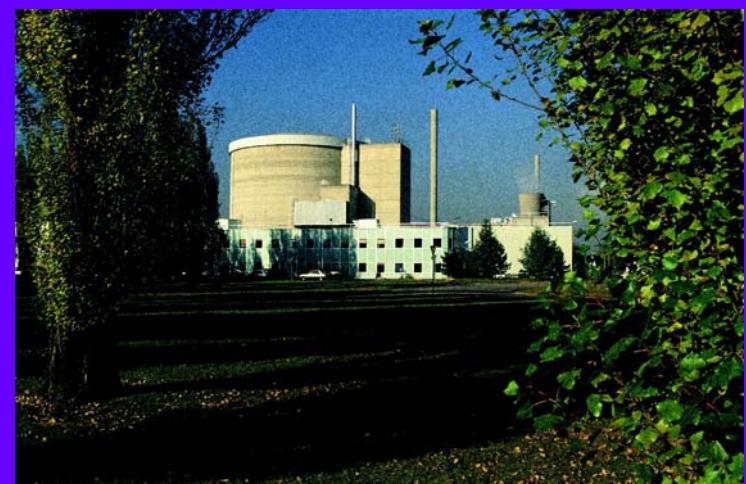
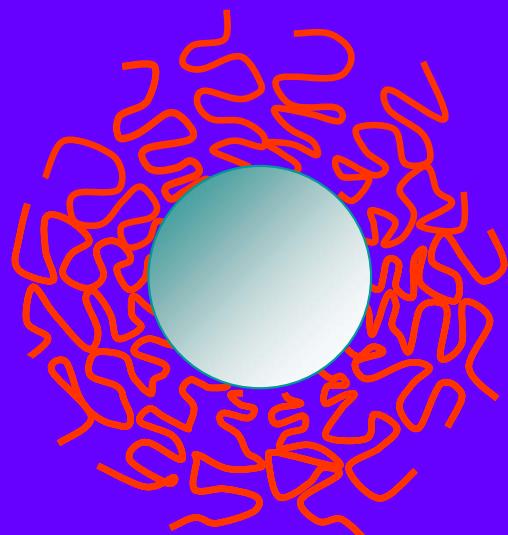


Nanoscale hybrid objects: from 3D SANS study to tunable 2D arrays formation

Géraldine Carrot

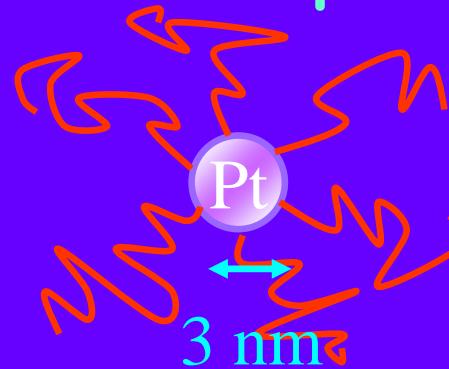
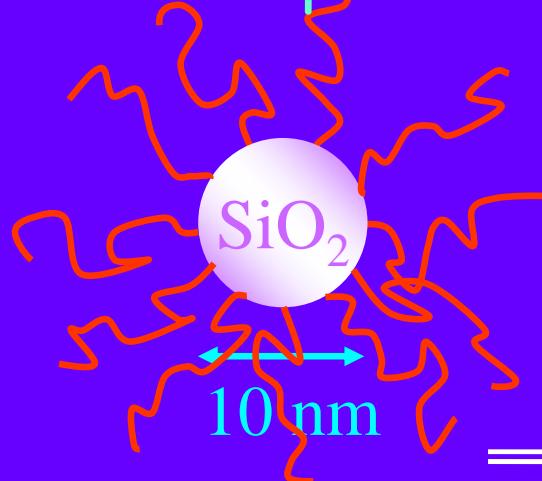
Laboratoire Léon Brillouin, CEA-Saclay.



Nano-objects based on polymer-grafted inorganic nanoparticles

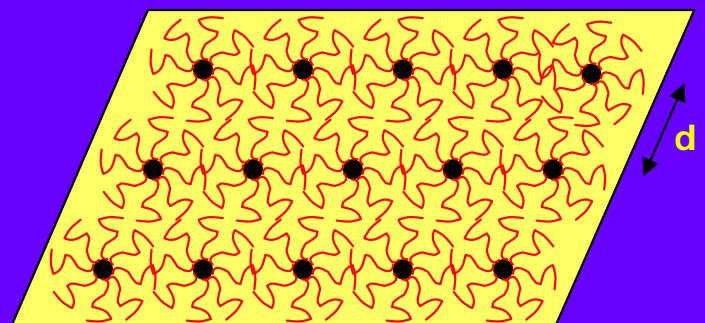
Platinum nanoparticles

Silica nanoparticles

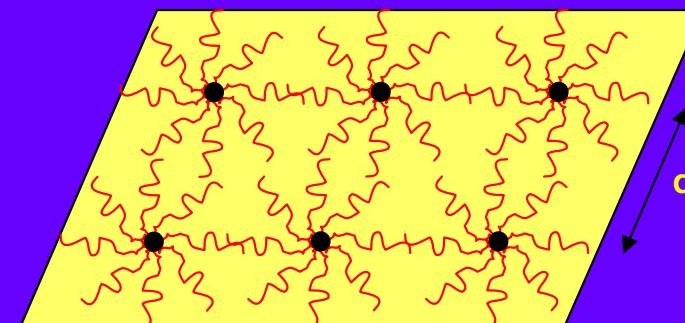


Bio-application as
bio-sensor
(glucose probe)

- Polymerization in organic or aqueous medium
- Study of the structure via SANS (3-D) Use of Contrast Matching
- Organization in 2D and neutron reflectivity



Short chains



Long chains

Colloidal suspension in water or in organic solvent

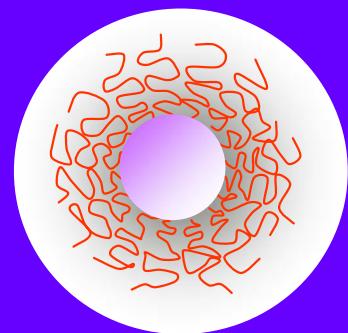


Necessary to avoid aggregation

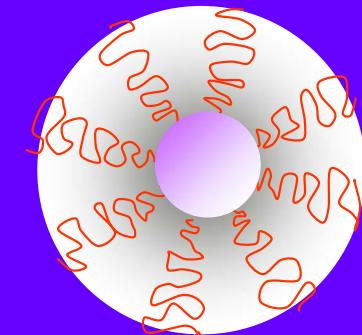
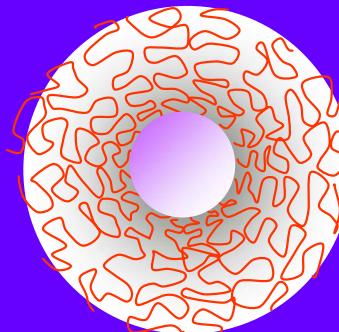


Control of the surface state

By grafting polymer chains:

