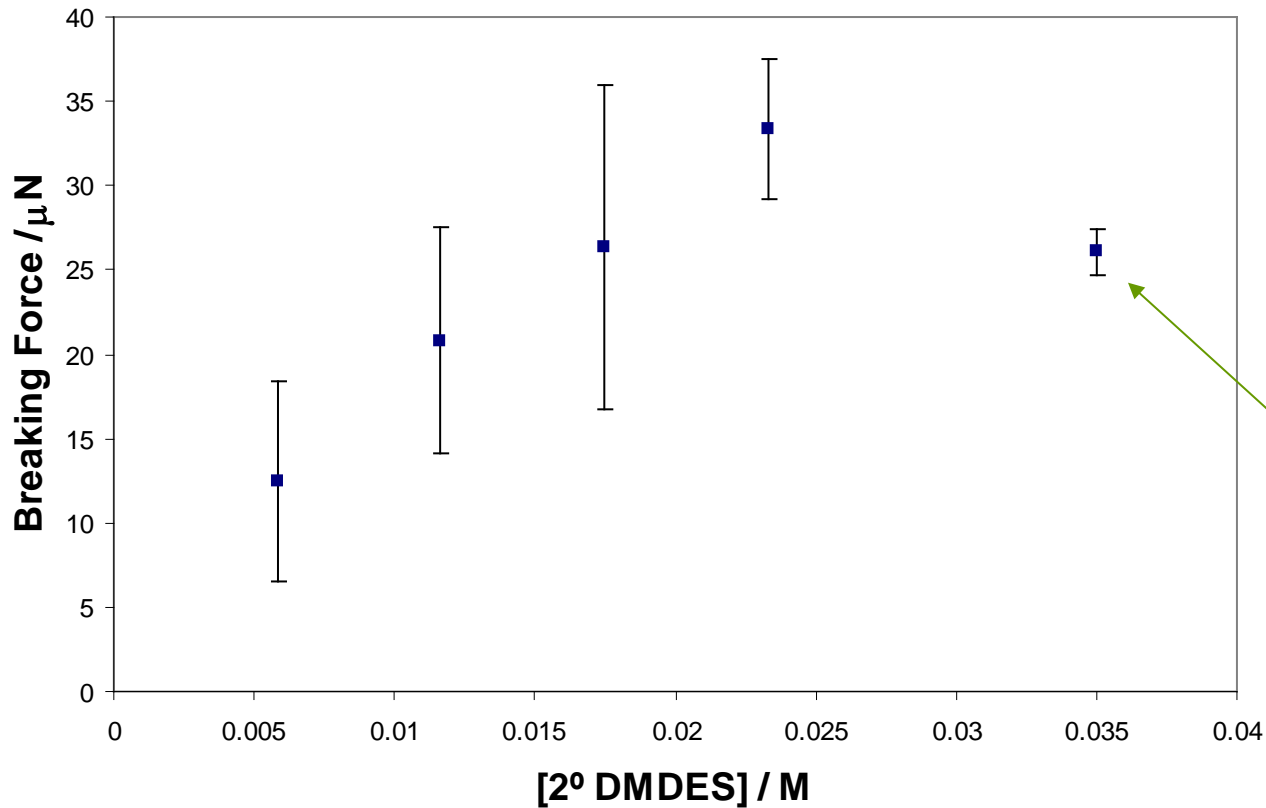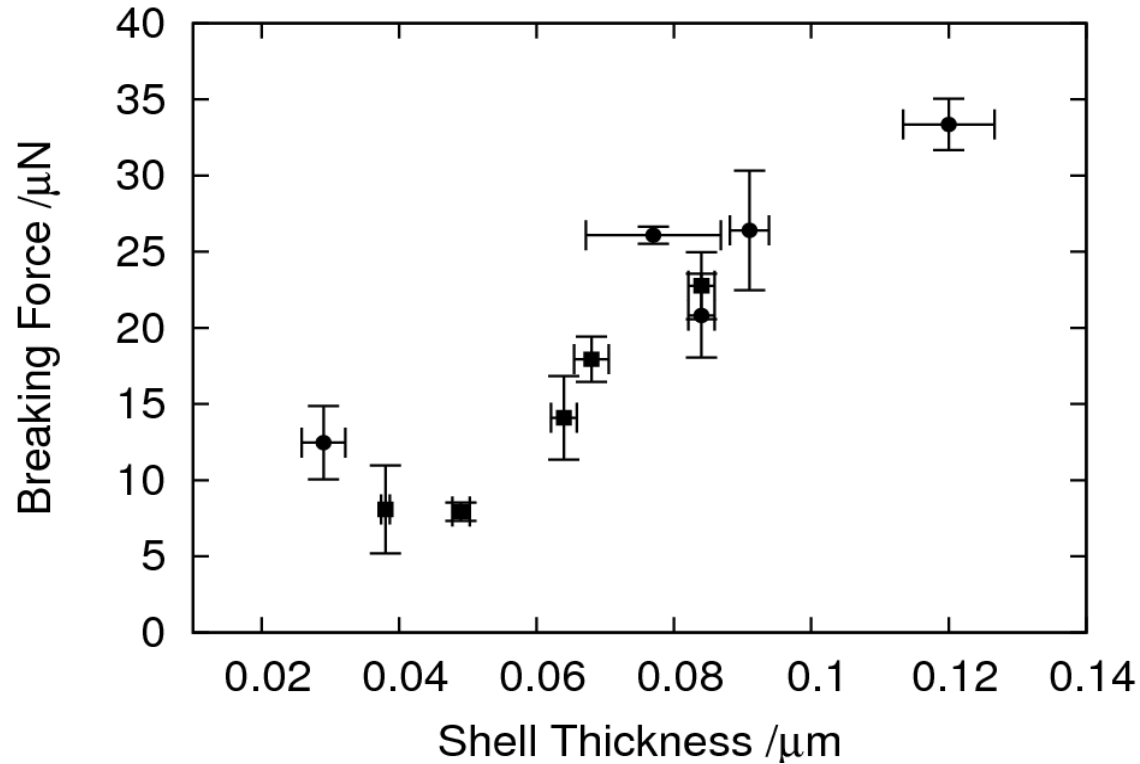
