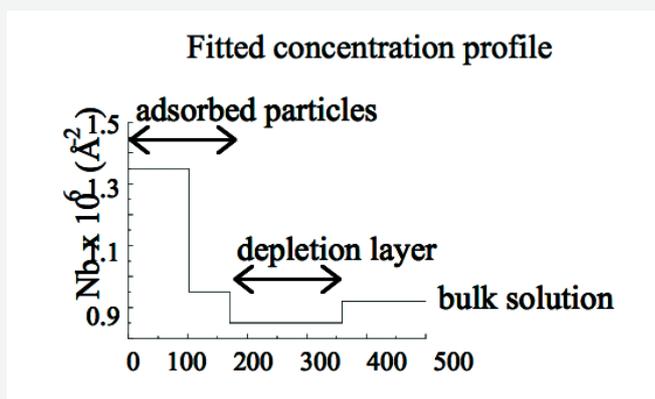
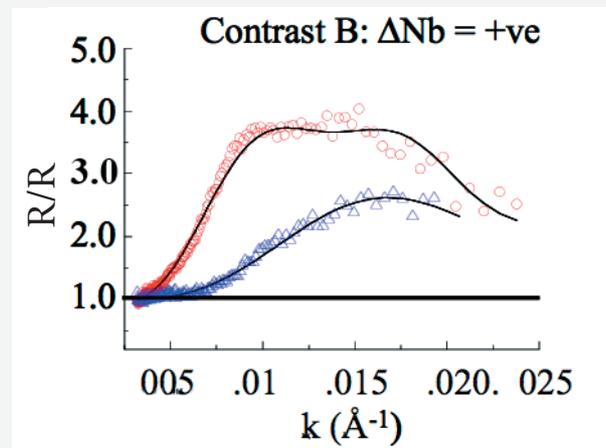
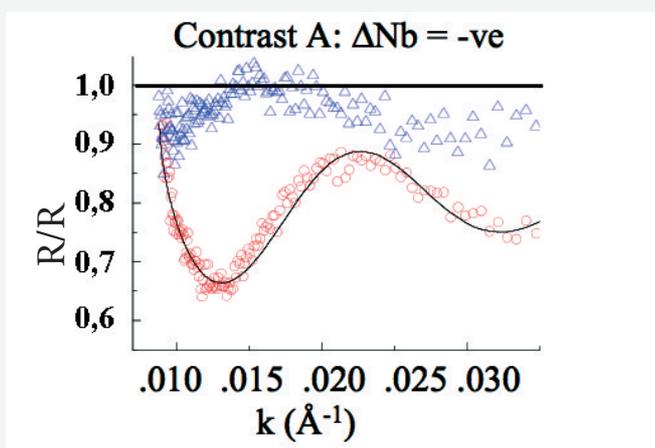


(ii) Thin-film liquid template for controlled nanoparticle organization Thin films of charged polymer solutions dewet a solid substrate to form complex patterns that depend on solution and drying conditions. The dewet morphologies offer a potential method for templating nanoparticles into 2-dimensional complex patterns. Here, we focus on forming nanoparticle chains. The method involves dragging the nanoparticles by the dewetting liquid followed by capillary attractions between particles; minimal nanoparticle-substrate attraction is thus required. For aqueous dispersions of charged polymers and nanoparticles deposited on hydrophilic substrate, 2-dimensional arrays of nanoparticle chains extending over several hundred microns can be formed (image above – cyclodextrin-grafted Au on mica, $d \sim 5$ nm). On hydrophobic substrate, this liquid-template system fails. Neutron reflectivity results show that while nanoparticle (silica and gold colloids) adsorption to hydrophilic substrate (water-silica) is undetectable, adsorption at a hydrophobic surface (water-air) is significant and is mediated by the adsorbed polymer (PNIPAM). Addition of SDS reduces adsorption of the nanoparticles; interestingly, the concentration profile shows a depletion layer, indicating a progressive transformation from a hydrophobic to hydrophilic surface. This effect should enhance dewetting and nanoparticle organization.