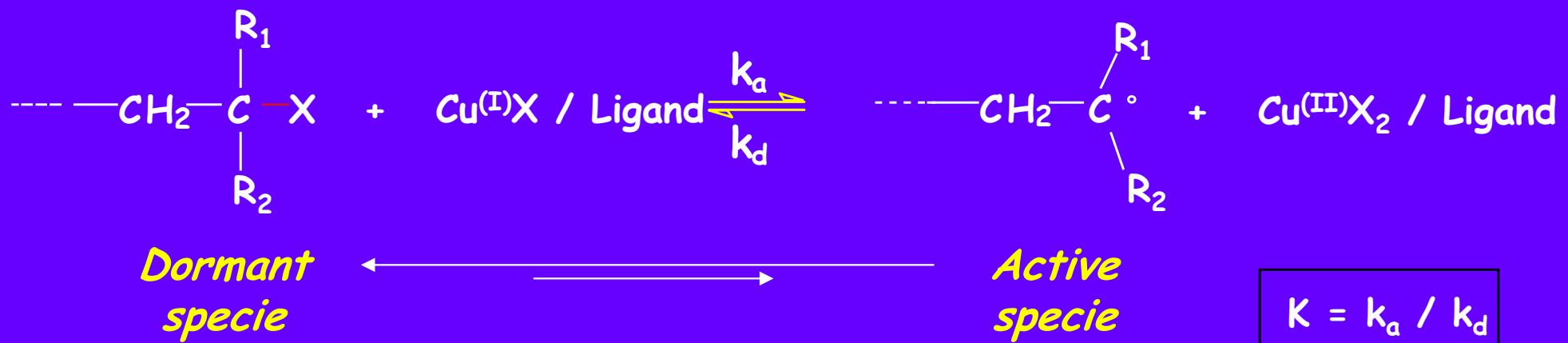


Chain lengths

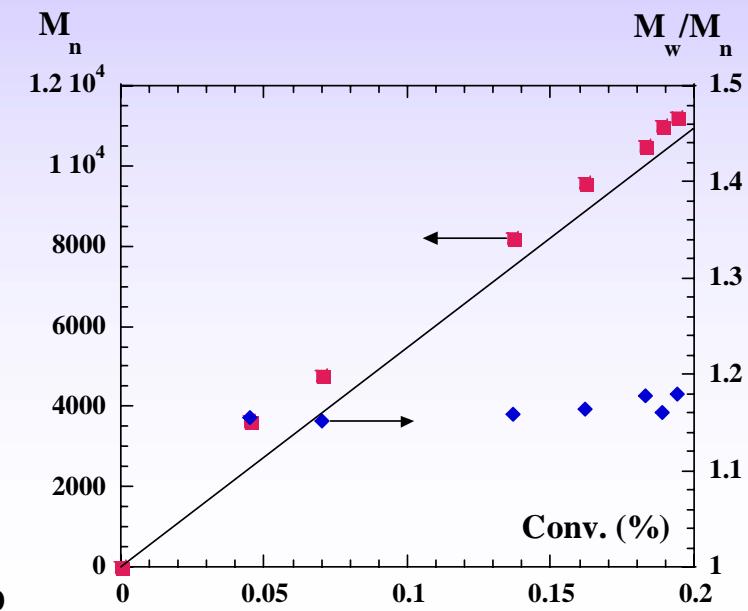
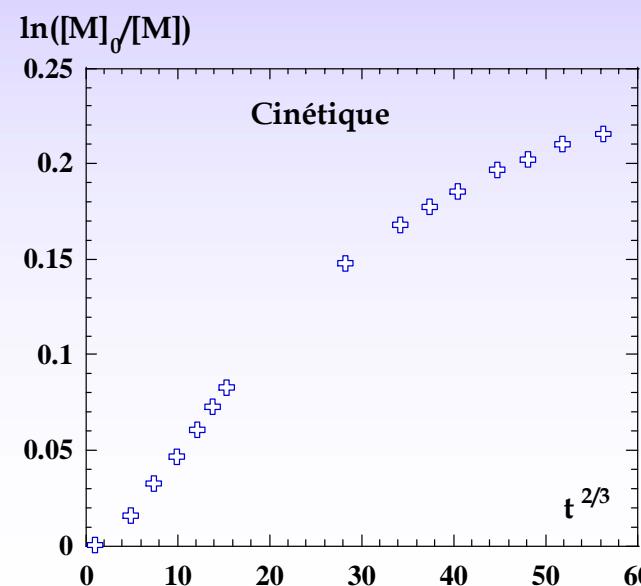
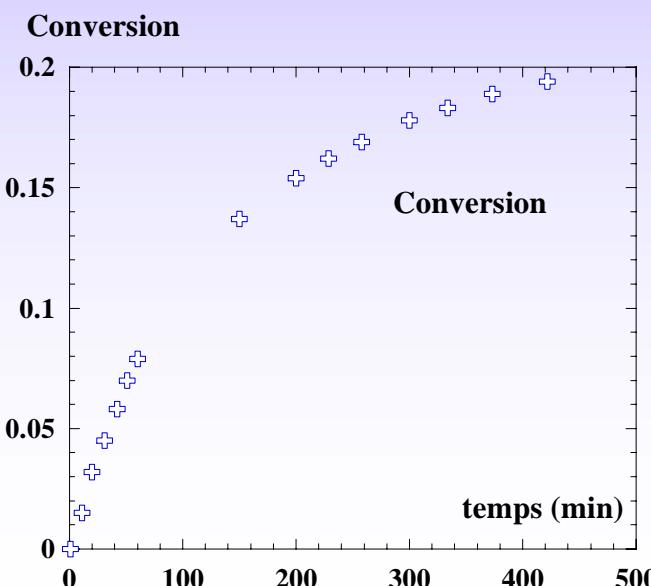
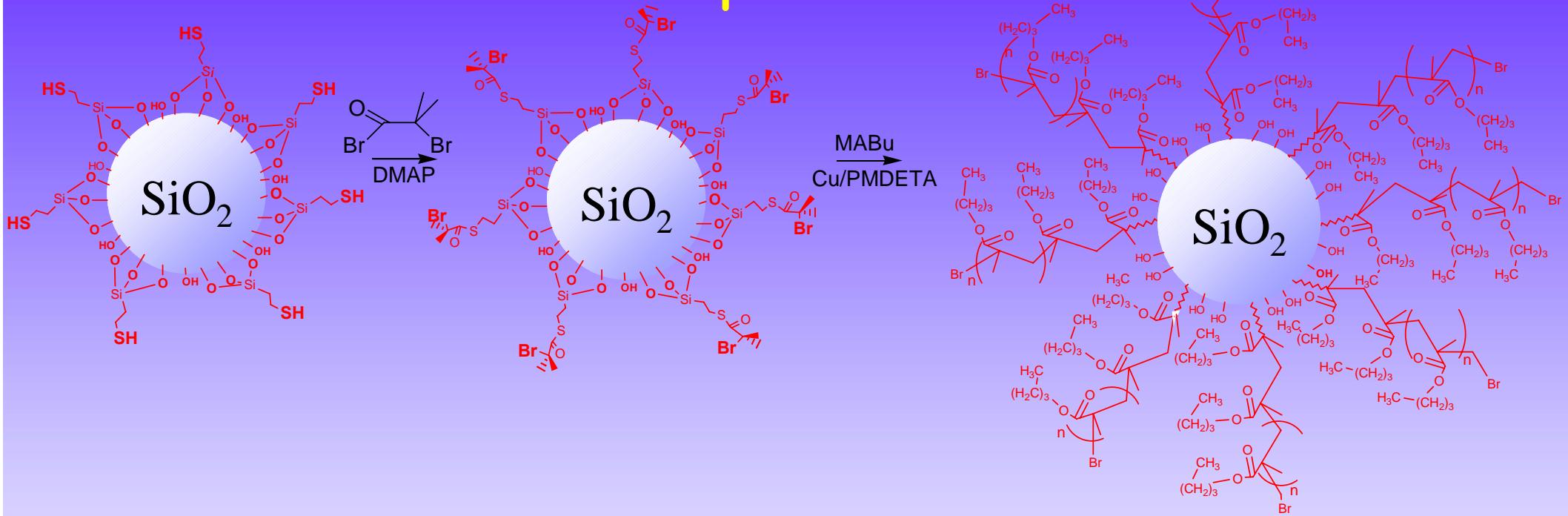


Density of chains

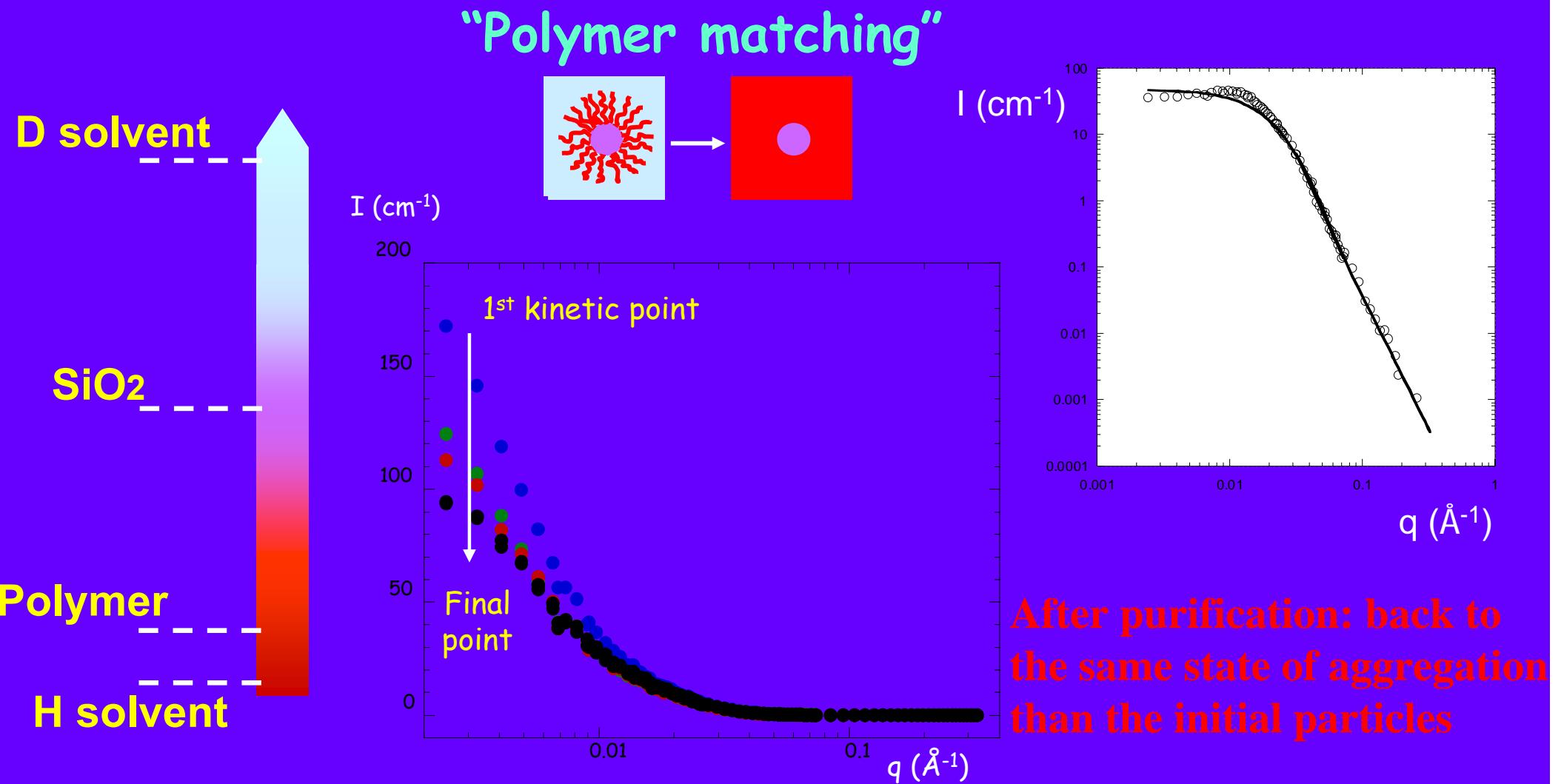
Controlled polymerization principle:



Controlled radical polymerization from silica nanoparticles



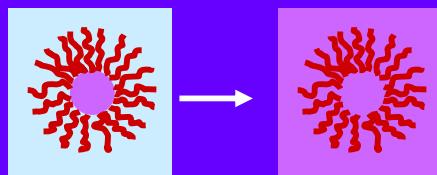
Kinetic study of the polymerization via SANS : dispersion state of particles



