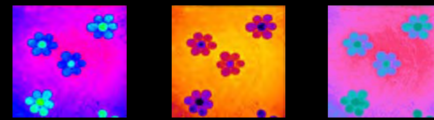


From shape-controlled nanoparticles to "colloidal molecules"

Prof Etienne DUGUET

Institut de Chimie de la Matière Condensée de Bordeaux

Colloids: Towards higher complexity and functionality

Colloidal stability

Size

Size-polydispersity

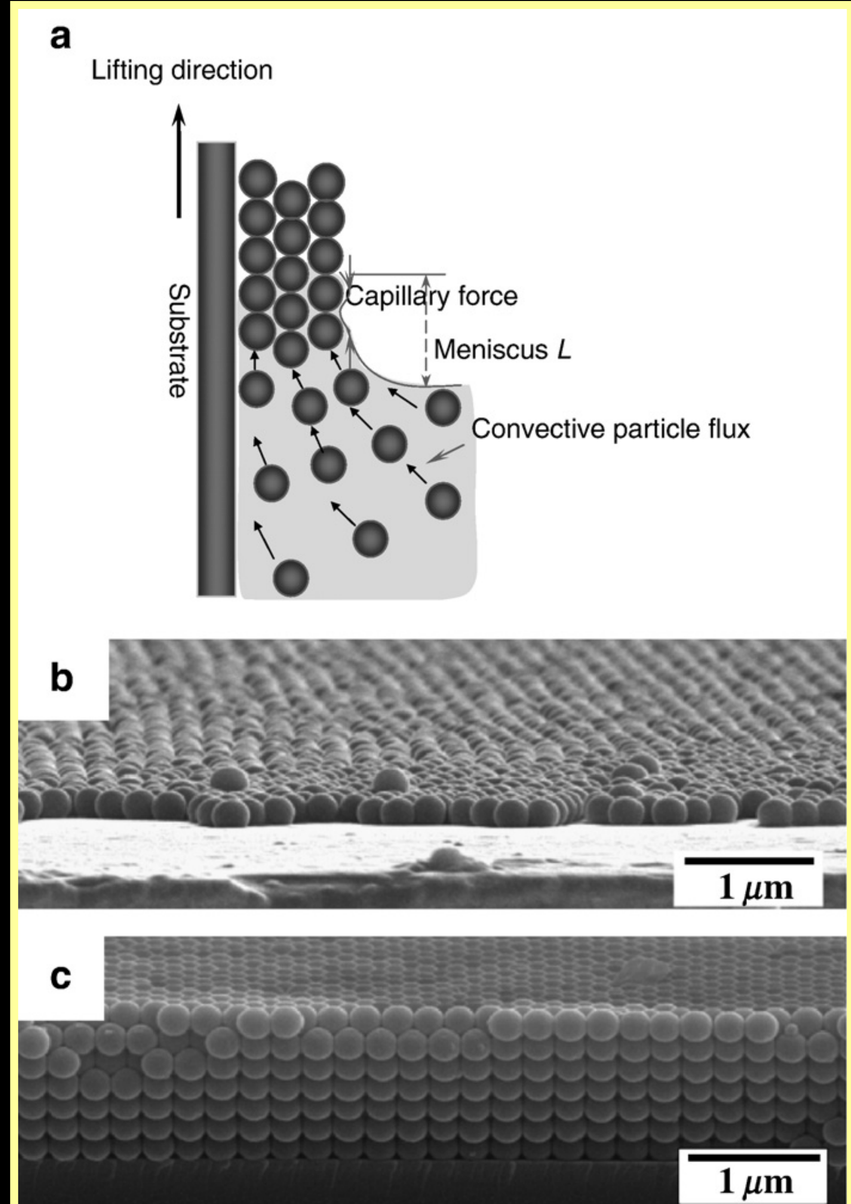
Chemical composition

Surface groups

Shape

Self-assembling ability

"spherical colloids can be treated as if they were atoms"



Wang and Keddy, *Adv. Colloid Interf. Sci.* **2009** 147–148 ,319

Colloids: Towards higher complexity and functionality

Colloidal stability

Size

Size-polydispersity

Chemical composition

Surface groups

Shape

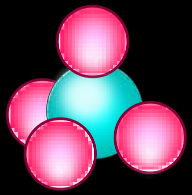
Self-assembling ability

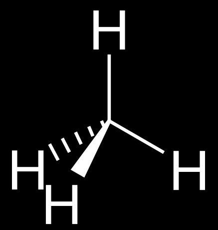
"spherical colloids can be treated as if they were atoms"

and

"molecules form more complex materials than do atoms"

