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SYNTHESIS AND FUNCTIONALIZATION OF ROD-LIKE IRON OXIDE NANOPARTICLES



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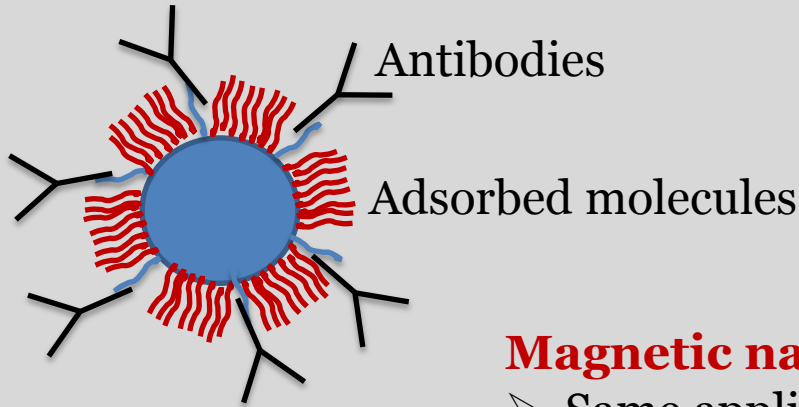
²University Pierre and Marie Curie, PHENIX, France

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⁴Nuclear Gamma Resonance Laboratory, Lithuania

**⁵Scientific-Practical Materials Research Centre of the National Academy of
Sciences of Belarus**

Introduction



Magnetic micro- or nanobeads:

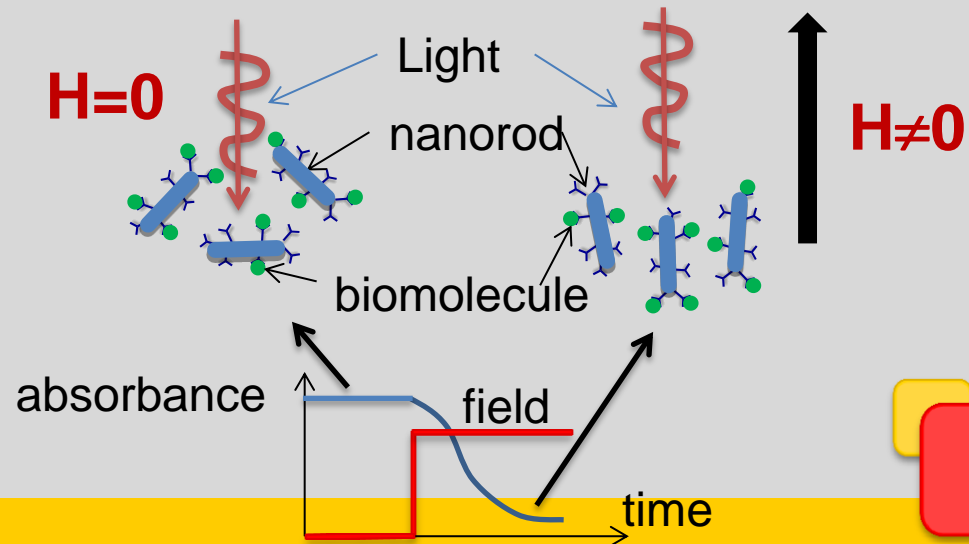
- MR imaging;
- Cell separation;
- Hyperthermia;
- Detection of biomolecules by ELISA

Magnetic nanorods:

- Same applications with **enhanced magnetization**
- Detection of biomolecules by **magneto-optic effects**

- Follow light absorption by nanorod suspension in response to \mathbf{H}
- Relate C_{ads} to change of relaxation time

Start-up **CMD** (Exeter, UK)

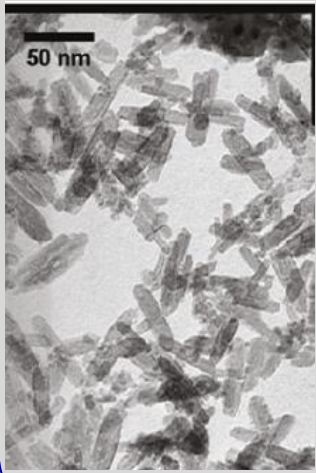


Objectives and State of the Art

We seek for iron oxide nanorods:

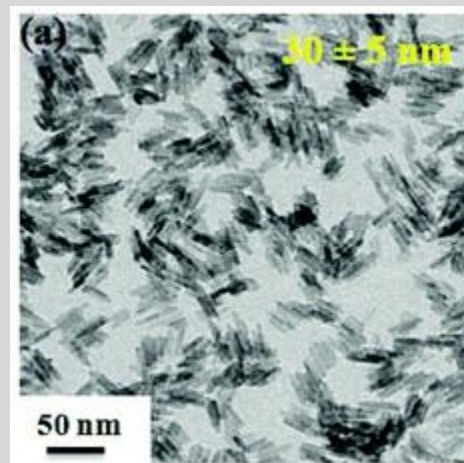
- High specific surface → small enough
 - High interaction with **H** → large enough
 - Strong MO response → $L/d > 5$
 - Well dispersed in water → graft **polymers/polyelectrolytes**
- If using **B~1 mT**
d~5 nm
L ~ 25 nm

Milosevic *et al.*
J. Phys. Chem. (2011)



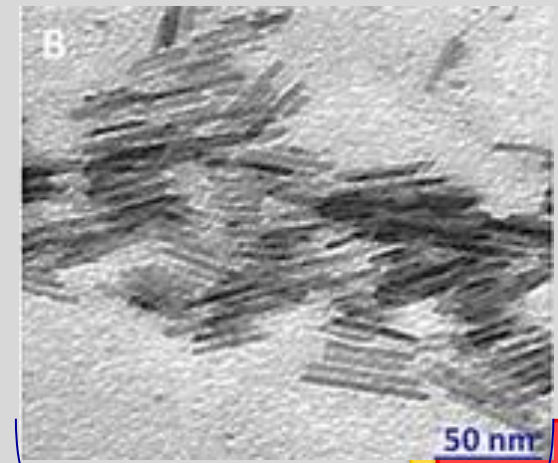
No stabilization

Mohaparta *et al.*
Nanoscale (2015)



Stabilization by PEI

Orza *et al.*
ASC Appl. Mater. Int. (2017)



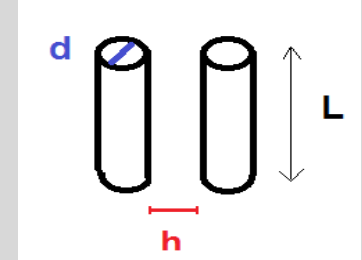
Stabilization by PEG-NH₂

Why nanorods are so unstable as compared to nanobeads?

Key question

van der Waals interaction is much stronger for rods than for beads
(larger contact area)

$$U_{vdw} = -\frac{A_H}{24\sqrt{2}} \frac{L}{d} \left(\frac{d}{h}\right)^{\frac{3}{2}} \sim -60k_B T$$



$L \sim 30\text{nm}$, $d \sim 6\text{nm}$;

$h \sim 0.5\text{ nm}$ – two water layers separating particle surfaces

To get $U_{vdw} \sim 1k_B T \rightarrow$ separate nanorods at $h \sim 7\text{-}8\text{ nm}$ using a polymer



Detailed study of nanorod stability is missing

Our work: go further in realization and understanding of nanorod dispersion

Outline

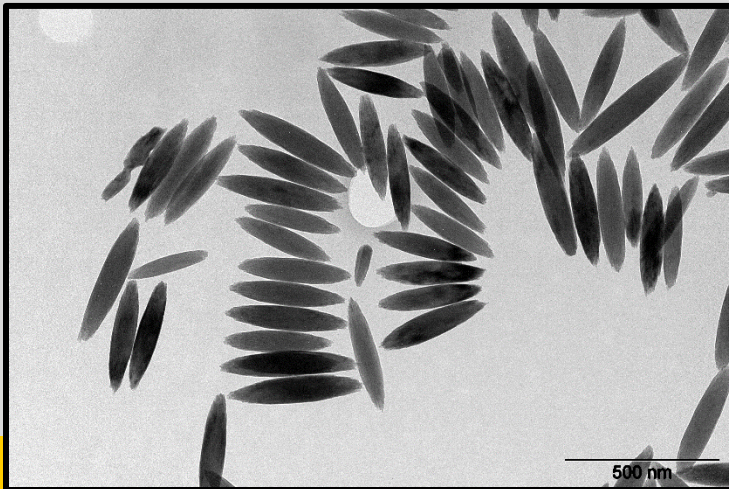
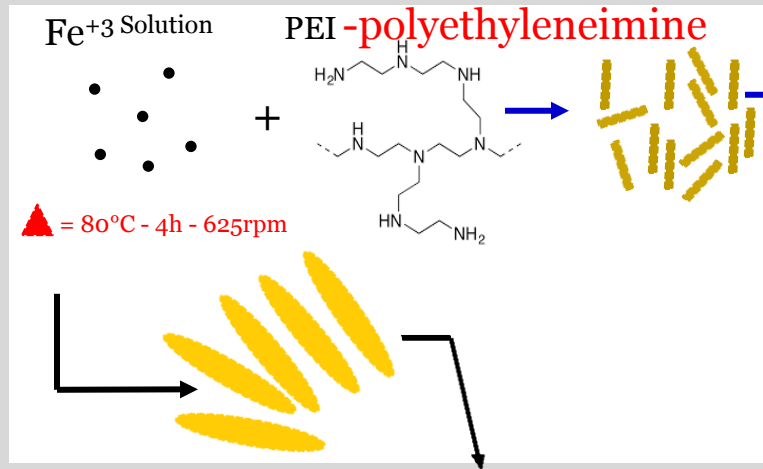


- Two –step synthesis of iron oxide nanorods
 - ❖ Akaganéite
 - ❖ Iron oxide
- Water stabilization of iron oxide nanorods
 - ❖ Functionalization
 - ❖ Characterization
 - ❖ Stability diagrams
- Conclusions