Desaggregation of the particles as the polymerization proceeded

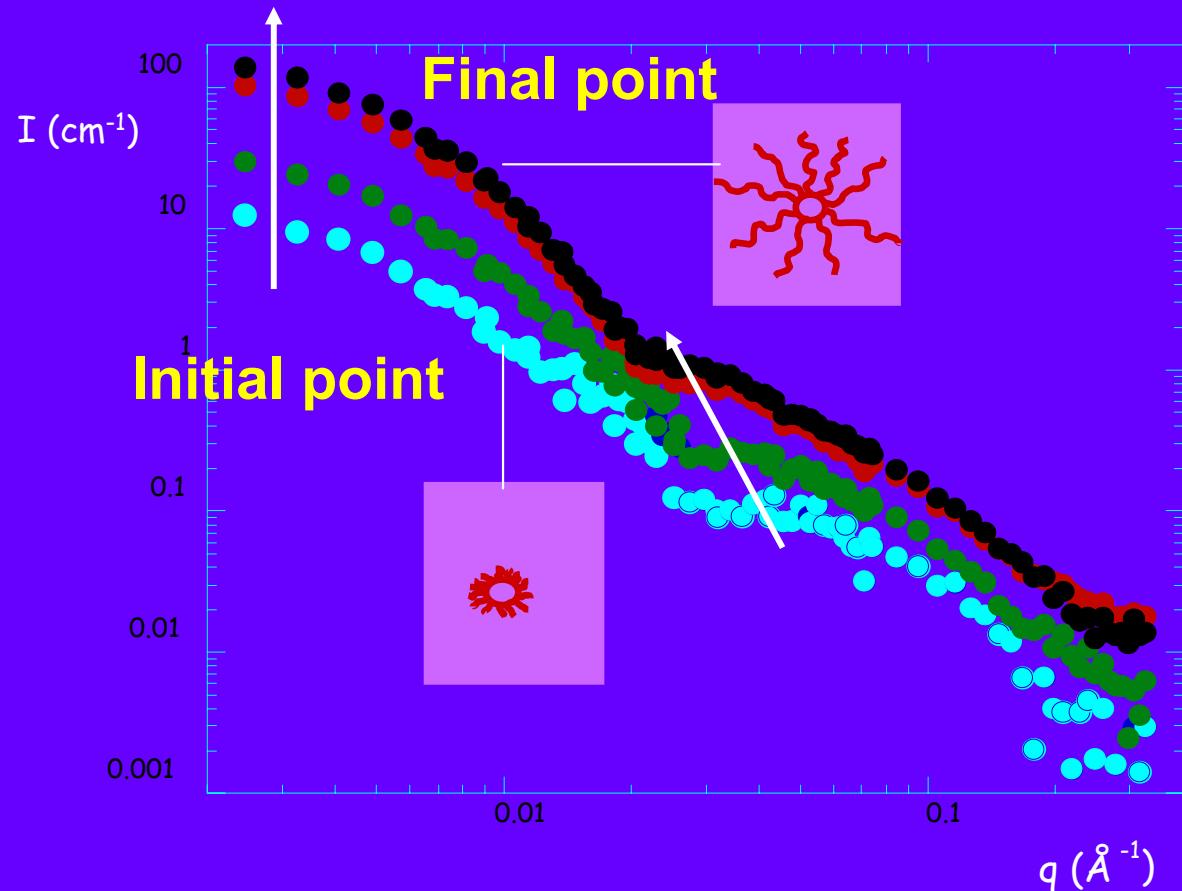
Kinetic study of the polymerization via SANS : Corona growth

“Silica matching”



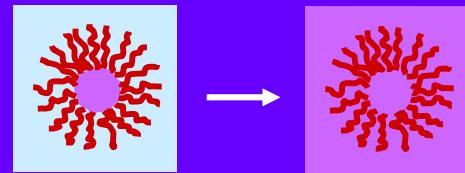
Polymerization time

- 30 min
- 60 min
- 230 min
- 420 min



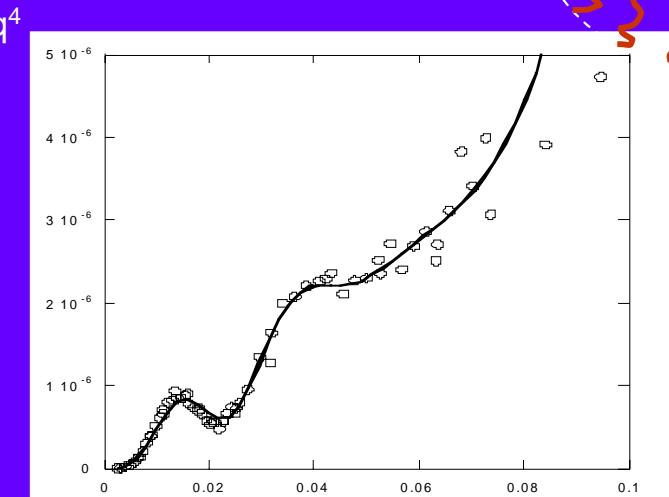
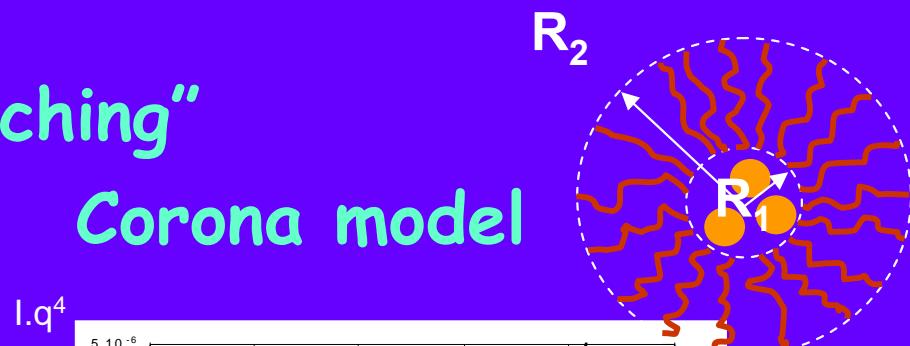
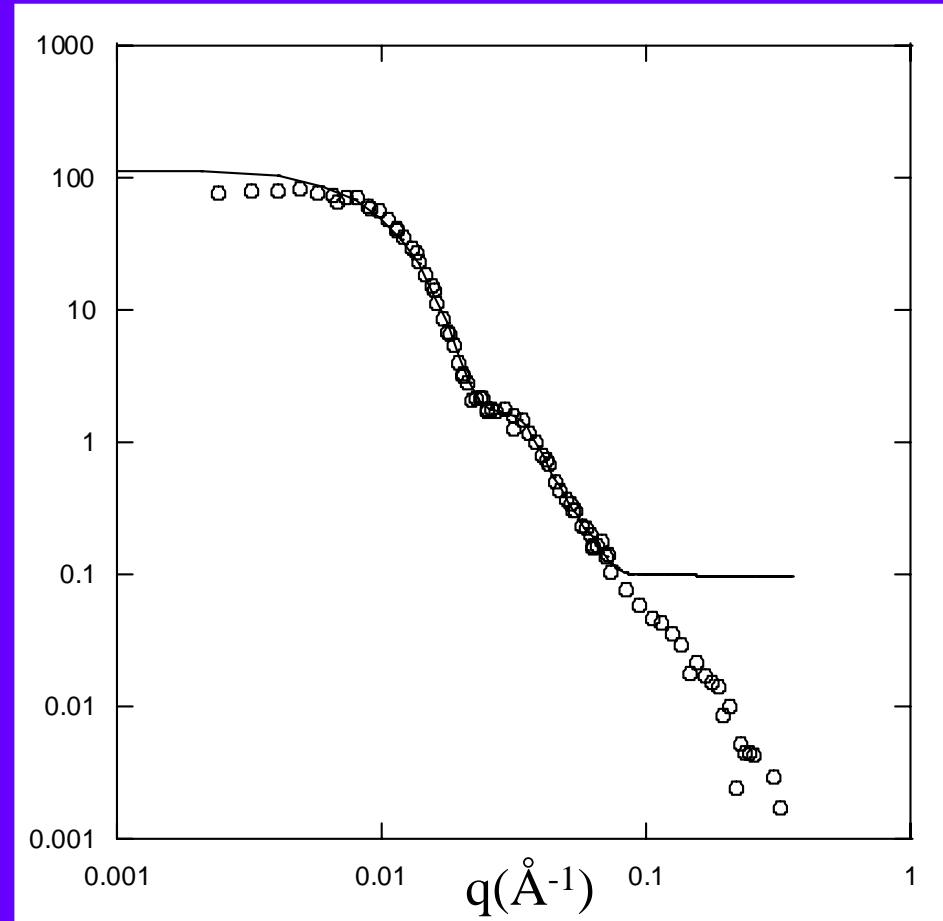
↗ of the signal at low q ↗ of the quantity of polymer
Oscillation at the intermediate q with a shift toward low q
↔ Increase of the corona size

Polymer-grafted silica nanoparticles after purification: corona characterization



“Silica matching”

Corona model



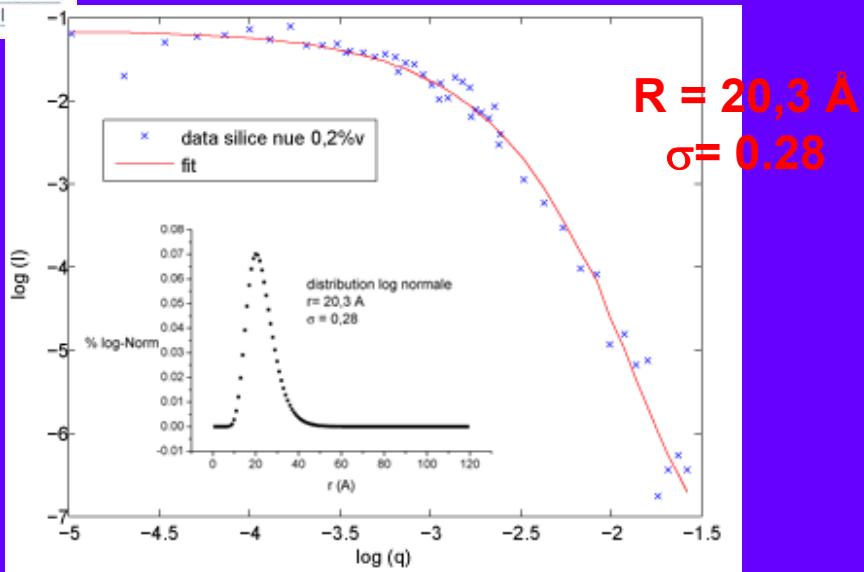
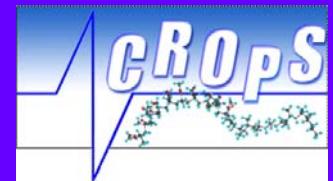
$N_{\text{agg}} = 5$
 $e \approx 70 \text{ \AA}$ with 30% of polymer