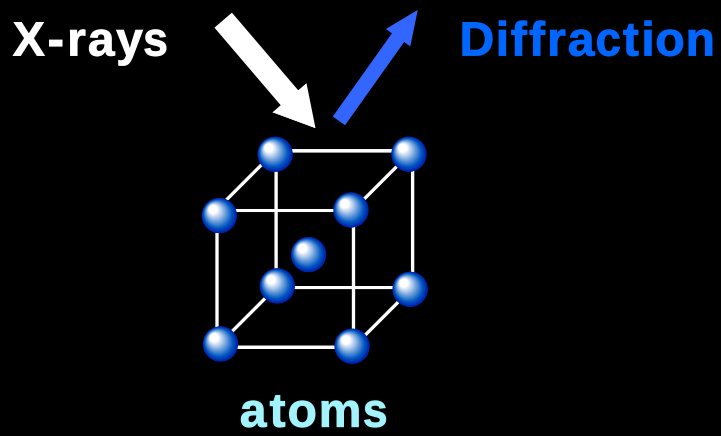
Colloidal Molecules

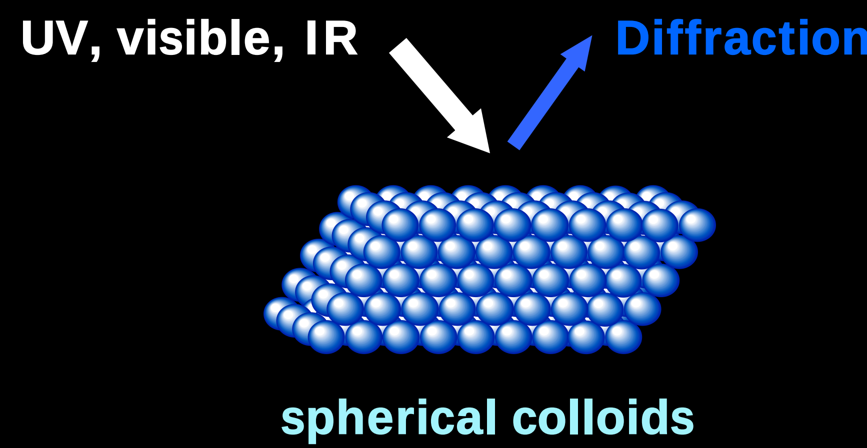




Van Blaaderen, *Science* **2003** 301, 470

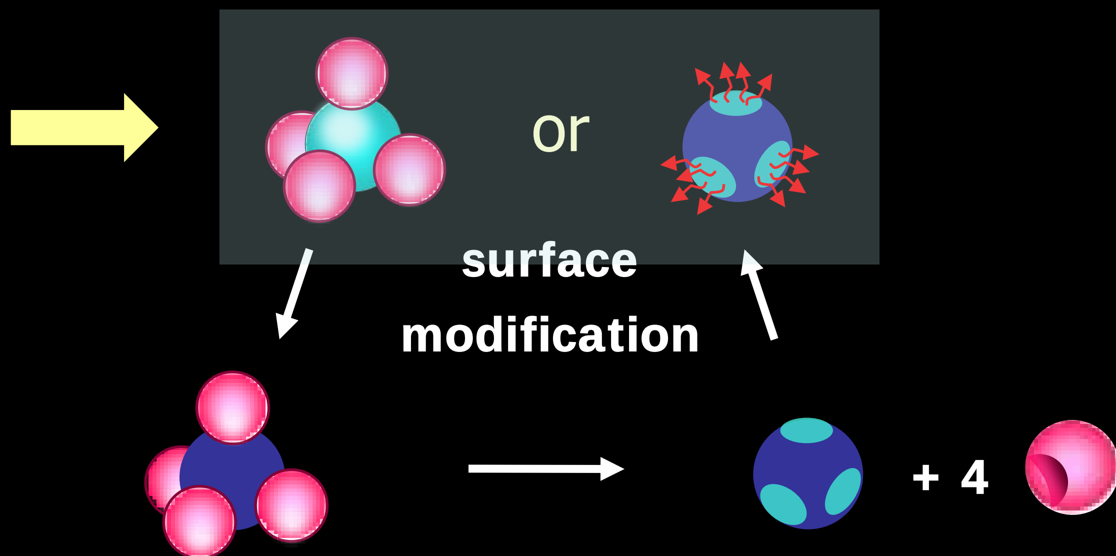
Photonic crystals with full bandgap



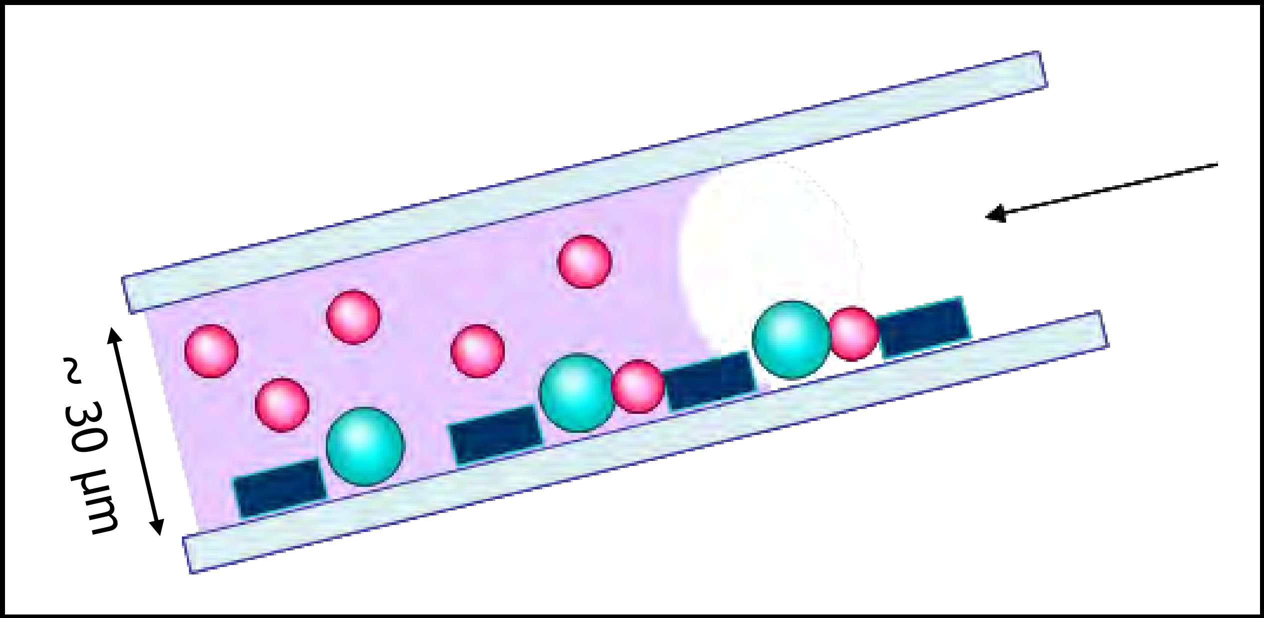


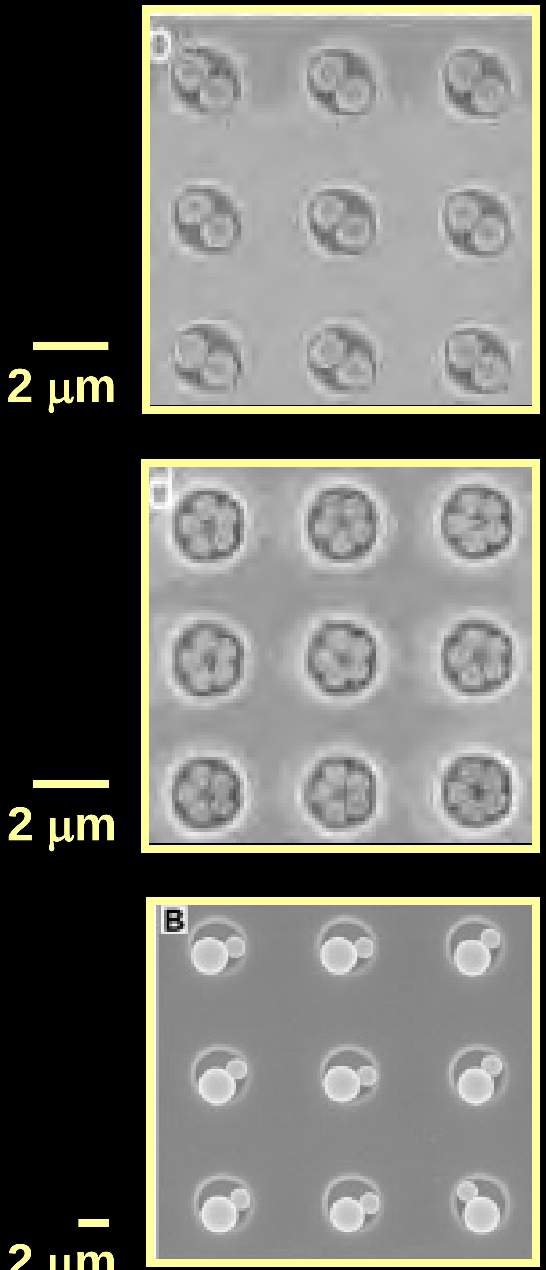
fcc or hcp structure ➔ no full photonic bandgap

full photonic bandgap
➔ diamond-like structure



Template-directed self-assembly route

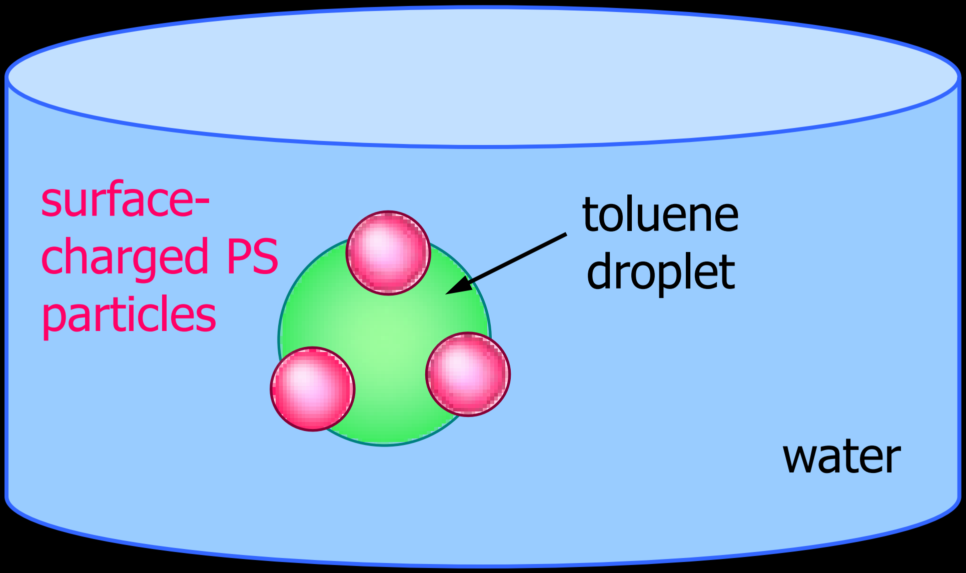


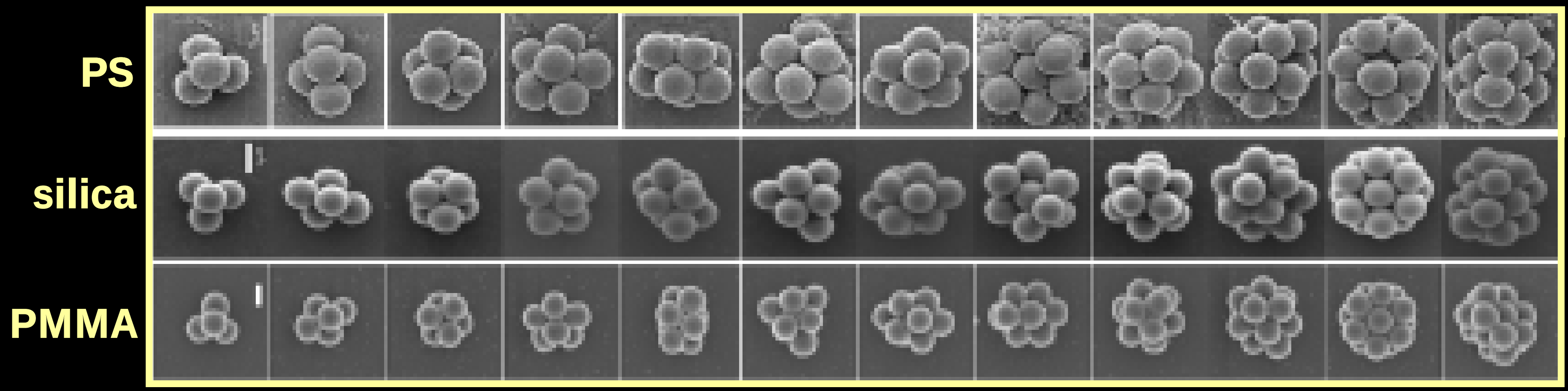


Combined effect of geometrical confinement and attractive capillary forces

Yin and Xia, *Adv. Mater.* **2001** 13, 267
Yin, Lu and Xia, *J. Am. Chem. Soc.* **2001** 123, 771

Emulsion-confined self-assembly route





scale bar : 1 µm

Manoharan, Elsesser and Pine, *Science* **2003** 301, 483
Pine and coll., *Adv. Mater*. **2004** 16, 1204

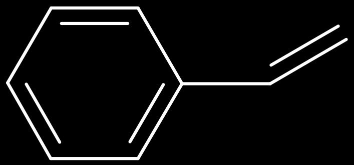
Our route based on
the controlled surface nucleation/growth
of PS latex particles onto silica seeds