[Collaborations: L.T. Lee, LLB; C. Rezende, F. Galembeck, University of Campinas, Brazil; F. Cousin, LLB]



Normalized reflectivity for silica nanoparticle ($d \sim 15$ nm) adsorption at water-air interface in two contrast schemes.

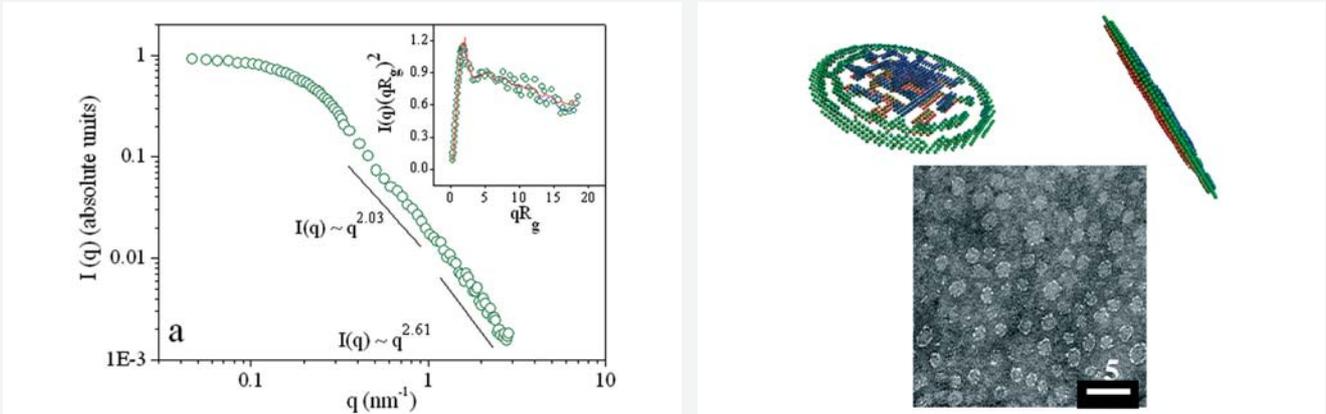
In this representation, all deviations from $R/R_F = 1$ are due only to the adsorbed layer. ΔN_b = difference in scattering length density between nanoparticle and solvent. Polymer solution (circle), polymer+surfactant solution (triangle).

Perspectives: Current studies concentrate on modulating the concentration profiles of nanoparticles at interfaces with special interests in stabilization of soft interfaces, and in optical properties. Emphasis is placed on the thermosensitive nature of PNIPAM-based polymers to produce reversible stimulus-responsive systems.

[C9. C. Sanchez] **Conformation of arabinogalactane-peptide from Acacia gum: a new model based on SANS and *ab initio* calculations.**

Biopolymers of the arabinogalactane-protein (AGP) type are everywhere in vegetal world, with many biological functions. Those extracted from Acacia gum are largely used in industry (stabilisation, emulsion, dispersion or adhesion). Conformation of the major molecular fraction, F1, an arabinogalactane-peptide ($M_w : 2.86 \cdot 10^5$ g.mol⁻¹), is highly hypothetical. SANS (Fig.1) is used here, together with *ab initio* calculations and microscopy (MET, cryo-MET, AFM), to propose a first model: a flat oblate ellipsoid of diameter ~ 20 nm, thickness ~ 1.5 - 1.9 nm et and radius of gyration ~ 6.5 nm. The central part resembles a fractal-like network of branches and aggregates, $d_{\text{fractal}} = 2.6$, a seen directly on the scattering.

[Collaboration : C. Sanchez ENSAIA-INPL, Nancy, A. Lapp, LLB, C. Schmitt & E. Kolodziejczyk, Nestlé, Lausanne, C Gaillard & D Renard, INRA-Nantes].



Form factor (SANS) of F1 at 25°C in D2O 50 mM NaCl, ab initio model and cryoTEM picture

[C10. C. Gerardin] Hybrid polyion complex micelles precursors for Highly stable metal [C. hydroxide colloids].

