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”

Colloids: Towards higher complexity and functionality

- Colloidal stability
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- 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”

Van Blaaderen, *Science* 2003 301, 470
Photonic crystals with full bandgap

X-rays Diffraction

atoms

UV, visible, IR Diffraction

spherical colloids

fcc or hcp structure ➔ no full photonic bandgap

full photonic bandgap ➔ diamond-like structure

surface modification

+ 4
Template-directed self-assembly route

Combined effect of geometrical confinement and attractive capillary forces

Emulsion-confined self-assembly route

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**

Initiator: **Na₂S₂O₈**

\[
S₂O₈^{2-} \xrightarrow{\Delta} 2 \text{SO}_₄^{-\circ}
\]
Styrene emulsion polymerization

- [styrene] = 100 g/L
- [NP30] = 20*CMC
- [Na$_2$S$_2$O$_8$] = 0.5 g/L
- T = 70°C

Monomer-to-polymer conversion %

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

(D$_n$)$_{TEM}$ number-average diameter of latex nm

Time (min)

0 500 1000 1500

0 50 100 150 200 250 300
Styrene emulsion polymerization

**Experimental**

- [styrene] = 100 g/L
- [NP30] = 20*CMC
- [Na$_2$S$_2$O$_8$] = 0.5 g/L
- T = 70°C

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

**Figure:** Coagulation phenomenon

- Latex number: $10^{15}$ L$^{-1}$
- Time: min

**Graph:**

- X-axis: Time (min)
- Y-axis: Latex number
- Data points and error bars indicate the coagulation phenomenon over time.
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

What happens in the presence of Stöber silica

Latex number $10^{15}$ L$^{-1}$

Silica diameter $nm$

- 450 nm
- 127 nm
- 50 nm

At maximal conversion

Time: 120 min
Conversion: ~20%
Scale bar: 200 nm
Styrene seeded-emulsion polymerization

Macromonomer pre-adsorption onto Stöber silica

\[
\text{H}_3\text{C} \quad \text{CH}_2 \quad \left(\text{O-CH}_2\text{CH}_2\right)_n\text{O-CH}_3 \quad n \sim 23
\]

+ free latex

500-nm silica

[styrene] = 100 g/L
[NP30] = 20*CMC
[Na$_2$S$_2$O$_8$] = 0.5 g/L
T = 70°C

500 nm silica

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

TEM

Styrene seeded-emulsion polymerization

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

**Experimental Conditions**
- [styrene] = 100 g/L
- [NP30] = 20*CMC
- [Na$_2$S$_2$O$_8$] = 0.5 g/L
- $T = 70^\circ$C
- [macrom.] = 0.1 g/L
Styrene seeded-emulsion polymerization

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

<table>
<thead>
<tr>
<th>Silica Size</th>
<th>Concentration</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 nm</td>
<td>[silica] = 0.2 g/L</td>
<td>120 min</td>
</tr>
<tr>
<td>64 nm</td>
<td>[silica] = 0.5 g/L</td>
<td>120 min</td>
</tr>
<tr>
<td>85 nm</td>
<td>[silica] = 1.2 g/L</td>
<td>90 min</td>
</tr>
<tr>
<td>127 nm</td>
<td>[silica] = 3.2 g/L</td>
<td>60 min</td>
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Styrene seeded-emulsion polymerization

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

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

- **silica 127 nm**
  - $[\text{silica}] = 3.2 \text{ g/L}$
  - 60 min

- **silica 170 nm**
  - $[\text{silica}] = 4.7 \text{ g/L}$
  - 25 min

- **silica 212 nm**
  - $[\text{silica}] = 4.7 \text{ g/L}$
  - 20 min

120 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

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

120 min

TEM grid
Styrene seeded-emulsion polymerization

Silane surface treatment of “Stöber” silica

\begin{center}
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_2\text{Si} \quad \text{OC}_2\text{H}_5 \\
\text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5
\end{align*}
\text{methacryloxyethyltriethoxysilane (MMS)}
\end{center}

Silane-saturated surface

\begin{center}
\begin{tabular}{ccc}
50 nm & 127 nm & 450 nm \\
\end{tabular}
\end{center}

experimental

\begin{itemize}
\item \([\text{styrene}] = 100 \text{ g/L}\)
\item \([\text{NP30}] = 20 \times \text{CMC}\)
\item \([\text{Na}_2\text{S}_2\text{O}_8] = 0.5 \text{ g/L}\)
\item \(T = 70^\circ\text{C}\)
\item \([\text{silica}] = 10 \text{ g/L}\)
\item \([\text{silane}] = 16.6 \mu\text{mol/m}^2\)
\item conversion \(\sim 20\%\)
\end{itemize}

scale bar : 200 nm
Styrene seeded-emulsion polymerization

Silane unsaturated surface

- [styrene] = 100 g/L
- [NP30] = 20*CMC
- [Na₂S₂O₈] = 0.5 g/L
- T = 70°C
- [silica] = 10 g/L
- [silane] = 1.66 µmol/m²
- Conversion ~20%
- 120 min

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

Scale bar: 200 nm
Styrene seeded-emulsion polymerization

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


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

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

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

Styrene seeded-emulsion polymerization

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

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Scale bar: 200 nm
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 latex number
- **5 min**: 10-15 latex number
- **10 min**: 10-15 latex number
- **20 min**: 8-10 latex number
- **30 min**: ≤ 8 latex number
- **40 min**: ≤ 8 latex number
- **50 min**: ≤ 8 latex number

→ coagulation phenomenon occurs also on the surface

Scale bar: 100 nm
Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation/growth study

Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation/growth study

Styrene seeded-emulsion polymerization

Cryo-TEM / tomography for nucleation/growth study

Wetting efficiency of the growing latex particle towards the inorganic core

Ideal core-shell
Excentered core-shell
Dumbbell-like or snowman-like
No encapsulation
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
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