

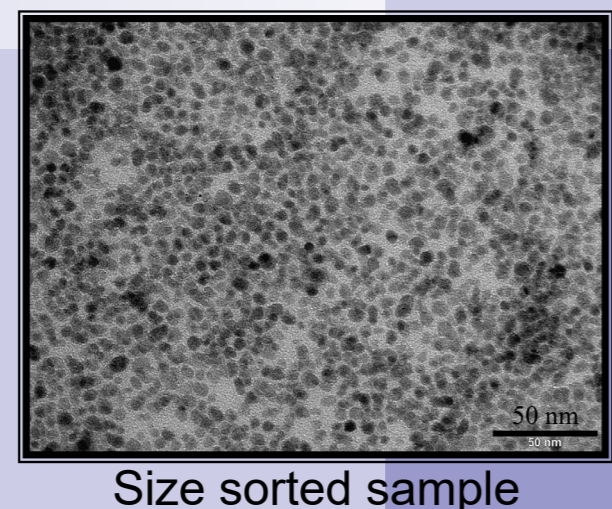
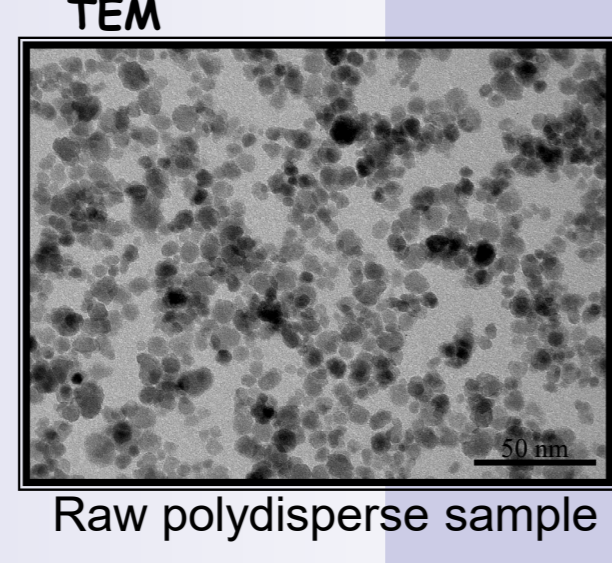
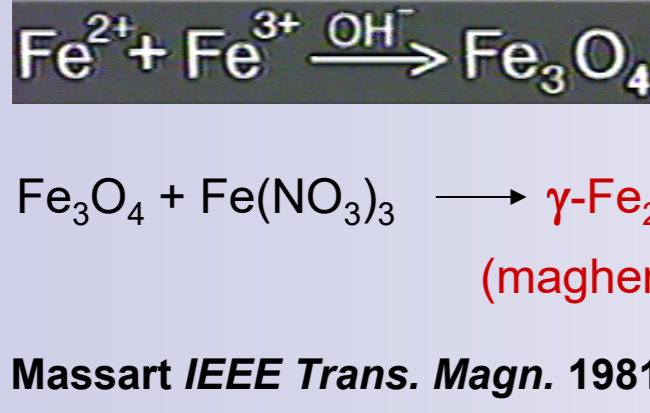
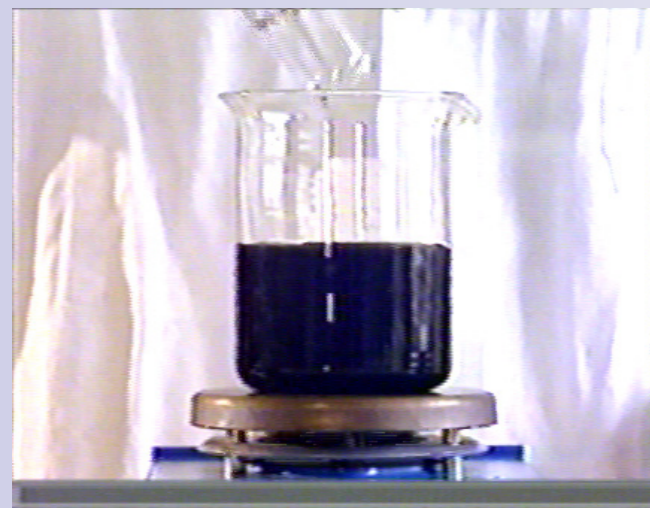
Probing the internal structure of magnetic nanocomposites – thermo-sensitive gels and lamellar films – respectively by small angle neutron scattering and neutron reflectivity

Siham Douadi-Masrouki¹, Delphine El kharrat¹, **Olivier Sandre**¹, Maud Save², Bernadette Charleux² and Valérie Cabuil¹

¹LI2C UMR7612, ²LCP UMR76120, Centre National de la Recherche Scientifique / Université Pierre et Marie Curie - 4 place Jussieu case 51 75252 Paris Cedex 5 France