Emulsion polymerization background

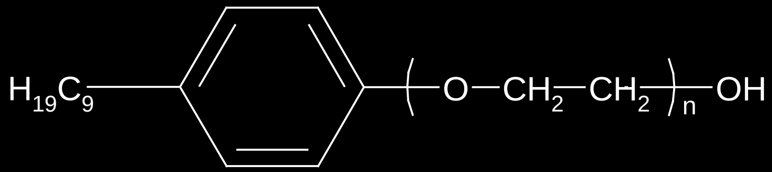
Styrene emulsion polymerization

Our polymerization system

Monomer : **styrene**



Surfactant : **NP30**



n ~ 30

CMC = 0.15 g.L^{-1}

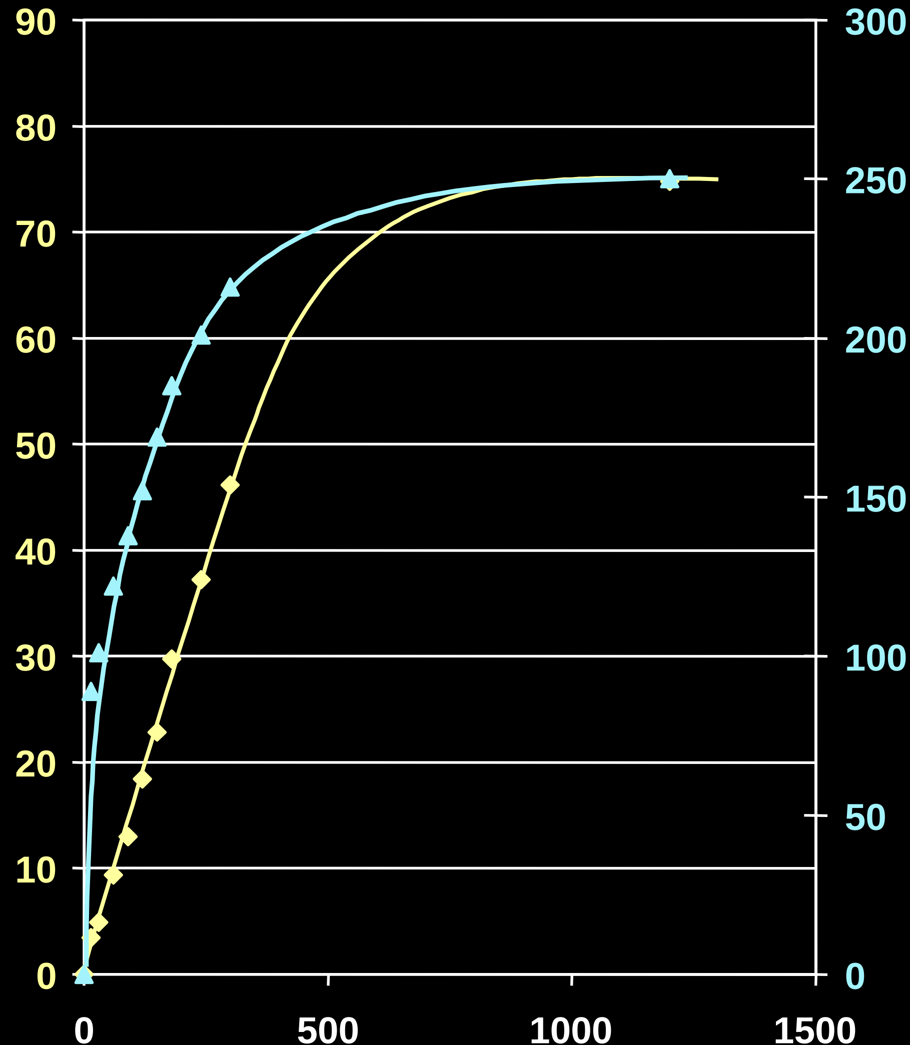
Initiator : **$Na_2S_2O_8$**

$$S_2O_8^{2-} \xrightarrow{\Delta} 2\ SO_4^{-\circ}$$

Styrene emulsion polymerization

experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C

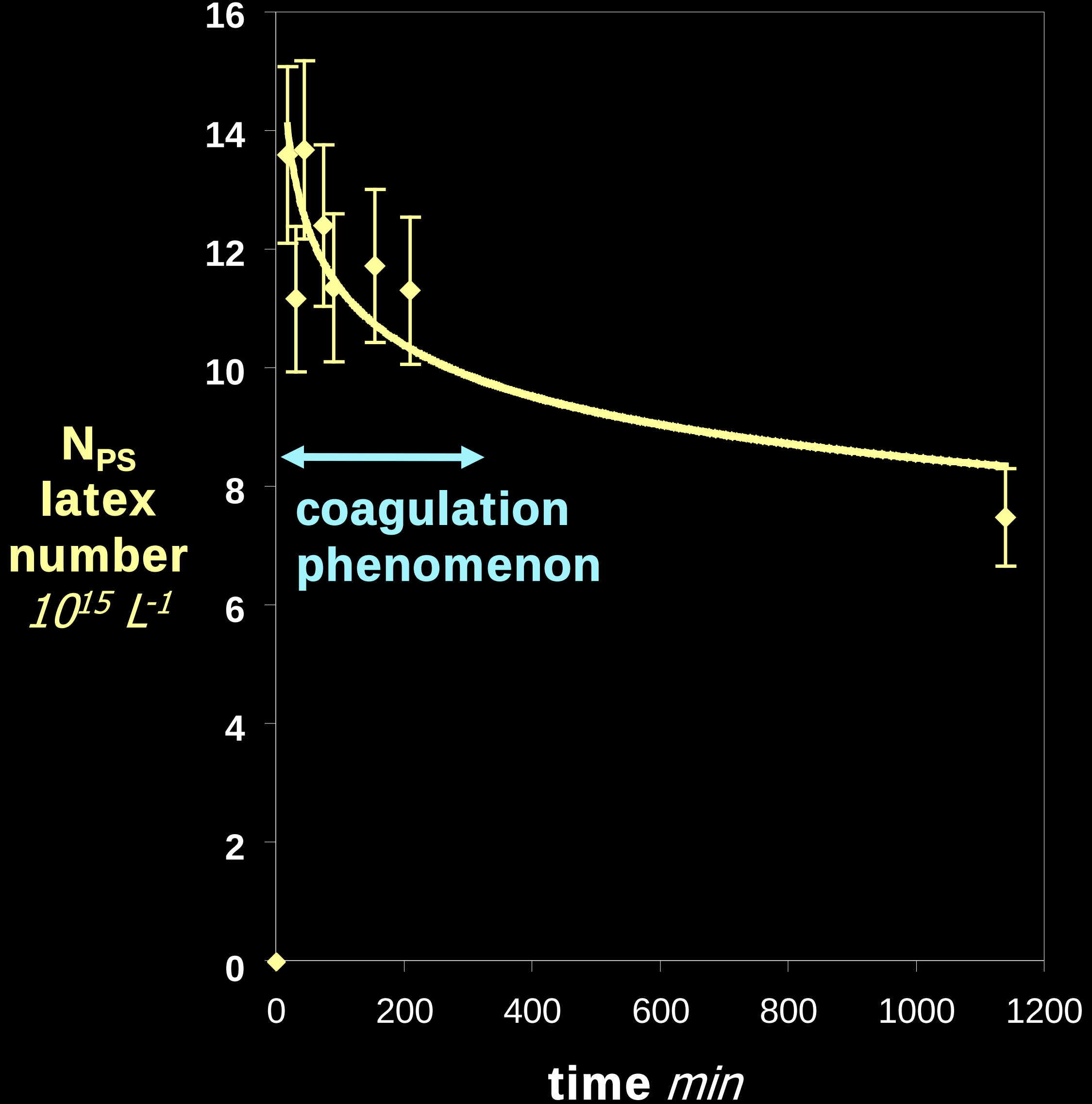


$$\%_{conv} = \frac{[m - m_{Si}] * 100}{m_{monomer}}$$

Styrene emulsion polymerization

experimental

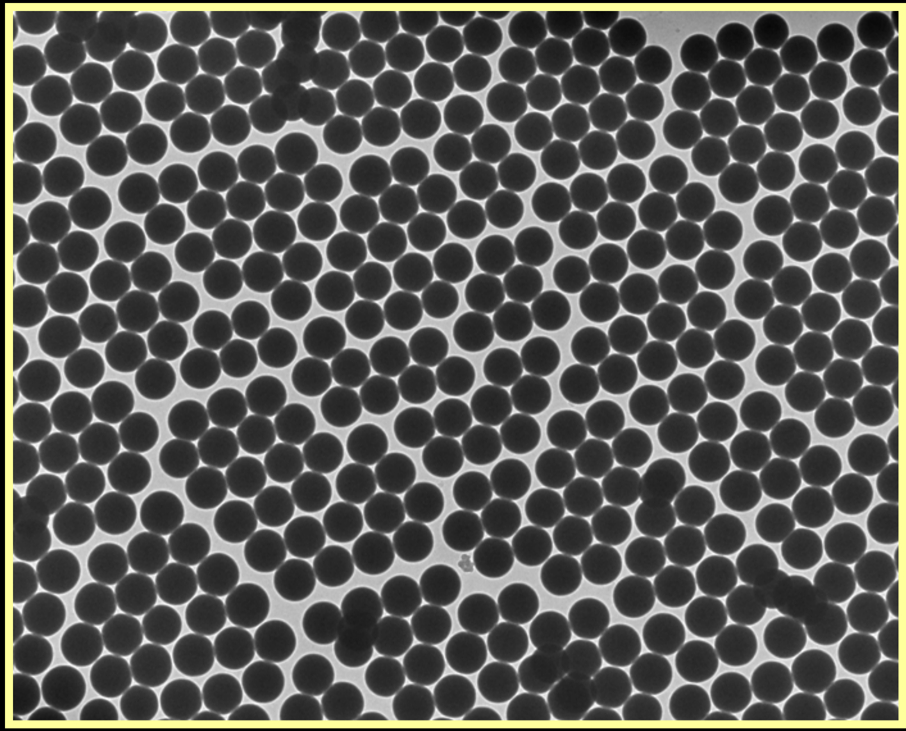
[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C



$$N_{PS} = \frac{[m - m_{Si}] * 10^{21}}{(\pi/6)(D_n)_{TEM}^3 \rho}$$

Styrene emulsion polymerization

What happens in the presence of Stöber silica



Stöber and coll., *Colloid Interface Sci*. **1968**, 26, 62
Kang and coll., *Polymer* **2001** 42, 879

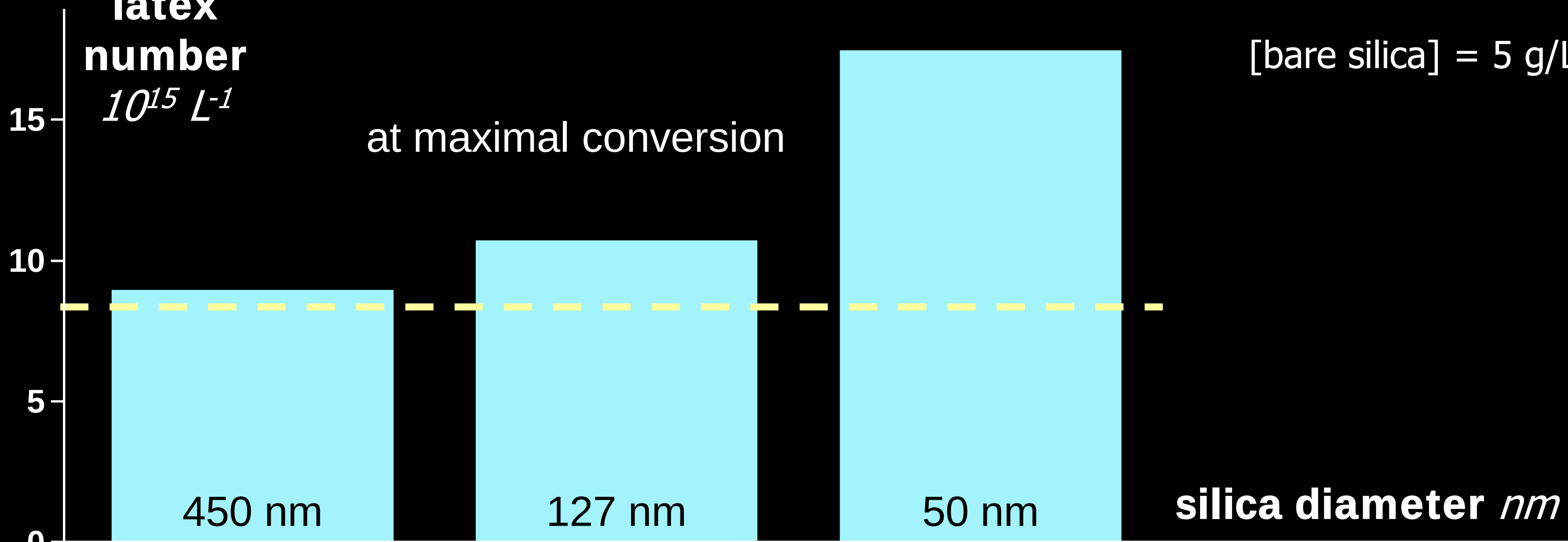
Styrene emulsion polymerization

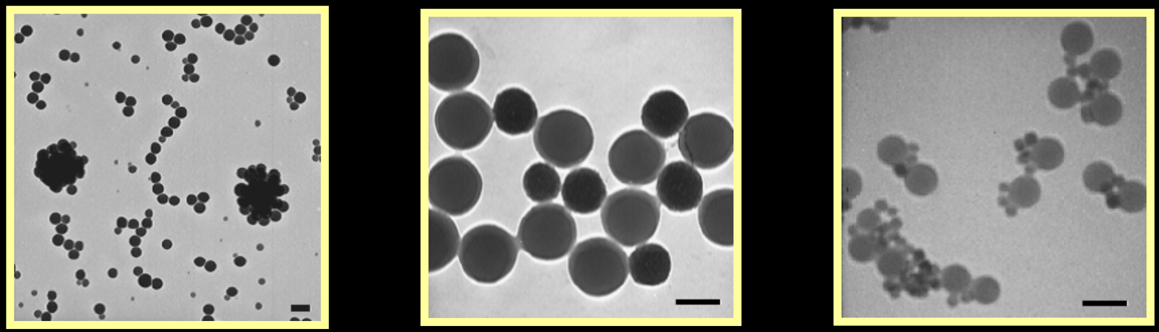
experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
[$Na_2S_2O_8$] = 0.5 g/L
T = 70°C

