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

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

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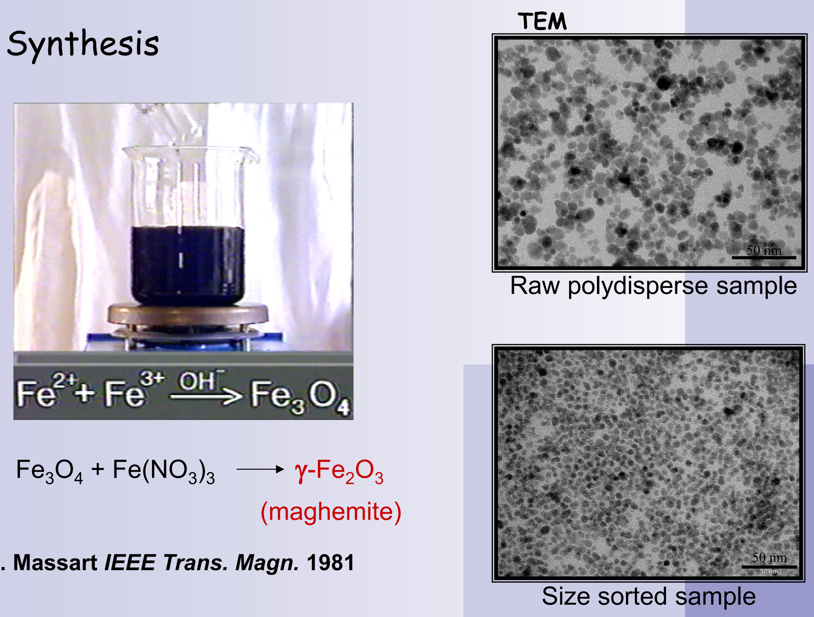
Magnetic nanoparticles (NPs) as building blocks

1) Synthesis

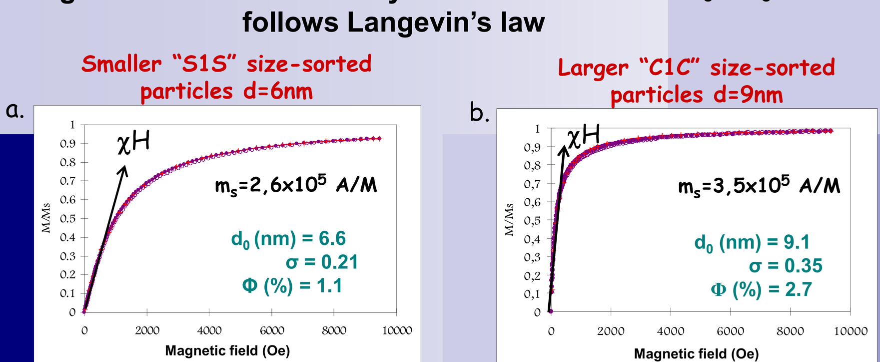


Fe_3O_4 + $Fe(NO_3)_3$ ⟶ γ-Fe_2O_3 (maghemite)