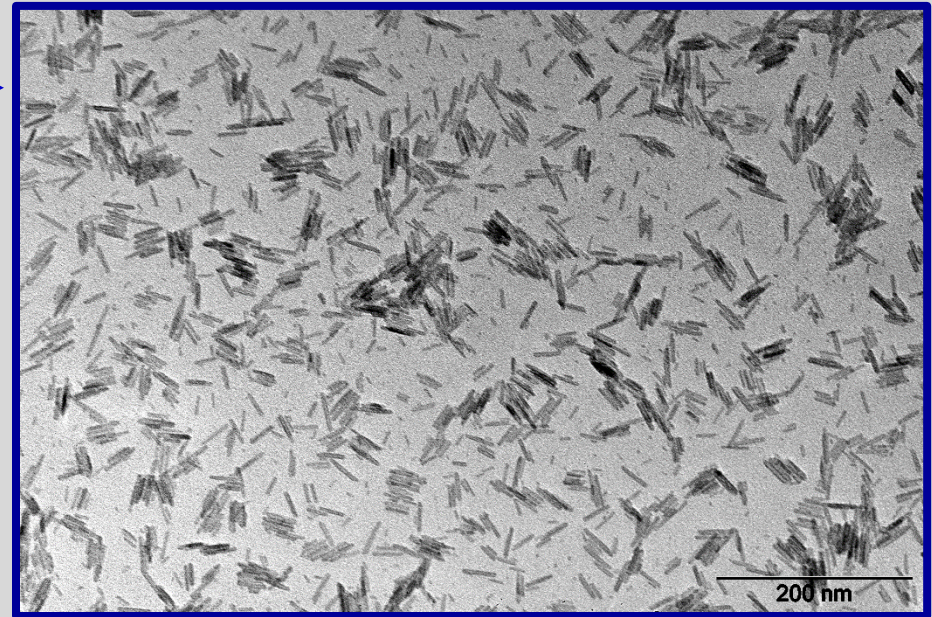
Akaganéite β -FeOOH

Synthesis

Hydrolysis of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 80°C



The protocol with PEI Mohaparta *et al.* Nanoscale (2015)



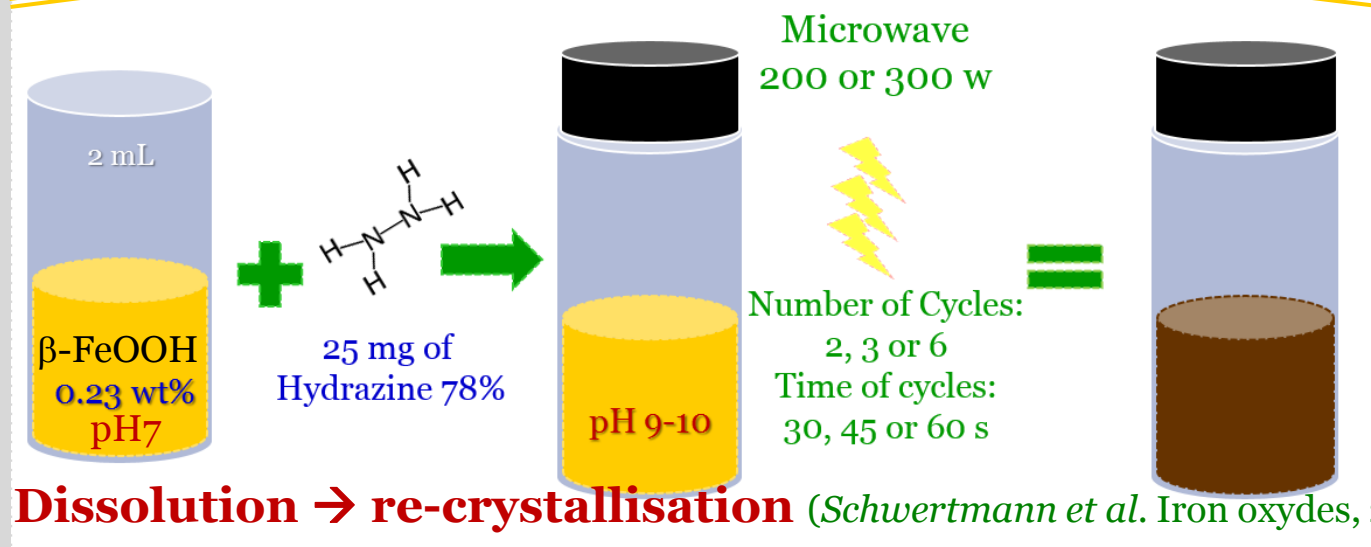
NH₂ groups → affinity with specific crystal phases → **anisotropic crystal growth**

The protocol without PEI

Blesa *et al.* Reactivity of Solids (1986)

Iron oxide – Reduction of β -FeOOH

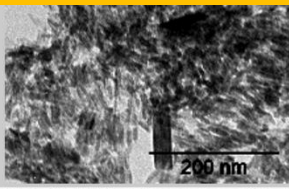
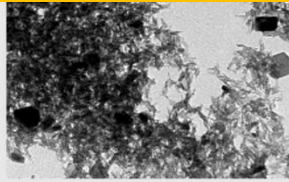
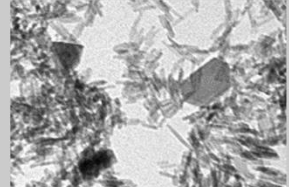
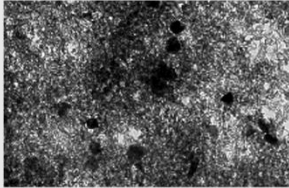
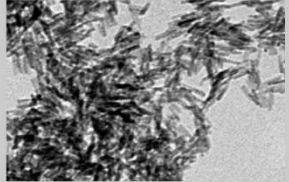
Synthesis

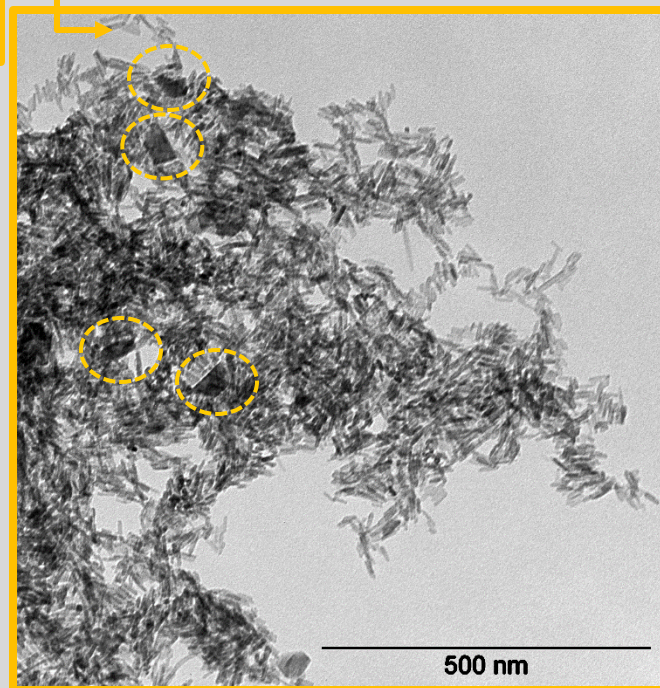


Iron oxide – Reduction of β -FeOOH

Results

Effect of number of cycles, duration and microwave power

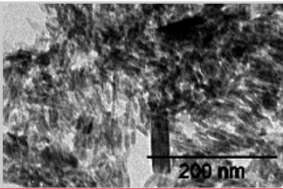
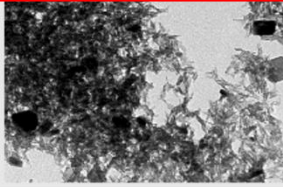
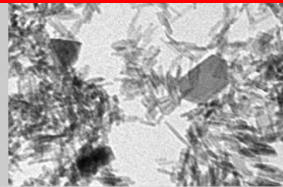
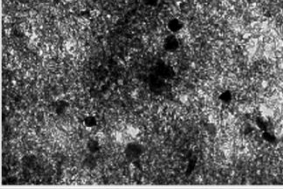
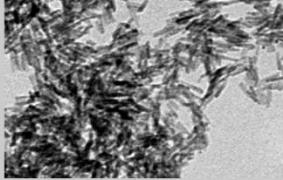
Number of cycles	Time (s)	Power (w)	Magnetization	Form	TEM
2	60	200	weak	cubic/ rod	
6	30	200	strong	cubic/ rod	
3	30	300	strong	cubic/ rod	
2	60	300	strong	cubic/ rod	
3	45	200	strong	rod	

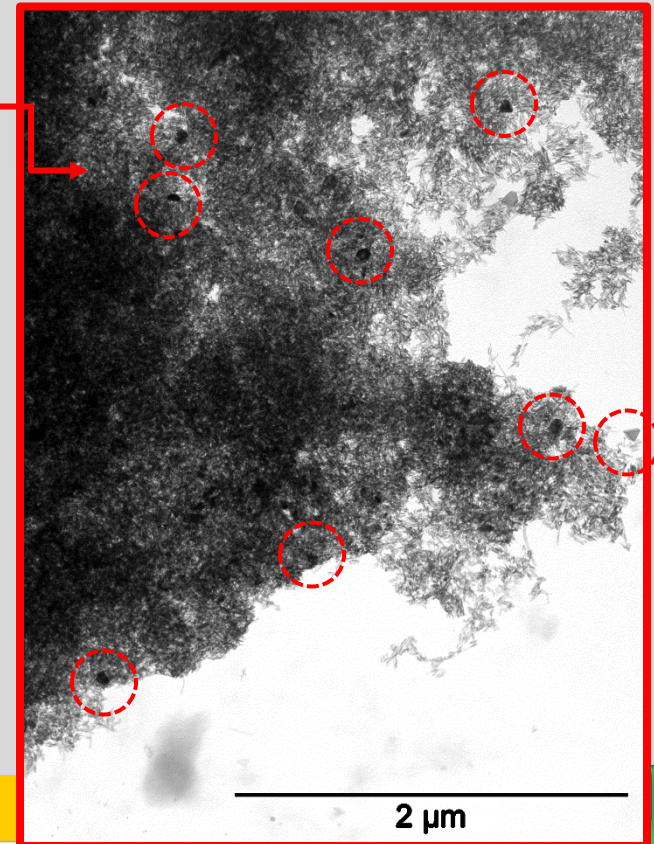


Iron oxide – Reduction of β -FeOOH

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Effect of number of cycles, duration and microwave power