$\rho_{\text{core}} = \rho_{\text{solvant}}$

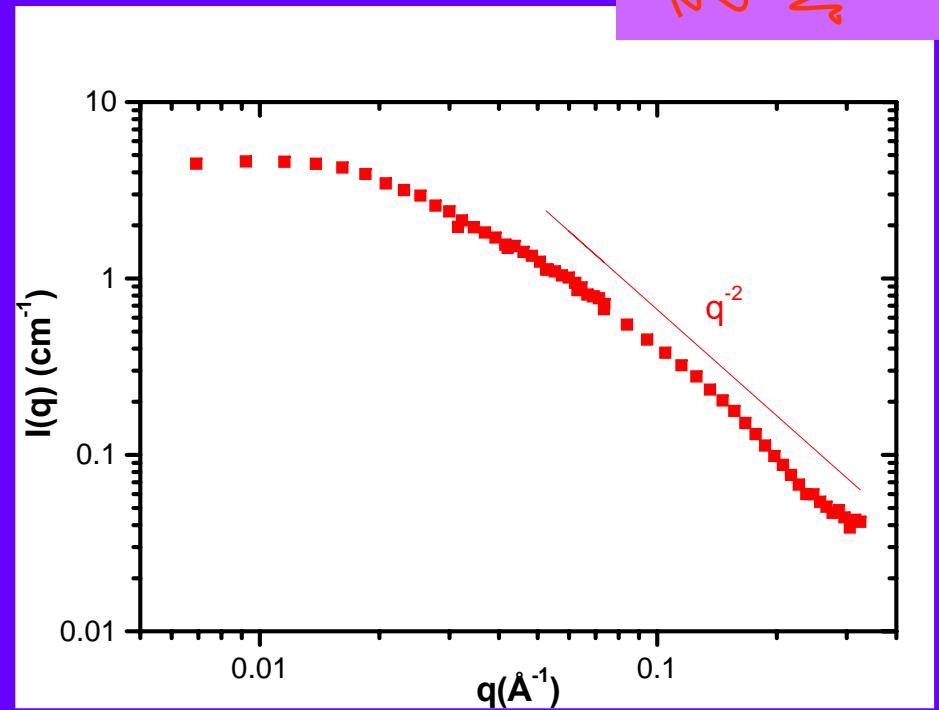
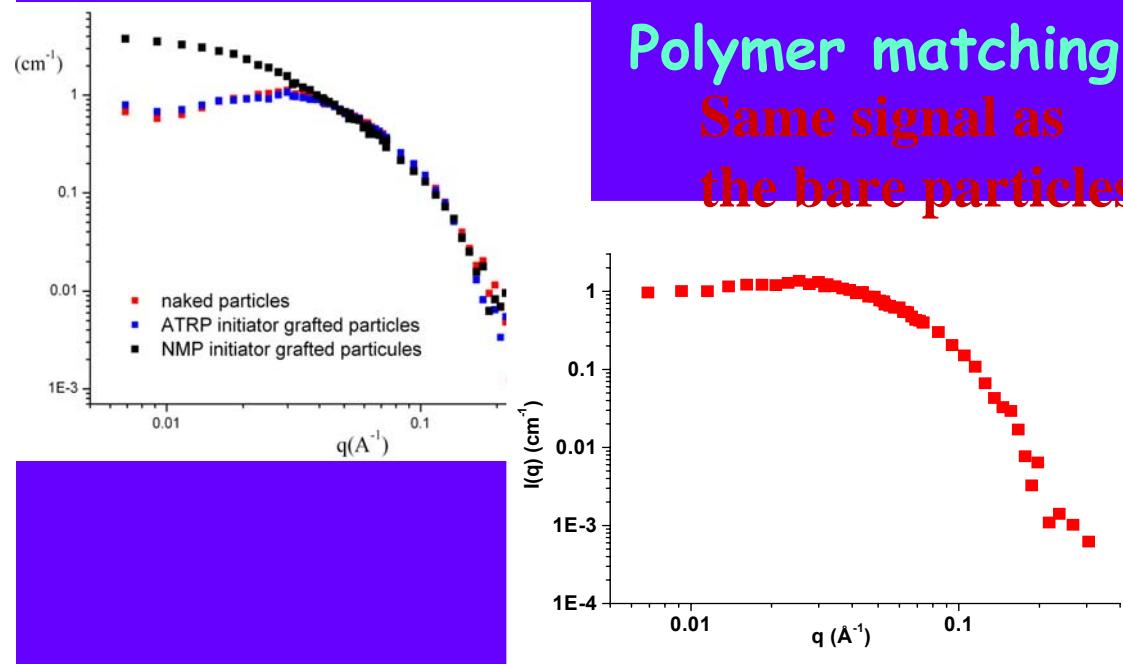
→ $V_{\text{corona}} = 1.28 \cdot 10^{-17} \text{ cm}^3$
 $M_{\text{corona}} = 4.0 \cdot 10^{-18} \text{ g}$
With $M_w = 12000 \text{ g/mol}$

→ 198 chains per particle

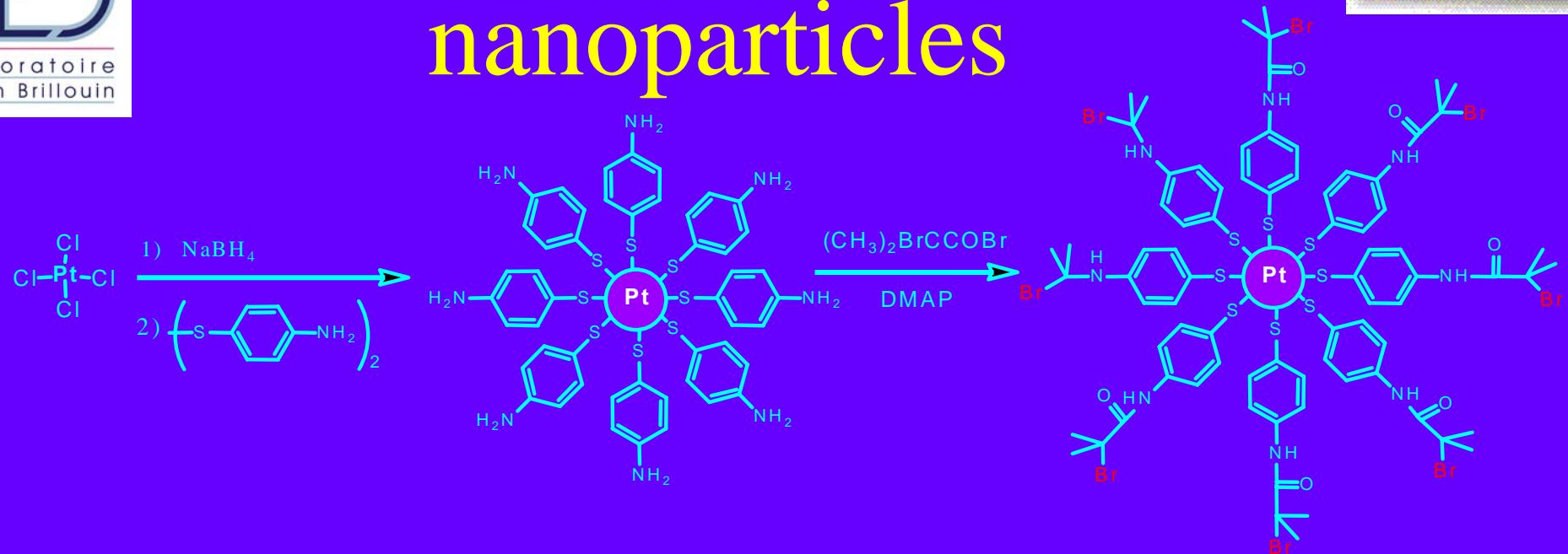
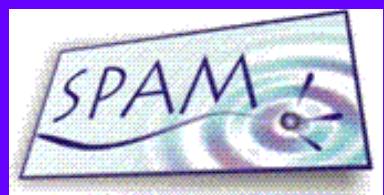
Grafted silica nanoparticles in aqueous phase*



