



SOFT MATTER

LABORATOIRE LÉON BRILLOUIN

SOFT MATTER

A- Introduction

Future axes of research in soft matter will develop, by mutual enrichment, in external teams, mixed collaborations and in-house research; finding new routes is a commitment for the LLB team.

The contribution below covers different trends, taking the opportunity to put into perspective related recent work, by ourselves and/or others, including highlights and clips. These trends include **New synthesized polymers**, a field of obvious interest, to **Systems under external constraints**, currently raising much interest, and **Confinement and surface effects**, a recent trend gathering several LLB projects, to finish with **Ternary mixed systems**, the largest set of various situations involving many teams. Our knowledge based on polymers, has evolved towards **mixed systems involving polymers**. Among the different specific advantages of neutron radiation, **deuterium labelling** is the one which should benefit this kind of system, as well as other subjects, in the different techniques: SANS, reflectivity, as well as quasielastic scattering.

B- New synthesized polymers

New synthesis routes for polymers are constantly being developed by chemists; LLB has the right experience to analyse the chain conformation and arrangement. **Deuteration**, which implies additional synthesis (that of the deuterated monomer), is a very powerful tool and is particularly worth achieving.

Let us refer to recent studies such as **polyelectrolytes with a conjugated backbone**, which enables us tuning the right correct the good water solubility theoretical ingredients of a “wormlike chain to globule” conformational transition, addressing in particular the question of annealed versus frozen charge distribution along the chain [*CI*, P. Vallat] (thesis) - Rawiso).

Other research for new polymers has been conducted and will be developed, for instance on conjugated conducting polymers (G. Hadziioannou, Strasbourg)

Another theme, which is currently rising, is polymers resulting from **supramolecular associations**: systems come from J. M. Lehn team (E. Buhler), and other laboratories. These systems exploit the potential of deuteration of a key chemical group (P. Mésini), or solvent trapped inside the molecular thread (L. Bouteiller). Other associations give birth to polymer-like objects: for example, in polyrotaxanes, between a POE chain and cyclodextrins. This subject was studied by LLB associate team (L. Auvray - P. Guégan, Evry), and recently revisited (Hadziioannou-Lapp).

C - Systems under external constraints

A more widespread group of projects corresponds to polymers which are often well known at rest, but not understood when subjected to the various environments and constraints of real life. For that purpose, in addition to the aforementioned strength of the technique, rather thick and complex sample environment devices can be used owing to **high penetration power of neutron**.

1 - PRIMARY MIXTURES UNDER MECHANICAL CONSTRAINTS

Primary mixtures are made of object which are all identical, except for a fraction of them which is deuterated, permitting unique studies of the individual objects and of their interaction. We focus first on pure polymer systems, for which mechanical deformation behaviour is of interest and sometimes of prime importance to industrial applications. Studies of conformation and arrangement of chains under shear or stretching deformation, now achieved only on simple linear polymers, will yield important information on other architectures. Beyond the behaviour of liquid crystalline polymers in shear induced phases which is studied in detail, (L. Noirez), and the fundamental questions on entanglement effects in stretched rings compared to linear chains (M. Rawiso, J. Combet), there is much to be done on architectures found frequently in real life high performance polymers. Starting with such a common polymer as polyethylene, which contains **branched chains** of different branching rates, we have studied how branched objects arrange and deform in monodisperse blends as well as in mixtures with less branched chains (modelled here by linear chains), in collaboration with the Laboratoire des Polymères Organiques de Bordeaux [*C2*, S. Desvergne] (thesis) - Brûlet). This kind of system should be studied more, in link with expert laboratories.

2 - ELECTRIC OR MAGNETIC FIELDS

As the materials need to be more and more multifunctional, a variety of external constraints should be explored in the near future, among which are the electric and magnetic fields. The experiments can be **static or oscillatory**, using cyclic measurements or time of flight focalisation as developed in Munich and Berlin (A. Wiedenman J. Gahler).

The behaviour of **ferrofluids** in several magnetic configurations has been initiated and performed at LLB. This includes studies on mixed systems. Previously, SANS has used visual techniques, to show accurately that magnetic nanoparticles can be included in the membrane of a polymer vesicle (“polymersome”), and SANS remains an easy direct way to show in situ that a **field deforms the membrane of the vesicle** [C3, O. Sandre].

The organization of **magnetic nanoparticles** along the field in a **polymer matrix** has been studied in a ferrolatex, derived from mixing polymer latex and ferrofluid colloidal suspensions. Application of a constant magnetic field during water casting induces anisotropy in the filler network [C4, F. Cousin].

3 - BINARY POLYMER-PARTICLE SYSTEMS: MECHANICAL CONSTRAINTS AND REINFORCEMENT.

Constraint effects have been extended to **binary mixed systems**, in particularly soft polymers associated with hard nanoparticles at LLB. Various strategies of chemical synthesis of **grafted particles** are developed by G. Carrot at LLB and in collaboration with the CROPS laboratory of University of Marseille 1 (D. Bertin), in the thesis of J. Vinas [C5, J. Vinas] and with the SPAM (H. Perez), with the aim of applications in fuel cells (see Section Materials). Similar work has been performed by external teams (L. Billon, J. Peyrelasse, Pau) using other grafting routes also avoiding aggregation. The LLB project of relation, for a **nanocomposite** material, between **mechanical reinforcement** and the dispersion of grafted nanoparticles at rest, its evolution under deformation, and the deformation of labelled chains [C6, J. Jestin] is just now being developed in the thesis work of C. Chevigny.