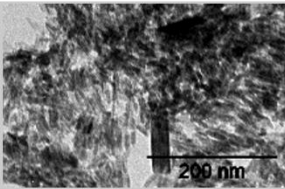
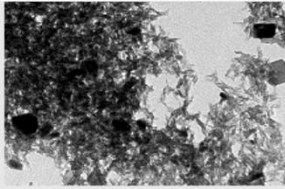
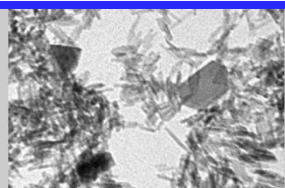
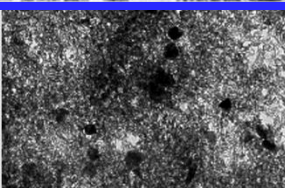
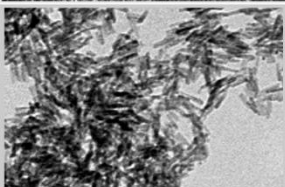
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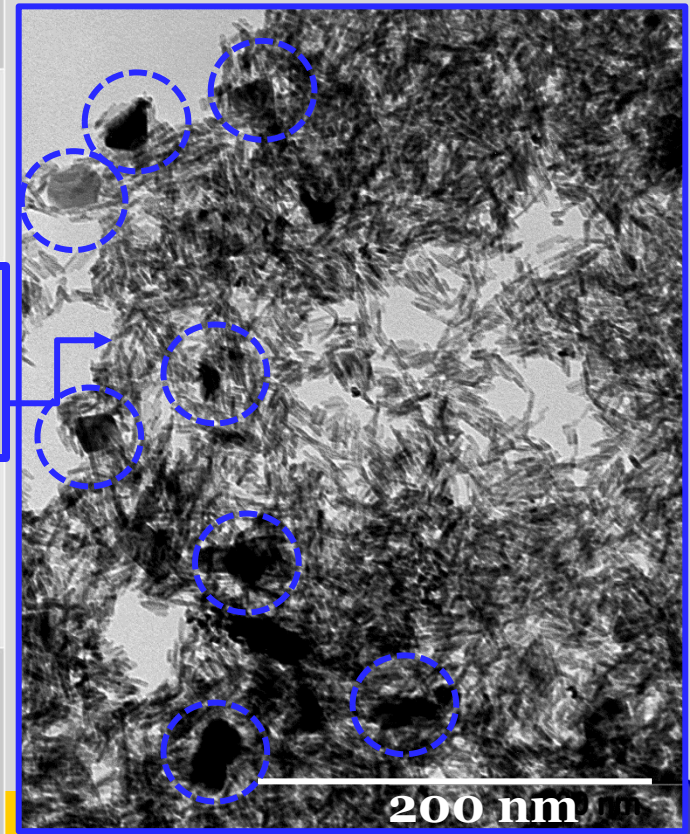


Iron oxide – Reduction of β -FeOOH

Results

Effect of number of cycles, duration and microwave power

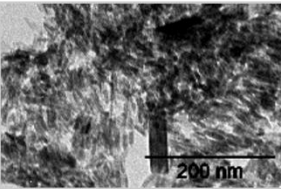
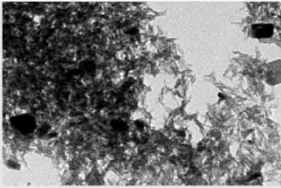
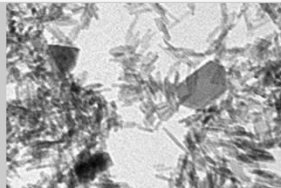
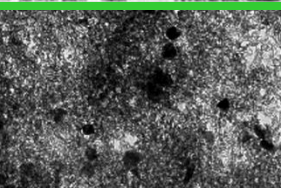
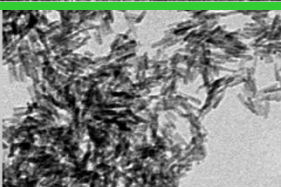
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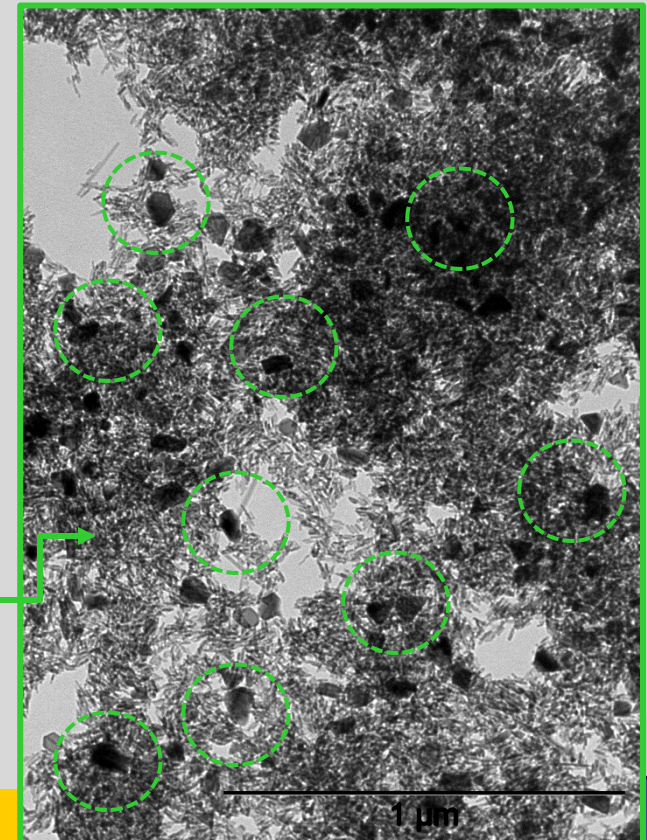


Iron oxide – Reduction of β -FeOOH

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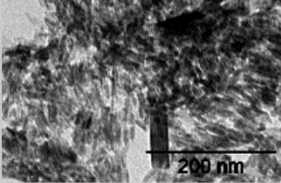
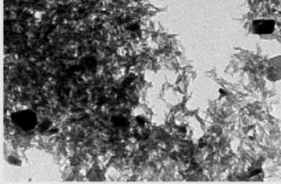
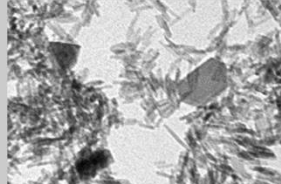
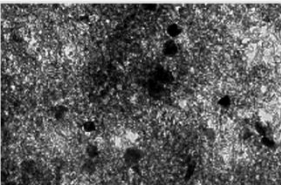
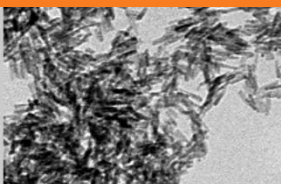
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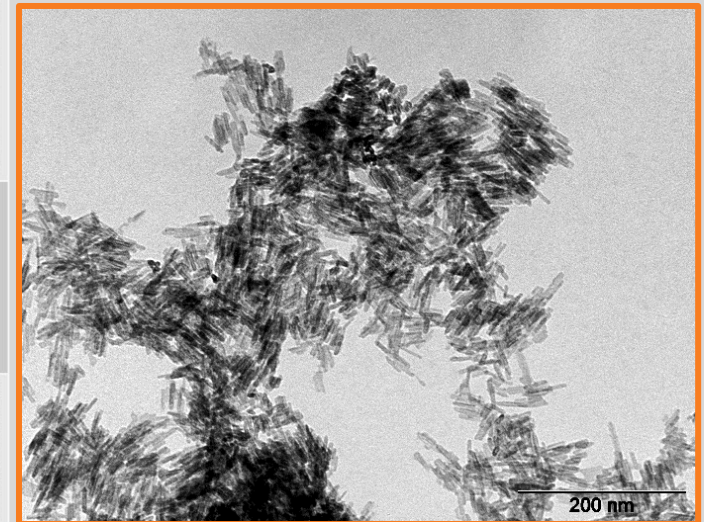


Iron oxide – Reduction of β -FeOOH

Results

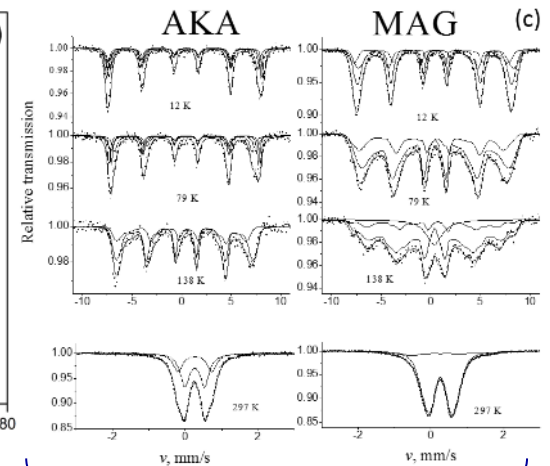
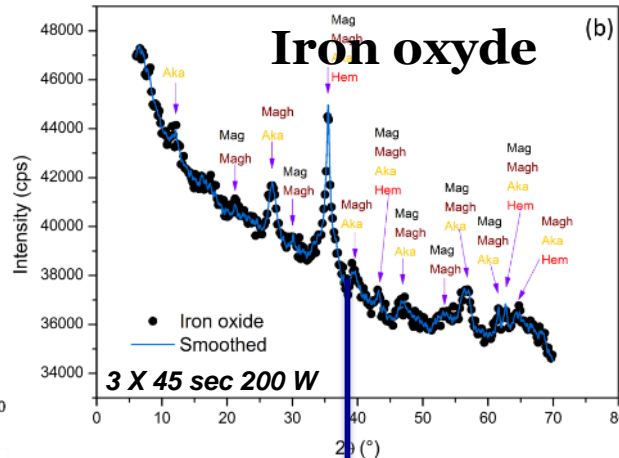
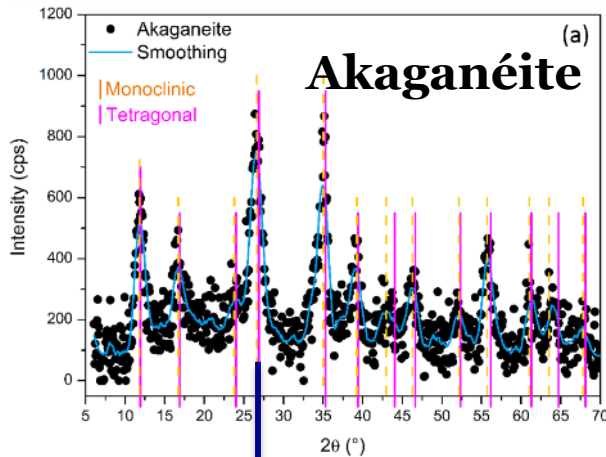
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2	60	300	strong	cubic/ rod	
3	45	200	strong	rod	