R. Massart *IEEE Trans. Magn.* 1981

Superparamagnetic behavior

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

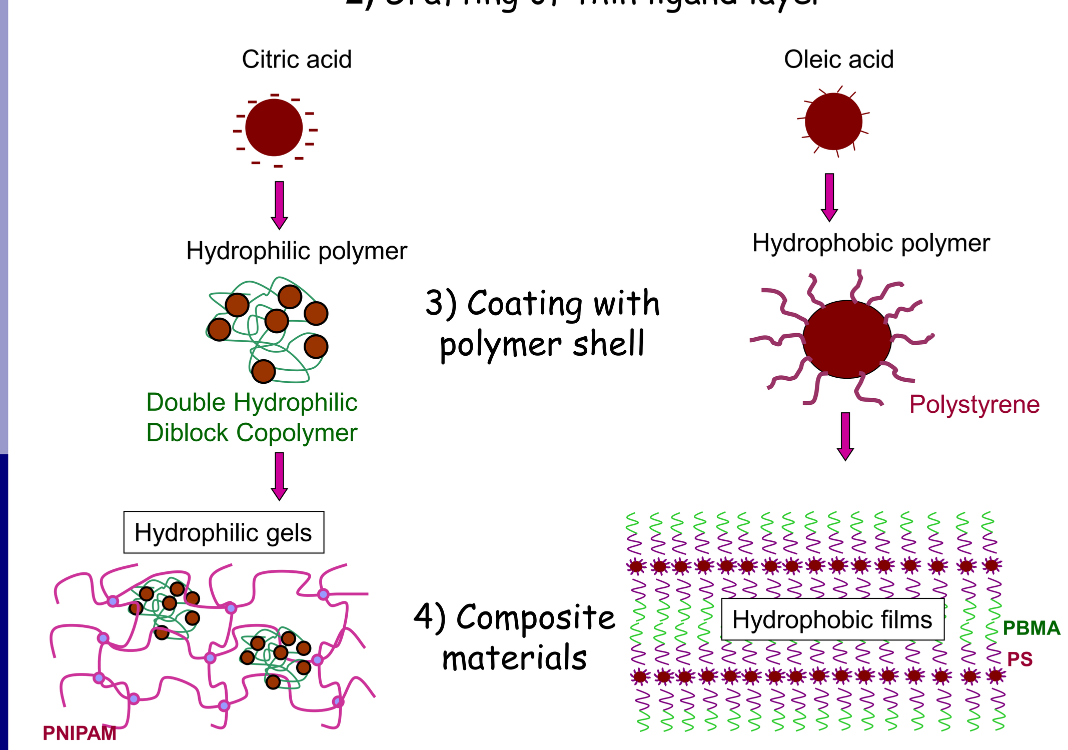


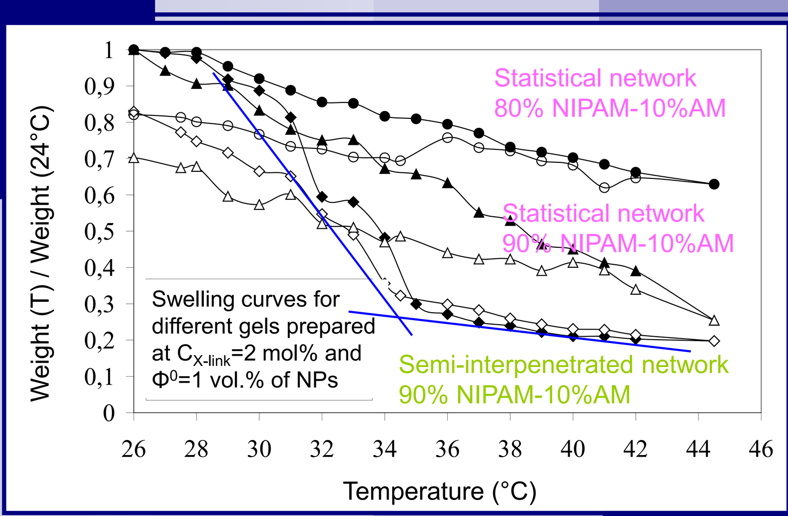
We study nanocomposites consisting of the same iron oxide γ-Fe_2O_3 nanoparticles embedded in polymer matrices:

I) a **gel matrix** exhibiting a swelling transition triggered by temperature;

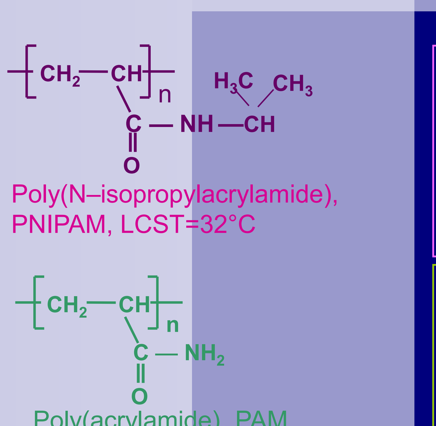
II) a **lamellar matrix** based on the self-assembly of a symmetrical diblock copolymer.

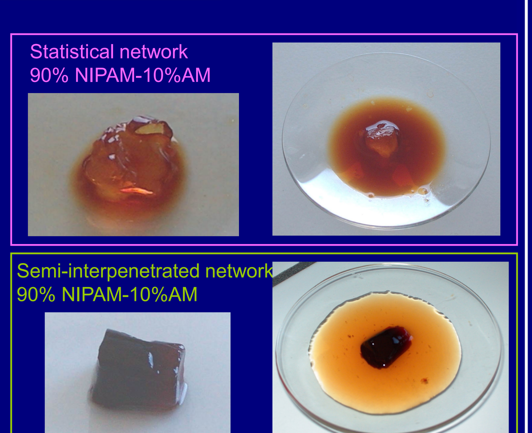
We use both neutron scattering & reflectivy techniques to probe the local structure at the mesoscopic scale.