Polymer signal in
Silica matching



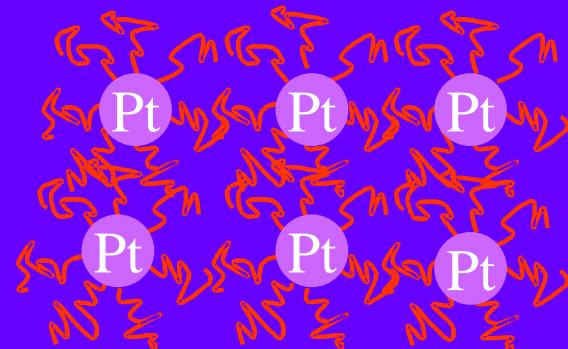
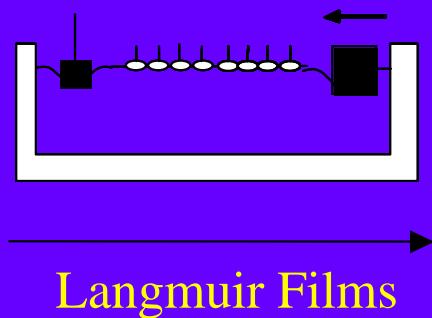
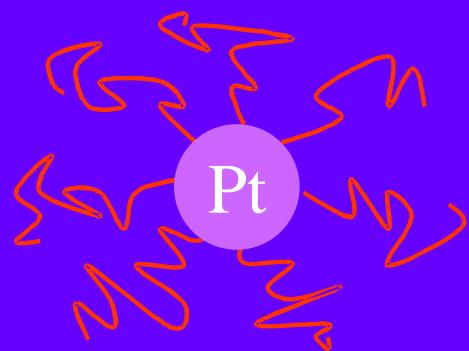
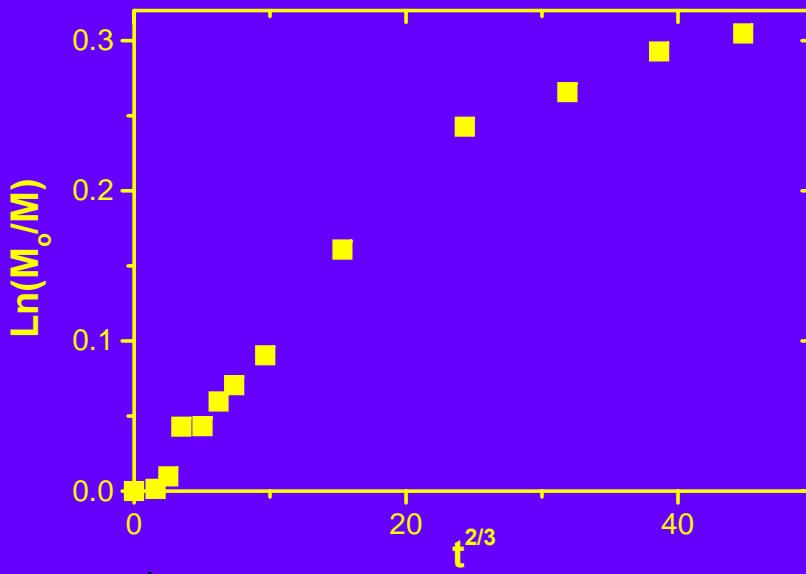
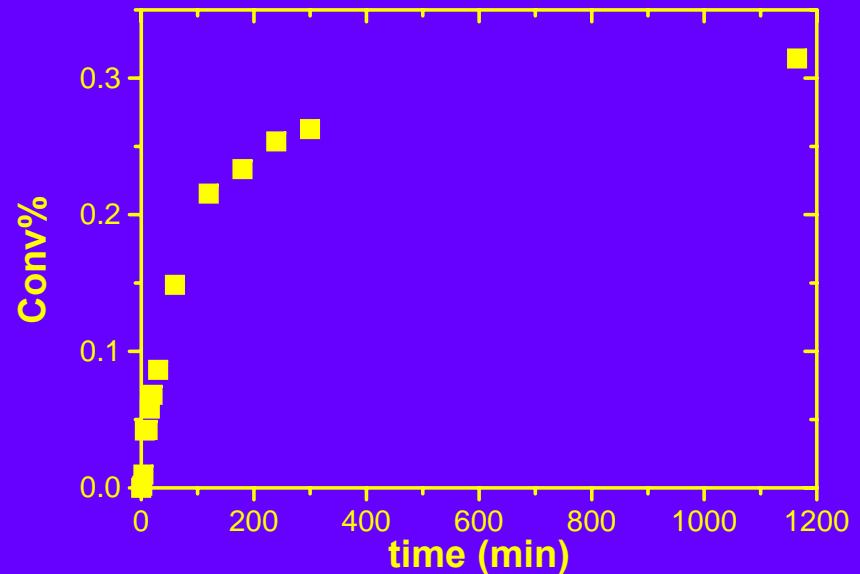
ATRP from platinum nanoparticles



Sample	Theoretical Mn	Reaction time	Conv. %	Polymerization batch	% Polymer	T_g (°C)
PtMAB7-1	100000	455	19.2	PtPMAB7	88.0	34.2
PtMAB7-2	100000	113	15.3	PtPMAB7	83.1	29.5
PtMAB8-1	100000	334	15.4	PtPMAB8	83.6	36.2
PtMAB8-2	100000	40	10.5	PtPMAB8	80.7	-

- (1) H. Perez et al. *Chem. Mater.* 1999, 11, 3460-3463. (3) G. Carrot, H. Perez *Polym. Prep.* 2006, 827
 (2) H. Perez et al. *Chem. Mater.* 2001, 13, 1512. (4) G. Carrot, F. Gal, H. Perez, *Langmuir*, in Press.

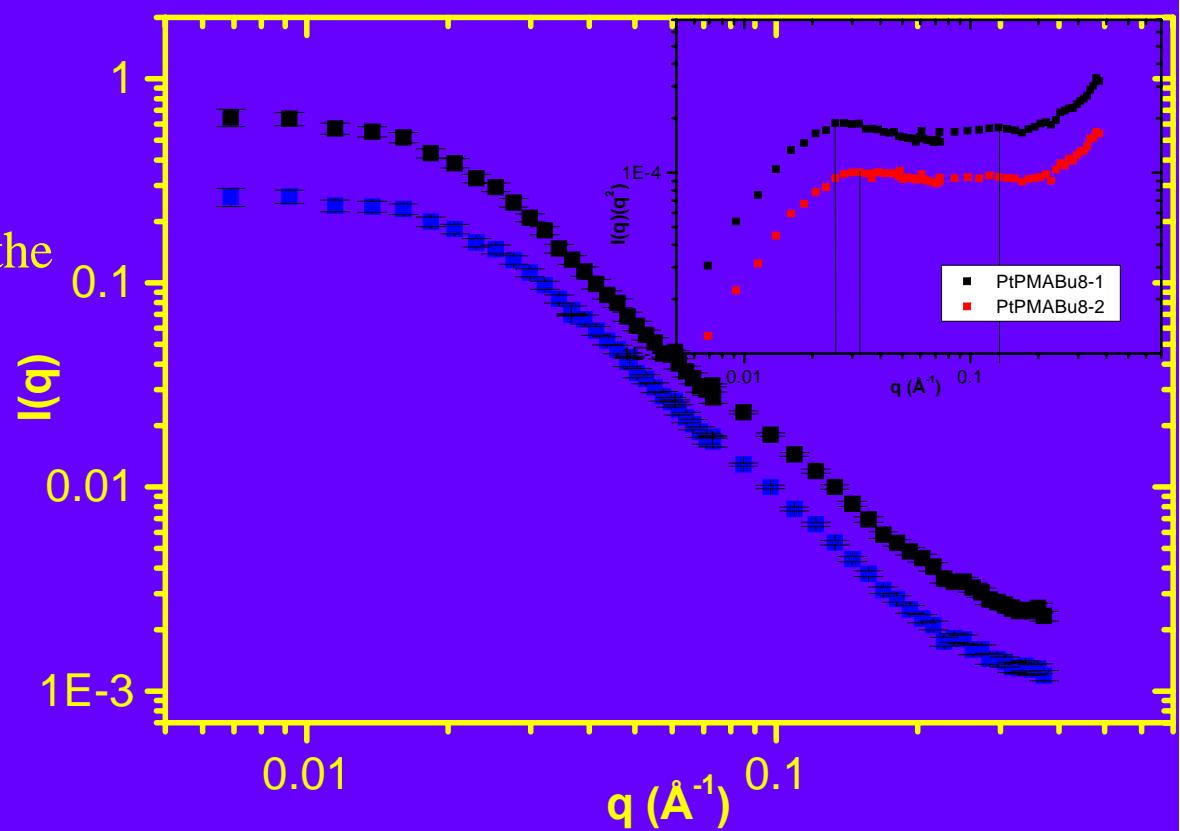
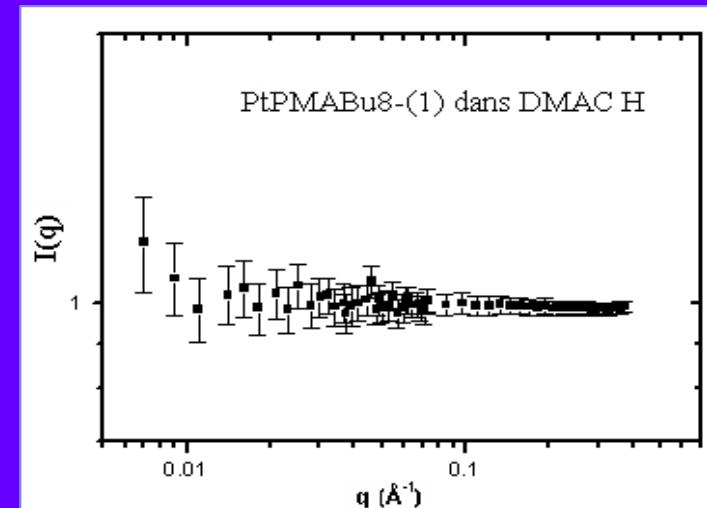
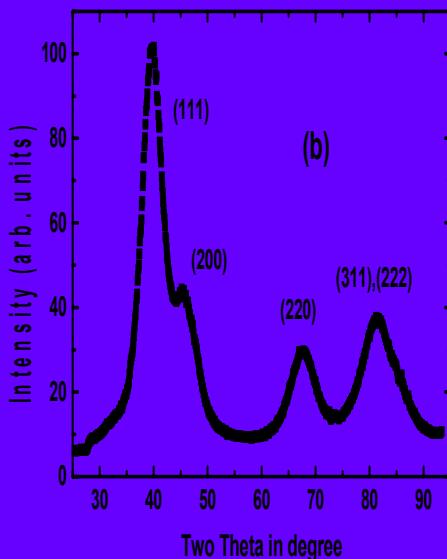
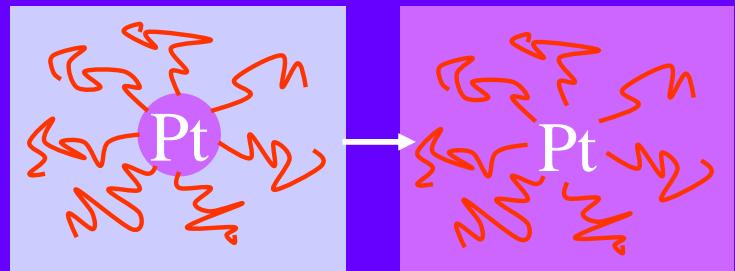
Surface polymerizations from platinum nanoparticles *



Study of the nano-objects in solution via SANS

“Polymer matching”