Akaganeite and iron oxide

Results



X-ray diffraction of akaganeite (a), iron oxide (b) and Mossbauer spectroscopy of akaganeite (AKA) and iron oxide (MAG) (c)

Peaks correspond to:

- **monoclinic** ← more peaks
- **tetragonal**

Peaks correspond to:

- **Magnetite**
- **Maghemite**
- **Akaganeite**
- **Hematite**

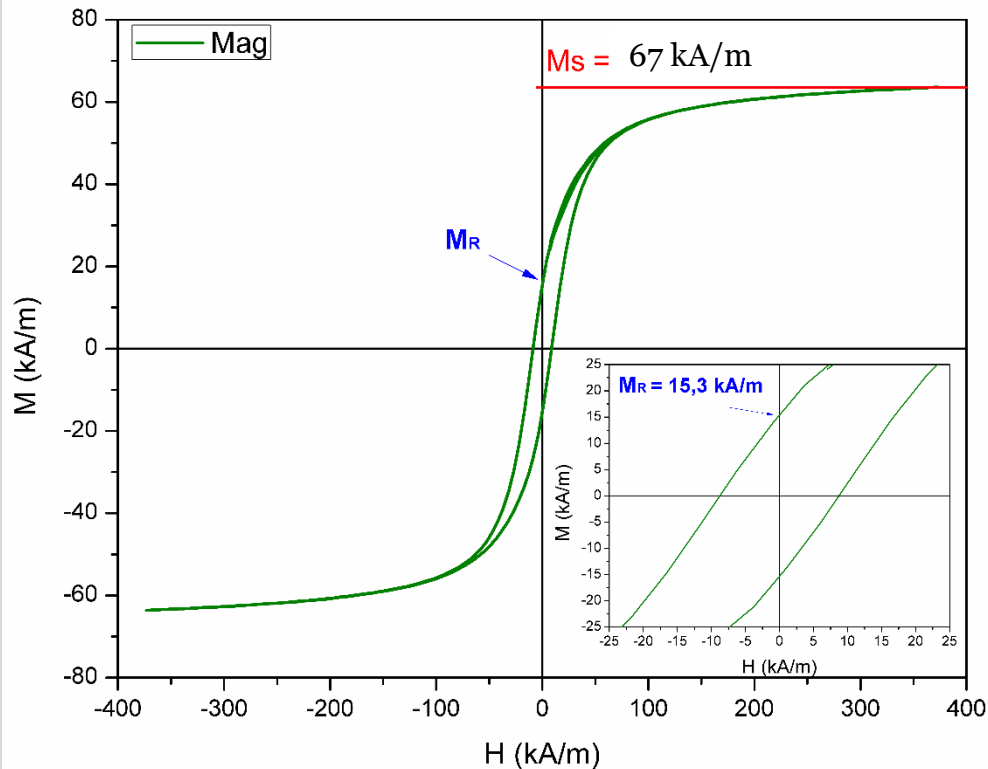
Only 3 peaks

Low hyperfine field,
no hematite

Iron oxide

Magnetization curve at room temperature

Results



Saturation magnetization :

$M_s = 67 \text{ kA/m}$ **Why so small?**

Remnant magnetization :

$M_R = 15 \text{ kA/m}$ **Why remnance?**

Mossbauer spectra:

11 % \rightarrow ordered magnetic phase
(**ferrimagnetic** $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$
giving **remnance**)

89 % \rightarrow disordered magn. phase
(**superparamagn.** $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$

+ non-transformed **weakly**
paramagnetic akaganeite
contributing to low M_s)

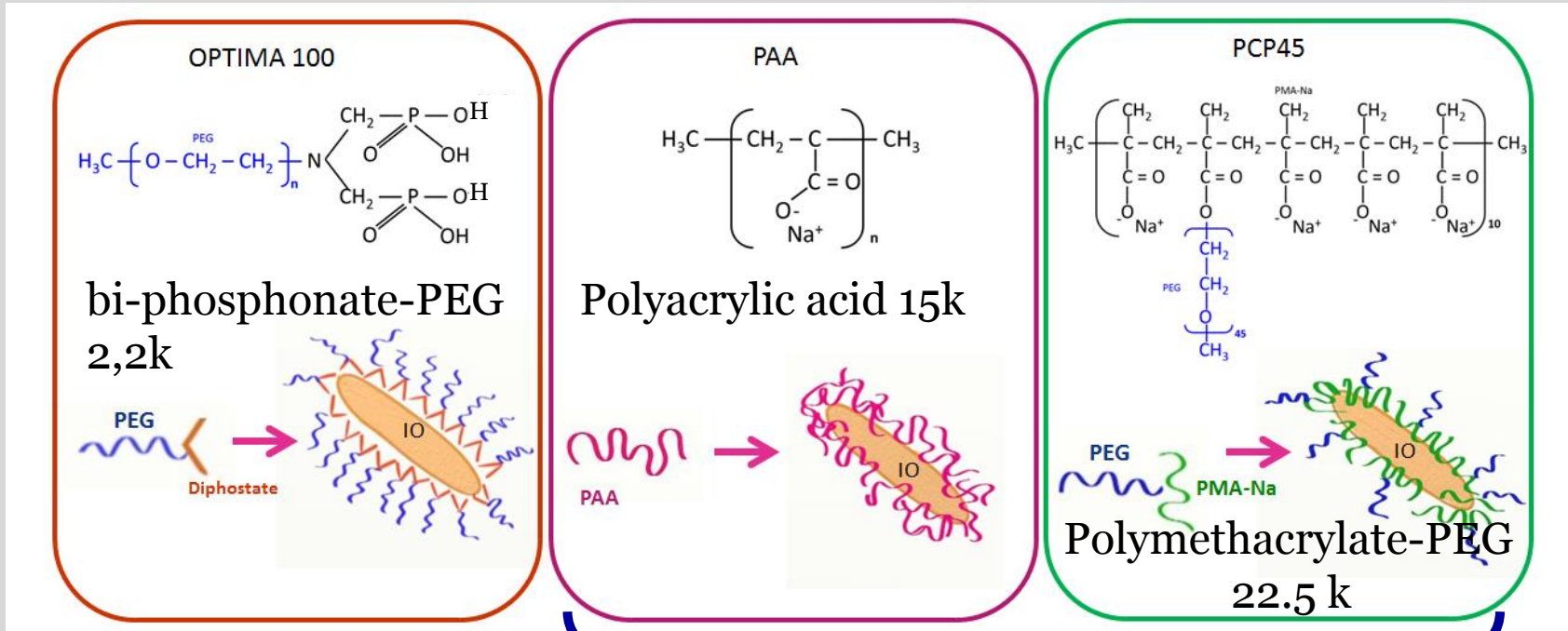
Water stabilization of iron oxide nanorods

Function-
alisation

Before: **pH=1.2** or **6**

pH=1.2

pH=1.2



After: **pH=1,2** or **3**
chemisorption
phosphonate on iron oxyde

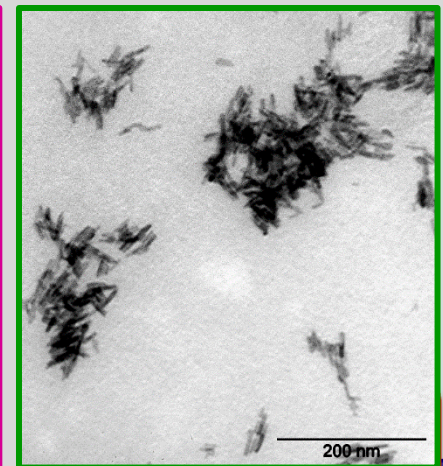
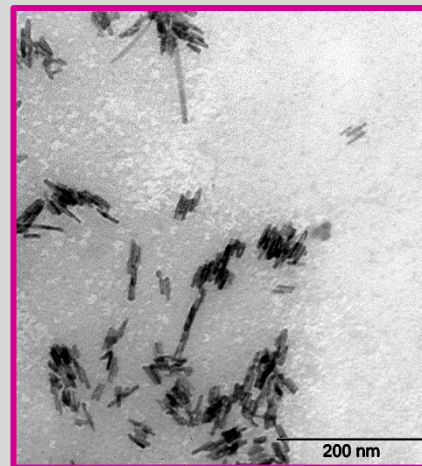
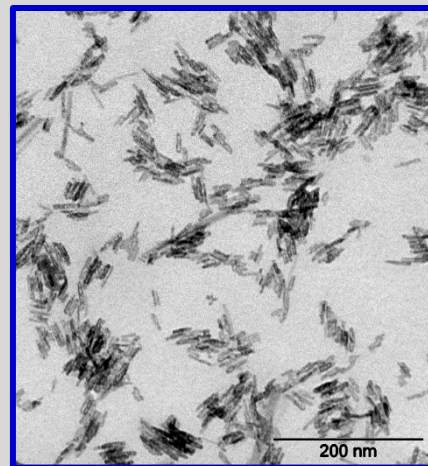
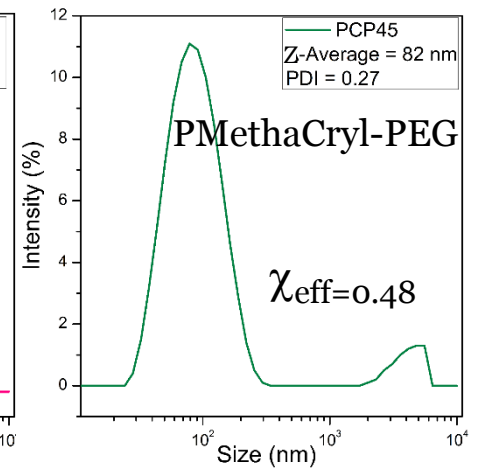
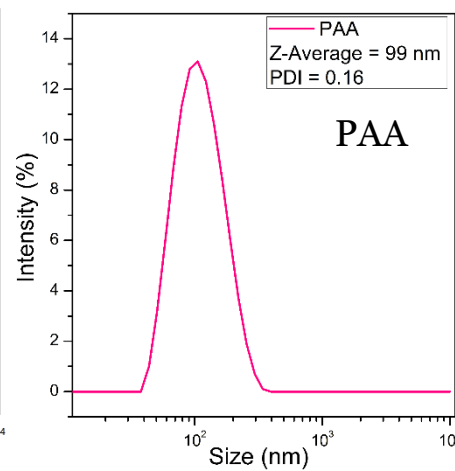
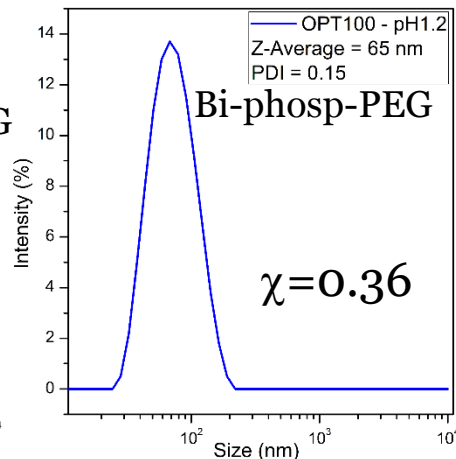
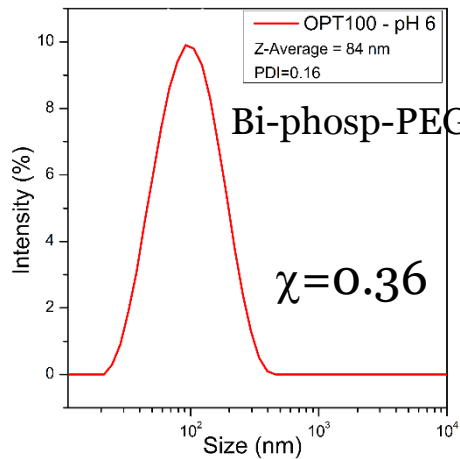
Adjustment of **pH to 8-9**
precipitation-redispersion
[Sehgal, ..., Berret, Langmuir (2005)]