Magnetic nanoparticles (NPs) as building blocks

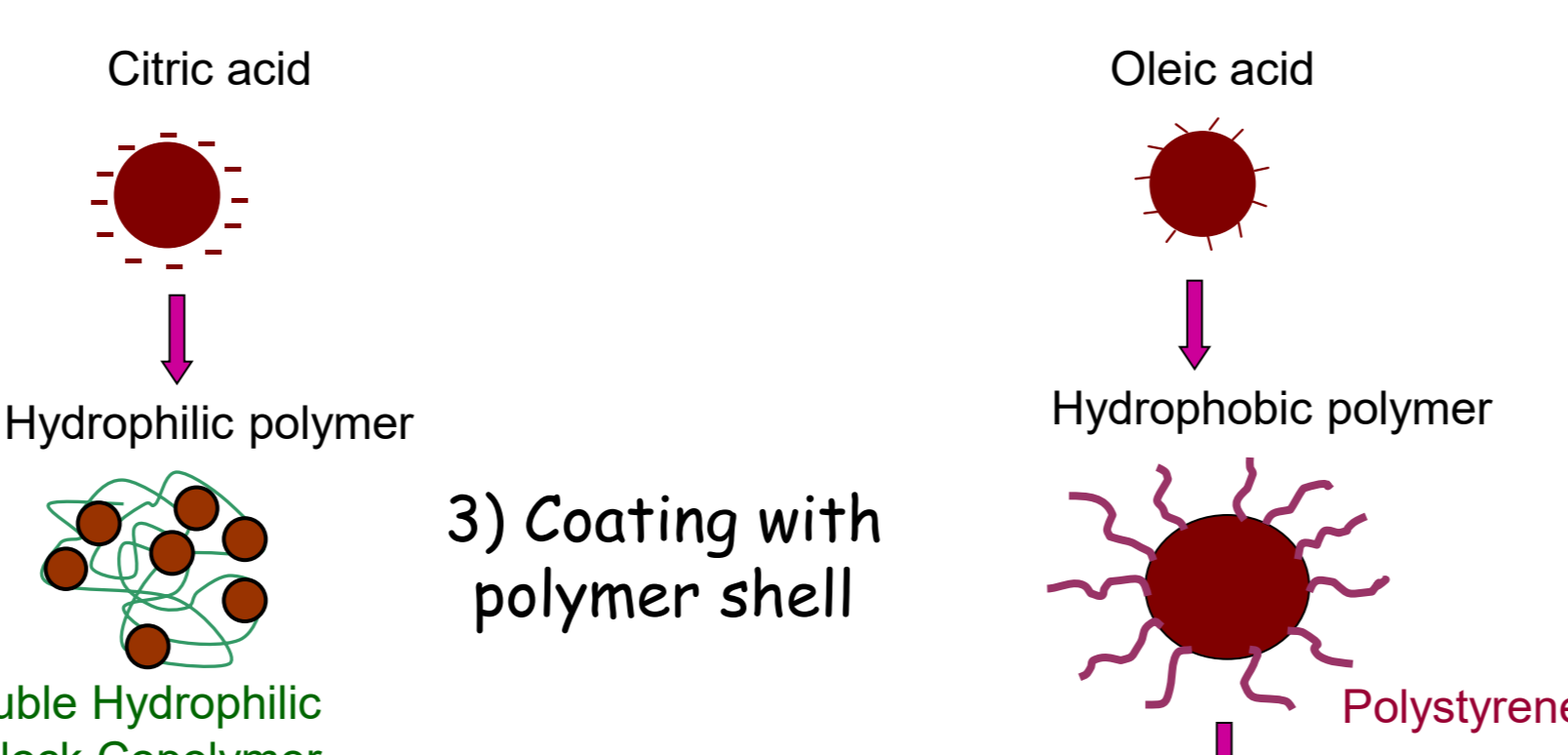
1) Synthesis



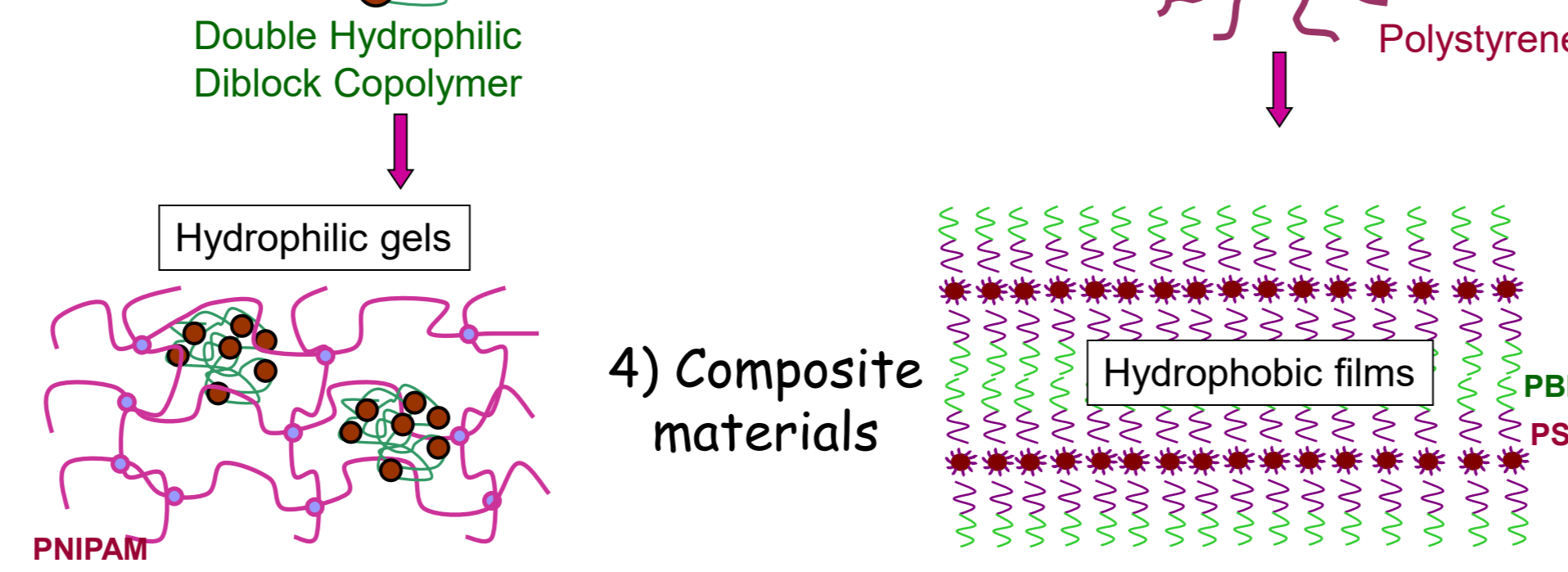
We study nanocomposites consisting of the same iron oxide $\gamma-Fe_2O_3$ nanoparticles embedded in polymer matrices:

- I) a **gel matrix** exhibiting a swelling transition triggered by temperature;
 - II) a **lamellar matrix** based on the self-assembly of a symmetrical diblock copolymer.
- We use both neutron scattering & reflectivity techniques to probe the local structure at the mesoscopic scale.

2) Grafting of thin ligand layer



3) Coating with polymer shell

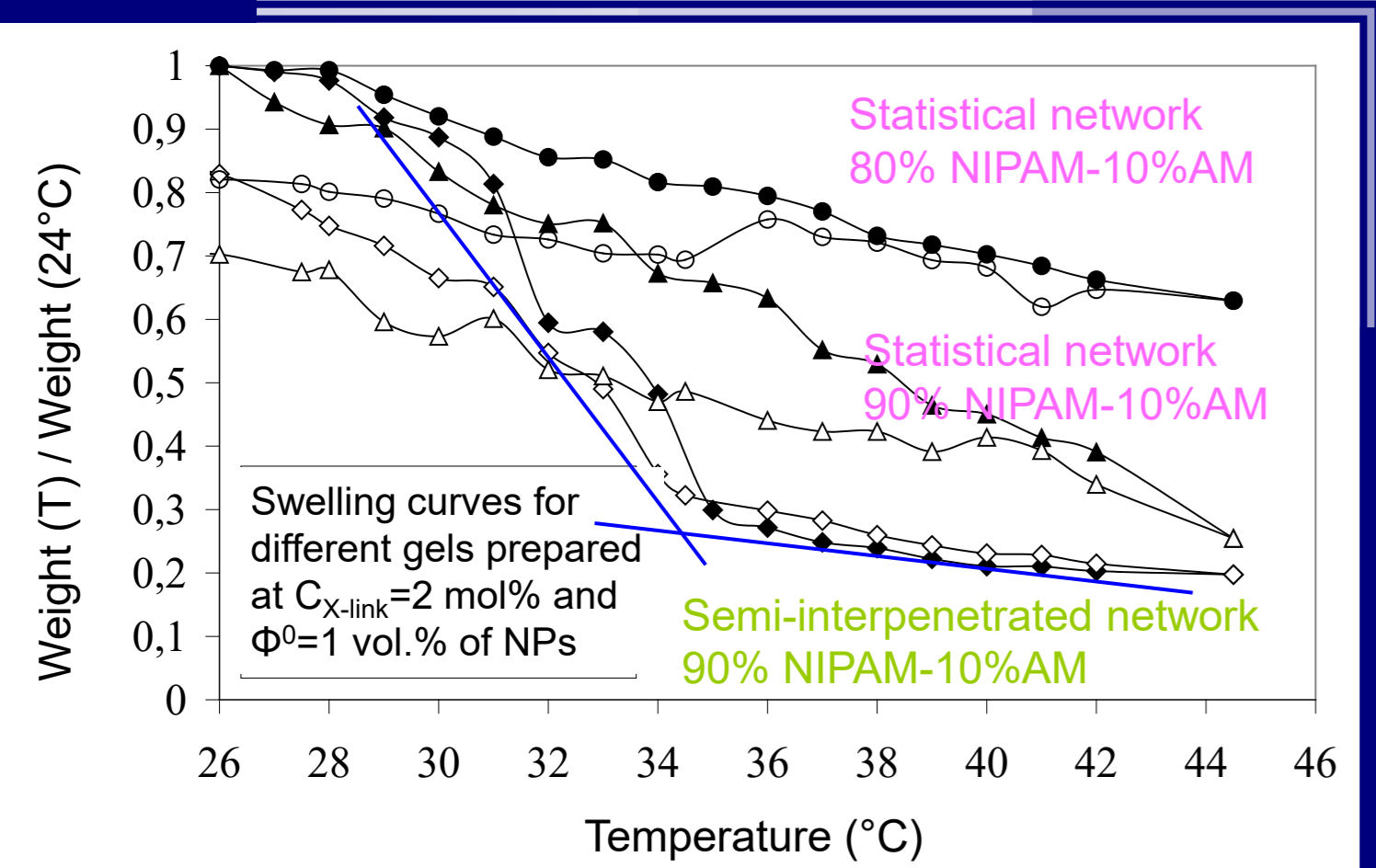
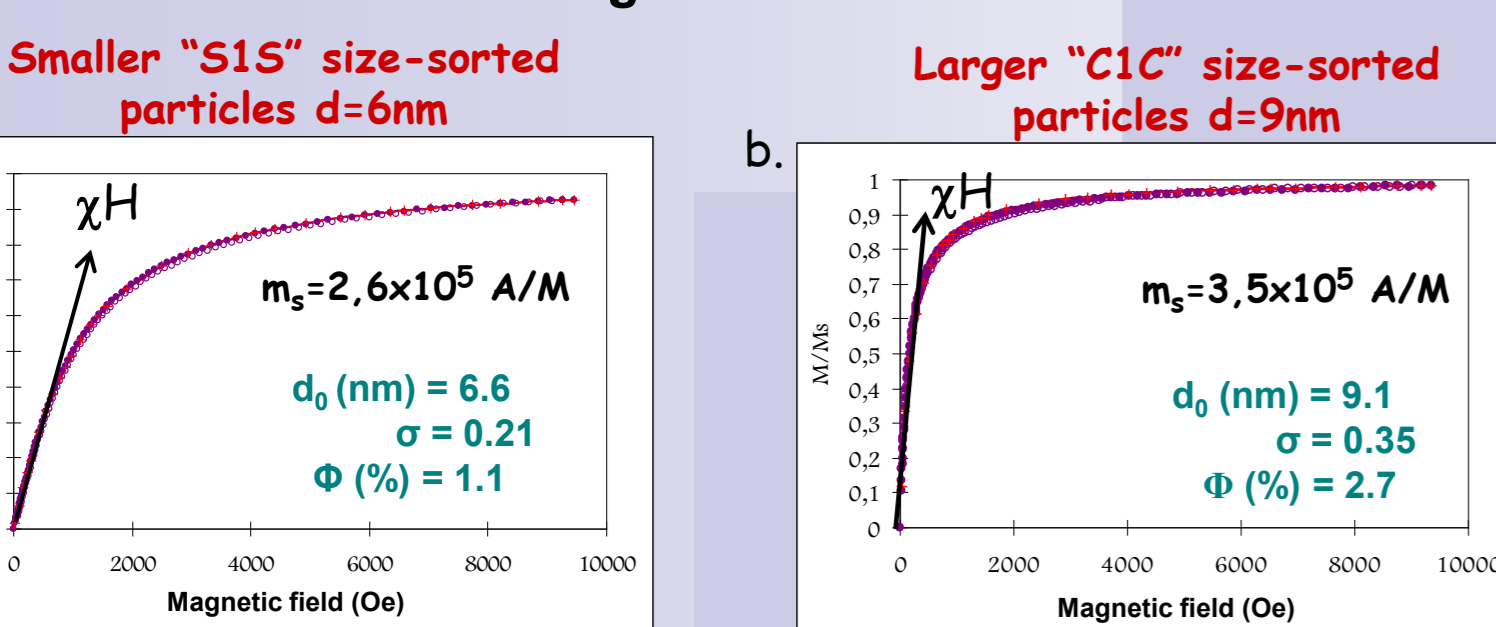