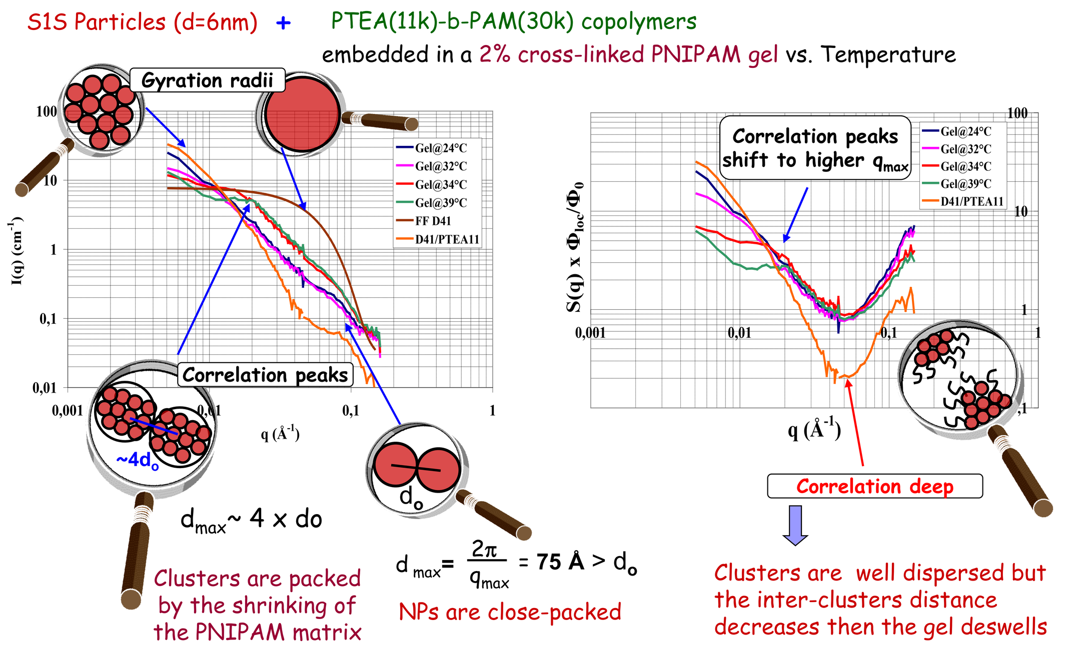
I) Thermosensitive PNIPAM gels doped with magnetic NPs



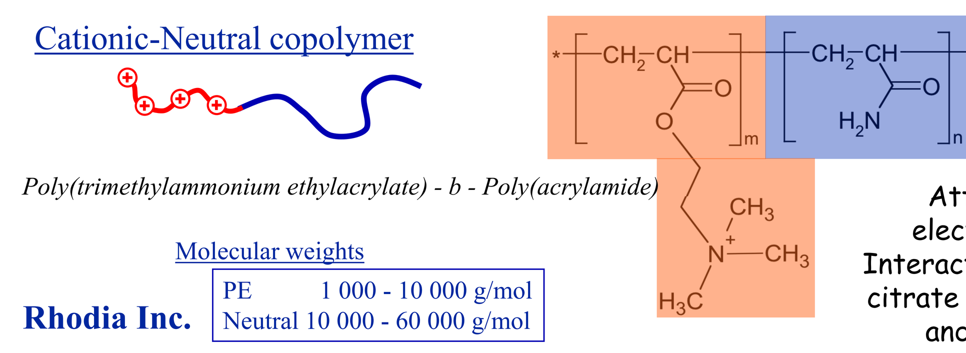


STRUCTURAL STUDY BY SMALL ANGLE NEUTRON SCATTERING (SANS)

S1S Particles (d=6nm) + PTEA(11k)-b-PAM(30k) copolymers embedded in a 2% cross-linked PNIPAM gel vs. Temperature