[bare silica] = 5 g/L

What happens in the presence of Stöber silica

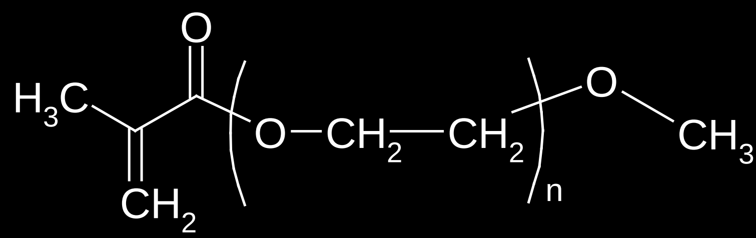




time : 120 min
conversion ~20 %
scale bar : 200 nm

Styrene seeded-emulsion polymerization

Macromonomer pre-adsorption onto Stöber silica

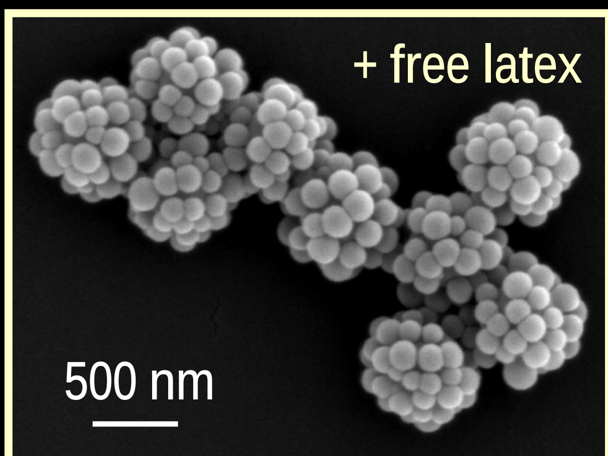


n ~ 23

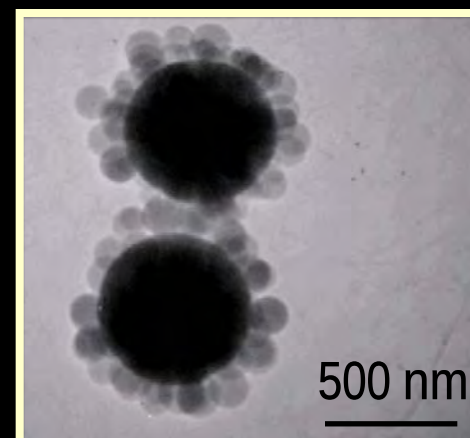
experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C

500-nm silica
[silica] = 10 g/L
[macrom.] = 0.1 g/L
conversion ~30 %



SEM



TEM

raspberry-like silica / PS particles

Duguet and coll, *Chem. Mater.* **2002** 14, 2354

Styrene seeded-emulsion polymerization

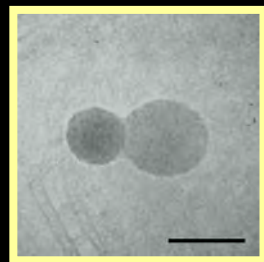
experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C

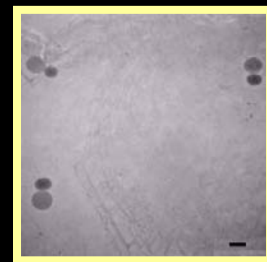
[macrom.] = 0.1 g/L

Influence of silica concentration: $N_{PS/Si} = N_{PS} / N_{Si}$?

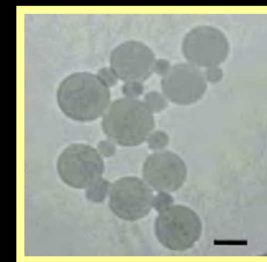
N_{Si}/N_{PS} = 1
silica 64 nm
[silica] = 4.6 g/L



30 min



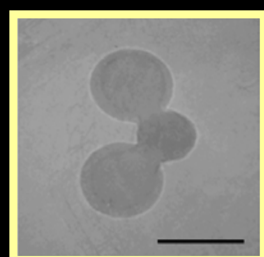
60 min



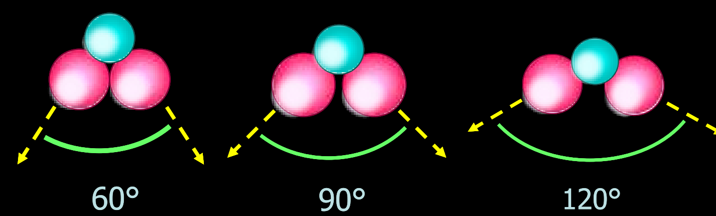
120 min

scale bar : 100 nm

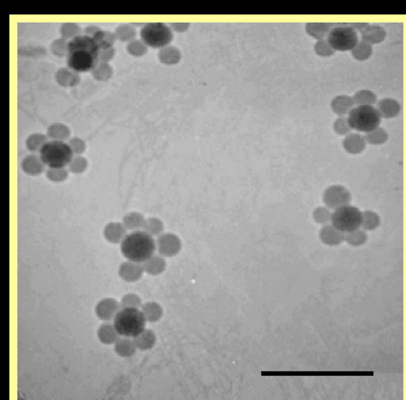
N_{Si}/N_{PS} = 1/2
silica 93 nm
[silica] = 7.5 g/L



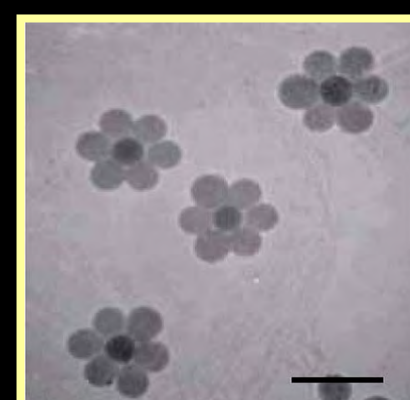
120 min
scale bar : 200 nm



N_{Si}/N_{PS} = 1/6
silica 127 nm
[silica] = 4.8 g/L



30 min



60 min

scale bar : 500 nm

Styrene seeded-emulsion polymerization

experimental
idem

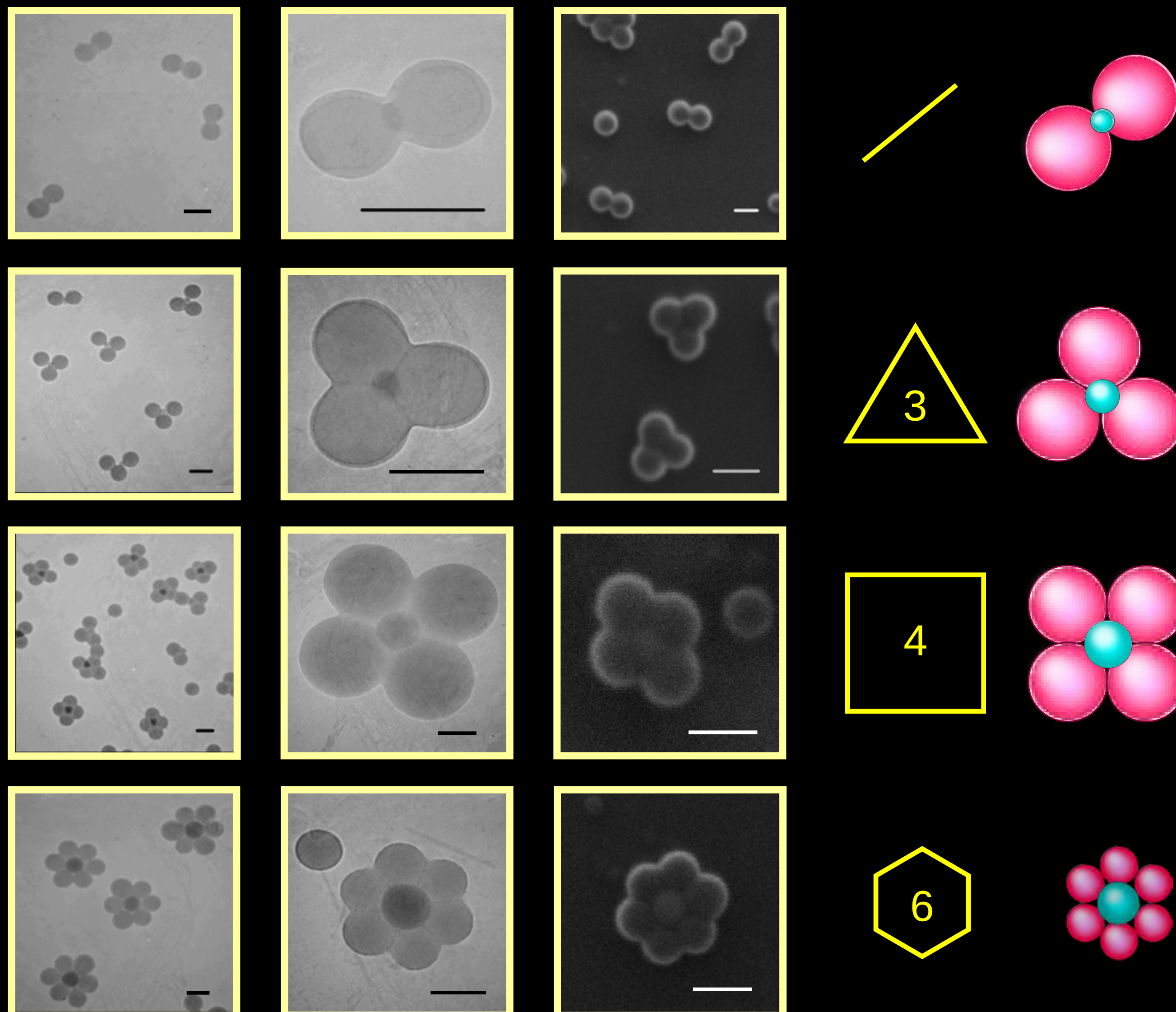
Influence of silica size ($N_{Si} << N_{PS}$)

silica 42 nm
[silica] = 0.2 g/L
120 min

silica 64 nm
[silica] = 0.5 g/L
120 min

silica 85 nm
[silica] = 1.2 g/L
90 min

silica 127 nm
[silica] = 3.2 g/L
60 min



Styrene seeded-emulsion polymerization

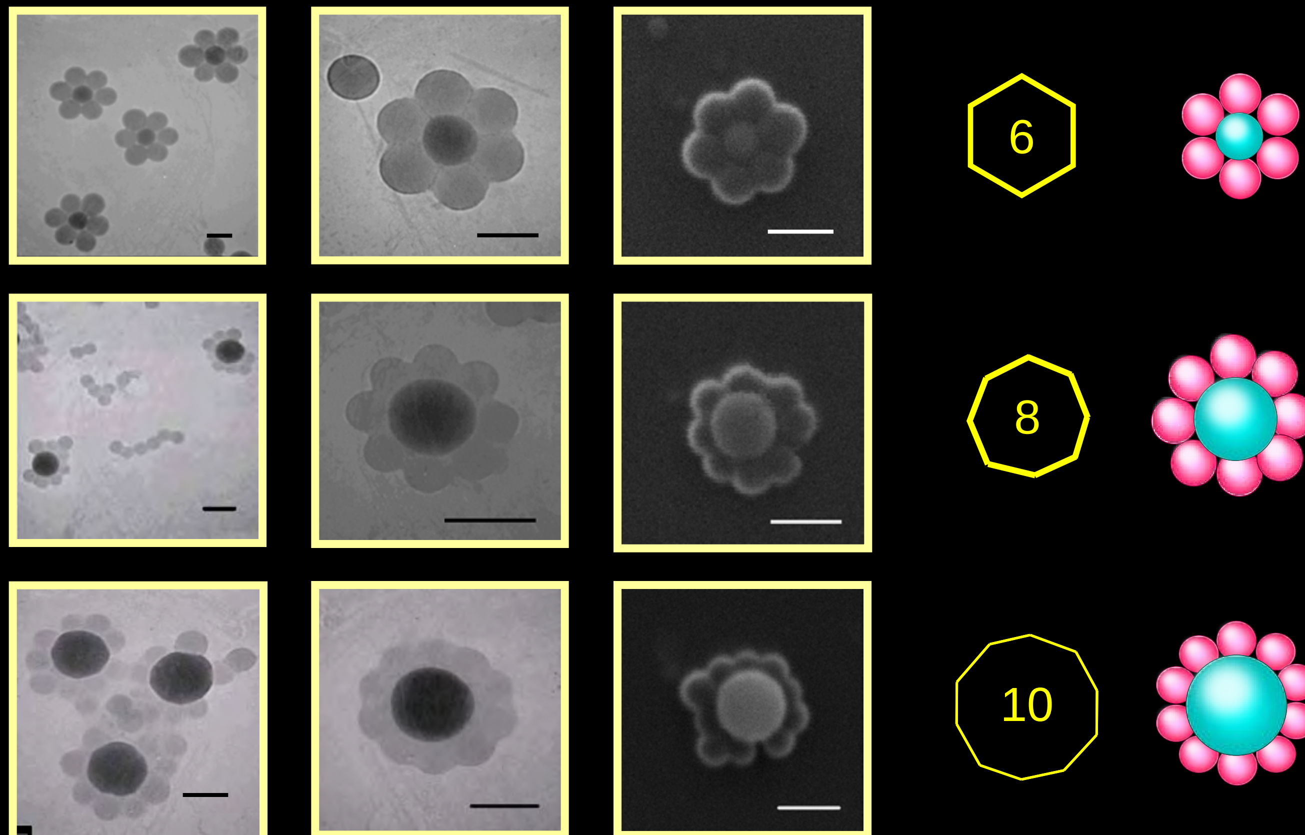
experimental
idem

Influence of silica size ($N_{Si} < N_{PS}$)