4) Composite materials

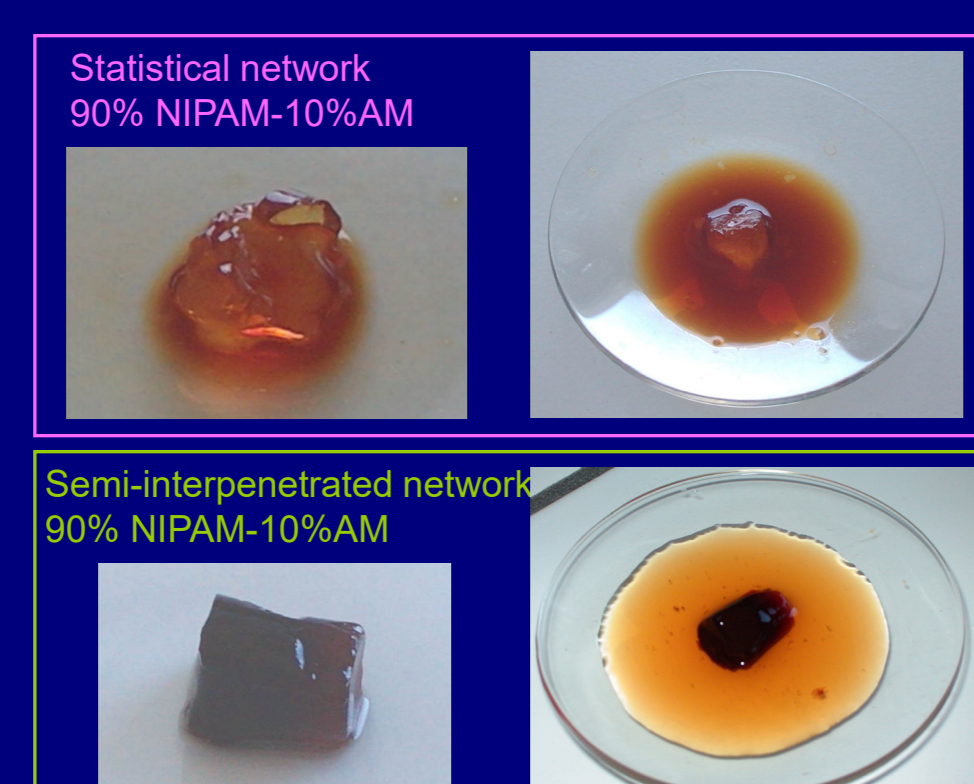
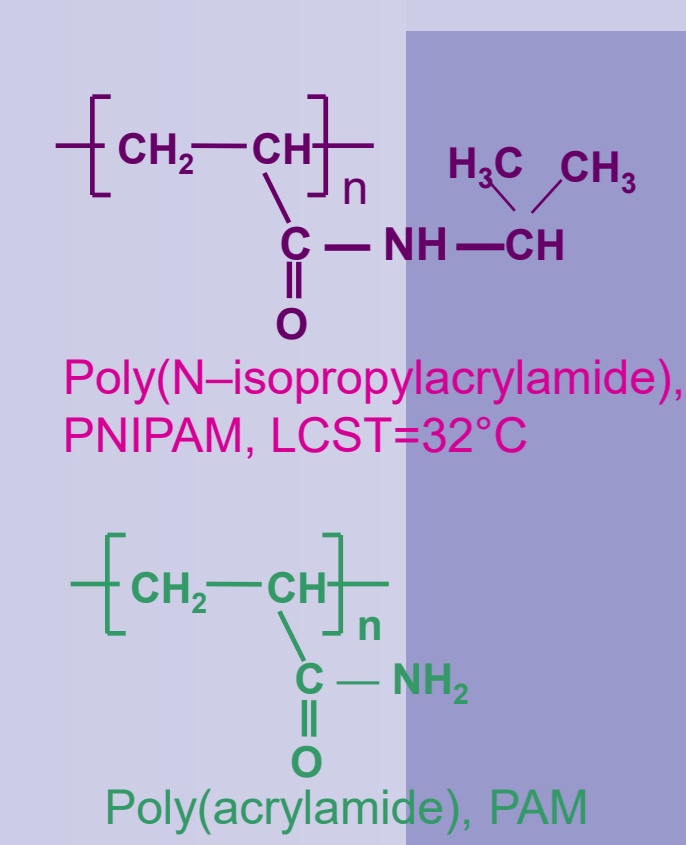


Superparamagnetic behavior

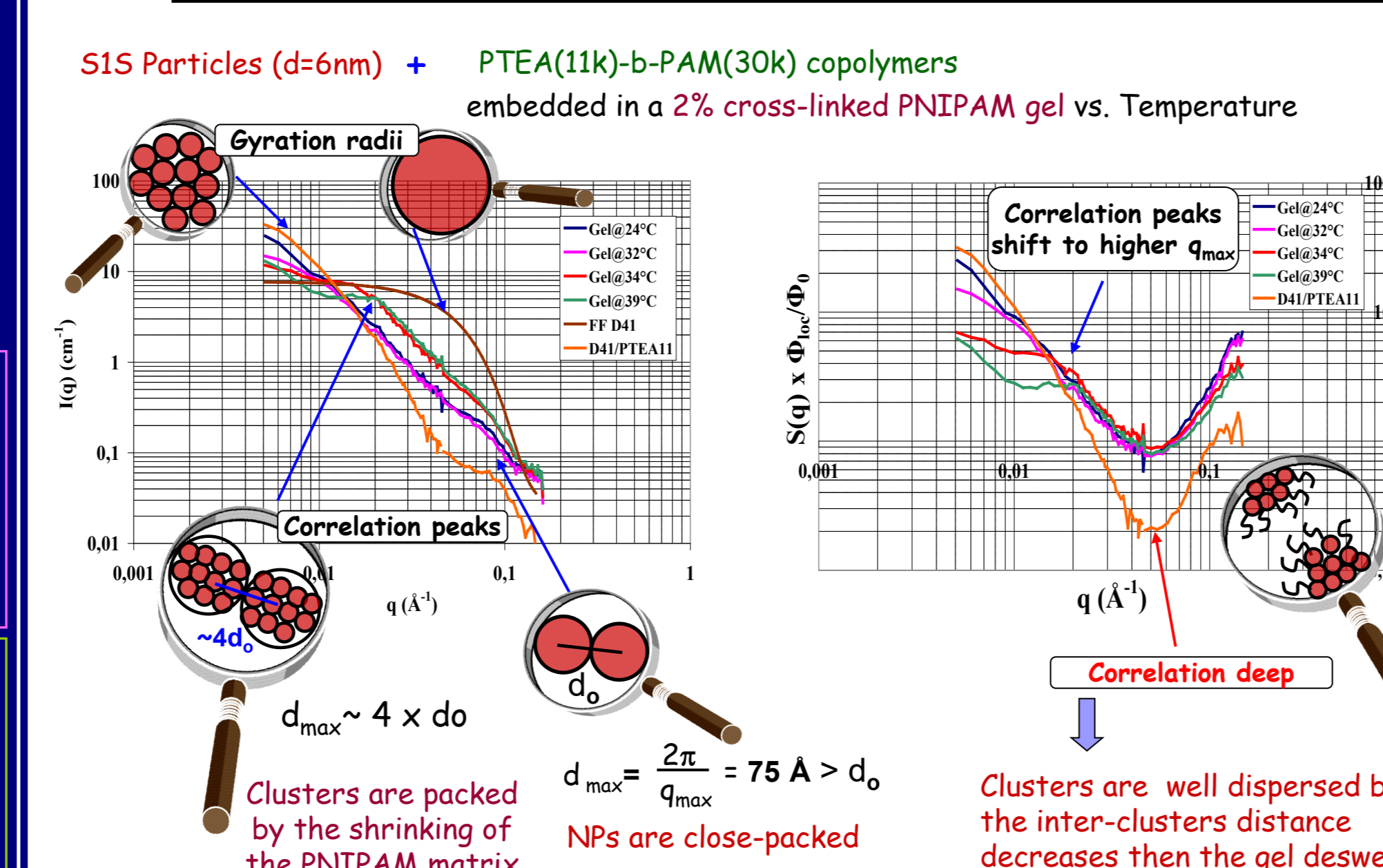
Magnetization normalized by its saturation value $M_s = m_s \Phi$ follows Langevin's law