Force transducer
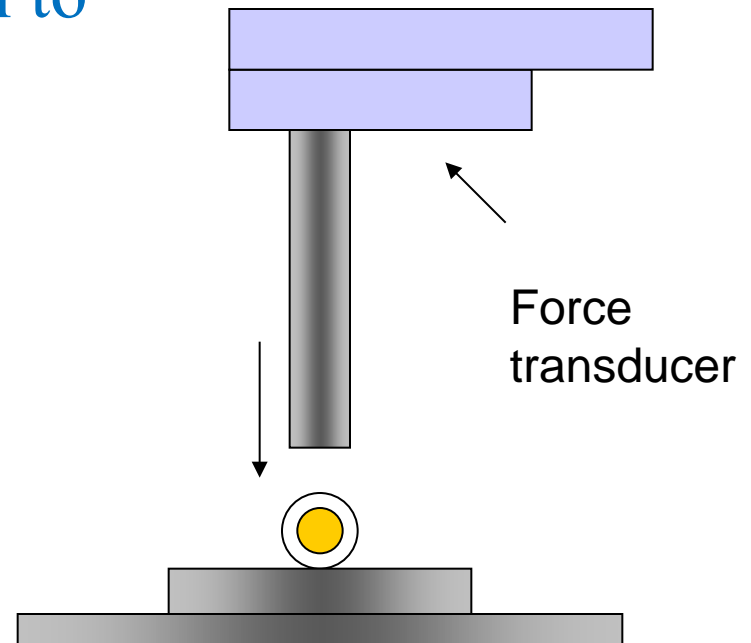
The Equipment