silica 127 nm
[silica] = 3.2 g/L
60 min

silica 170 nm
[silica] = 4.7 g/L
25 min

silica 212 nm
[silica] = 4.7 g/L
20 min



Duguet *and coll., J. Mater. Chem.* **2009** in press

Styrene seeded-emulsion polymerization

experimental
idem

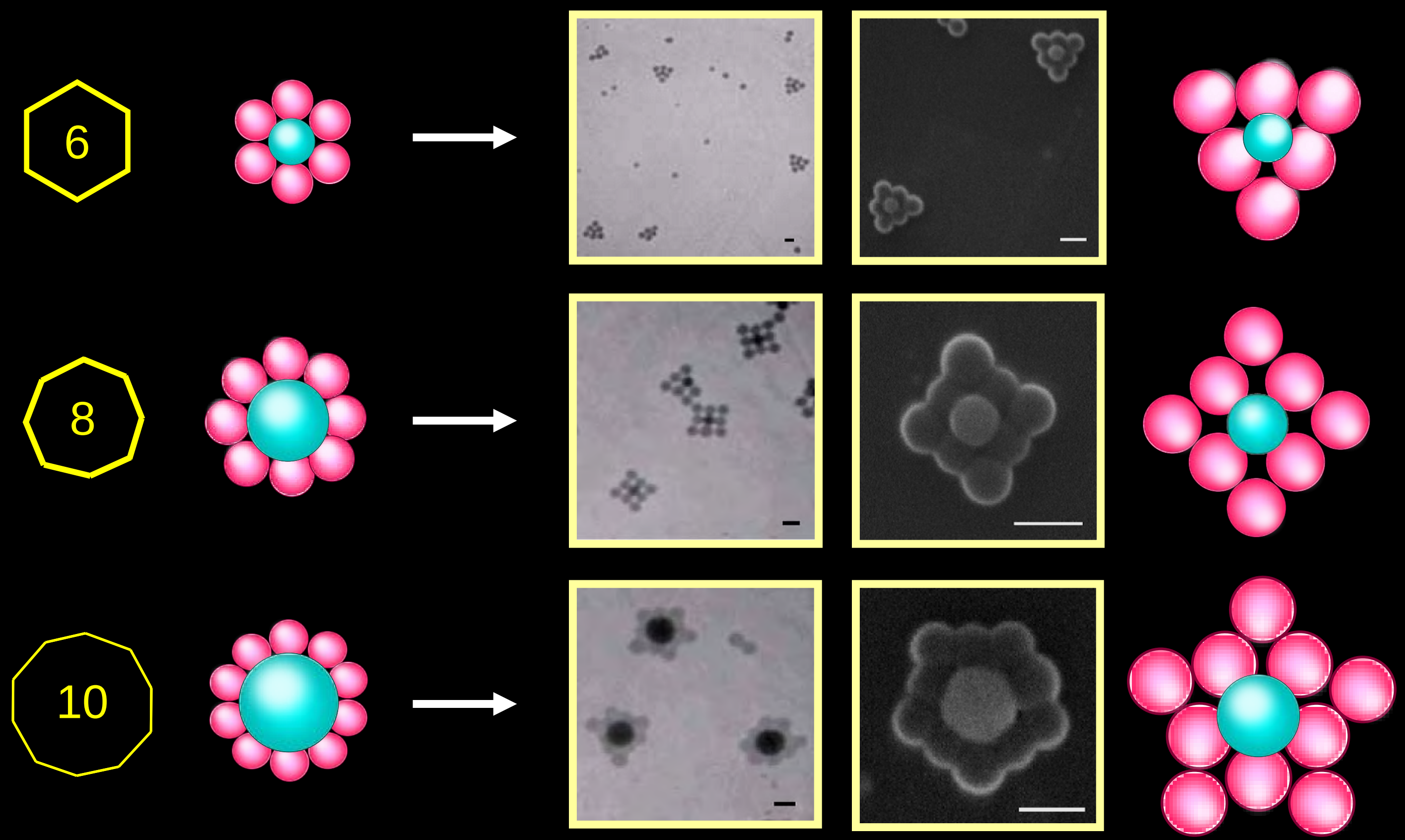
Influence of conversion ($N_{Si} < N_{PS}$)

120 min

silica 127 nm
[silica] = 3.2 g/L
60 min

silica 170 nm
[silica] = 4.7 g/L
25 min

silica 212 nm
[silica] = 4.7 g/L
20 min

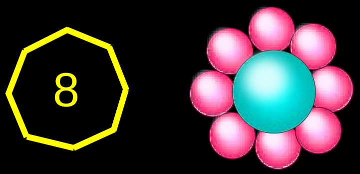


Are our colloids really planar ?

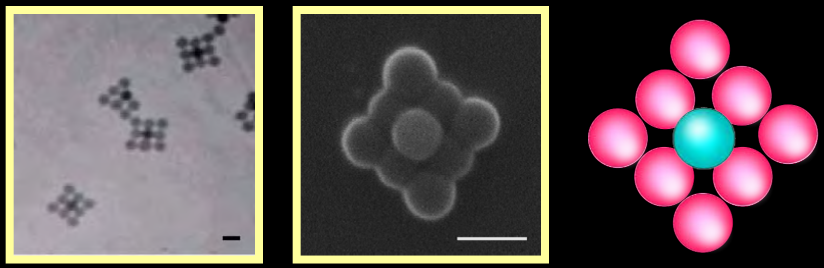
Duguet *and coll.*, *J. Mater. Chem.* **2009** in press