Double Hydrophilic Diblock Copolymers

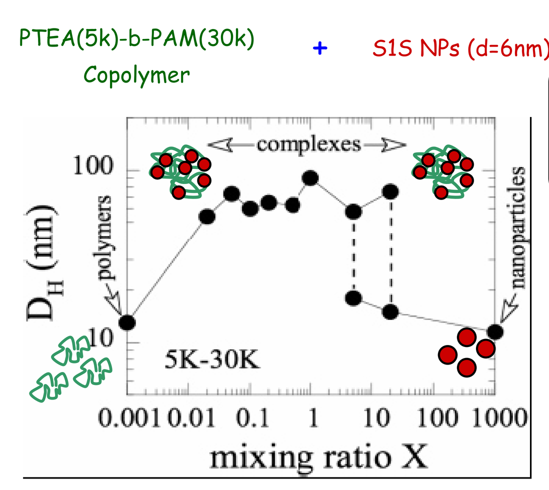


Attractive electrostatic Interaction between citrate grafted NPs and DHBCs

DHBC – particles solutions

DYNAMIC LIGHT SCATTERING

PTEA(5k)-b-PAM(30k) Copolymer + S1S NPs (d=6nm)

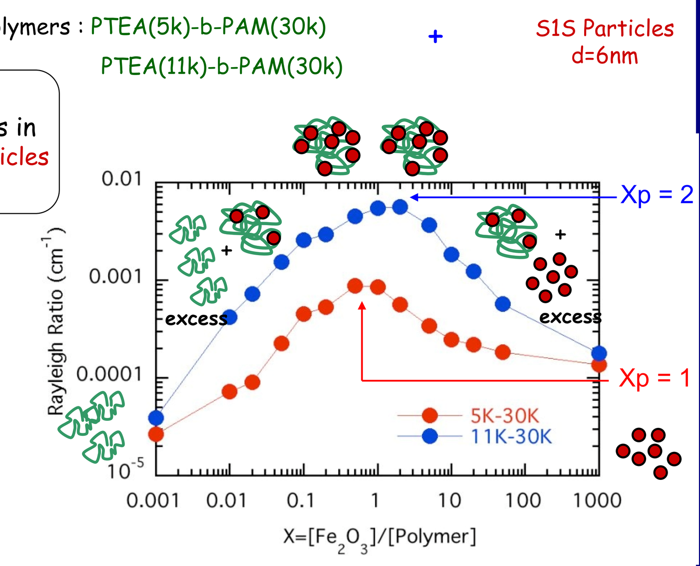


At X=Xp: 100% species in polymer – particles clusters

60 nm < D_H < 80 nm

STATIC LIGHT SCATTERING

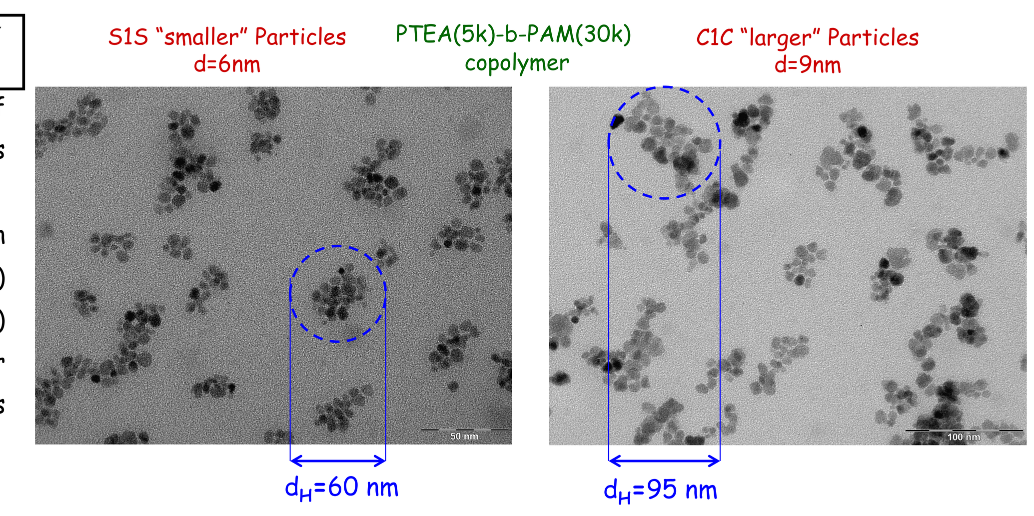
2 copolymers : PTEA(5k)-b-PAM(30k) PTEA(11k)-b-PAM(30k) + S1S Particles d=6nm