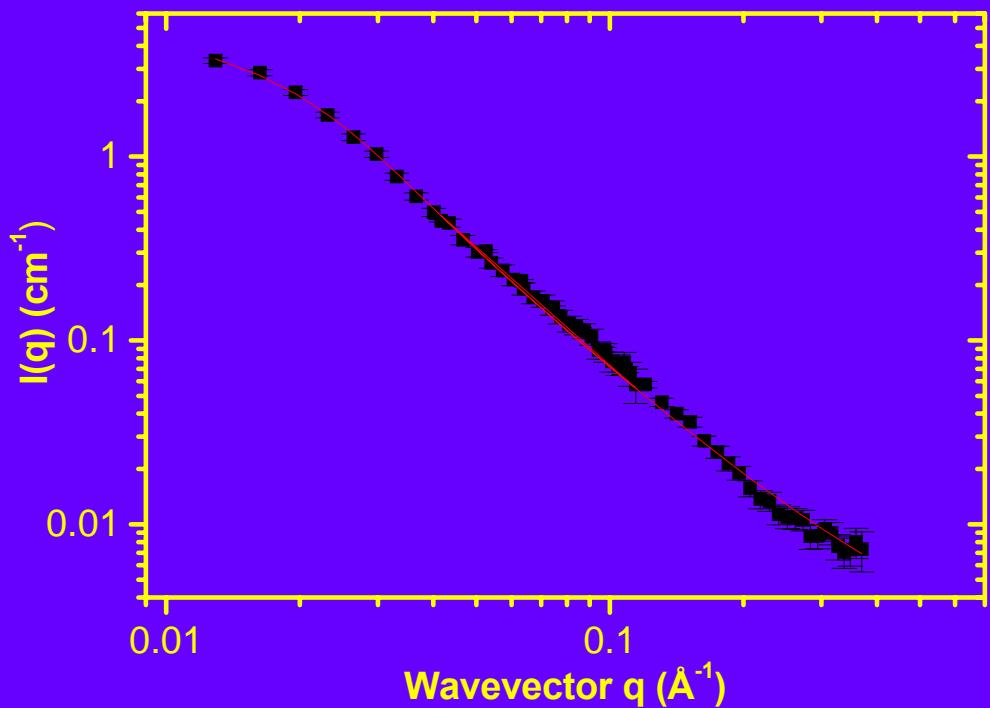
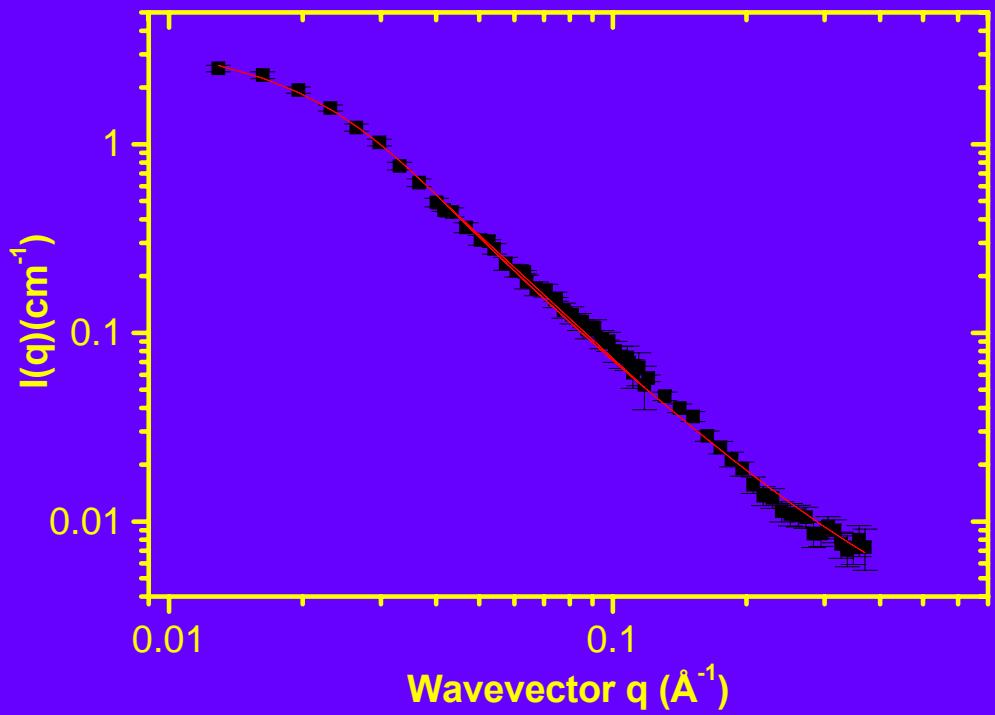
“Platinum matching”



Radius of giration obtained by the fit of the signal in the Guinier regime

Samples	Rg (Å)
PtPMA7-(1) p=20 %	95
PtPMA7-(2) p = 15.4 %	75
PtPMA8-(1) p = 15.4 %	68
PtPMA8-(2) p =10.5 %	57

Fit of the spectra with a Star model

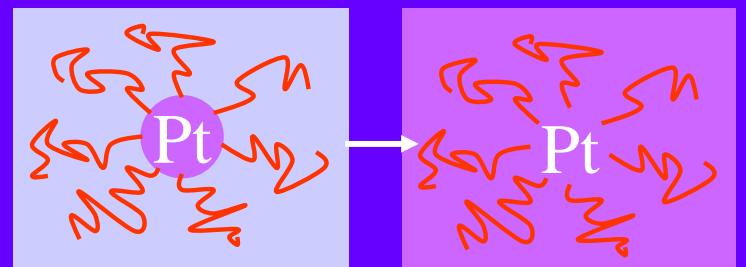


Zimm-Stockmayer-Benoît model:

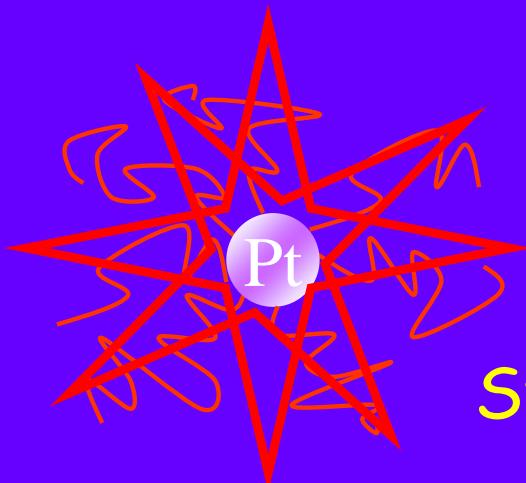
$$F(x) = \left[\frac{2}{x^2} \left(\frac{f}{2} (f-1) \exp\left(-2\frac{x}{f}\right) - f(f-2) \exp\left(-\frac{x}{f}\right) + x + \frac{f}{2} (f-3) \right) \right]$$

$$x = (qR_g^L)^2 = (qR_g^B)^2 f = (qR_g^E)^2 \frac{f^2}{(3f-1)}$$

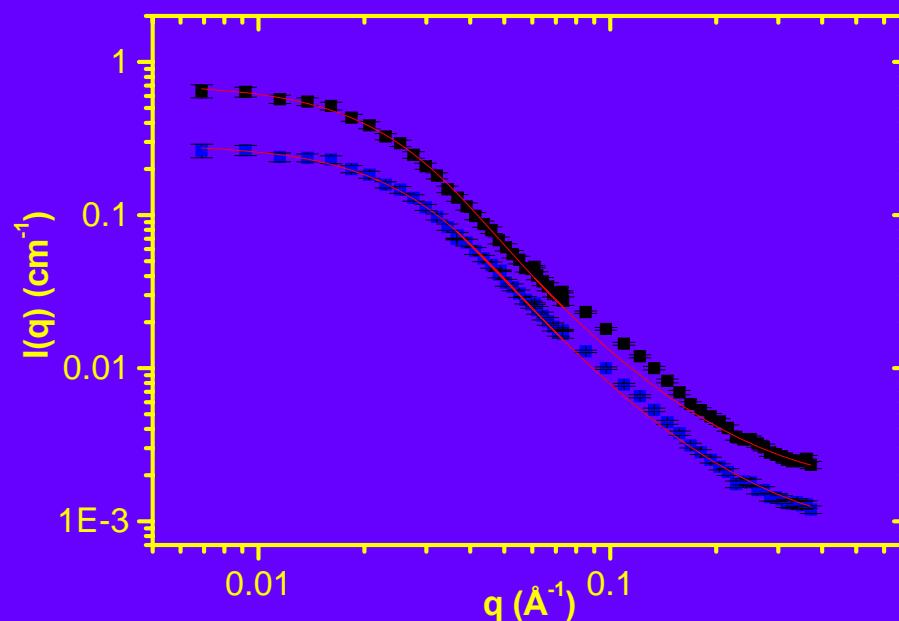
“Platinum matching”