Breaking Force/Displacement

Breaking Force Against Added DEODMS conc.
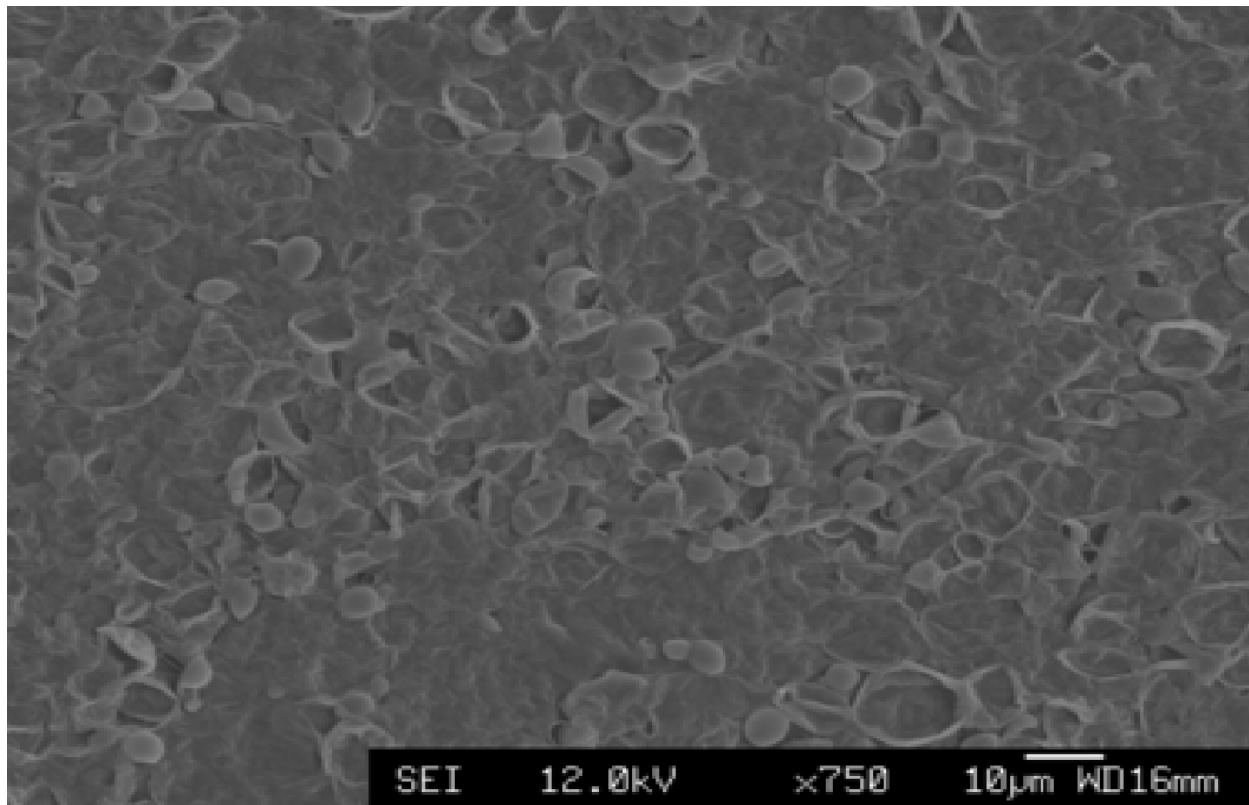
Breaking force as a function of shell thickness

■ *in situ* (Zoldesi) method; ● post-addition method.

WATER-CORE / SILICA SHELL PARTICLES

Shells grown around water droplets in hexadecane, stabilised with "*Tegopren 8700*", by adding DEODMS + TEOS mixtures.

NB the particles may be transferred into water by centrifugation.

O'Sullivan, Vincent   J. Colloid Interface Sci., 2010 **343** 31

CONCLUSIONS

- liquid core/ "silica" shell particles for the protection and / or controlled release of active materials have been prepared by an interfacial polymerisation route.

- the cores may be oil or water

- oils other than silicone oil have been successfully used also (e.g. vegetable oils).