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

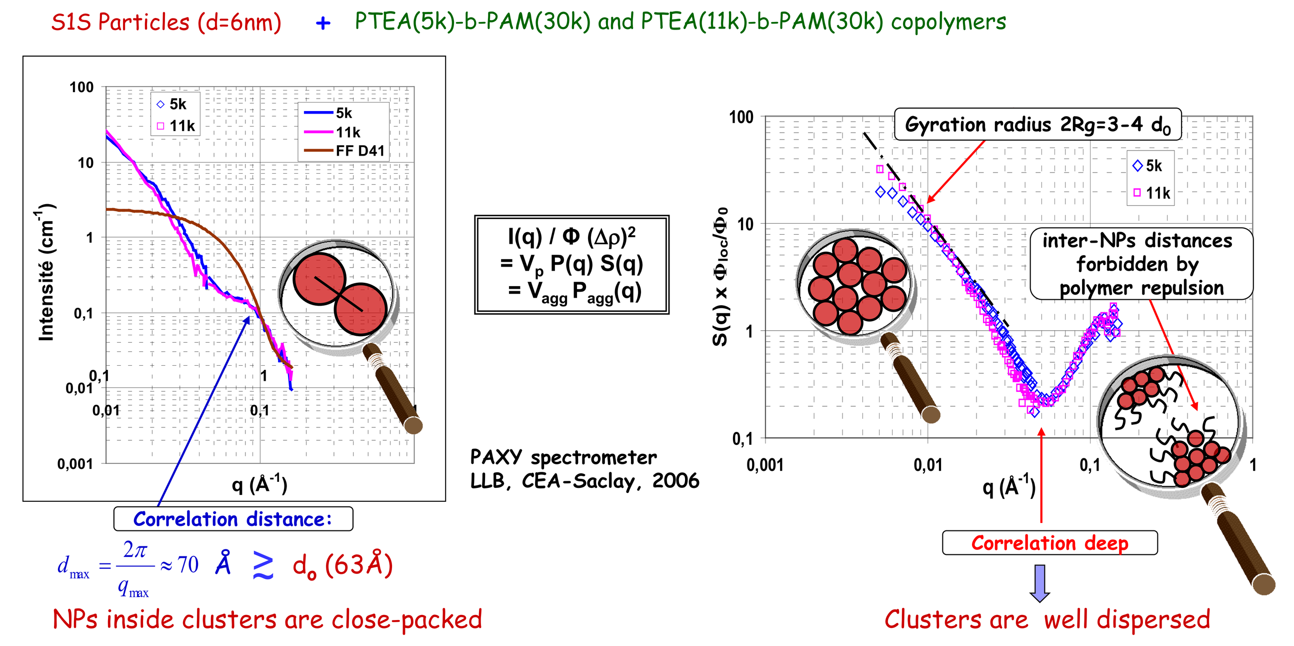
CLUSTERS MORPHOLOGY BY TEM

- 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)