Also, a study of **natural latex** mixed with natural (and dried) **clay** is currently running in collaboration with Campinas University (T. Doi, post-doc, L. T. Lee). The stretching of the sample has shown the importance of other entities, such as calcium aggregates, present in these systems.

Combinations of mechanical and magnetic field deformation have been recently explored. The competing effects of mechanical rotation and applied field at constant orientation results in orientation of the ferrofluids structure at an intermediate direction which is q dependent, in agreement with calculations (E. Dubois, R. Perzynski, E. Cebers, Univ. Paris 6). The response to a mechanical **deformation** of the **field oriented ferrolatex** described above [C4, F. Cousin] shows a clear orientation dependent modulus, which should allow better understanding of reinforcement. Studies of ferro - polymersomes [C3, O. Sandre] under shear are being attempted.

Association of hard particles with the liquid crystalline systems formerly studied in Montpellier are also planned (J. Oberdisse).

D - Confinement and surface effects

With the rapid development of nanotechnology, the problem of confinement is met in a large variety of situations where degrees of freedom are reduced close to a surface. Polymer chains are thus particularly sensitive to such effects.

Here again, neutron scattering is a powerful tool: the spatial profiles can be studied by **reflectivity**, and the **chain conformation** by SANS. A first simple situation of confinement is that of a chain in a **thin film** of nanometric thickness lower than the “natural” global size of the chain in bulk. This is well suited to a “primary mixture” study by labelling some of the chains in order to measure their conformation. We showed formerly (A. Brûlet- J.P. Cotton) that this conformation remains Gaussian at intermediate sizes, while apparent stretching appeared at large q (small distances), linked to the presence of surface, either acting on some chains, or giving additional scattering, as proposed by other authors (Russel et al). Extension of these studies can make use of **Quasi-Elastic Neutron Scattering** (QENS), combined with deuteration, as proposed by A. Brûlet. Indeed, low thickness also induces some apparent changes of T_g , as explored by many authors in macroscopic experiments. The corresponding change in the dynamics of dynamics has scarcely been studied (Frick, ILL).

Using deuteration again, one can observe how confinement affects deformation, modulus and T_g shift in **small nanolatex beads** immersed in an elastic latex matrix [H1, Y. Rharbi].

Other confined systems involve polymer © particle binary systems. The study of polymer conformation in nano-cylindrical

mesopores has been started in external collaboration (C. Stilling - L. Noirez). An LLB thesis is ion-conducting polymer inside non-porous aluminium films, with application to fuel cells (J.M. Zanotti, K. Grenet) is detailed in Section *Nanomaterials*. See also the effect of confinement on liquid crystal transitions (D. Morineau) in the Section *Phase transition*.

A very rich new class of binary **polymer particle** systems related to confinement is nanoparticles inside the polymer matrix. Beyond the “filler network” effect due to connectivity of particles aggregates, it has long been suspected that the solid particles give birth to a kind of “**less mobile**” **polymer layer** near their surface, which also plays a role in reinforcement. Such aspect of chain dynamics in a confined geometry is now revisited by many groups. **Quasi-Elastic Neutron Scattering** (QENS), combined with deuteration, in a bulk sample is planned in the thesis of N. Jouault (codir. S. Said, Y. Grohens, Lorient).

Finally, beyond confinement, novel experimental observations carried out by controlling the boundary conditions between various polymer and their substrates give new perspective on their nature. Indeed, it has been shown [H2, H. Mendil], PhD, that the molten state of these polymers, far from any transition, reveal hitherto unknown long range correlations.

E - Ternary mixed systems

Probably the widest part of future activity at LLB in terms of systems and users is **mixed systems**, which associate polymers, surfactants and particles. Their technological future spans many applications: food and agricultural products, pharmaceuticals, biotechnology, even biology. Neutrons are useful because of the possibility of **contrast variation**.

1 - BULK

A good example of system allowing many ways of using contrast is water, **polyelectrolyte and proteins**: here one can use mixtures of water and heavy water which match the protein, the polymer or the deuterated version of the same polymer. This enables us to “see” the different species separately, and even some deuterated chains among other non deuterated ones, or labelled counterions [H3, J. Gummel]. Such detailed insight helps understand similar protein-polymer complexes studied by external users (M. Axelos, Nantes), for which deuteration is not available, or where it has been achieved (C. Tribet, ESPCI, P. Dubin, Amherst-US). One group is currently studying an **acacia gum** component macromolecule associating polysaccharide and protein moieties [C49, C. Sanchez]. Complexes can also involve cationic polymers (L. Auvray, M. Zeghal, Evry) or surfactants (D. Langevin) complexed with flexible or more rigid (**DNA**) polyelectrolytes; this is related to cell targeting for pharmaceuticals or **gene therapy** (cancer treatment, for example). Adding polymer can also modify the rheology of well-known surfactant structures like giant micelles (C. Ligoure - L. Ramos, Montpellier).