Determination of the number of chains and molecular weight

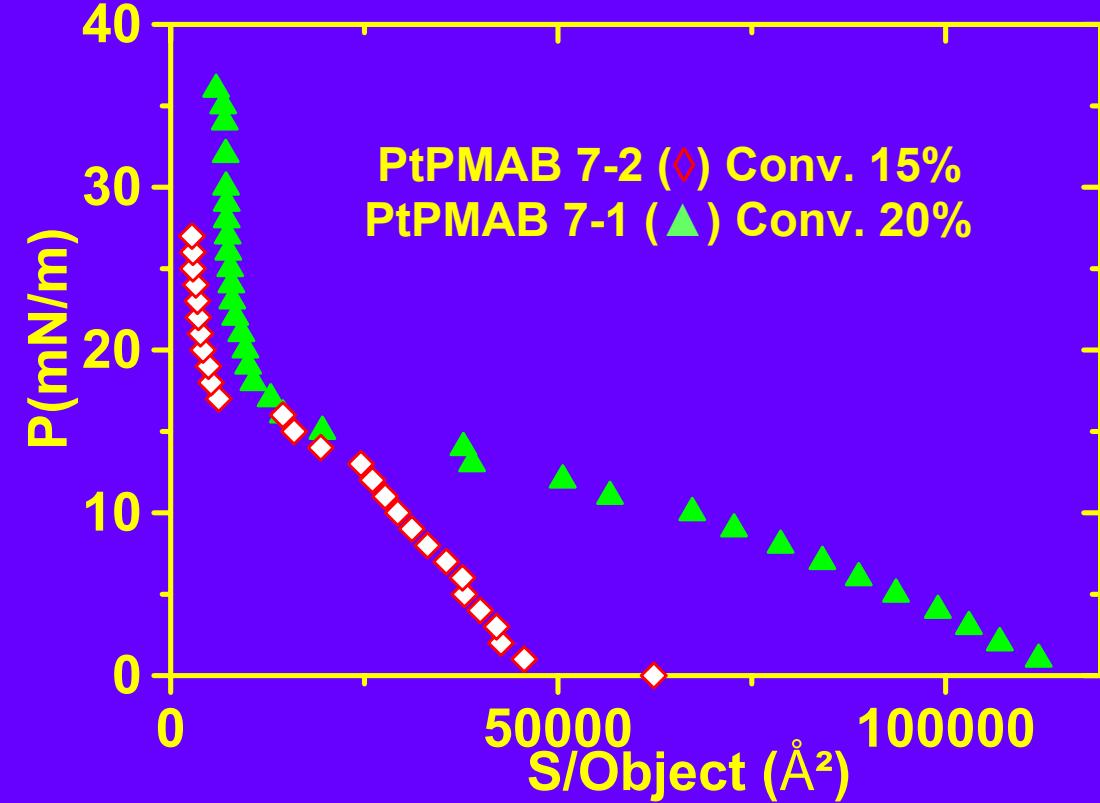
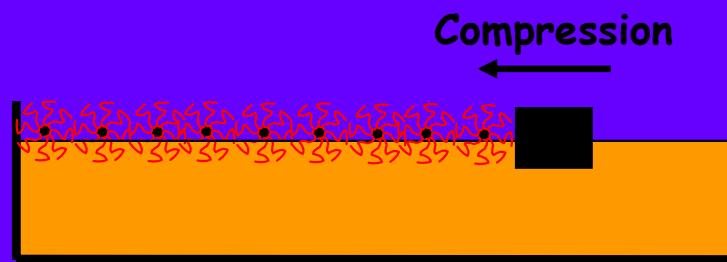


Star model



Sample	Number of branche, f	R_g gaussienne R_g^L (Å)	R_g branche R_g^B (Å)	Rg Star, R_g^E (Å)	Number of chains per nm ²	Mn of 1 branche, M_B (g.mol ⁻¹)	Mn from TGA (g.mol ⁻¹)
PtPMA7-1	5.3	122	53	85.8	0.42	12055	13222
PtPMA7-2	5.2	102	44.3	72.33	0.42	8600	11000
PtPMA8-1	8	119	42.4	70.35	0.63	7723	8558
PtPMA8-2	7	97	36.9	60.8	0.55	5844	7940

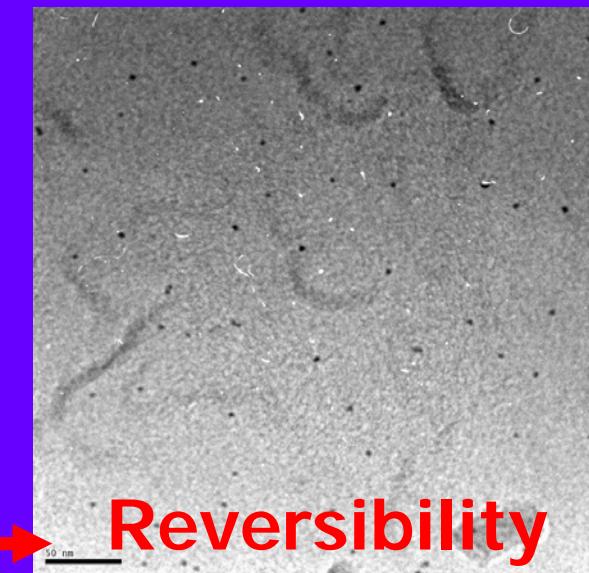
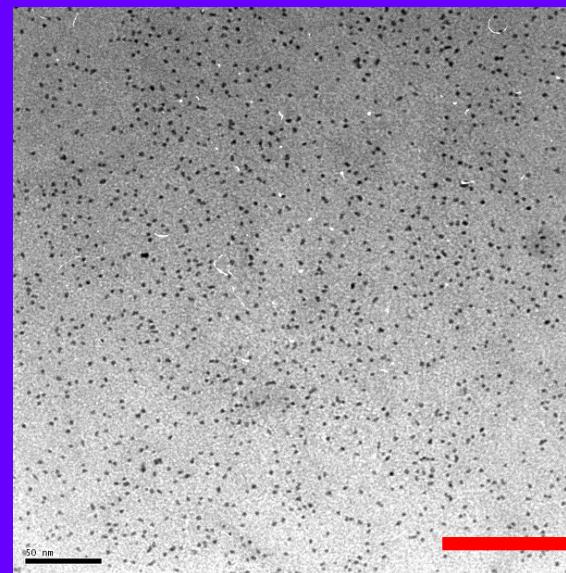
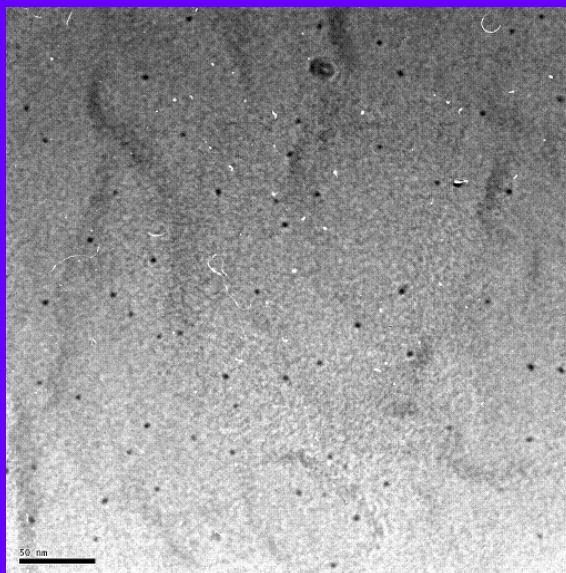
Langmuir Films-Compression Isotherms



Compression at 2 mN/m

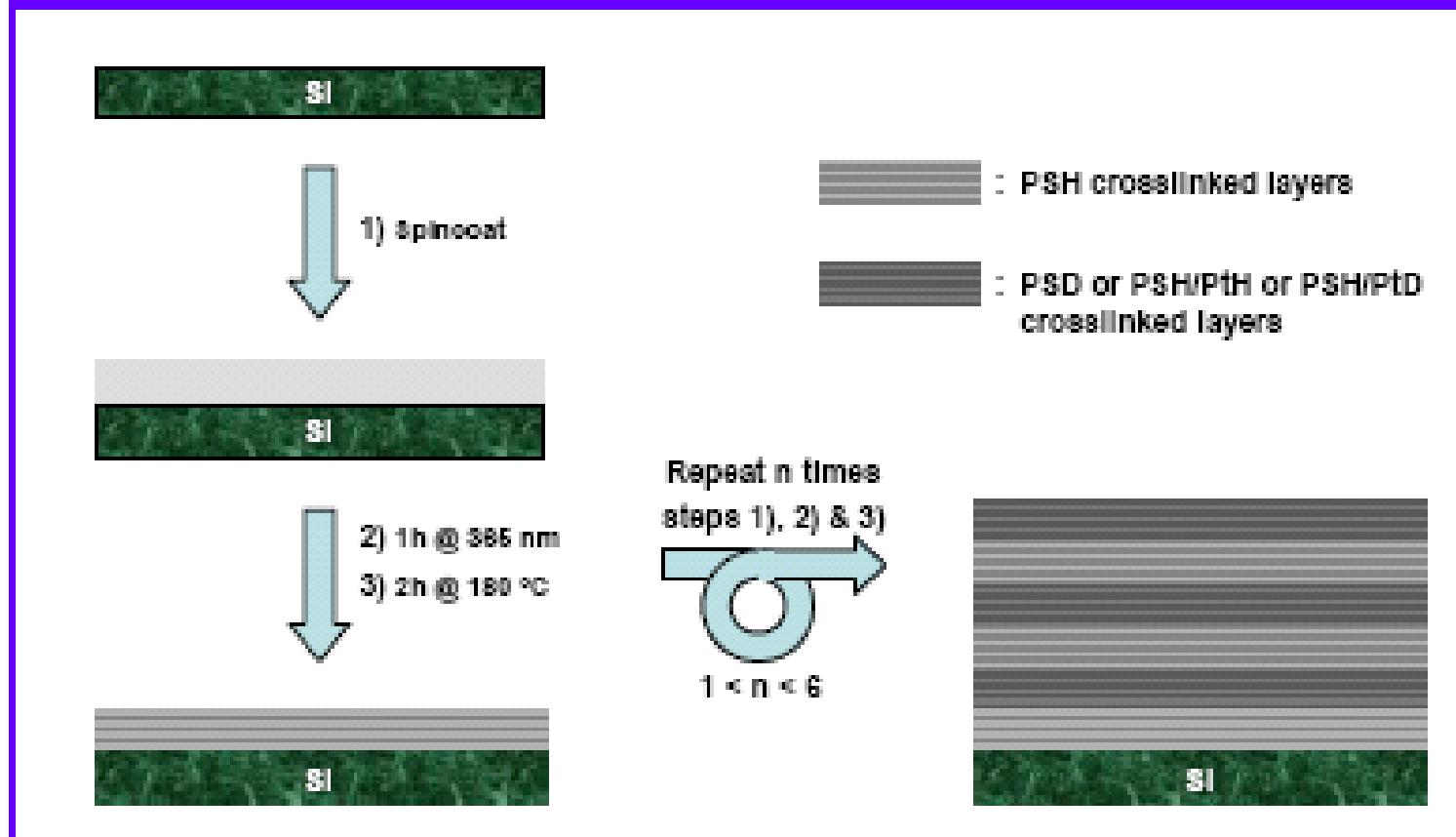
26 mN/m

Decompression at 2mN/m



3D-Organization of particles in 2D films

Dispersion of PS-g-Pt NP in cross-linked films via spin-coating and N₃ reactions



cross-linked
multilayers
(with or without Pt)