S1S Particles (d=6nm) + PTEA(5k)-b-PAM(30k) and PTEA(11k)-b-PAM(30k) copolymers



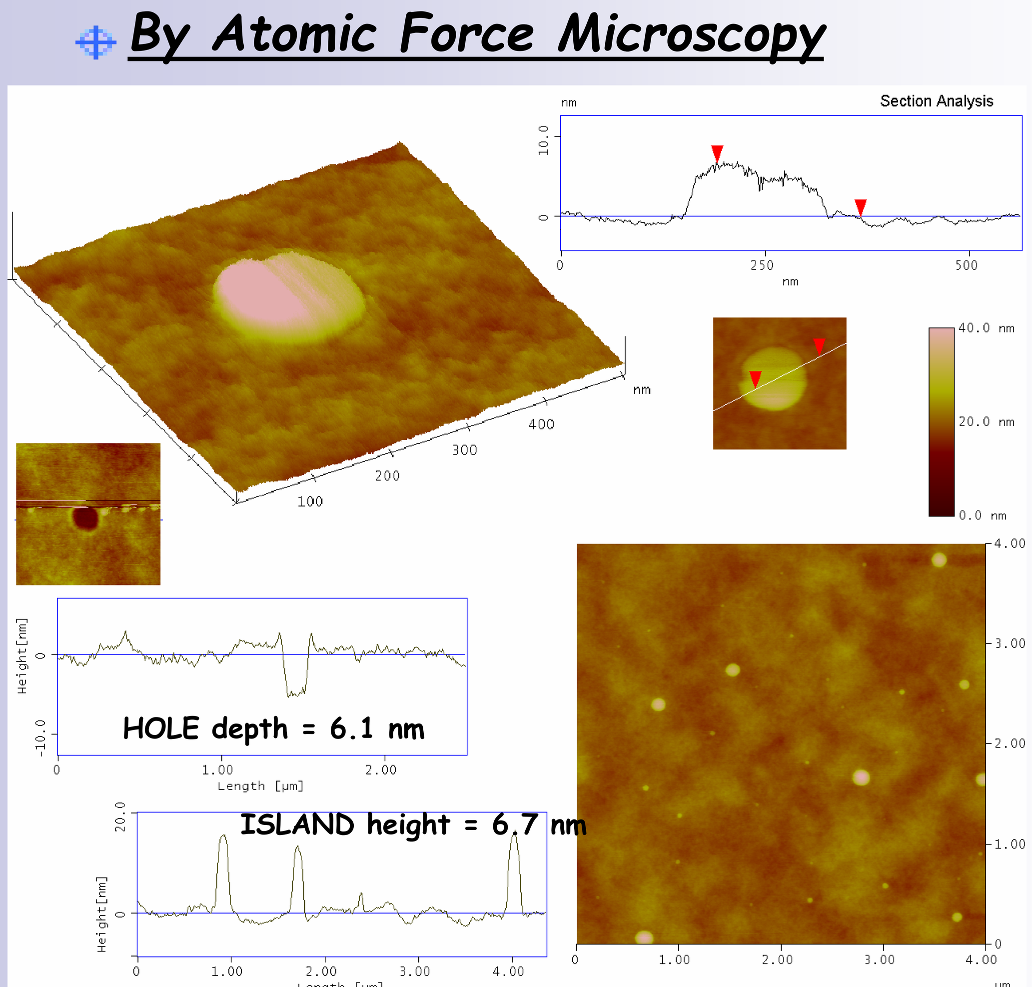
$d_{max} = \frac{2\pi}{q_{max}} \approx 70$ Å ≳ d_o (63Å)

NPs inside clusters are close-packed

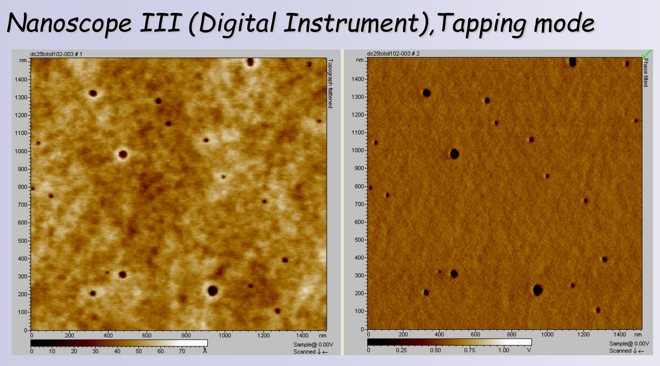
Clusters are well dispersed

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

By Atomic Force Microscopy



Nanoscope III (Digital Instrument),Tapping mode



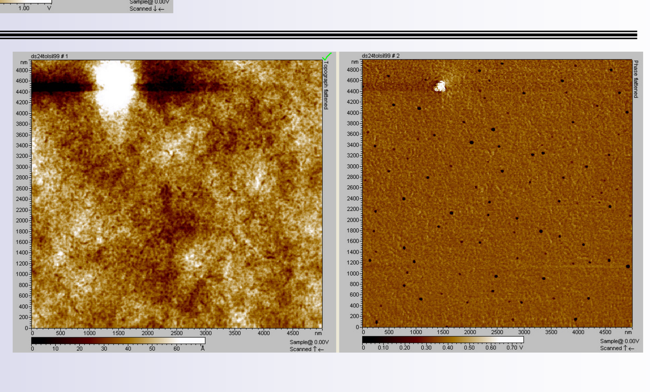
P(nBMA)$_{425}$-b-PS$_{490}$ Film deposited on silicon