Studies also deal with polymer plus nanoparticles colloids in a solvent. For example, PNIPAM polymer adsorbs on silica, which creates a composite gel, with thermosensitive rheology properties induced by PNIPAM collapse above a threshold of the order of 40 °DC (D. Hourdet - L. Petit (thesis), ESPCI). Polymer can also stabilize quantum dot nanoparticles in a solvent, for which the final colour of the dispersion depends on the sizes involved (N. Lequeux, A. Fragola, ESPCI - C.Chassenieux, Le Mans). Systems of polymer plus mineral particles, in solution, are also present when studying (**bio**)**mineralisation** as currently performed [C10, C. Gérardin], or planned for the case of diatomea silica backbone (J. Bibette - A. El Harrak).

Indeed the number of expected new systems is very large. In **pharmacology**, drug release is associated with trapping molecules in complexes, or networks; other biotechnological networks can be studied, benefitting from former basic studies on networks in LLB-ICS teams. To conclude, let us cite a bit more far-fetched systems, such as these gathered from the Autoassemblages de Biomolécules Végétales research group, which associates physico-chemistry with food and agronomy. As an already advanced study, let us mention the work on derivatives of cutin and suberin, some biopolymers of the “plant skin”, which can form membranes, but also original hollow microtubes (J.P. Douliez, INRA, L. Navailles, F. Nallet, CRPP). Meanwhile, **ABV** interest is growing in various types of associations: proteins with polyphenols in fruit juices or wines (as modelled already by catechine - β -casein association), starch with proteins, triglycerides with phospholipids), combined growth of amylose with amylopectine inside starch grains...

Achievement for these systems would be complete if a dream became reality: a technological jump in **deuteration of natural products**.

2 - PLANAR SURFACES: REFLECTIVITY

In parallel with SANS, surface reflectivity studies of the same kinds of mixed systems **use and will use the same possibilities of contrast variation**. In some cases, the third component is only the substrate. In a study of pH-responsive interfaces grafted with polyelectrolyte or polyampholyte, what is important is a good contrast with respect to substrate and solvent, here D₂O, together with the accuracy of the analysis [H4, Y. Tran].

The swelling dynamics of the ultra-thin polyacrylamide (PAM) spin-coated films in saturated vapor of water were studied by measuring the profile of D₂O or H₂O fraction in the film (725 Å) at different exposure times. Interestingly, the chain diffusion coefficient was found to be an order of magnitude higher in D₂O, due to the stronger D₂O-PAM interaction [C12, J. Daillant]. Real ternary systems in contact with surface are a field where the reflectivity team is expert. Accompanying such studies is now

a trend for links with other properties. First example, the structural properties of adsorbed poly(N-isopropylacrylamide), PNIPAM, and mixed PNIPAM-SDS layers are correlated to **gas permeation behaviour of thin foam films** [C7, L. T. Lee]. Second example, depositing **nanoparticles on a solid substrate** can be done by dragging the nanoparticles by the dewetting of particle-surfactant-polymer solutions, followed by capillary attractions between particles; minimal nanoparticle-substrate attraction is required, hence it is important to know the correlation particles to substrate. A hydrophobic surface is modelled by the air-water surface, and the contrast of silica can be varied in the ternary system, allowing a definite conclusion on the existence of depletion layer [C8, L. T. Lee]. A project of L. T. Lee is to study the typical distances involved for nanoparticles deposited on a surface, both along the perpendicular direction and along the surface plane. An **easily reversibly tuning** of these distances will be provided by the use of a three-component system : particles plus solvent plus thermosensitive polymer. In the case of optosensitive particles (quantum dots) these distances will control optics of the coating. Finally, going towards more bio-inspired systems, organisation of **cellulose with xyloglucan** at the surface of the primary cell wall has been mimicked by multilayers of cellulose whiskers and polyelectrolytes of the opposite sign and is studied by reflectivity [C11, B. Jean].

3 - SURFACE IN VOLUME, AND FROM VOLUME TO SURFACE.

Other systems enable us to study surfaces, from a volumic sample. Beyond previous work on **foams**, recently refocused on single films (J. Etrillard, E. Terriac, Rennes), are **emulsions** promising systems: here, even if the sizes of the droplets are microns, much larger than the accessible range, a large enough quantity of interface is dispersed inside the sample volume. It can be shown that its structure involves nm scale in asphaltene-based emulsions created during the production stage, since drilling brings water together with oil [H5, J. Jestin], while other asphaltene emulsions can be studied for transportation application (F. Argylier, IFP-D. Langevin, Orsay).

Particles also play a surfactant role for some so-called "**Pickering**" emulsions; some of these particles are studied in bulk (P. Perrin, A. Roudot, ESPCI). Emulsion associating particles and PNIPAM for temperature tuning are also part of L. T. Lee's project.

It has also been possible to observe silica particles **both dispersed in volume** (using SANS) and **on a silicon wafer** in contact with the dispersion, using **grazing incidence small angle scattering**; one observes a characteristic length in both situations on the spectrometer PAPHYRUS [C13, G. Chaboussant]. Though flux is low, neutrons provide some advantages (contrast, penetration) for such a combined study.

We have also proposed to study the relation **between volume and surface** situations by observing what happens to bulk complexes when transferred from the bulk dispersion to the surface. The surface can be an air-water one; presently in progress are studies of protein-based objects (aggregates, protein-polymer or surfactant complexes) in volume and surface, to end with studies of the same systems in foams - which can be seen as a reflectivity study (M. Axelos, B. Novales, INRA Nantes).