I) Thermo-sensitive PNIPAM gels doped with magnetic NPs

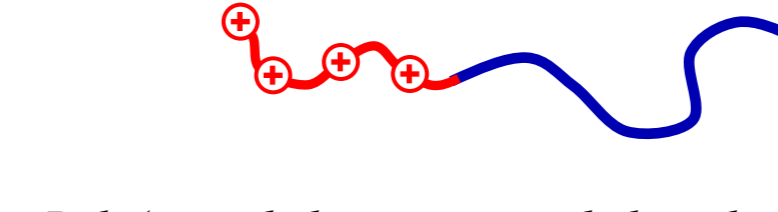


STRUCTURAL STUDY BY SMALL ANGLE NEUTRON SCATTERING (SANS)



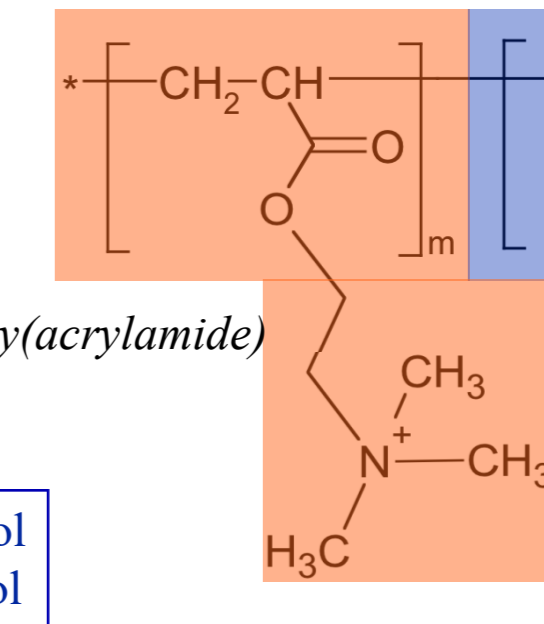
Double Hydrophilic Diblock Copolymers

Cationic-Neutral copolymer



Poly(trimethylammonium ethylacrylate) - b - Poly(acrylamide)

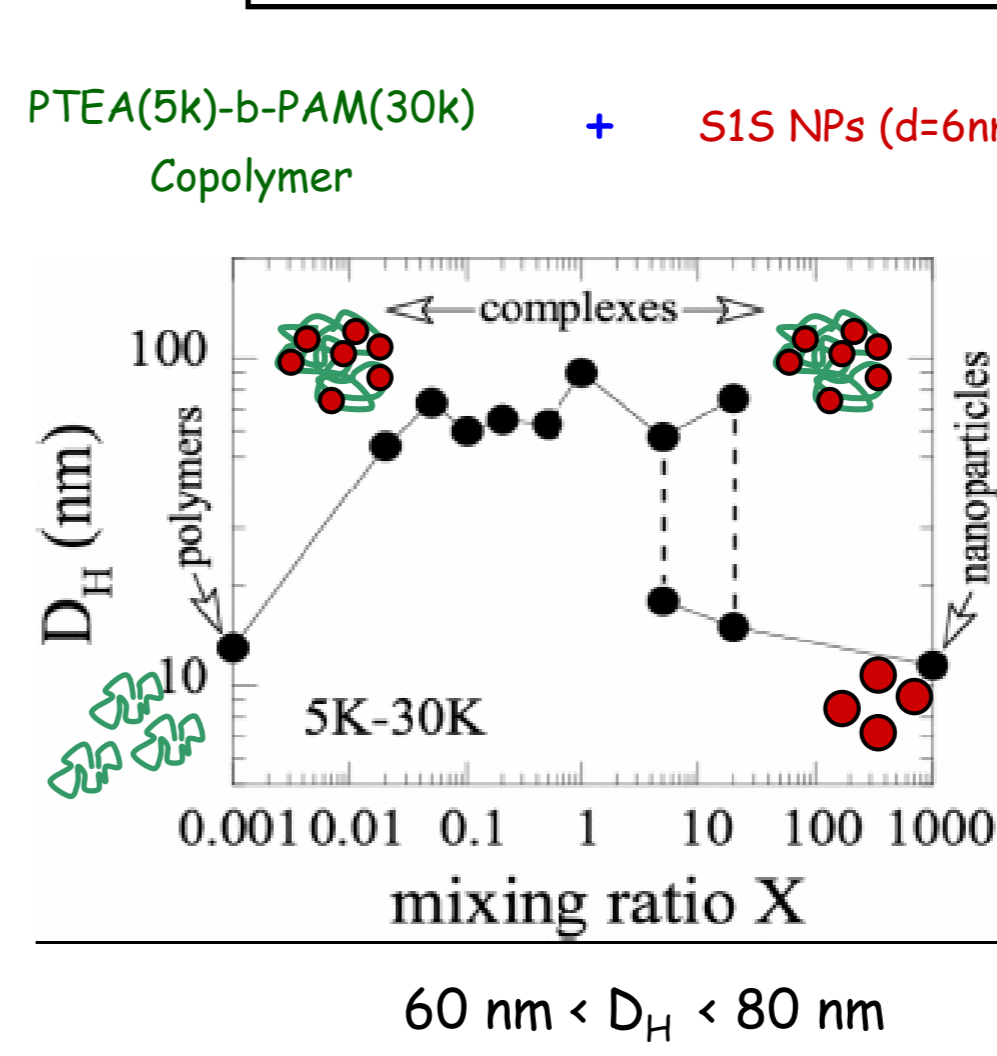
Molecular weights
Rhodia Inc. PE 1 000 - 10 000 g/mol
Neutral 10 000 - 60 000 g/mol