Water stabilization of iron oxide nanorods

Results

DLS intensity-average distribution of diameters

Useful method for comparative study

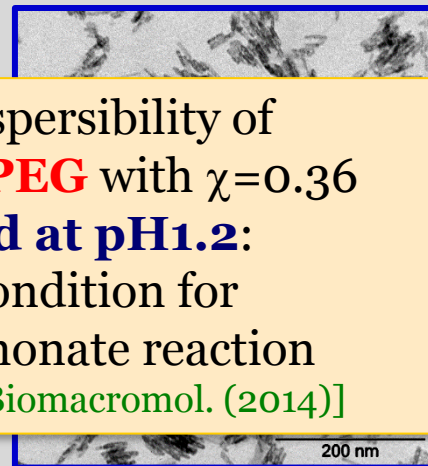
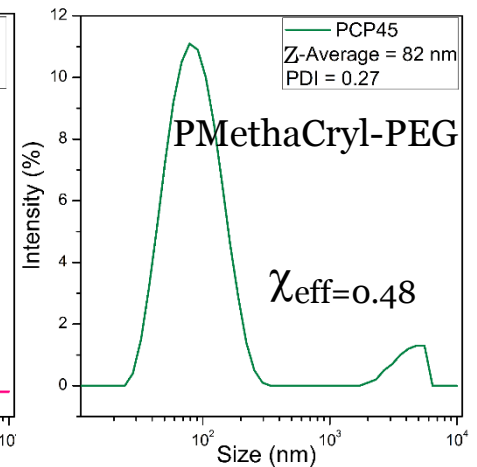
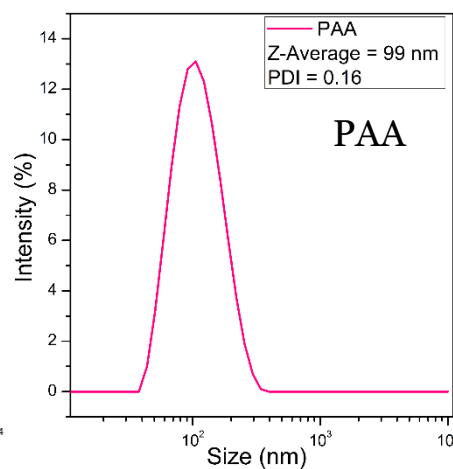
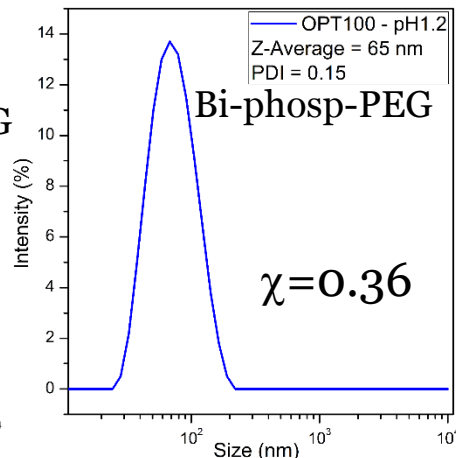
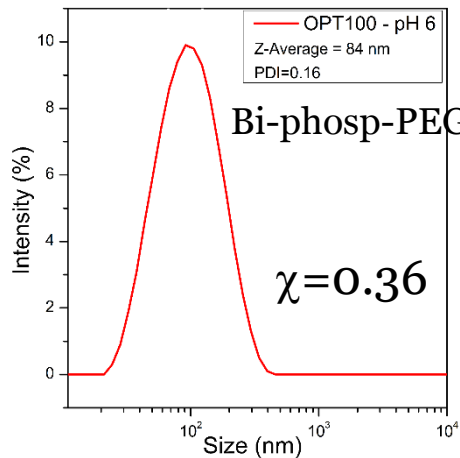


Water stabilization of iron oxide nanorods

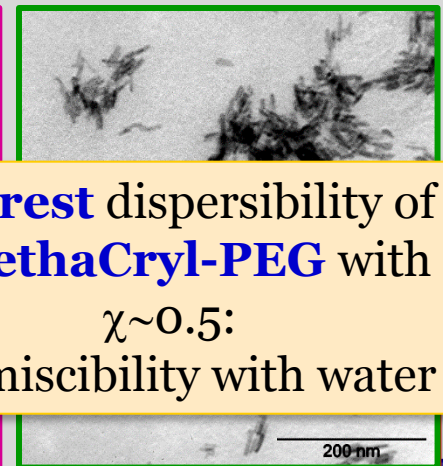
Results

DLS intensity-average distribution of diameters

Useful method for comparative study



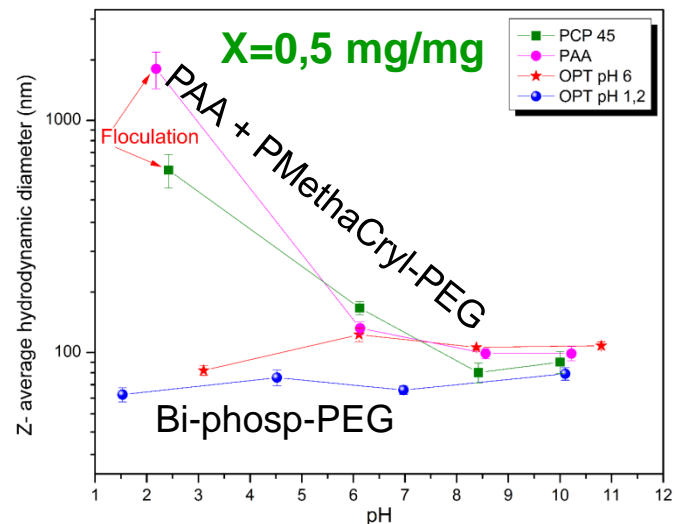
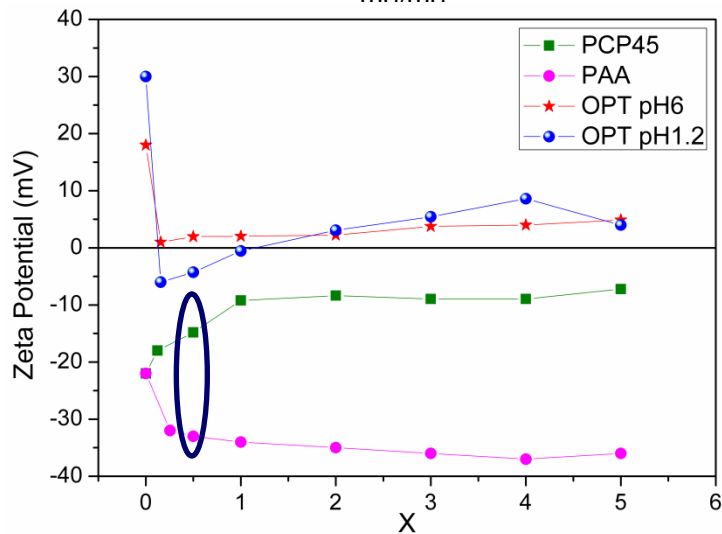
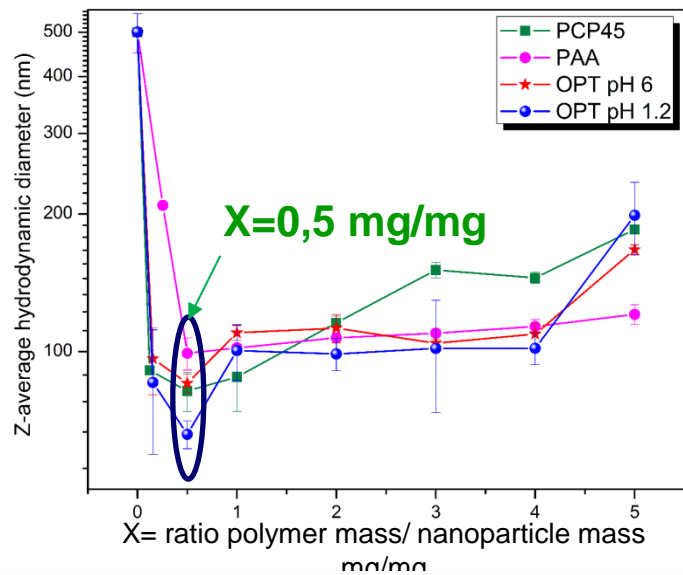
Best dispersibility of
Bi-phosp-PEG with $\chi=0.36$
grafted at pH1.2:
Best condition for
IO-phosphonate reaction
[Torrise et al. Biomacromol. (2014)]



Poorest dispersibility of
PMethaCryl-PEG with
 $\chi\sim 0.5$:
Poor miscibility with water