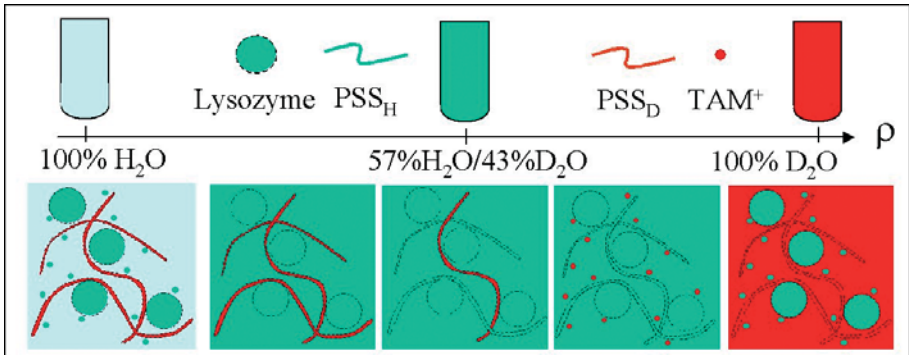
The surface can also be a hard substrate: by creating a polyelectrolyte layers or multilayer, **lysozyme surface traps** can be created by similarity with polyelectrolyte-lysozyme complexes in volume with enzymatic activity control (project of F. Cousin). This is very similar to former studies of biochips. Such systems can also be created at the surface of particles.

F - New instrumentation and new systems

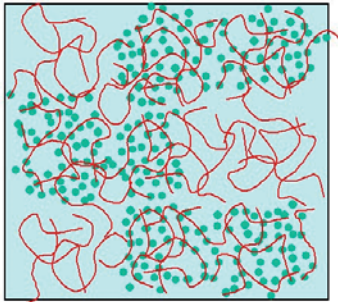
A *fourth* class of systems is only just emerging, as it is **linked with instrumentation** progress in the Small Angle techniques, namely **VSANS** ("TPA", see *Instrumentation* section). Access to lower values of q ($5 \cdot 10^{-4} \text{ \AA}^{-1}$), will enable the study of larger objects, when contrast variation is useful, or when **light scattering is impossible or difficult** (e.g. dark or very turbid inhomogeneous systems). To start with, we will study compact objects since their scattering cross-section is higher for the same size. Thus systems involving larger particles or larger aggregates are good candidates. This is obviously consistent with some of the projects discussed above in mixed systems; like confined systems, soft-hard composites, and complexes between polymers and surfactant or proteins.

Last, but not least, a large new instrument now exits one mile from the LLB site, namely the **SOLEIL** synchrotron. For example, **X + N combined studies** of the same system, which can be seen as a contrast variation, are very interesting. These have been done successfully in polyelectrolyte systems by M. Rawiso and J. Combet. We have to develop the complementarities between neutron and X rays radiations both for the projects of our users as well as our own.

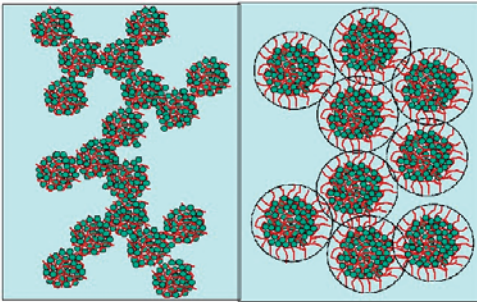
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(a)



(b)



(c)



- H1. Nanomechanics and glass transition of confined polymers within spherical nanosized particles
Y. Rharbi, N. Bassou, F. Boué
- H2. Novel frontier between liquid and solid states in polymers: identification of a macroscopic solid-like mode in the molten state.
H. Mendil, P. Baroni, L. Noirez
- H3. Chain form factor and counterions release in polyelectrolytes-proteins complexes : beyond the usual contrast matching method
J. Gummel, F. Cousin, F. Boué
- H4. pH-responsive interfaces grafted with polyelectrolyte or polyampholyte
Y. Tran, S. Sanjuan, N. Pantoustier, P. Perrin
- H5. A SANS study of the adsorbed asphaltene layer in water-in-hydrocarbon emulsions
J. Jestin, S. Simon, T. Palermo, L. Barré

[C1. P. Vallat]

Molecular structure of conjugated polyelectrolytes

[C2. S. Desvergne]

Two polymers made of the same segments which do not mix because of their different architecture

[C3. O. Sandre]

Smart hybrid magnetic polymersomes

[C4. F. Cousin]

Anisotropic reinforcement of latex films by magnetic nanoparticles

[C5. J. Vinas]

Stimuli-sensitive hybrid nano-objects: polymerisation from silica nanoparticles synthesized in aqueous medium.