Styrene seeded-emulsion polymerization

silica 170 nm
[silica] = 4.7 g/L
25 min

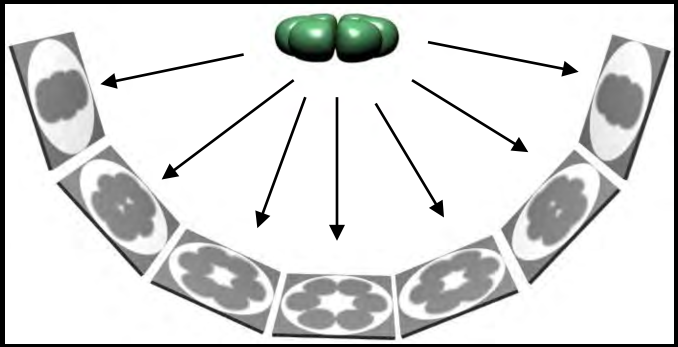


120 min

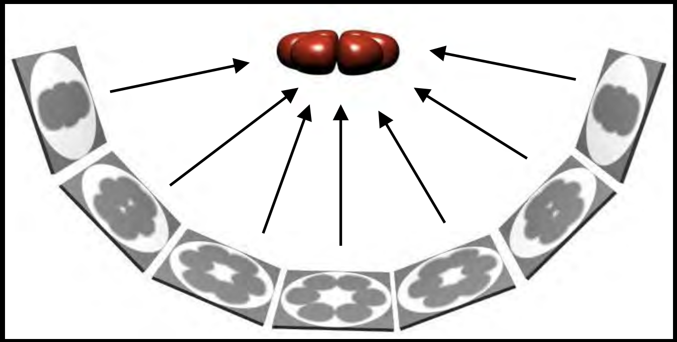


Electronic tomography

acquisition of tilt series
from -60° to +60° every 2°



3D-reconstruction
from these projections

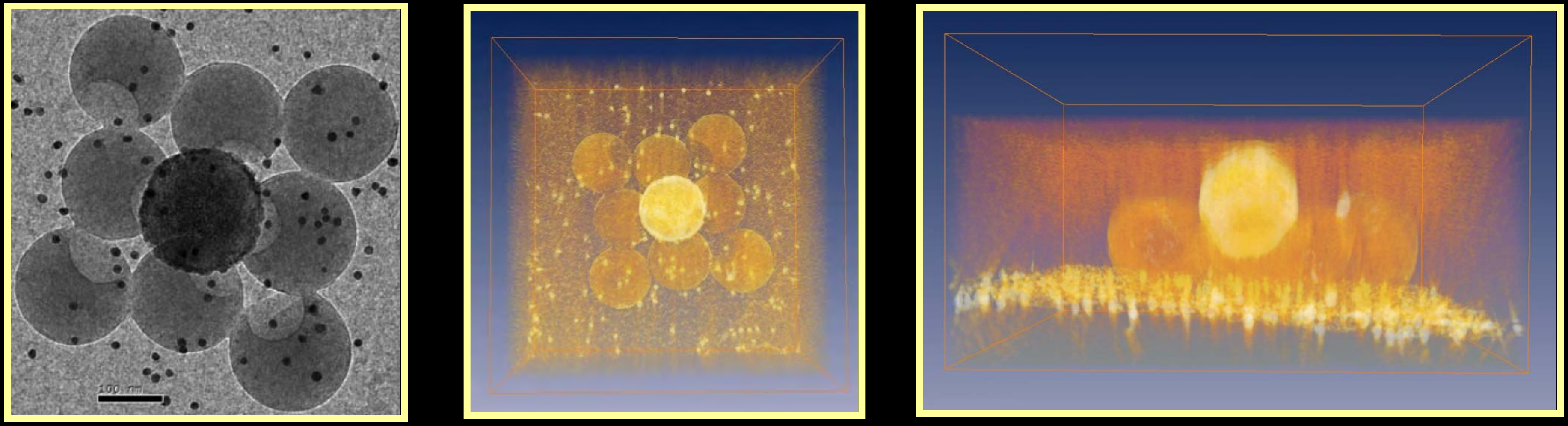


Duguet *and coll., J. Mater. Chem.* **2009** in press

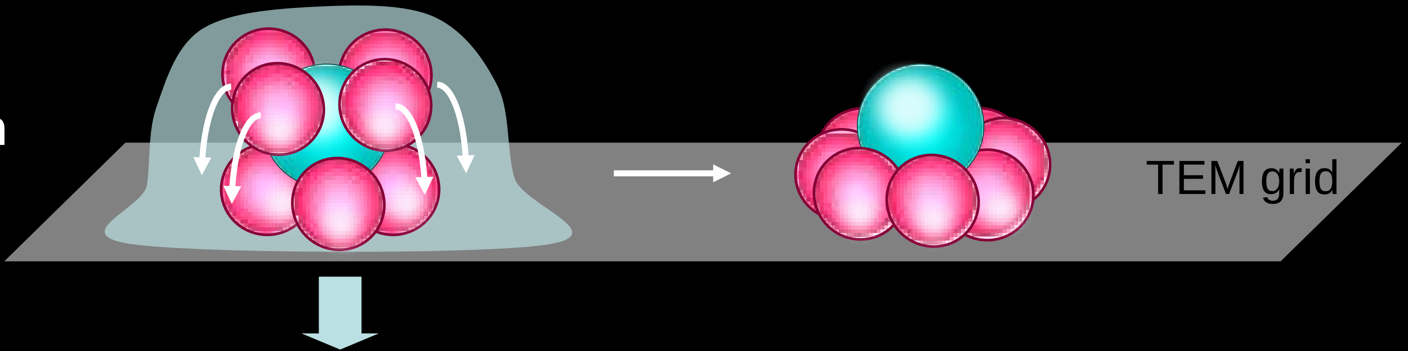
Styrene seeded-emulsion polymerization

silica 170 nm
[silica] = 4.7 g/L
25 min

Electronic tomography

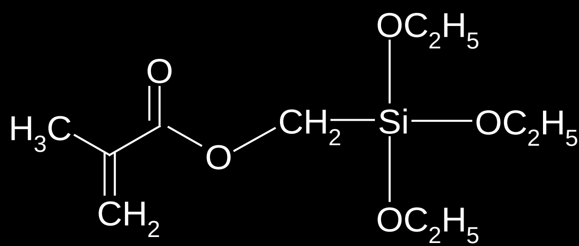


Falling-in mechanism



Styrene seeded-emulsion polymerization

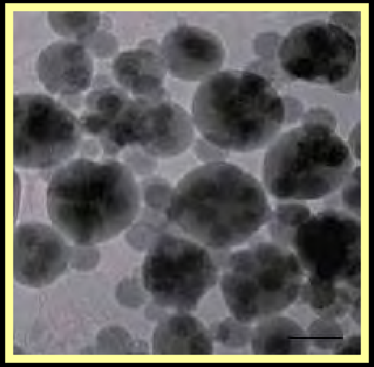
Silane surface treatment of “Stöber” silica



methacryloxymethyltriethoxysilane (MMS)

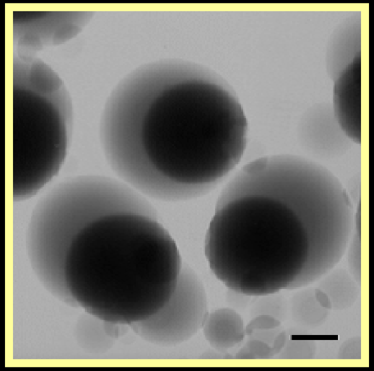
Silane-saturated surface

50 nm



127 nm

450 nm



scale bar : 200 nm

experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C

[silica] = 10 g/L
[silane] = 16.6 μmol/m^2
conversion ~20 %

Styrene seeded-emulsion polymerization

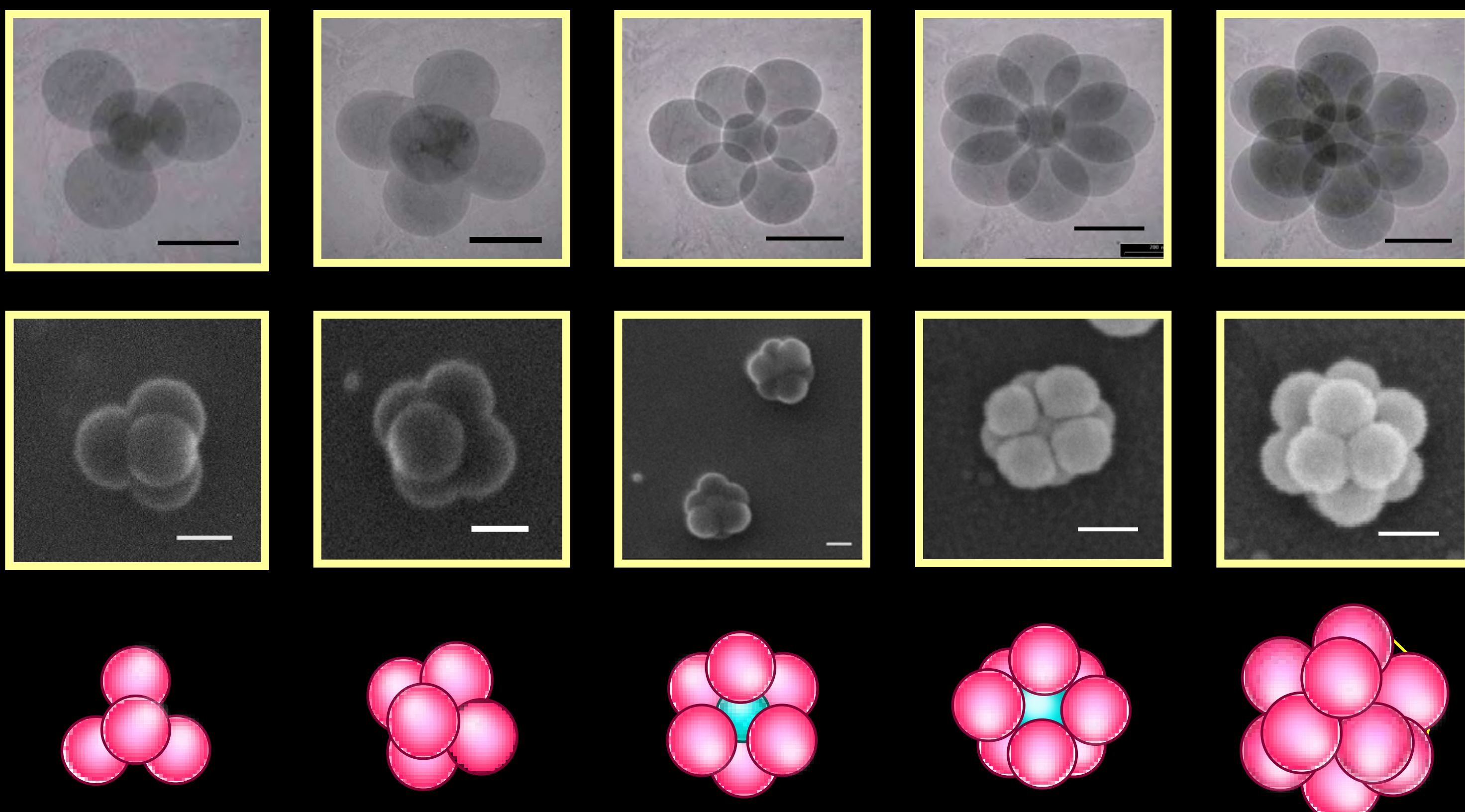
Silane unsaturated surface

experimental

[styrene] = 100 g/L
[NP30] = 20*CMC
$[Na_2S_2O_8]$ = 0.5 g/L
T = 70°C

[silica] = 10 g/L
[silane] = 1.66 µmol/m^2
conversion ~20 %
120 min

85 nm	106 nm	127 nm	170 nm	255 nm
1.2 g/L	2.0 g/L	3.2 g/L	4.7 g/L	4.7 g/L



scale bar : 200 nm

Styrene seeded-emulsion polymerization

About $(D_n)_{Si}$ and $N_{PS/Si}$ correlation

Minimization of the energy of n points whose positions are unconstrained on the surface of a sphere:

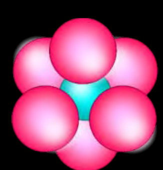
$$E_P = \sum_{i}^{n} \frac{1}{2} |x_i|^2 - \sum_{i}^{n} \sum_{j<i} x_{ij}$$

attraction towards the centre of the sphere

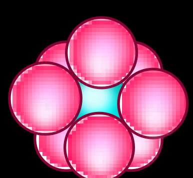
two-body particle repulsions

Battye *et al., J. Math. Phys.* **2003** 44, 3532

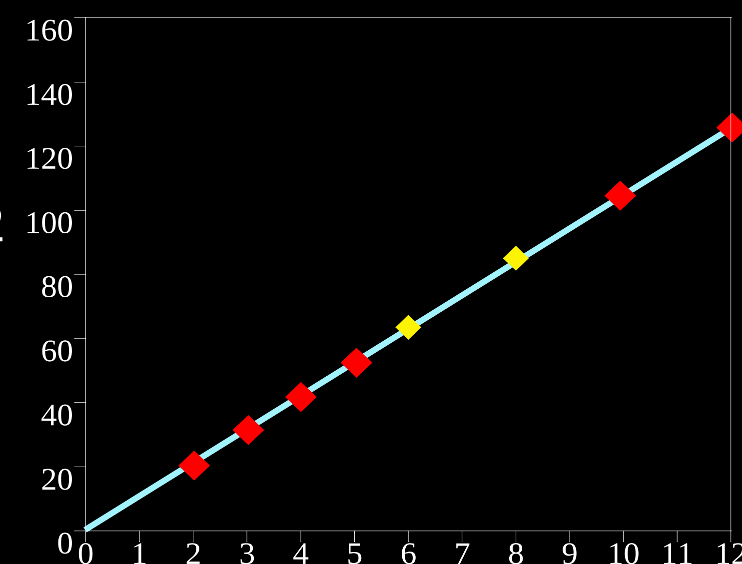
$$\frac{D_{Si}}{2} = K\left(\frac{2N_{PS/Si}}{3} - \frac{1}{2N_{PS/Si}}\right)$$