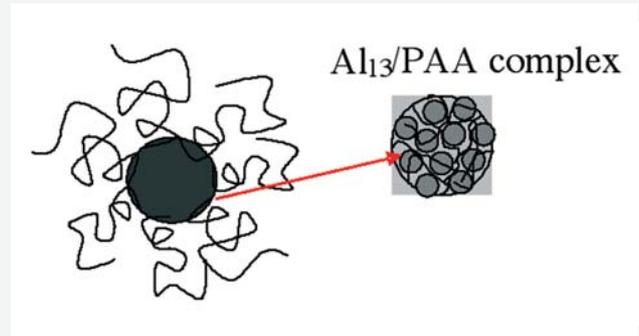
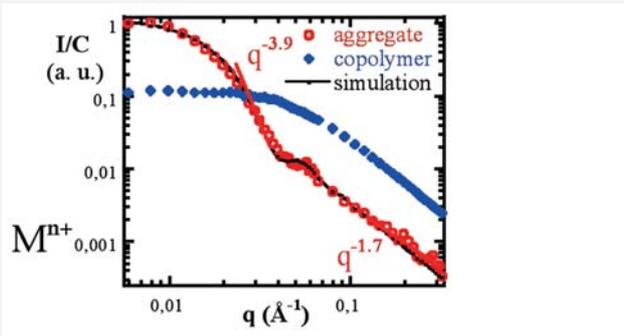
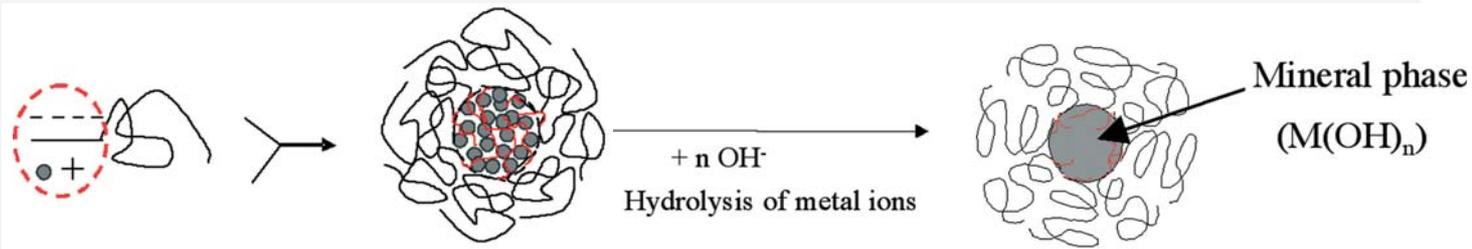
Anionic-neutral double hydrophilic block copolymers are used to control the growth and morphology of inorganic particles and directly prepare sterically stabilized suspensions of metal hydroxides. Metal hydroxides are obtained by hydrolysis of metal cations in the presence of the copolymers. The metal-complexing polyelectrolyte block ensures a *controlled growth of the inorganic phase* since the complexing functions act as poisons of the inorganic polycondensation reactions, whereas the neutral block ensures steric stabilization of the colloids.

The first synthesis step is the *induced assembly* of the copolymers in the presence of the oppositely charged multivalent inorganic species. The formation of the hybrid polymeric-inorganic nanoaggregates is induced by complexation of the inorganic ions. The micellar aggregates present a core-corona architecture characterized by scattering techniques (SANS and DLS).

The micelles are then used as *adjustable supramolecular precursors* for the formation of metal hydroxide particles. Hydrolysis of metal ions in the micellar core leads to *mineralization* of the colloids. The size of the stabilized particles can be tuned by adjusting the copolymer-to-metal ratio, the metal prehydrolysis ratio and the polymer block lengths. Finally, the morphologies of the hairy particles vary with the nature of the metal and with some synthesis parameters.

Gérardin et al *Angew. Chem. Int. Ed.*, **2003**, 42, 31, 3681. Sanson et al. *Phys. Chem. Chem. Phys.*, **2004**, 6, 1463.

[Collaboration : C. Gerardin, N. Sanson, M. In, L. Auwray, UMR5618 ENSCM UM1 CNRS Montpellier]



Comparison of SANS curves : Polymer alone (blue) and aggregate (red) of Al₁₃ + PAA 1900 -b- PHEA 8200, at the same polymer concentration.