[C6. J. Jestin]

Dispersions of polymer grafted nanoparticles in a same polymer matrix: the effect of deformation

[C7 et C8 L.T. Lee]

Interfacial and thin-film properties of complex systems

[C9. C. Sanchez]

Conformation of arabinogalactane-peptide from Acacia gum: a new model based on SANS and ab initio calculations

[C10. C. Gerardin]

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

[C11. B. Jean]

Cellulose whiskers-based multilayers

[C12. J. Daillant]

Effect of solvent-polymer interaction in swelling dynamics of ultra-thin polyacrylamide films: A neutron and x-ray reflectivity study

[C13. G. Chaboussant]

Study of adsorbed nanoparticles at a solid-liquid interface by neutron surface scattering

H1. NANOMECHANICS AND GLASS TRANSITION OF CONFINED POLYMERS WITHIN SPHERICAL NANOSIZED PARTICLES

Y. RHARBI^{1*}, N. BASSOU¹, F. BOUE²

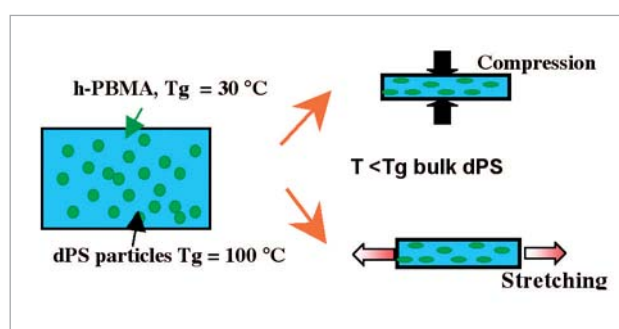
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It is most likely that a polymer's environment affects its dynamics, rheological properties and more particularly its glass transition temperature (T_g). This idea is backed up by "Brillouin Light Scattering", and ellipsometry results from Forrest and al.^{1,3}, and Keddie and al.² on both supported and free standing ultrathin films. They suggest that the T_g of polystyrene is reduced below the bulk values with a decrease in film thickness (h) for $h < 50$ nm. For free standing film, where thickness $h \sim 20$ nm, the T_g is reduced by about 60°C below the bulk value. Other experiments suggest that the T_g of supported polymethyl methacrylate (PMMA) on certain solid surfaces, increases with decreasing film thickness.⁴ However, the situation of a polymer confined within another polymer has not been thoroughly investigated. This situation is particularly crucial for a good number of applications; polymer blends, copolymers, composites... In this work we propose to study the influence of the proximity of two polymers on their glass transition and their dynamics.

We developed a method which combines Nanomechanics with Small Angle Neutron Scattering (SANS) to study the deformation modes of polymers confined within nanosized domains (20 to 200 nm). The work consists of analyzing the deformation modes of deuterated nanosized polymer particles, dispersed individually within matrices of another polymer using SANS (Schema 1). The project involves two major stages: 1) we prepare films containing deuterated polystyrene d-PS nanoparticles, dispersed in a perfectly individual manner within polybutyl methacrylate (PBMA) matrices. 2) Thereafter we apply mechanical stress to the films (compression), and we study the variations of the nanoparticles' form factor. Film preparation was carried out in two steps: 1) Synthesis, via emulsion polymerization, of deuterated d-PS nanoparticles ($T_g^{\text{bulk}} = 100^\circ\text{C}$, diameter ranging from 20 to 200 nm) and hydrogenated h-PBMA particles ($T_g^{\text{bulk}} = 28^\circ\text{C}$, diameter 50 nm). 2) Preparation of films via evaporation of a mixture of h-PBMA and dPS dispersions. PBMA particles were cross-linked during emulsion polymerization with 0, 1, 5 and 10% ethylene glycol dimethacrylate (EGDA). Small angle neutron scattering (SANS) experiments were carried out on the spectrometer PAXY (Saclay).



Schema 1. Experimental procedure

We optimized the experimental conditions for sample preparation in order to achieve perfect dispersion of the dPS particles within h-PBMA matrices. We obtained SANS spectra describing all the characteristics of the form factor of individual particles (Figure 1). The films were compressed at different temperatures in a home-made compression device.

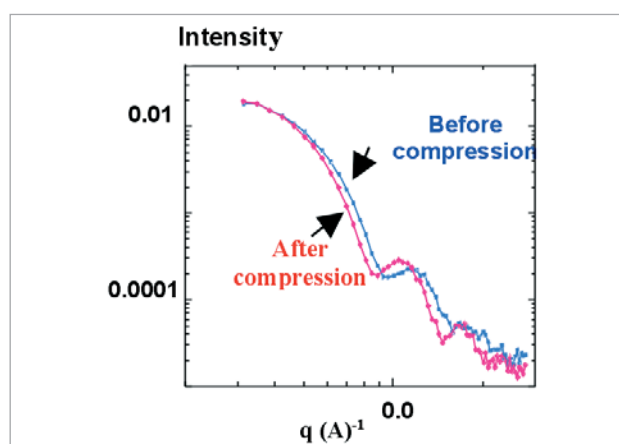


Figure 1. SANS spectra of dPS particles (90 nm, 2%) in crosslinked PBMA matrix (10 % crosslinker), before and after compression at 120°C .

In figure 1, we show the spectra of a film containing 90 nm dPS particles within a cross-linked PBMA matrix, before and after deformation. The form factor of the dPS particles changes upon compression which infers that the dPS nanoparticles undergo deformation within the PBMA matrix.