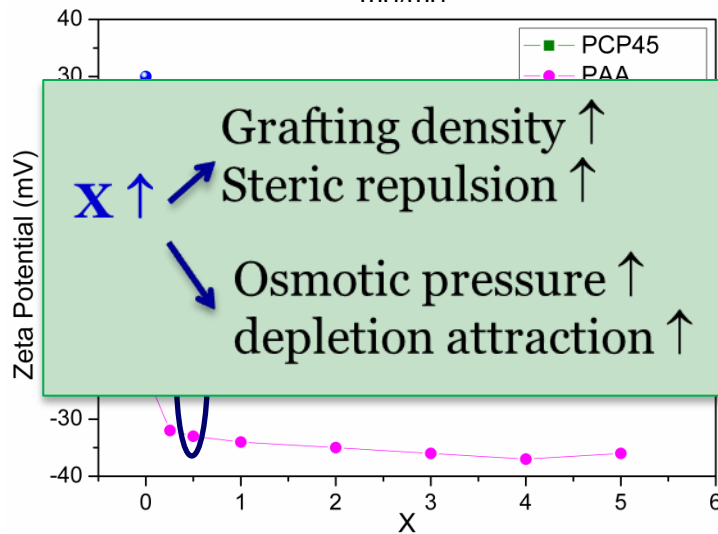
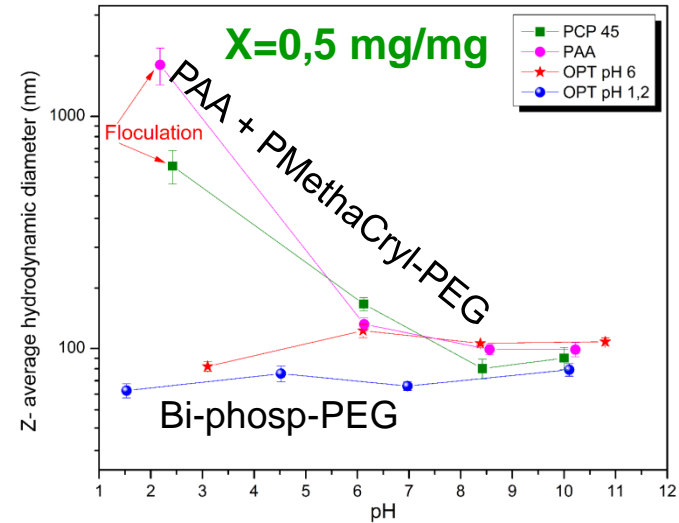
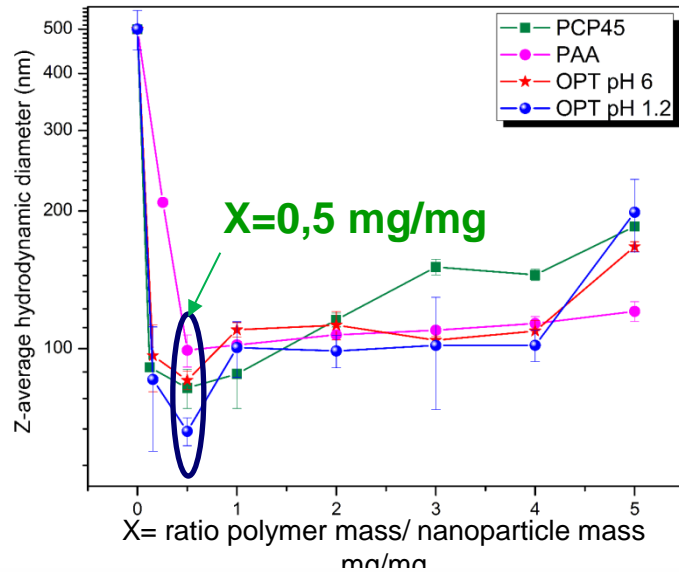
Water stabilization of iron oxide nanorods

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Water stabilization of iron oxide nanorods

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Bad conformation of PAA and PMethaCryl-PEG

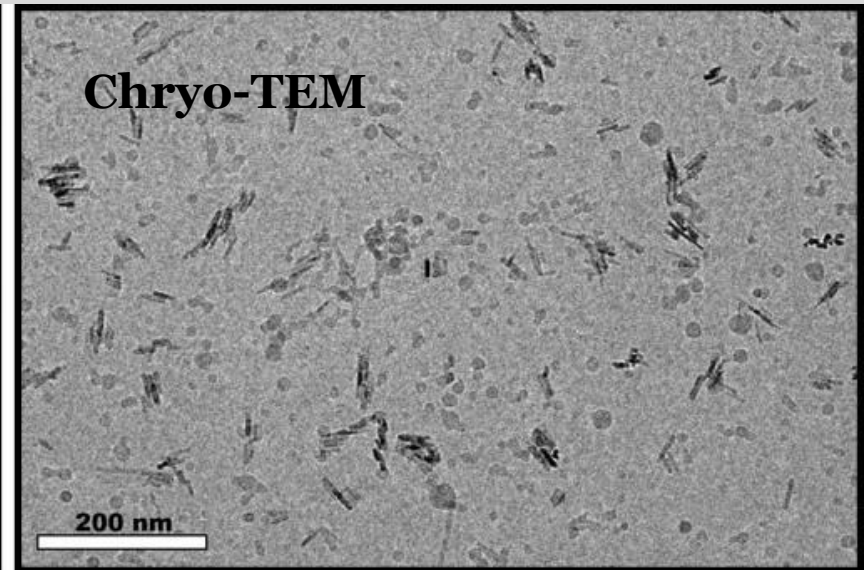
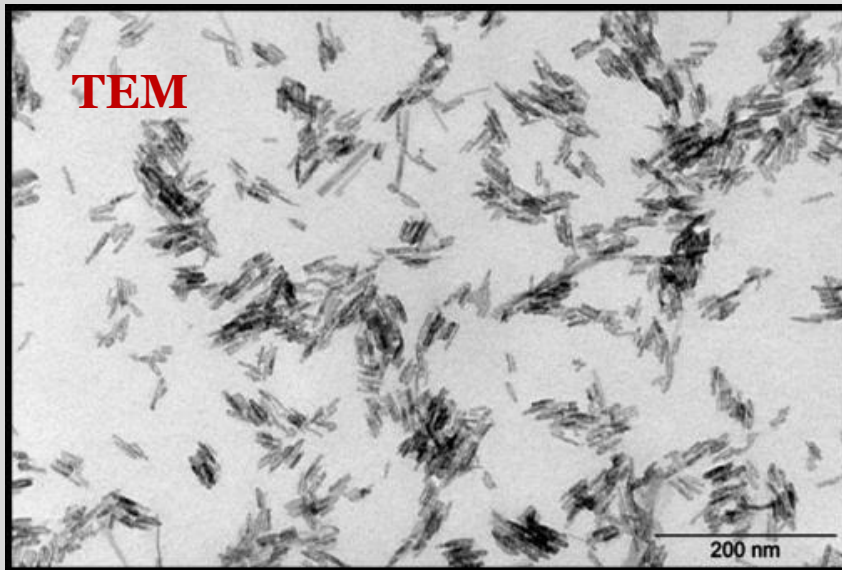
Adameczyk et al. (2006)

$\text{pH} \downarrow$ leads to:

- Bad conformation of PAA and PMethaCryl-PEG
- No strong effect on conformation of Bi-Phosp-PEG

Water stabilization of iron oxide nanorods

Best stabilization: PEG-bi-Phosphonate grafted at acidic pH at X=0.5 mg/mg



- Smaller aggregates in chryo-TEM pictures
- Lateral aggregation of rods

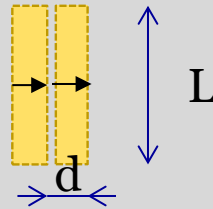
What leads to this aggregation?

Theoretical estimation of stability – Magnetic interaction

Two possible cases of remnant magnetization:

❖ (a)

$$U_{mag} = \frac{\pi\mu_0 M_r^2 dL^2}{32}$$



$M_r = 15 \text{ kA/m}$ remnant magnetization of particles

❖ (b)

$$U_{mag} = \frac{\pi\mu_0 M_r^2 d^4}{32L}$$



$$U_{mag} \ll k_B T$$

Theoretical estimation of stability - Depletion interaction

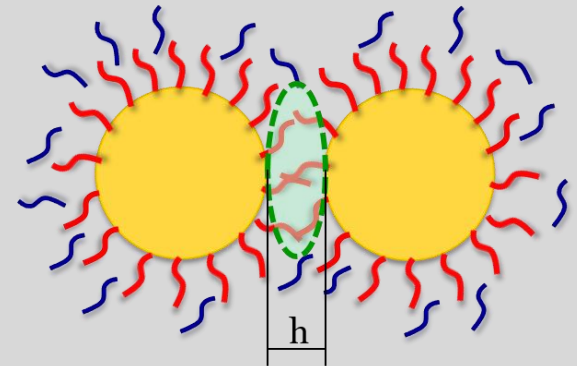
- ❖ Free polymer is squeezed out from the contact zone
- ❖ Osmotic pressure pushes the particles towards each other

Depletion interaction energy → excluded volume

$$U_{dpl} = - \Pi V_{exclu}$$

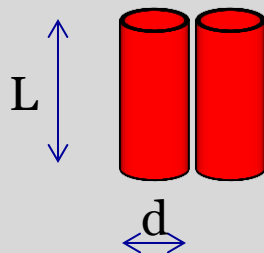
$$\frac{U_{dpl}}{k_B T} = - \frac{C_w N_A V_{exclu}}{M_w}$$

$$U_{dpl} < k_B T \text{ at } X = 0.5 \text{ mg/mg}$$



Theoretical estimation of stability - Electrostatic energy

Brenner & Parsegian, Biophys. J. (1974)



$$U_{el} = \frac{4\sqrt{2/\pi} q^2 \kappa^{-2} L}{\epsilon_0 \epsilon} \sqrt{\kappa d} e^{-\kappa h}$$

Surface charge density

$$q = \frac{\mu_E \eta}{\kappa^{-1}}$$

Electrophoretic mobility measured with ζ -sizer

Debye length estimated by conductivity meas.