D_{Si} = 127 nm ; $\mathbf{N_{PS/Si}}$ =6



D_{Si} = 170 nm ; $\mathbf{N_{PS/Si}}$ =8



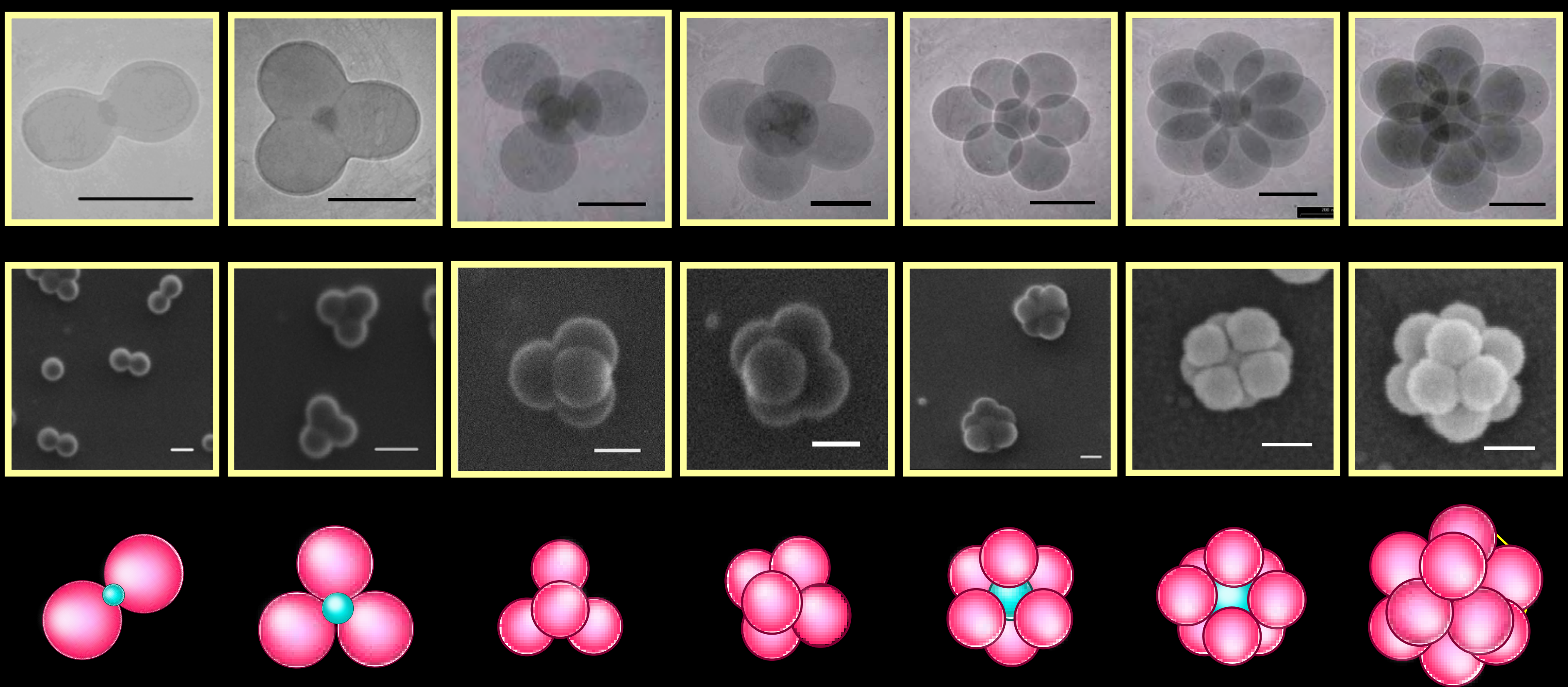
Duguet *and coll., Angew. Chem., Int. Ed.* **2009** 48, 361

Styrene seeded-emulsion polymerization

About $(D_n)_{Si}$ and $N_{PS/Si}$ correlation

scale bar : 200 nm

42 nm	64 nm	85 nm	106 nm	127 nm	170 nm	255 nm
0.2 g/L	0.5 g/L	1.2 g/L	2.0 g/L	3.2 g/L	4.7 g/L	4.7 g/L



Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation / growth study

0 min

5 min

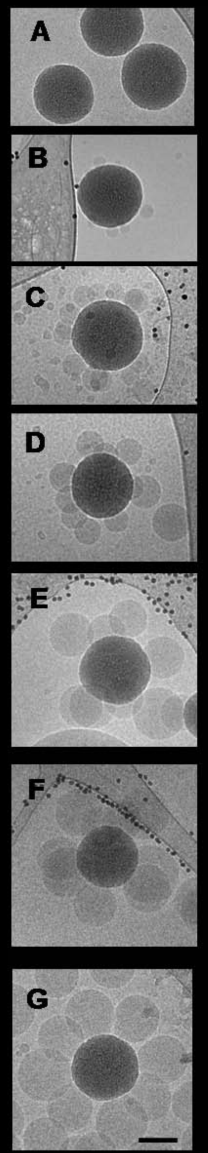
10 min

20 min

30 min

40 min

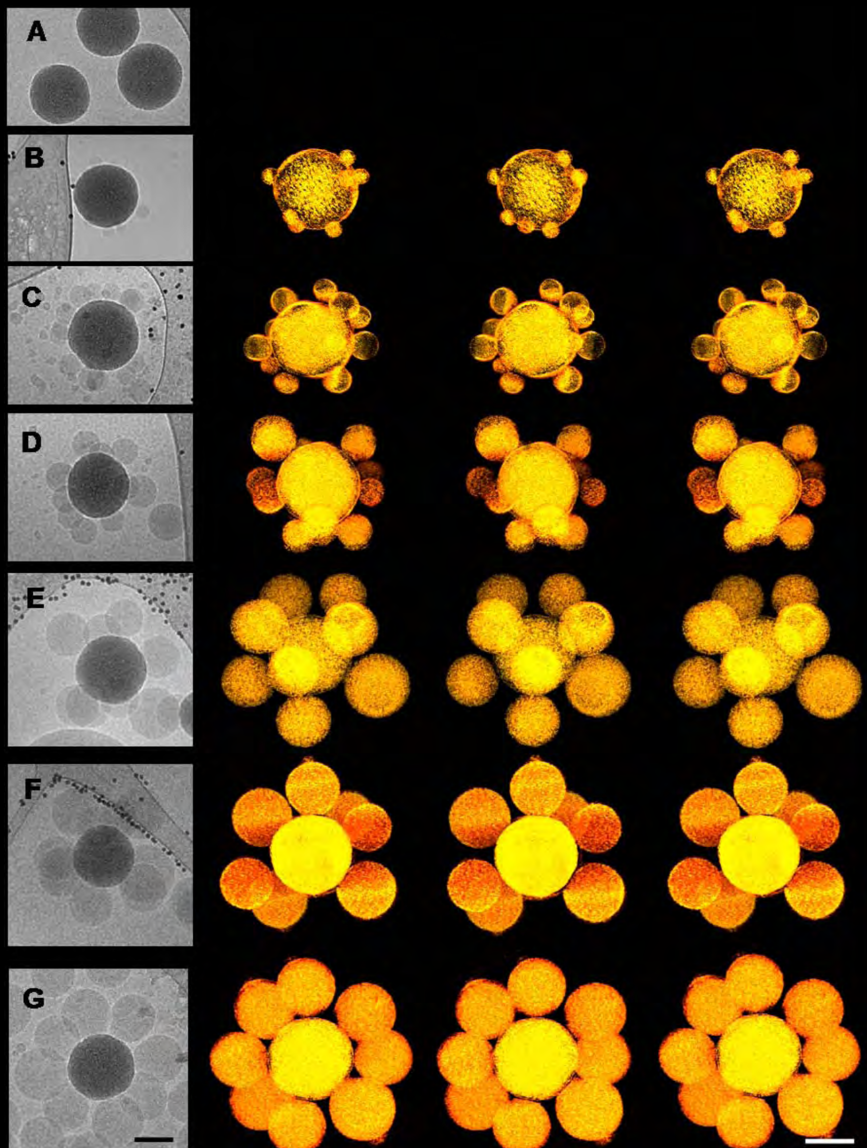
50 min



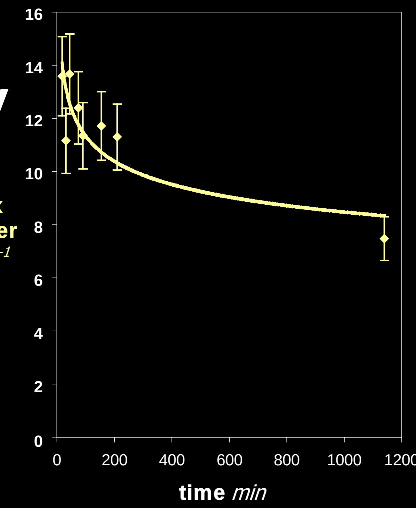
scale bar : 100 nm

Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation / growth study



0 min	0
5 min	10-15
10 min	10-15
20 min	8-10
30 min	≤ 8
40 min	≤ 8
50 min	≤ 8

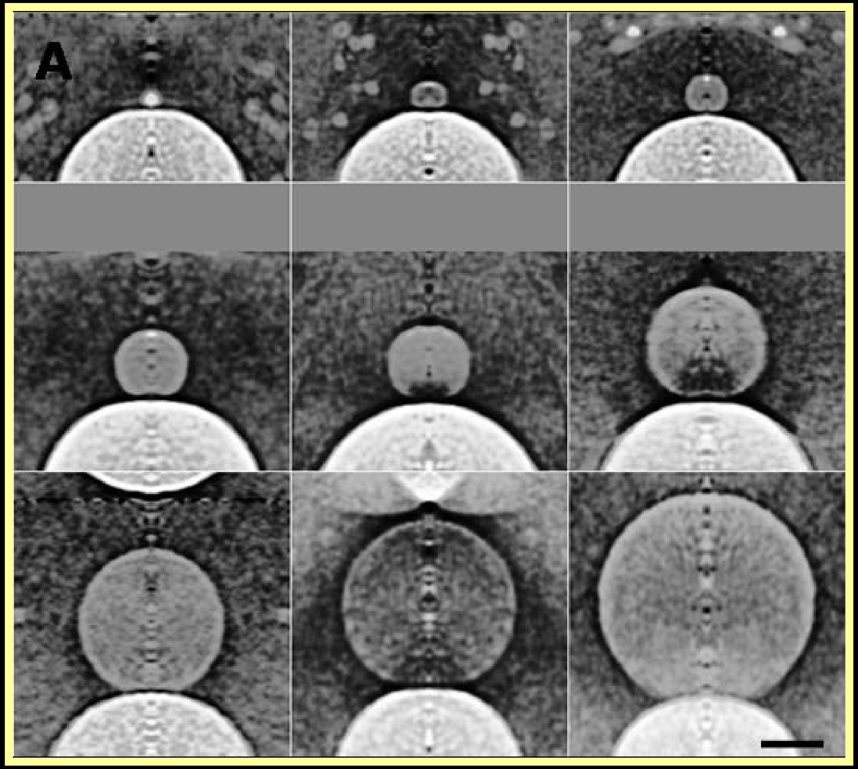


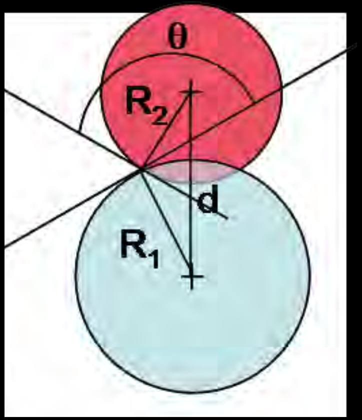
➔ coagulation phenomenon occurs also on the surface