We developed a model for analyzing the SANS spectra of compressed nanoparticles and for calculating the deformation rate λ . In figure 2, we show the nanomechanical spectra, λ vs. temperature for 90 nm and 27.4 nm dPS nanoparticles within cross-linked PBMA matrices (10% crosslink). The 90 nm sized d-PS particles undergo deformation, under compression, for temperatures $T > T_g$ of the bulk polystyrene (100 °C). Whereas the 27 nm sized dPS particles begin to deform at about 20°C below the bulk T_g (Figure 2). These results suggest that the nanomechanical properties and particularly the T_g of 90 nm sized d-PS particles are similar to those of the bulk polystyrene. On the other hand, the nanomechanical properties of 27 nm particles are influenced

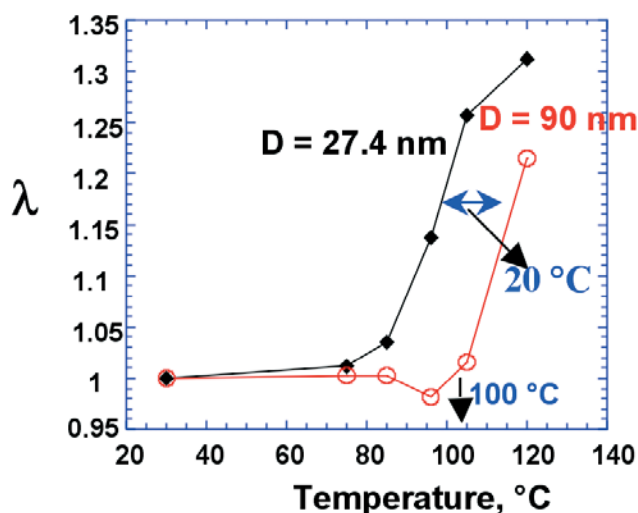


Figure 2. Nanomechanical spectra: deformation rate λ vs. temperature for 90 nm and 27.4 nm dPS nanoparticles in cross-linked PBMA matrices (10% cross-link).

by their environments and their T_g is about 20° C lower than that of bulk polystyrene (Figure 2). The onset temperature for the dPS deformation depends on the T_g of the confined polymer (T_g^{conf}) and is most likely similar to it. In Figure 3, we show the T_g^{conf} values vs. the dPS particle diameter. One can clearly see two behaviors: when the dPS particles are larger than 50 nm, T_g^{conf} is constant and similar to the bulk value. When the dPS particles are smaller than 50 nm, T_g^{conf} decreases continuously as the particle size decreases. This result is similar to that reported on ultra-thin polystyrene films¹⁻³ and is one of the first experiments that clearly show the similarity between confinement in thin polymer film and in blends.

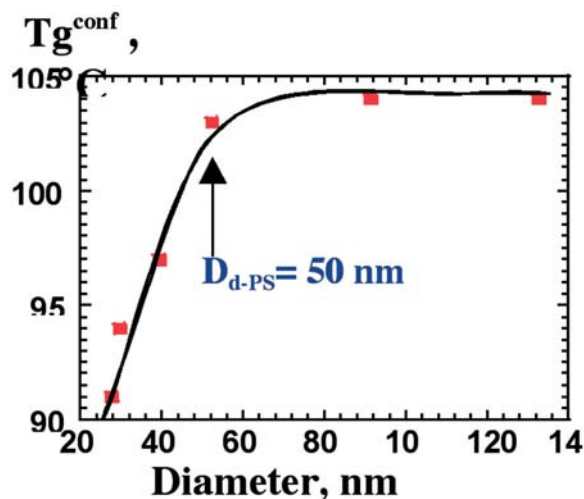


Figure 3. The onset temperature for the dPS nanoparticle deformation, calculated from figure 2, as a function of particle diameter. The PBMA matrices were crosslinked with 10 % cross-linker.

- [1] J.A. Forrest, K Dalnoki-Veress, J.R. Stevens and J.R. Dutcher, Phys. rev. Lett. 77, 2002-2005 (1996); 77, 4108 (1996).
- [2] Joseph L Keddie, Richard A.L. Jones and Rachel A. Cory, Europhys. Lett. 27,59, (1994)
- [3] J.A. Forrest, K Dalnoki-Veress, Advances in Colloids and interface Science, 94, 167, 2001
- [4] Joseph L Keddie, Richard A.L. Jones and Rachel A. Cory, Faraday Discuss.98, 219-230, (1994)

H2. NOVEL FRONTIER BETWEEN LIQUID AND SOLID STATES IN POLYMERS: IDENTIFICATION OF A MACROSCOPIC SOLID-LIKE MODE IN THE MOLTEN STATE.

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Polymers are produced and daily used but their dynamic properties far from being understood, fascinate by their puzzling properties. Indeed, polymers present unexplained large time scale relaxations; reinforced polymers display incredibly high moduli; the polymer dynamic at nanometric [1] and at filmic states [2] reveal solid-like characters incompatible with the conventional macroscopic viscoelastic properties [3]. Various flow behaviours display inexplicable instabilities. One of the most spectacular ones, is the shear induced phase transition observed in the liquid state of liquid-crystal polymer melts [see photograph below and reference 4].

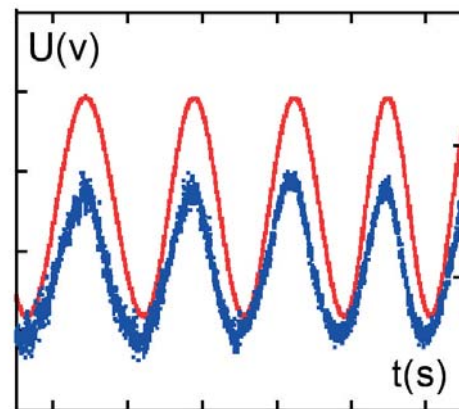
Novel experimental observations carried out at the LLB by controlling the boundary conditions between the polymer and its substrate, give a fresh perspective on their true nature. Indeed, the common and fundamental denominator in flow experiments is the no-slippage interacting condition between the fluid and the substrate(s). The several tens' years of apparent agreement between macroscopic rheological experiments and theoretical models, promoted the no-slippage condition as a postulate, reinforcing the idea that the no-slippage liquid-solid boundary is usually fulfilled.