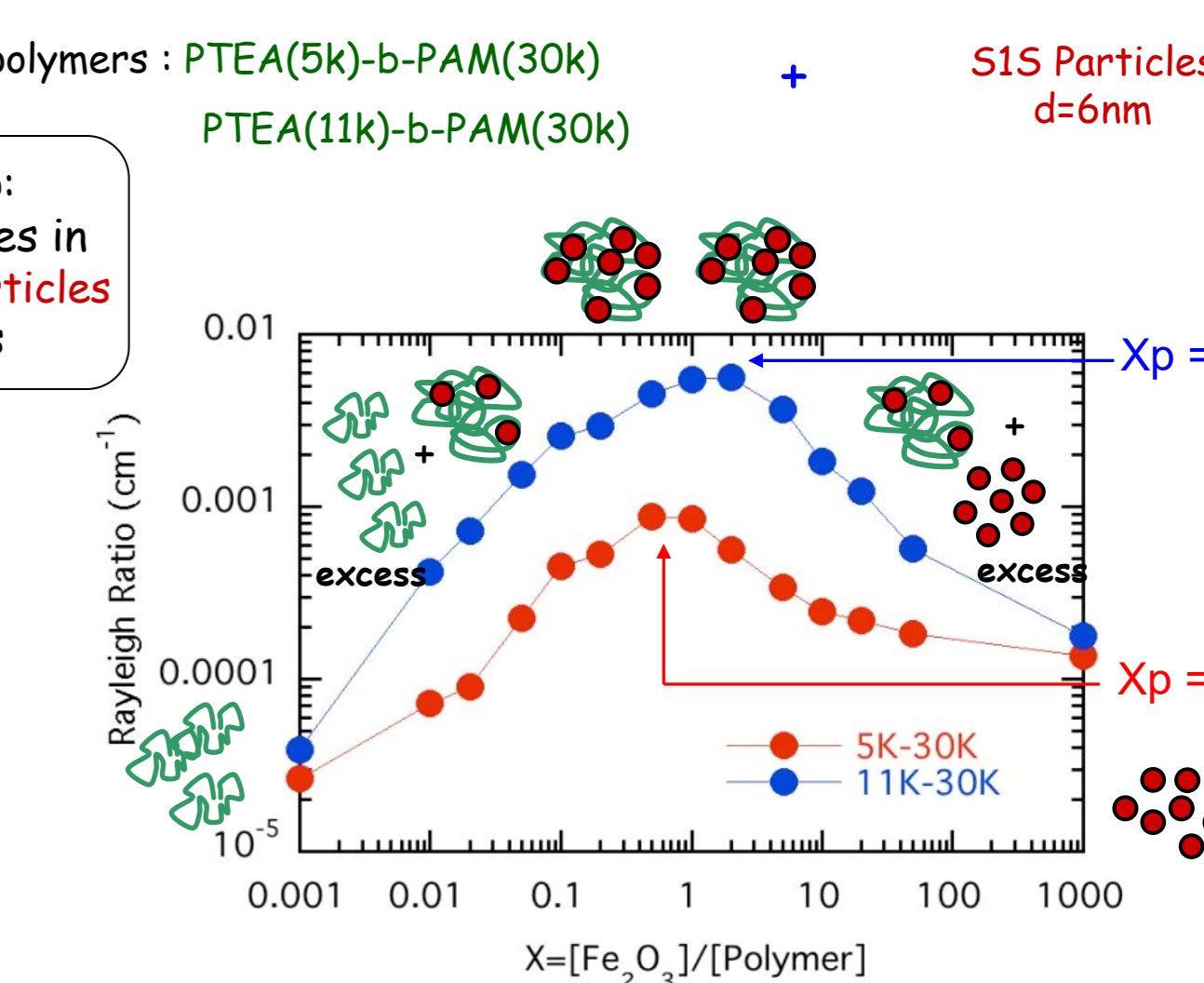
Attractive electrostatic Interaction between citrate grafted NPs and DHBCs

DHBC - particles solutions

DYNAMIC LIGHT SCATTERING



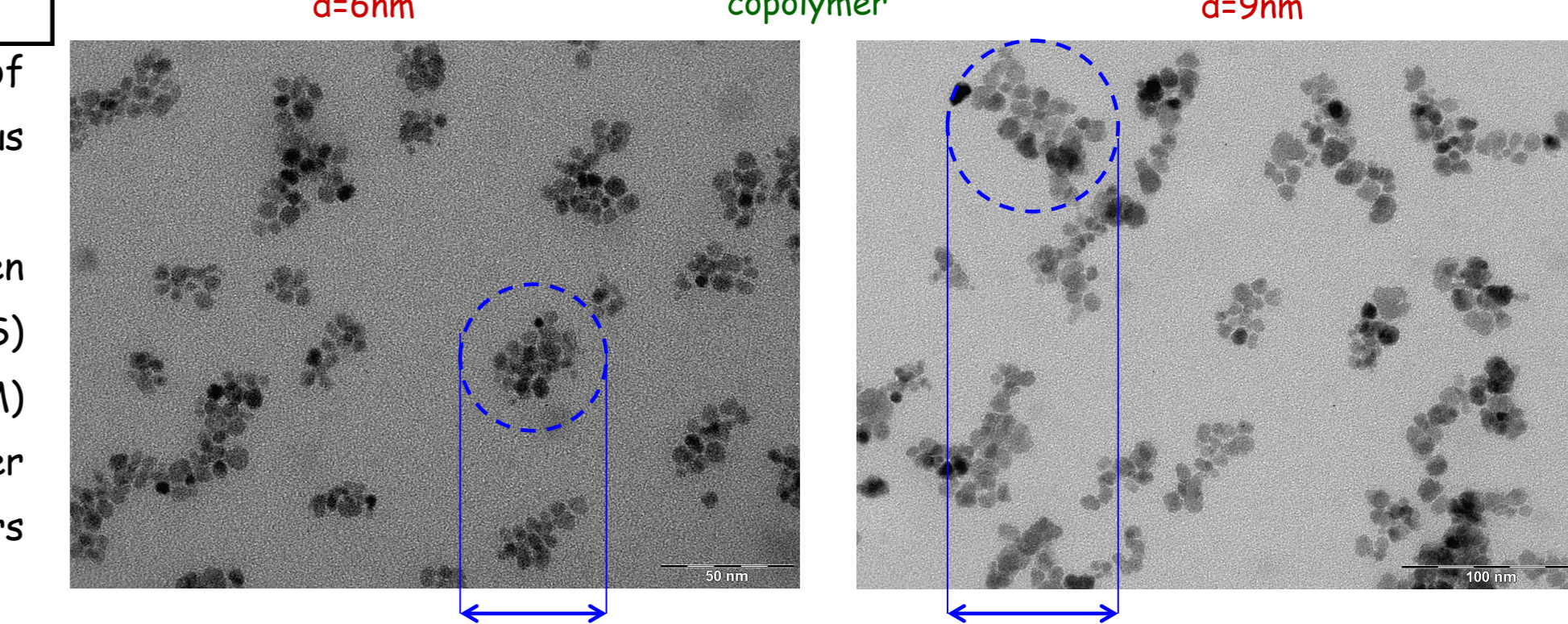
STATIC LIGHT SCATTERING



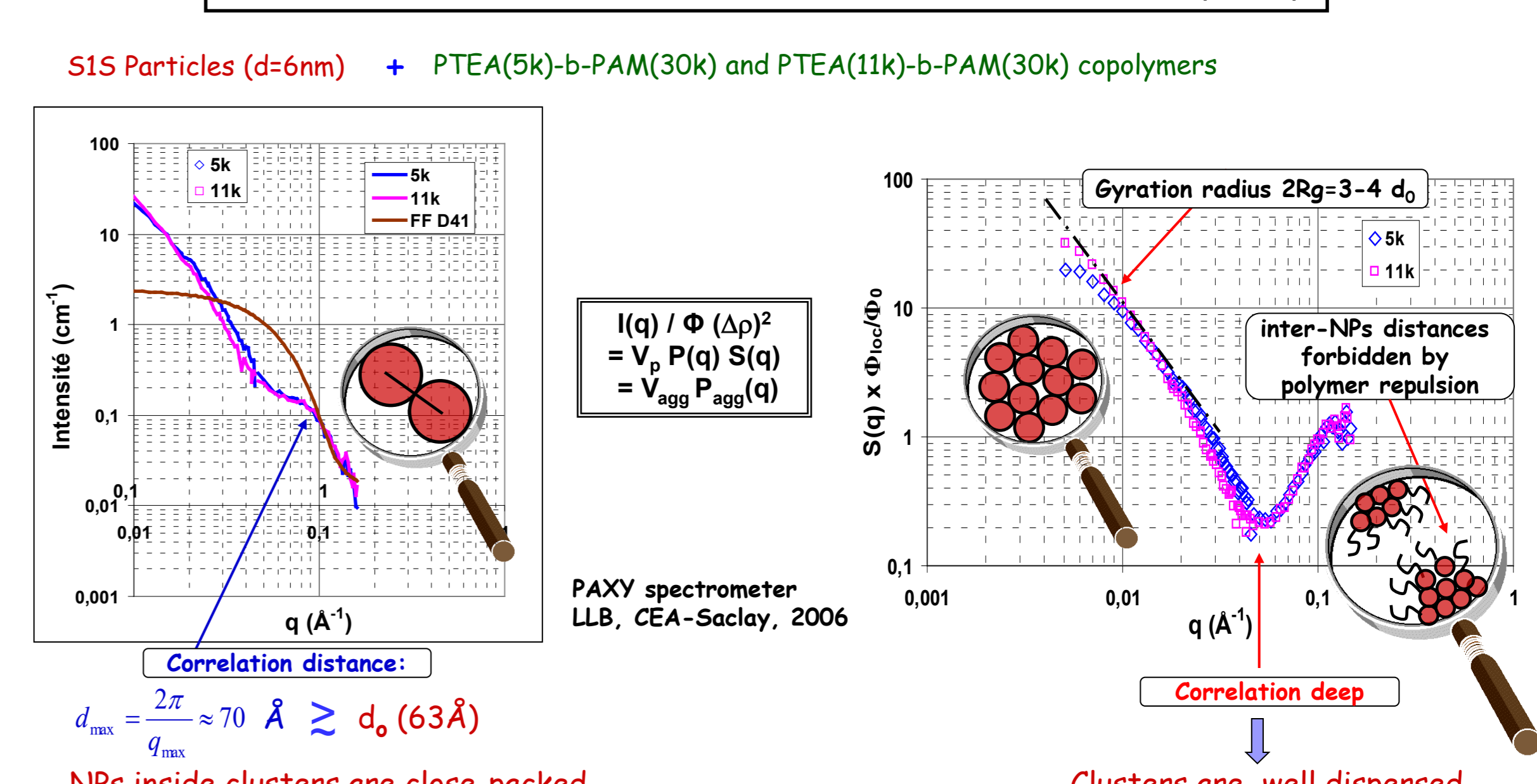
J-F. Berret, O. Sandre, D. El kharrat, JACS 2006

CLUSTERS MORPHOLOGY BY TEM

- Dense clusters of nanoparticles with various sizes and shapes.
- Difference between hydrodynamic size (DLS) and core size (TEM) ascribed to neutral polymer shell protecting the clusters against aggregation.