e = 60.3 +/- 2.8 nm

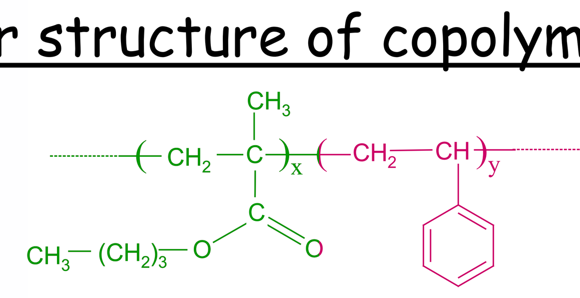
(ellipsometric thickness)

P(nBMA)$_{405}$-b-PS$_{460}$ Film deposited on silicon

e = 78.8 +/- 3.6 nm



Pico SPM LE (Molecular Imaging) Images by E. Lepleux (Scientec, Palaiseau, France)



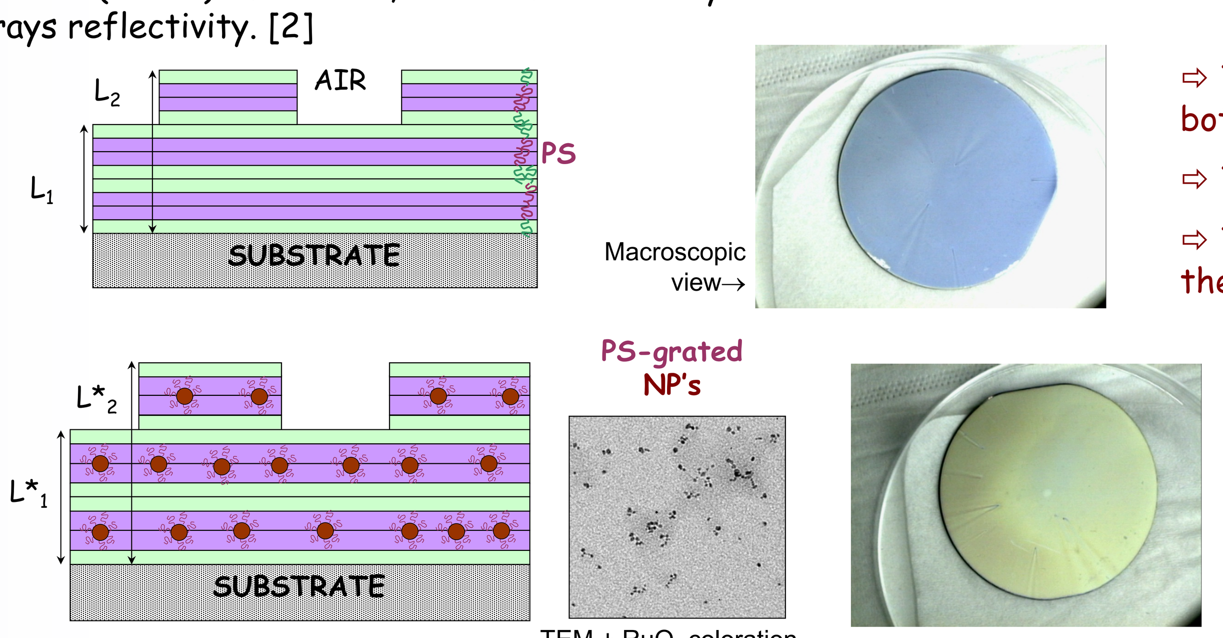
poly(n-butylmethacrylate)-b-poly(styrene)