Above a critical shear rate, the isotropic liquid of liquid crystal polymers (left photo) transforms in a strongly birefringent oriented phase (right photo). Photos are obtained between crossed polarisers in the (velocity, neutral axis) plane.

However, the emergence of new disciplines as microfluidics together with the observation of unexpected macroscopic instabilities as exposed above, shows that the fluid properties are actually strongly dependent on the scale of the observation and also on the nature of the surface interactions, driving numerous studies to reconsider now the static and the dynamic friction states between the fluid and the substrate. Combining the tribology to dynamic relaxation measurements (CEA patent), we propose a new type of dynamic experiment where the interaction of the polymer to the substrate is controlled. Under optimal conditions, we show that the molten state of polymers, far

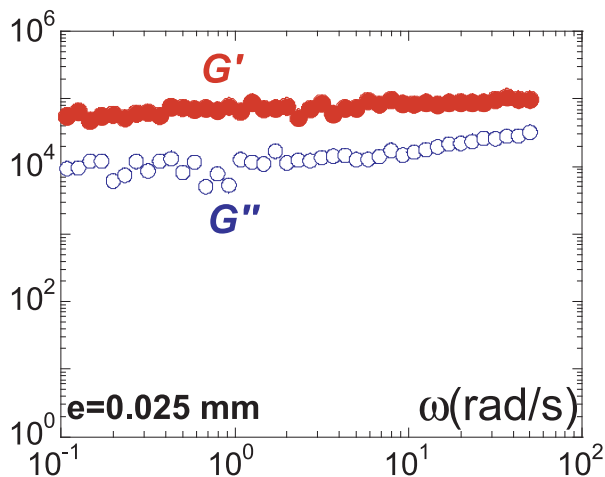
away from any transition, reveals so far unknown long range correlations [5]. The signature of an unpredicted elastic mode, is identified by the invariance of the dynamic response versus frequency and by the in-phase input strain and resulting output stress waves (see figure below).



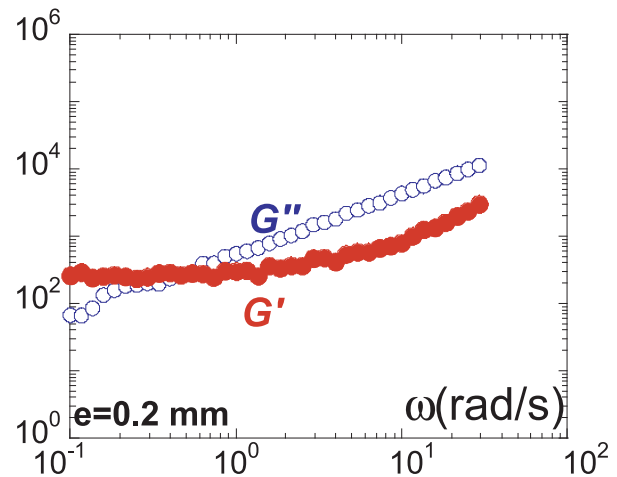
In phase entrance strain wave (red points) and resulting output wave (resulting torque - blue points) plotted versus time, evidencing a solid-like response for an ordinary polybutylacrylate at 100°C above the glass transition temperature ($M_w = 40000$, $I = 1.1$, $\omega = 0.1 \text{rd/s}$).

This elastic property is a dimensional parameter; it progressively vanishes by increasing the sample thickness, as shown in the following figures (from a to c). The solid-like response observed at low thickness (here 0.025mm) is no more measurable at large thickness (typically 1mm) and is progressively dominated by the conventional polymer viscoelastic response (figure c). The sample is an ordinary polymer measured about 100°C far away from the glass transition temperature.

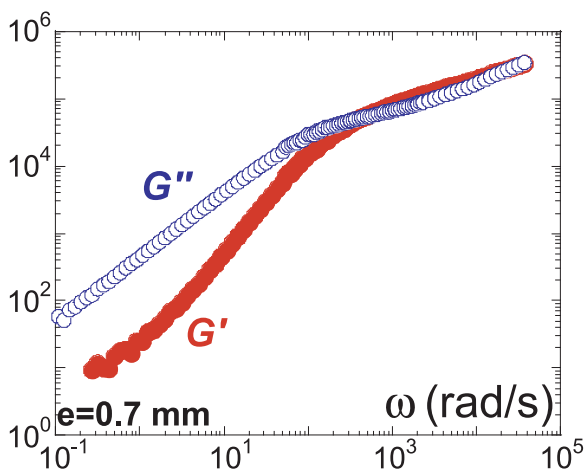
The identification of this size-dependent elasticity is of fundamental importance. It implies that the system contains unexpected giant time & length correlations at scales much larger than those described of the usual viscoelastic description (Rouse, reptation). Indeed, the low thickness solid-like response (typically measured at 0.020-0.040mm) corresponds to a gigantic scale with respect to the individual molecular scale (which is about 50-100Å). The definition of the conventional elementary polymer relaxation time described as the intercept of the ω and ω^2 scaling of the viscous and the elastic responses respectively, should be revisited since it does not reflect a terminal relaxation time.



a)



b)



c)

This experimental observation, carried out on various polymer types (LC-polymers, Polybutadiene, Polymethacrylates, Polybutylacrylates...) should shed light on various disagreements between experimental observations, theoretical developments and applications and open new routes for the understanding of polymer science and complex fluid dynamics, including the up to date active debate on the discontinuous dynamic behaviour from nanometric to macroscopic scale dynamics.