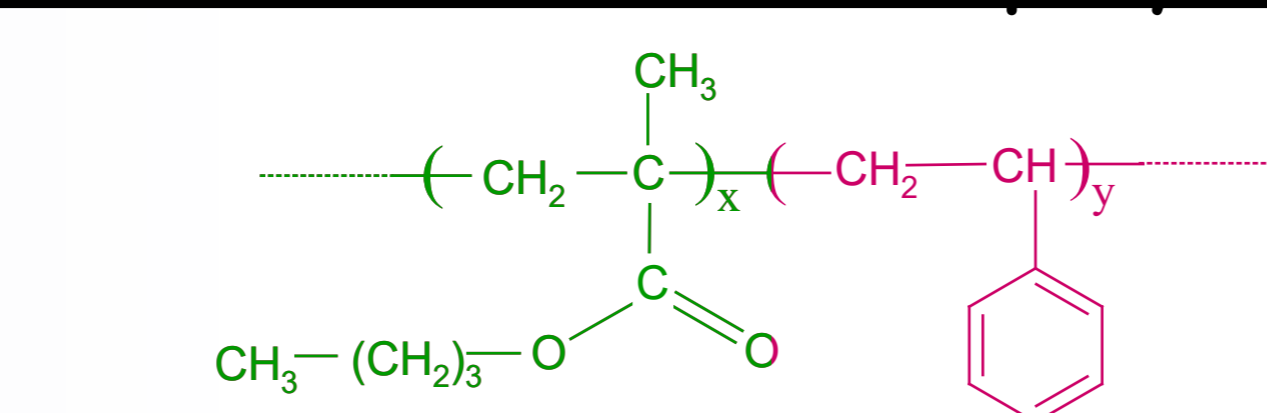


STRUCTURAL STUDY BY SMALL ANGLE NEUTRON SCATTERING (SANS)



II) Evidencing the lamellar structure of copolymer films doped or not with magnetic NPs

By Atomic Force Microscopy



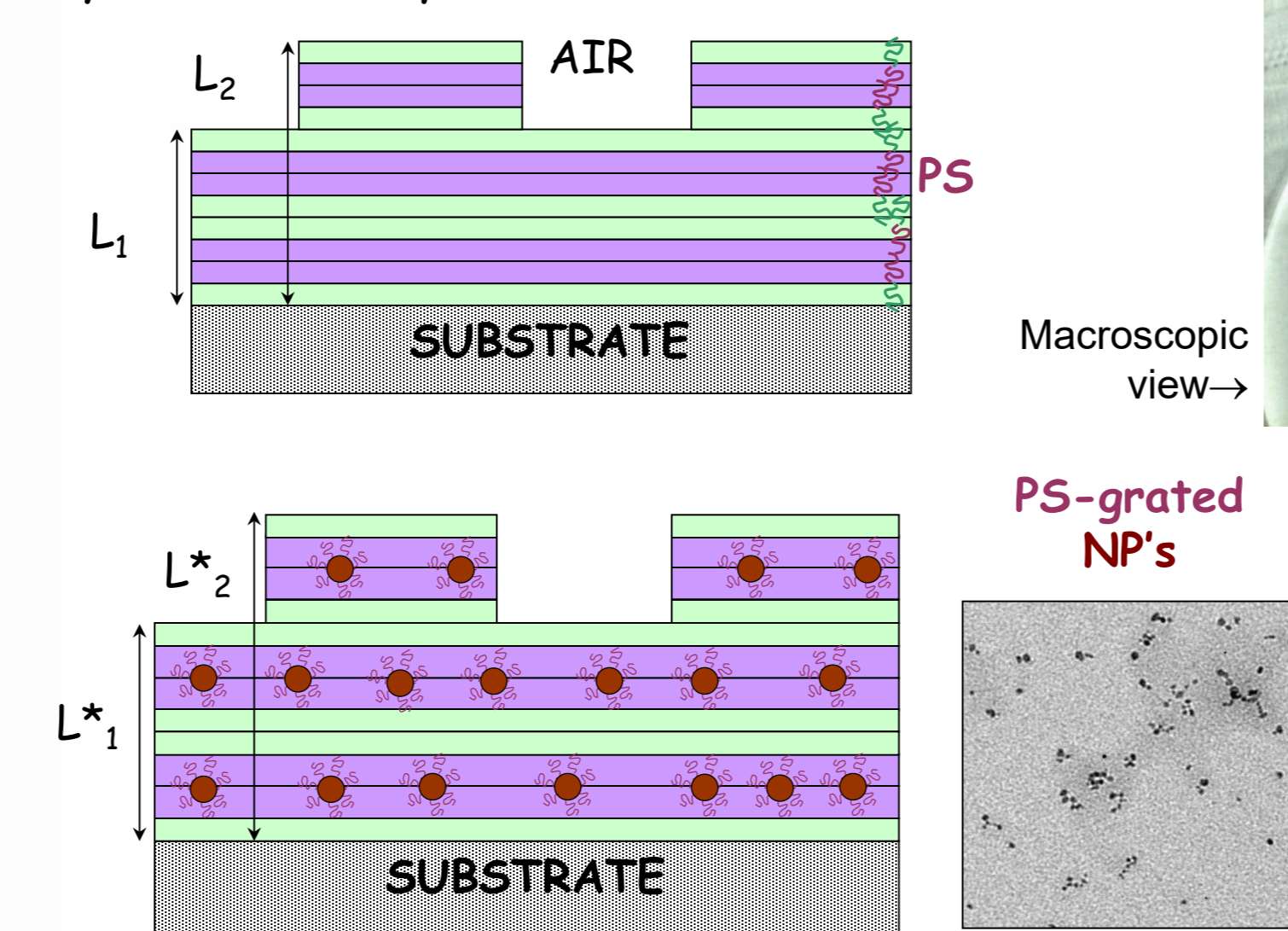
- > Atom Transfer Radical Polymerization (ATRP)
- > High molecular weight : Mn = 112 000 g/mol
- > Low polydispersity: Ip ≈ 1.4
- > Symmetrical Dibloc Copolymer: x=425 ≈ y=490

Preparation of thin lamellar film samples: Solutions of P(nBMA)-b-PS in toluene are "spin-coated" on smooth substrates (mica or silicone). After deposition, films are annealed at 150°C under vacuum for at least 48h. Their thickness is measured by ellipsometry.