Bi-phosp-PEG: $U_{el} \ll k_B T$ (low charge density q)

PMethaCryl-PEG & PAA: $U_{el} \approx (2 - 3)k_B T$ ($I \sim 0.1M, \kappa^{-1} \sim 1 \text{ nm}$)

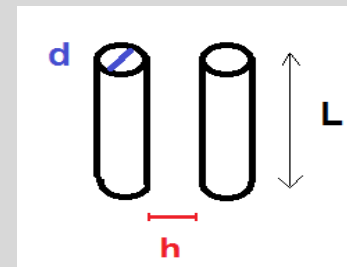
Theoretical estimation of stability - van der Waals interaction

Results

van der Waals force between two parallel cylindrical rods :

Van der Schoot & Odjik J. Chem. Phys. [1992]

$$F_{vdw} = - \frac{dU_{vdw}}{dh} = - \frac{1}{16\sqrt{2}} A_H L \left(\frac{d}{h^5} \right)^{\frac{1}{2}}$$



Theoretical estimation of stability - Steric interaction

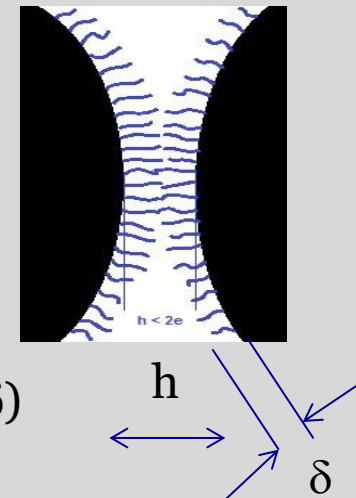
- *Milner et al. Macromolecules (1988)*

valid for **brush regime**
for **bi-phosp-PEG** at $\chi=0.36$

$$U_{st} = 2 \frac{k_B T}{d_a} (1 - 2\chi)^{2/3} N \left(\frac{a}{d_a} \right)^{2/3} \left[\frac{1}{2u} + \frac{u^2}{2} - \frac{u^5}{10} \right]$$

with $u=h/(2\delta)$

$$F_{st} = \pi d [U_{st}(h) - U_{st}(2\delta)] \quad \leftarrow \text{Derjaguin approach}$$

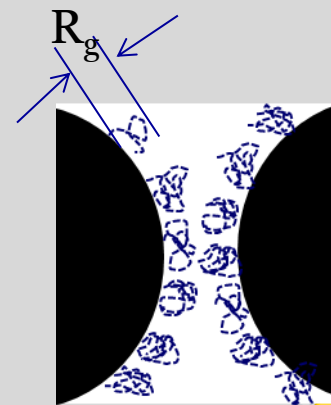


- *Patel & Russel, Coll. Surf. (1988):*

valid for **blob regime**
for **PMethaCryl-PEG** at $\chi = 0.48$

$$F_{st} = \pi d k_B T \frac{2R_g}{d_a^3} k_1^{1/4} k_2^{3/4} \left[\frac{1}{u^2} + u^2 - 2 \right]$$

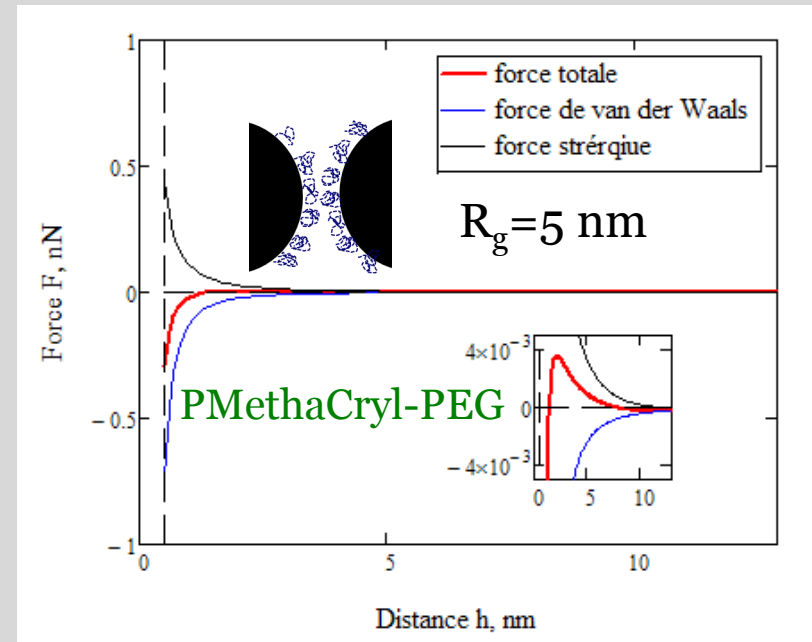
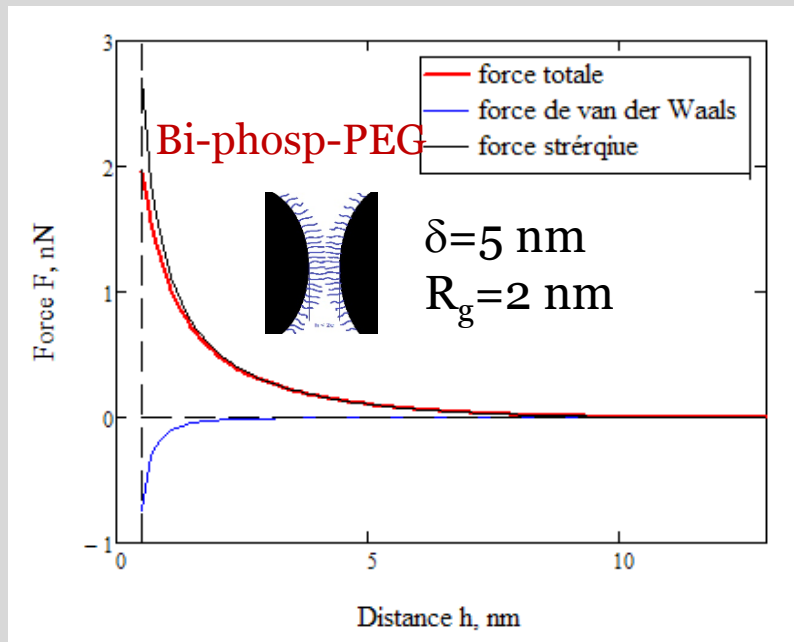
with $u=h/(2R_g)$



Theoretical estimation of stability - Total force

Magnetic, electrostatic and depletion energy are insignificant ($\ll k_B T$ or $\sim k_B T$).

Considered forces : **Van der Waals** and **steric interactions**



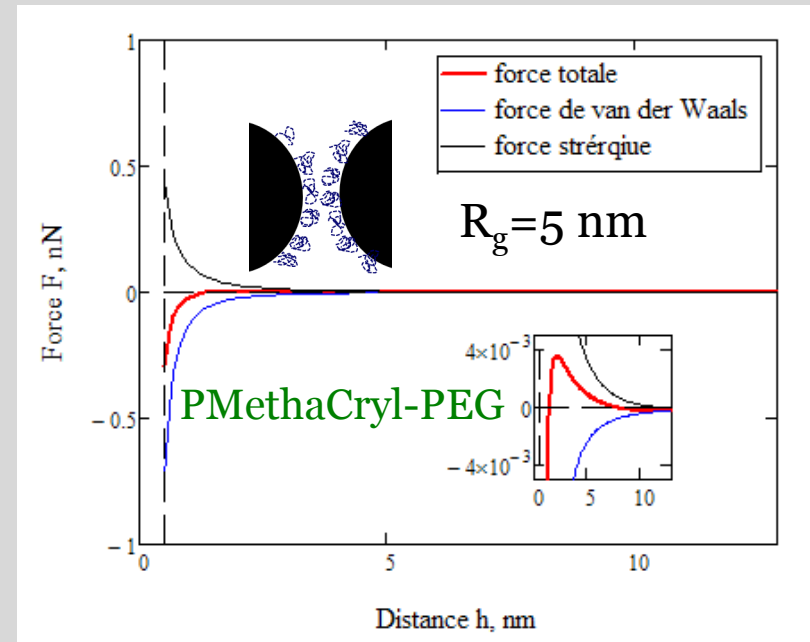
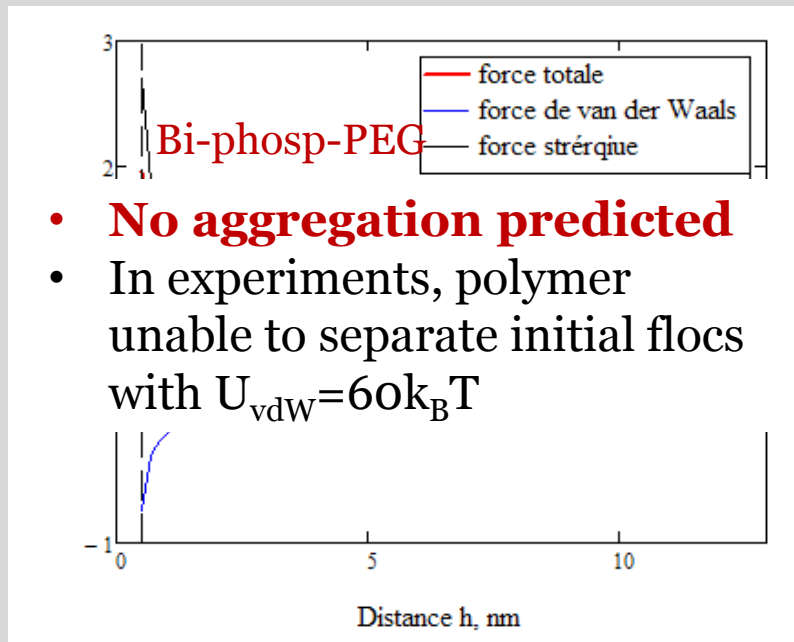
$U_{\text{tot}} = 23 k_B T$ at $h = \text{particle diameter}$

$U_{\text{tot}} \sim 1 k_B T$ at $h = 2 \text{ nm}$ (force barrier)