- 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

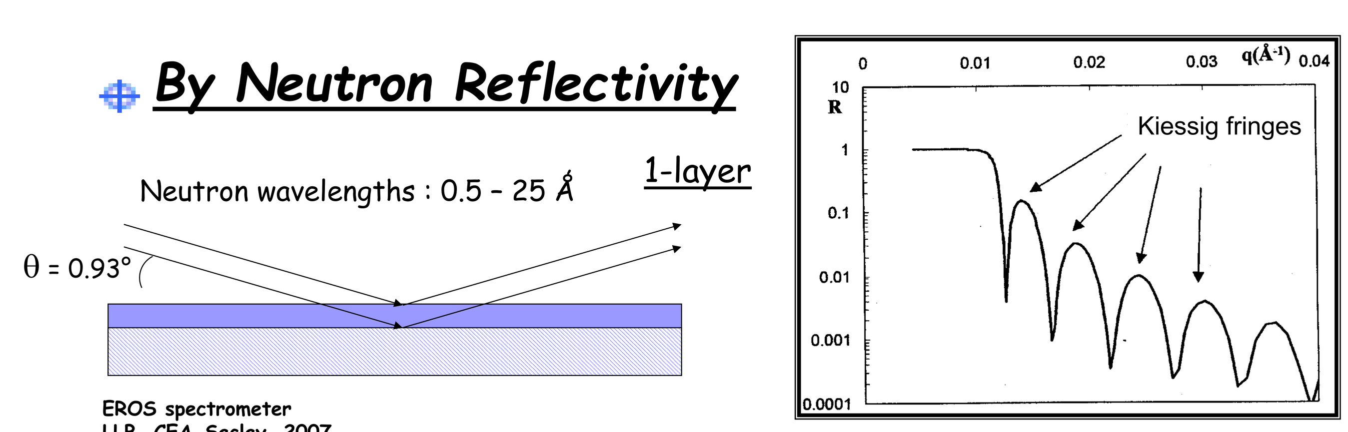
Preparation of thin lamellar film samples:

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.

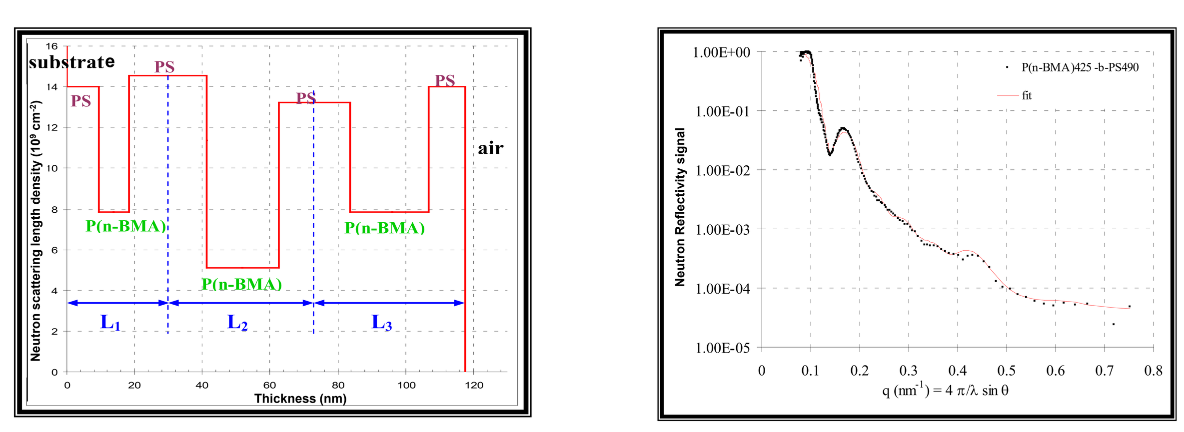
- Tapping mode AFM enables to image 2 types of defects at the surface of the films - **"islands"** and **"holes"** – typical of the lamellar order.
- The lamellar period should be measured from the height difference L_2-L_1 but the AFM tip is too large to reach the second bilayer.
- The lamellar period 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)



Bi-layer thickness ≈ 39 nm for the pure P(nBMA)$_{425}$-b-PS$_{490}$] copolymer

Film	Layer number and thickness (nm)				Total thickness (nm)		rough-ness
Φ_{NPs}	L_1	L_2	L_3	$L_{average}$	RN	Ellipsometry	
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-PS$_{490}$]=20 g/L doped with γ-Fe_2O_3@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_2O_3@PS	Layer number and thickness (nm)						Total thickness	
		L_1	L_2	L_3	L_4	L_5	L_{moy}	nm	roughness
20	γ-Fe_2O_3@PS3	31.2	45.3	41.5	-	-	39.3	117.9	±1.6
30	γ-Fe_2O_3@PS1	34.0	46.1	49.0	54.5	-	45.9	183.6	±4.9
40	γ-Fe_2O_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

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