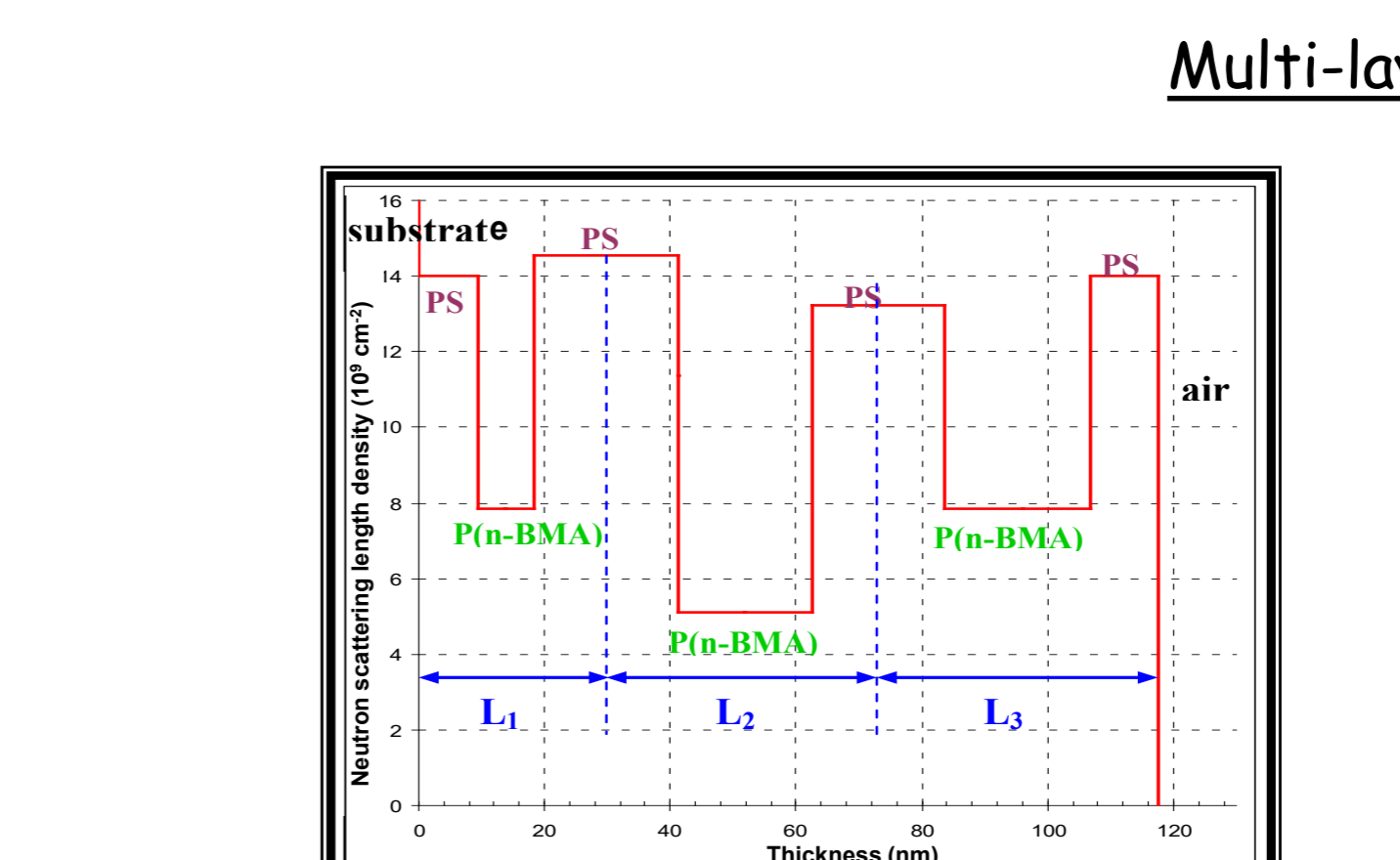
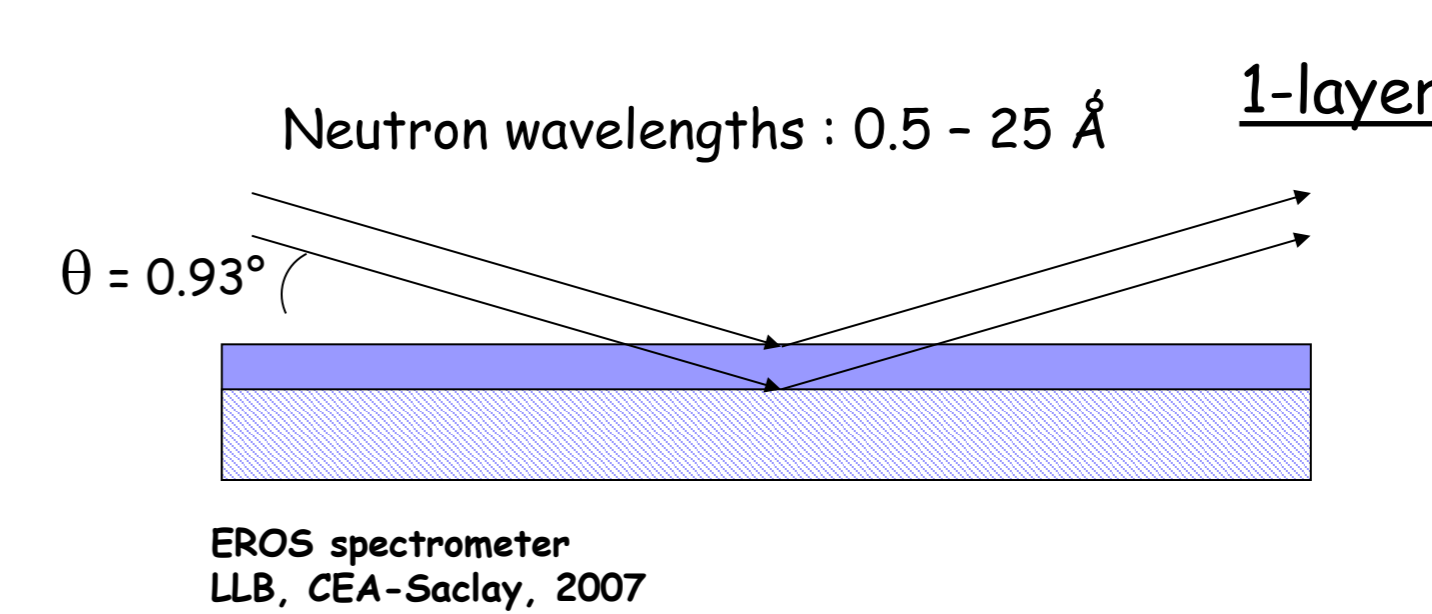
> Tapping mode AFM enables to image 2 types of defects at the surface of the films - "islands" and "holes" - typical of the lamellar order.

> The lamellar period should be measured from the height difference L₂-L₁ but the AFM tip is too large to reach the second bilayer.

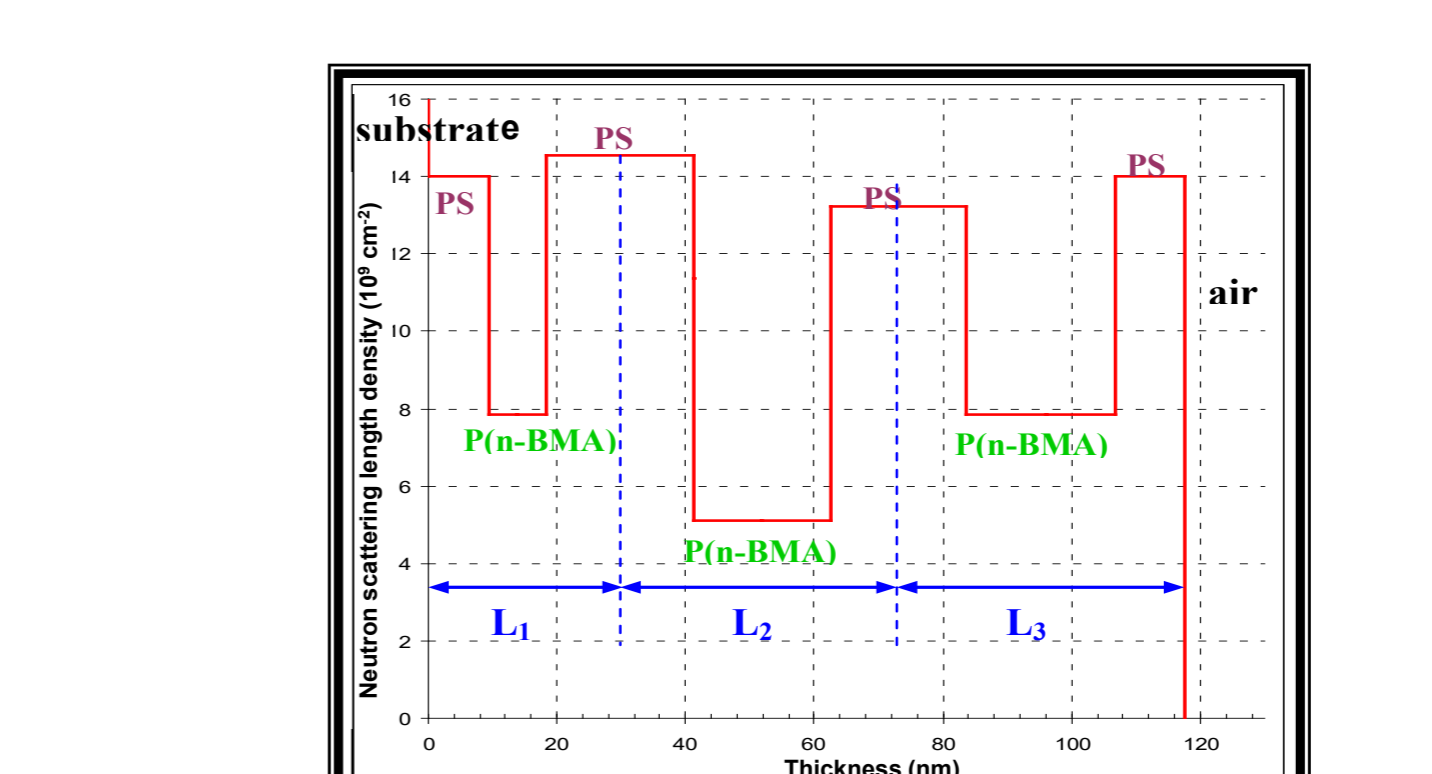
> The lamellar period is 28 nm for an analogous PS-b-P(nBMA) of Mw=82,000 as measured by X-rays reflectivity. [2]