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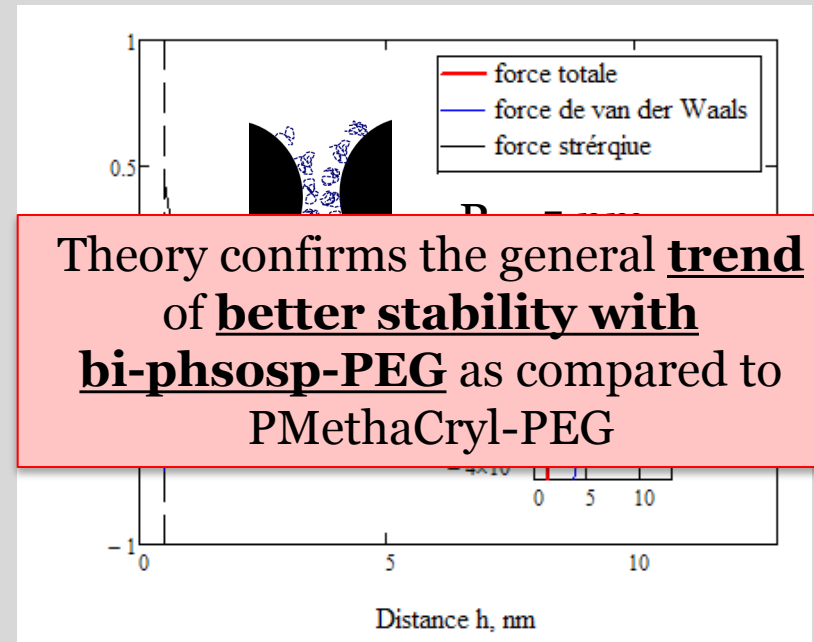
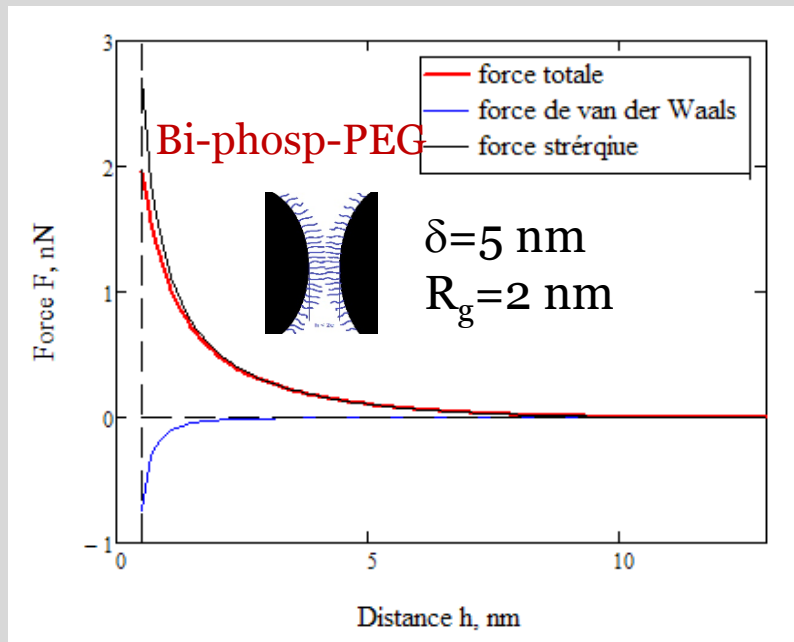
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Considered forces : **Van der Waals** and **steric interactions**



Theory confirms the general **trend** of **better stability with bi-phosp-PEG** as compared to PMethaCryl-PEG

$U_{\text{tot}} = 23 k_B T$ at $h = \text{particle diameter}$

$U_{\text{tot}} \sim 1 k_B T$ at $h = 2 \text{ nm}$ (force barrier)

Conclusions



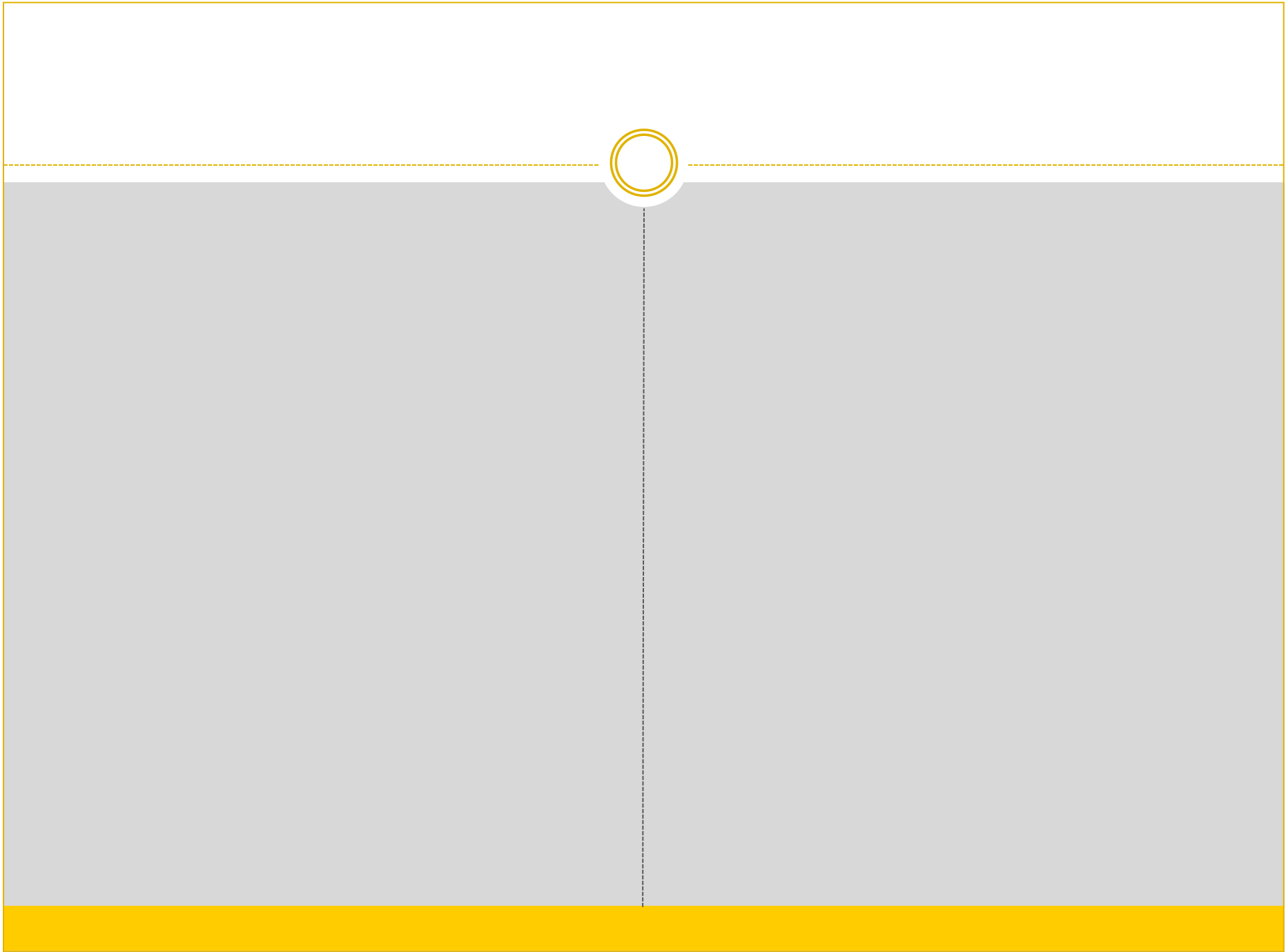
- ❖ **Two-step** nanorod **synthesis** + **grafting** of 3 different polymers/polyelectrolytes;
- ❖ **Optimum polymer amount** for minimal aggregation: interplay between increasing grafting density and depletion interaction;
- ❖ Nanorod with **PAA** and **Polymethacrylate-PEG**: stable at **$8 < \text{pH} < 11$**
- ❖ Nanorod with **bi-phosphonate-PEG**: stable at **$1.5 < \text{pH} < 11$**
- ❖ Best stability with **bi-phosphonate-PEG grafted at acidic pH**
- ❖ Theoretical estimations confirm general tendency of the stability diagrams

Thanks for your attention



This work was supported by CNPq





Washings

Akaganeite:

- After synthesis: centrifuging to remove polymer
- + washing with ethanol
- + drying at 25°C
- + washing with NaOH to increase the pH

Iron oxide:

- After synthesis: washing with water to remove hydrazine
- + after washing with HNO₃ to adjust pH to 1.2 or 6 for grafting
- After grafting of PAA, Pmethacrylate washing with ammonia to pH=8-9
- After grafting of bi-phosph-PEG no washing

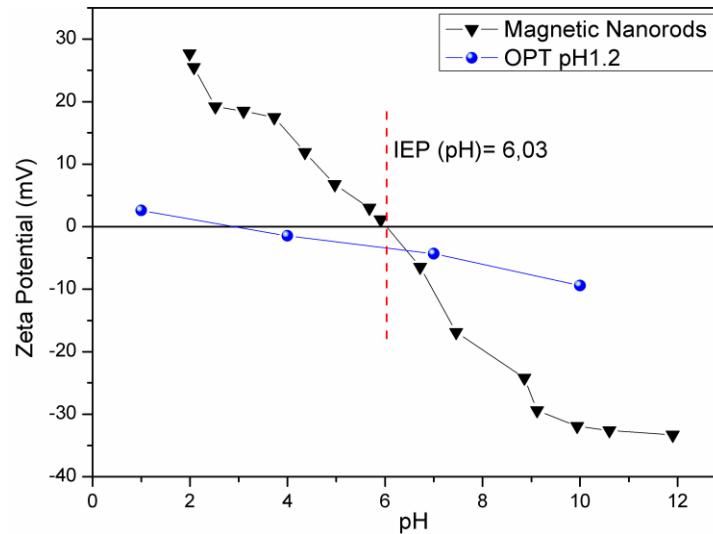
Estimation of polymer amount adsorbed
on the iron oxide surface

$$X_{theo} = M_{seg} \times N^{\circ}_{seg} \times S_{BET}$$

$$X_{theo} = 0,1 \text{ mg/mg for OPT}_{100}$$

$$X_{theo} = 0,07 \text{ mg/mg for PCP}_{45}$$

The quadrupole distribution fitted to room temperature spectrum of MAG3 sample is more uniform compared with that of akaganeite **which is like to be composed from two parts (Fig. 2)**. In addition, **11 %** area is attributed to magnetically ordered phase fitted to hyperfine field distribution $P(B)$ with the average hyperfine field 6.4 T



BET

Akaganeite (d=4 nm, L=29 nm) ~68 m²/g

Iron oxide (d=6 nm, L=31 nm) ~ 135 m²/g (particle porosity?)

$$A_H = 33 \cdot 10^{-21} \text{ J [Faure et al., Langmuir (2011)]}$$