scale bar : 100 nm

Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation / growth study

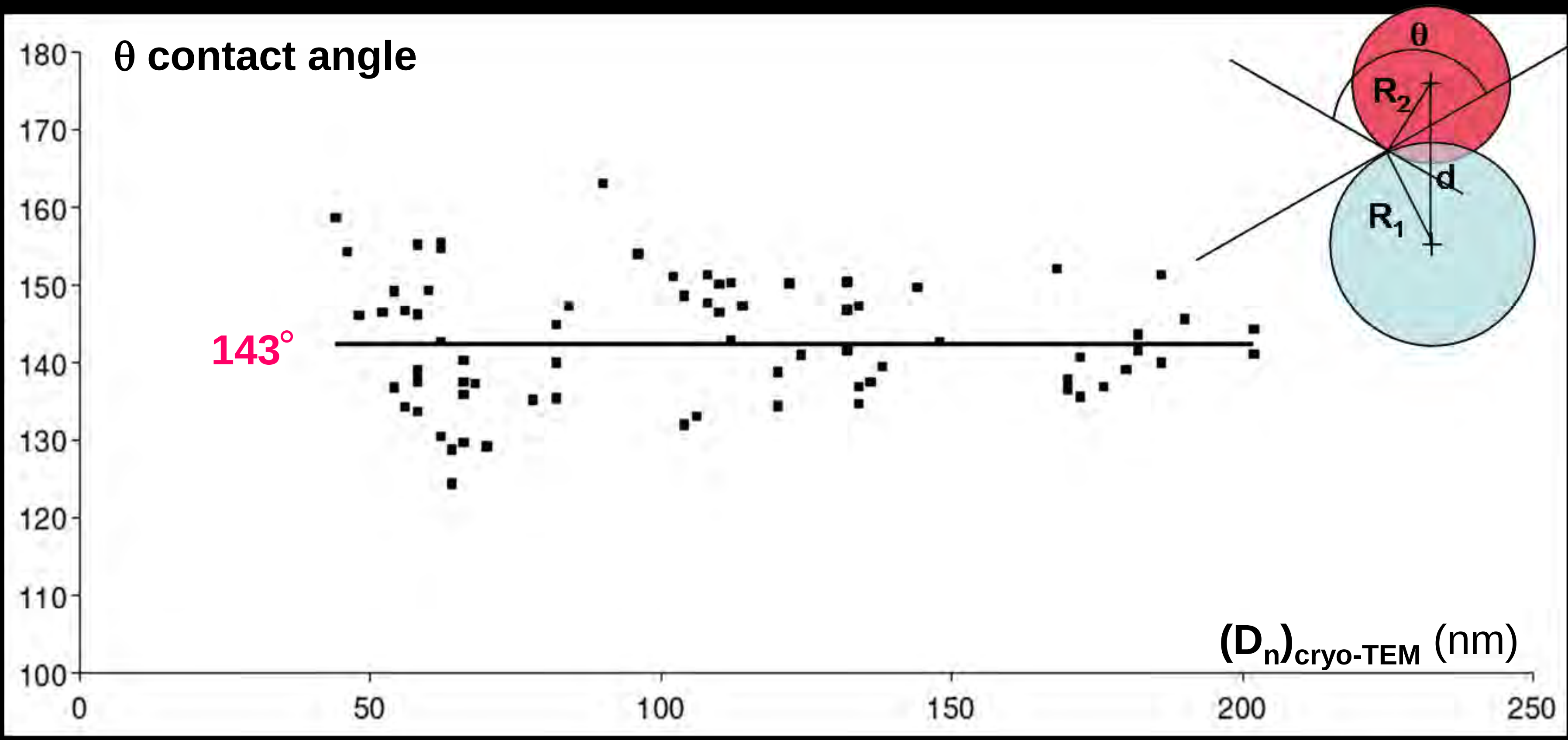




Duguet and coll, *Soft Mater.* **2008** 4, 311

Styrene seeded-emulsion polymerization

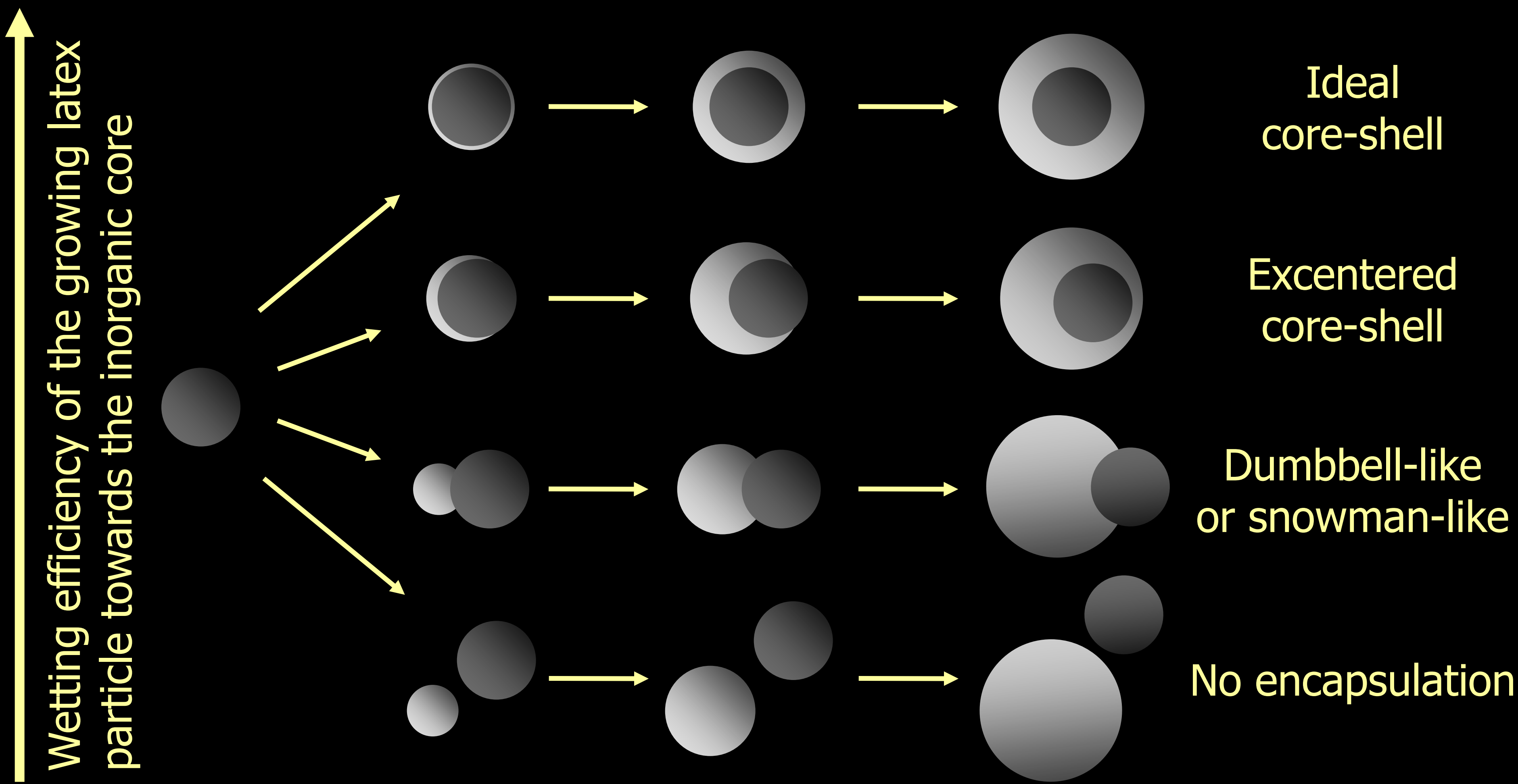
Cryo-TEM / tomography for nucleation / growth study



Duguet and coll, *Soft Mater.* **2008** 4, 311

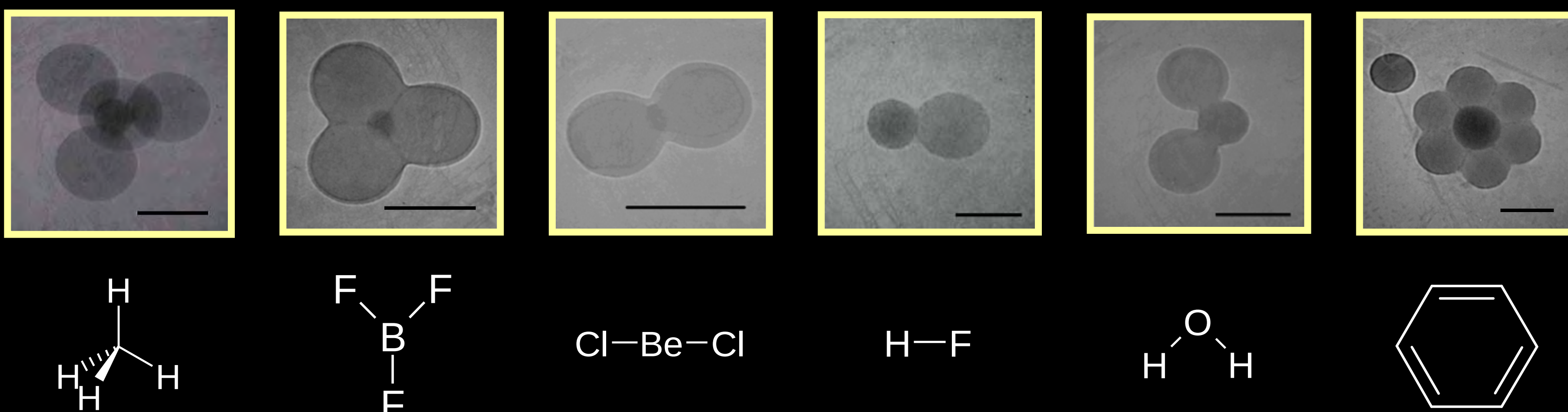
Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation / growth study



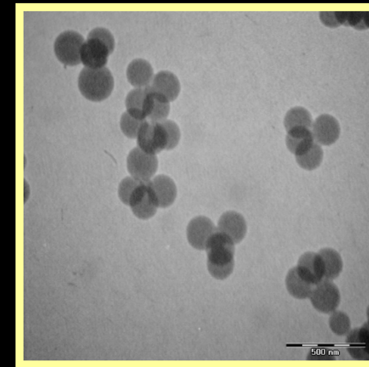
Summary

- **Hybrid structured nanoparticles with original 3-D morphologies**
- **Planar morphologies may result from 3-D particles instability**
- **Cryo-TEM / tomography is a powerful characterization tool**



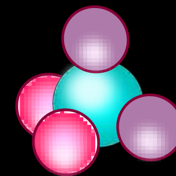
Efforts in progress

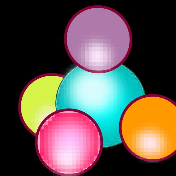
- **High yields of regular morphologies**



> 90 %

- **Complete bestiary of colloidal molecules made of a single central atom**

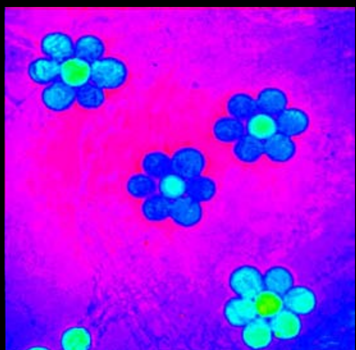


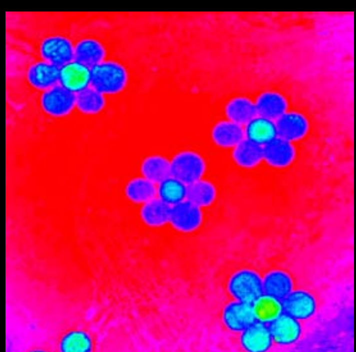


- **Study of colloid interactions**

- **Colloid packing into photonic crystals**

Acknowledgements





Adeline Perro, Stéphane Reculusa,

David Nguyen and Anthony Désert

Serge Ravaine *(CRPP/Bordeaux)*

Elodie Bourgeat-Lami *(LCPP/Villeurbanne)*

Olivier Lambert and Jean-Christophe Taveau *(IECB/Bordeaux)*

Elisabeth Sellier and Michel Martineau *(CREMEN/Bordeaux)*

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