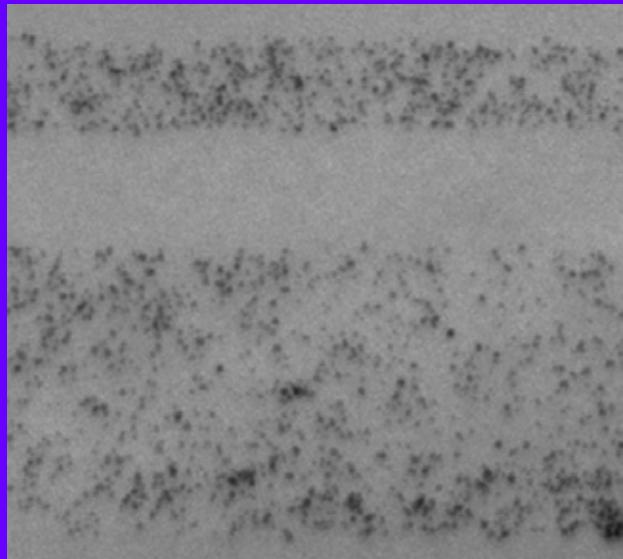
Alternating H and D

Neutron reflectivity

« 3D » cross-linked hybrid multilayer films

ANR 2007 Multiclick

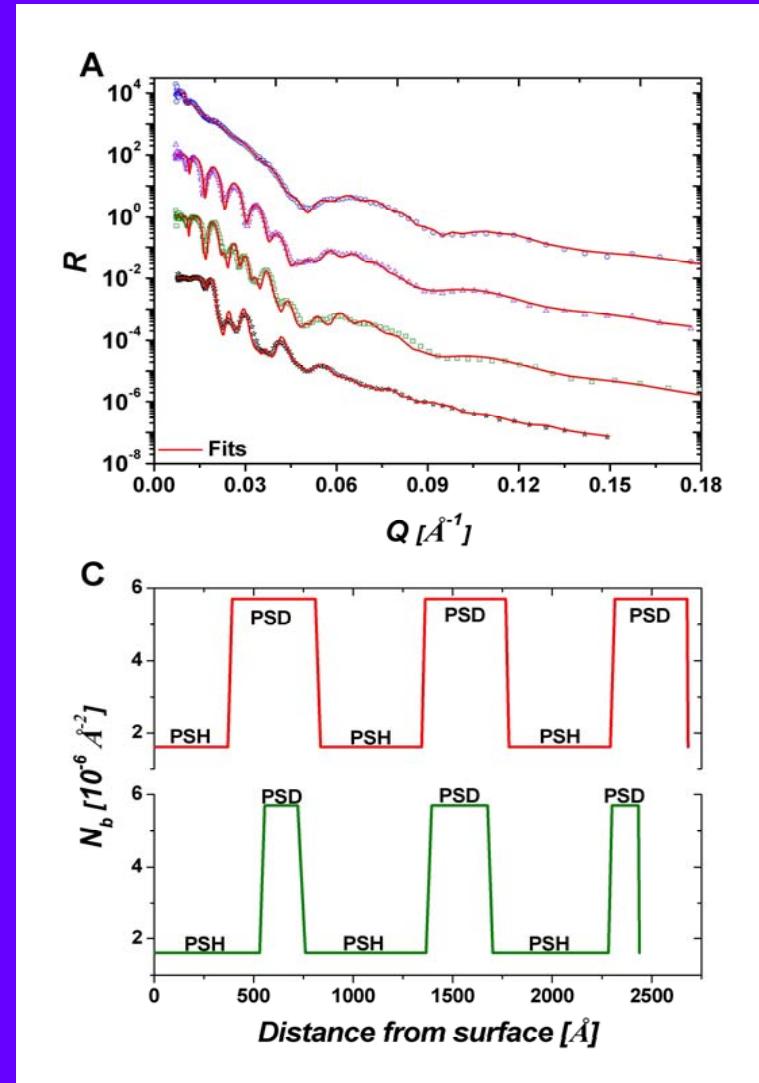
Neutron reflectivity



No interdiffusion
between layers

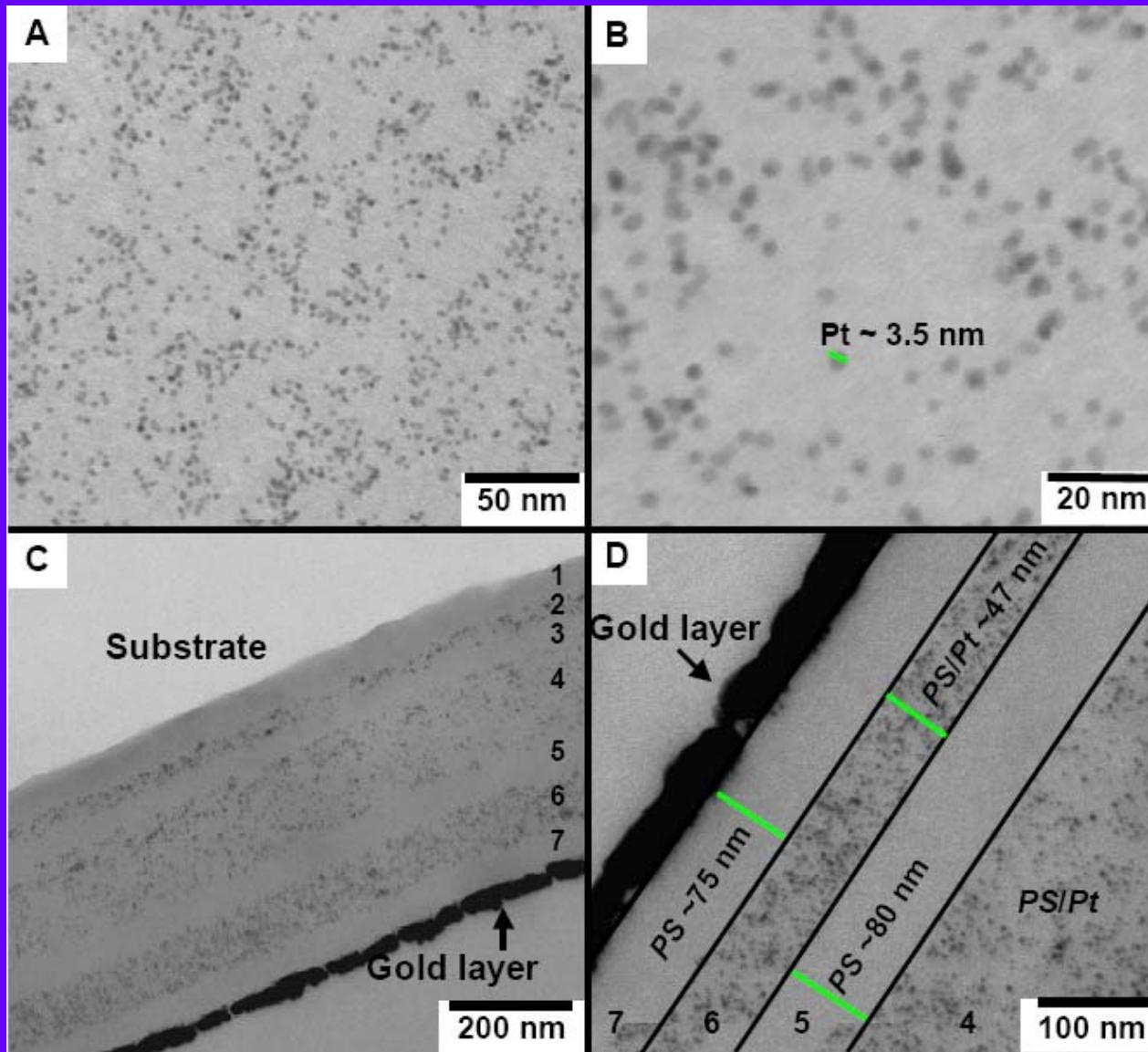


Alternated polymer
layers using H and D



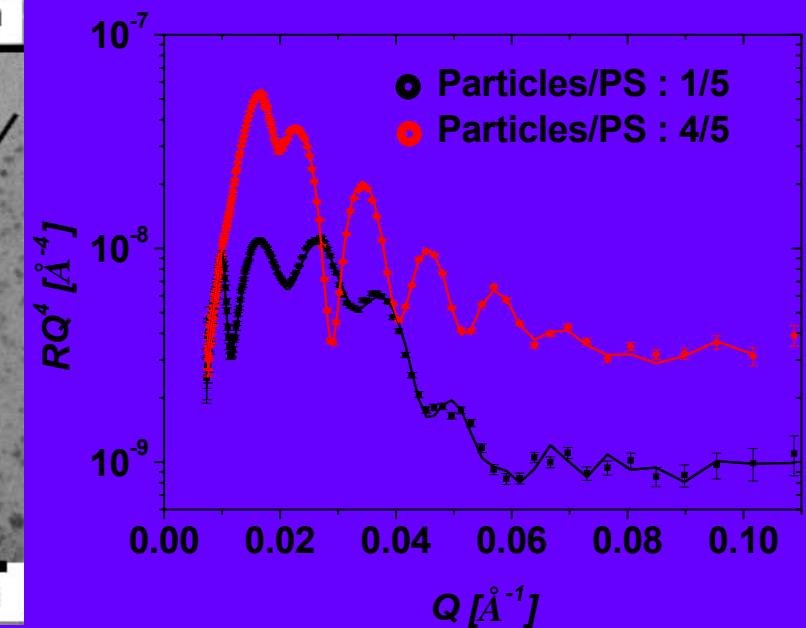
« 3D » multilayers films

ANR 2007 Multiclick



Neutron reflectivity

Dispersed Pt NP



Thanks



H. Perez, CEA, SPAM-DRECAM
François Gal, PhD student LLB



J. Oberdisse, Université de Montpellier
A. El Harrak, PhD student LLB,
J. Jestin, CNRS LLB, **F. Boué**, CNRS LLB



F. Cousin, CEA LLB

E. Drockenmuller, Université de Lyon

S. Al-Akhrass, Université de Lyon