By Neutron Reflectivity



Multi-layers → interferences (over-oscillations)



Film	Layer number and thickness (nm)					Total thickness (nm)	roughness
	L ₁	L ₂	L ₃	L ₄	L ₅		
0.05%	32.2	48.0	21.5	37.2	111.7	108.1	1.4
0.10%	32.8	48.0	33.3	38.0	114.0	109.4	3.5
0.15%	32.8	48.7	30.0	37.2	111.5	106.6	0.4

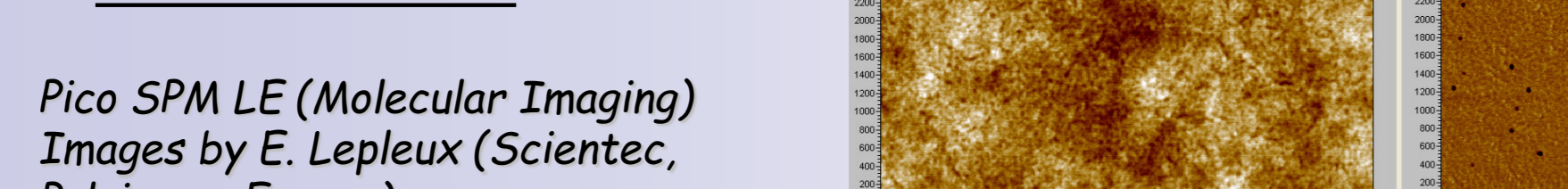
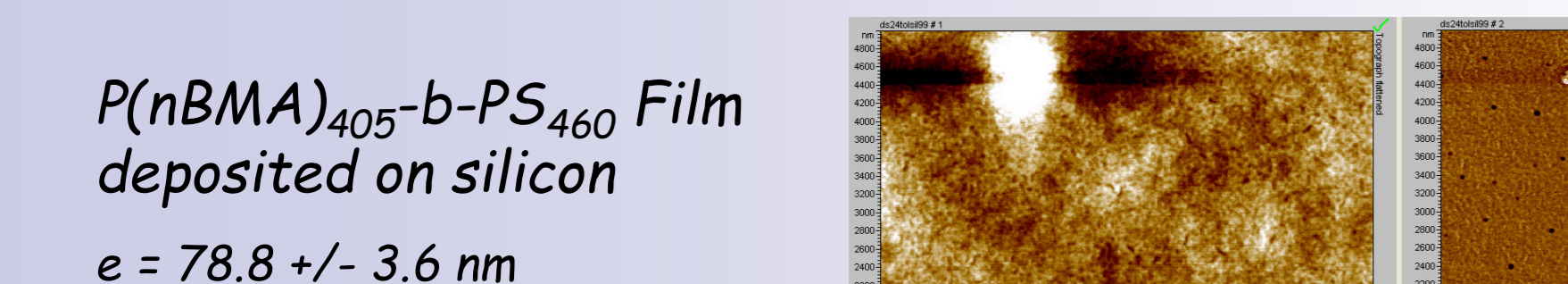
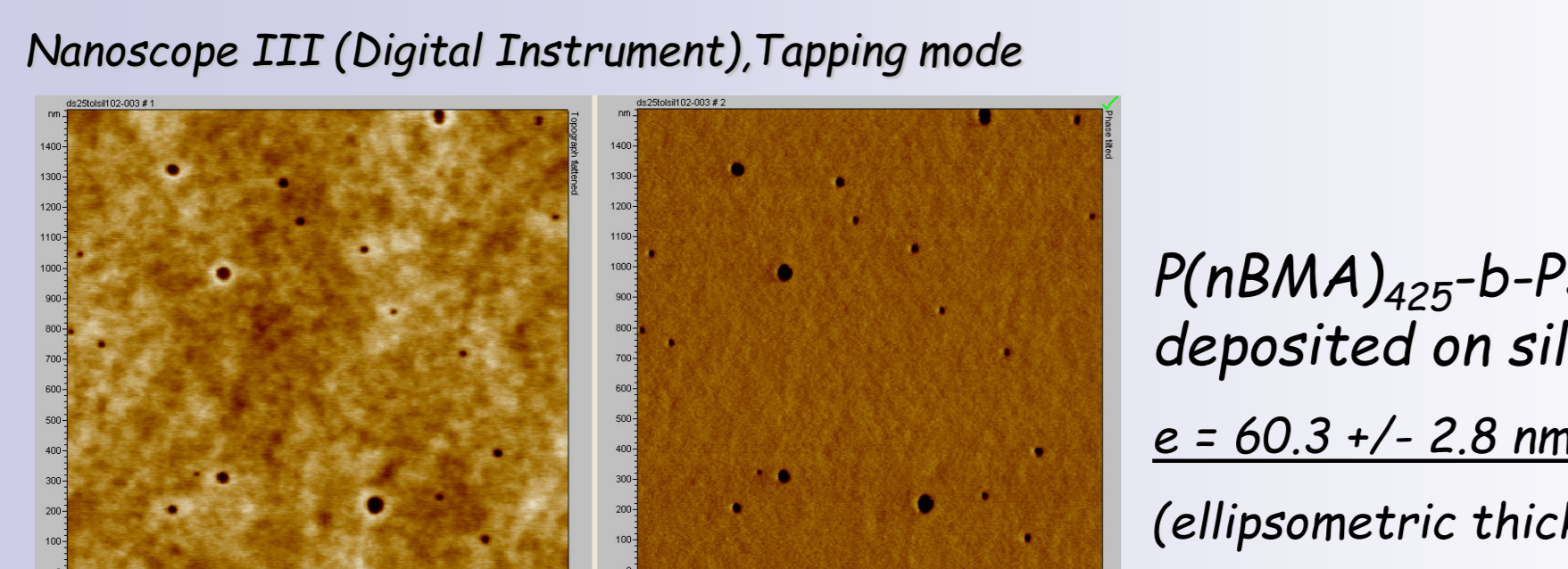
[P(nBMA)₄₂₅-b-PS₄₉₀]=20 g/L doped with γ-Fe₂O₃@PS1 at increasing volume fractions Φ_{NPs}

- ⇒ The insertion of increasing amount of magnetic nanoparticles leaves both the total thickness and the average period unchanged.
- ⇒ The nanoparticles are confined inside internal inter-penetrated layers.
- ⇒ The total thickness of the film and its roughness are proportional to the deposited materials amount.

C g/L	γ-Fe ₂ O ₃ @PS	Layer number and thickness (nm)						Total thickness (nm)	roughness
		L ₁	L ₂	L ₃	L ₄	L ₅	L _{moy}		
20	γ-Fe ₂ O ₃ @PS3	31.2	45.3	41.5	-	-	39.3	117.9	±1.6
30	γ-Fe ₂ O ₃ @PS1	34.0	46.1	49.0	54.5	-	45.9	183.6	±4.9
40	γ-Fe ₂ O ₃ @PS1	47.3	45.9	47.0	44.4	45.7	46.1	230.3	±17.4

Films doped at constant volume fraction Φ_{NPs} = 0.025 vol% and increasing deposited materials amount

Nanoscope III (Digital Instrument), Tapping mode



Bibliography:
[1] G. Coulon, B. Collin, D. Chatenay, Y. Gallot, "Kinetics of islands and holes on the free surface of thin diblock copolymer films", J. Phys. II France 3 (1993) 697
[2] G. Vignaud, A. Gibaud, G. Grubel, S. Joly, D. Aussere, J-F. LeGrand, Y. Gallot, "Ordering of diblock PS-BMA thin films: An X-ray reflectivity study" Physica B 248 (1998) 250
[3] B. Toperberg, V. Lauter-Pasyuk, H. Lauter, O. Nokonov, D. Aussere, Y. Gallot, "Morphology of off-specular neutron scattering pattern from islands on a lamellar film", Physica B 283 (2000) 60