Dynamic relaxation spectra showing the linear response of the viscous (G'') (●) and the elastic (G') (●) moduli versus frequency, at different sheared thicknesses ($e=0.025\text{mm}$, 0.2mm , 0.7mm). The sample is a monodisperse polybutylacrylate ($M_w=47000$) measured at $T=T_g + 90^\circ\text{C}$.

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H3. CHAIN FORM FACTOR AND COUNTERIONS RELEASE IN POLYELECTROLYTES-PROTEINS COMPLEXES : BEYOND THE USUAL CONTRAST MATCHING METHOD

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Understanding the mechanisms driving the formation of complexes of polyelectrolytes and proteins of opposite charges is of a fundamental importance as such complexes are often encountered in biological or industrial situations [1]. A large variety of macroscopic structures can be formed depending on the kind and strength of the interactions involved in the system. We show here how the combination of SANS with contrast matching permits the full determination of the structures formed by a model system. This system, made of lysozyme (positively charged protein) and PSSNa (negatively charged polyelectrolyte), is both model from the physico-chemical point of view and from a neutron contrast point of view because PSS can be easily deuterated and $\rho_{\text{PSSH}} = \rho_{\text{lyso}}$.

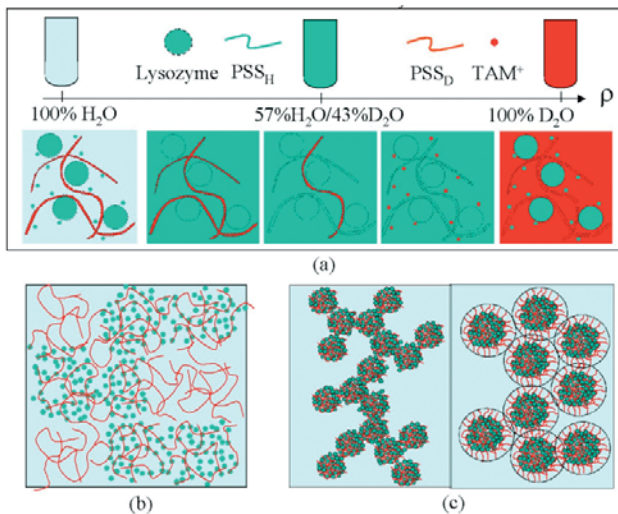


Figure 1. (a) Neutron density length ρ in the system (b) Gel structure (c) Globular structure.

Firstly, we have used PSSD to watch separately the protein and the polyelectrolyte inside the complexes. Three main structures can be formed in the system when changing the ratio of negative to positive charges $[-]/[+]_{\text{intro}}$ and the length of the PSS chains [2] for a given pH and a given ionic strength (50mM) : (i) For $[-]/[+]_{\text{intro}} < 5$ and for long PSS chains, the structure is a network formed by PSS chains cross-linked by lysozyme (Fig 1.b). Macroscopically, samples are gels. (ii) For $[-]/[+]_{\text{intro}} < 5$ and for short PSS chains, lysozyme and PSS chains are embedded in dense 3-D aggregates that arrange in a fractal network at a larger scale (Fig 1.c). Macroscopically, samples are liquid. (iii) For $[-]/[+]_{\text{intro}} > 5$ and whatever the chain length, the internal structure of the lysozyme changes. After an initial strong electrostatic

binding, lysozyme is progressively unfolded thanks to an hydrophobic contact with PSS. The two chainlike objects are finally organized in a homogeneous costructure (not shown here). We focus then on the role of $[-]/[+]_{\text{intro}}$ structure on the dense 3-D aggregates formed by small chains [3]. The primary complexes are always formed with radii around 10 nm and organize at a higher scale in aggregates of fractal dimension 2.1. The systematic use of the contrast matching of PSS_D in SANS have allowed the determination of the species composition and the water content, yielding the compactness and the inner charge ratio $[-]/[+]_{\text{inner}}$. The primary complexes have : (i) an inner charge ratio $[-]/[+]_{\text{inner}}$ close to 1 whatever $[-]/[+]_{\text{intro}}$, (ii) a high total volume fraction (0.25 to 0.4), (iii) an increases of the radius with an increase of $[-]/[+]_{\text{intro}}$ (from 75 Å up to 150 Å) and a (iv) a shell of PSS chains when $[-]/[+]_{\text{intro}} > 1$. There are free proteins if $[-]/[+]_{\text{intro}} < 1$ and free PSS chains if $[-]/[+]_{\text{intro}} \gg 1$. This inner charge stoichiometry is recovered for different charge density of components (tuned by pH for lysozyme and by sulfonation rate for PSS) and proves the dominant role of direct electrostatic interactions in complexation. The primary complexes aggregate at a higher scale with a fractal dimension of 2.1 characteristic of Reaction Limited Colloidal Aggregation often found in charged systems. The size of primary complexes is limited by the total ionic strength of solution.

We present now to experiments with specific labelling tricks that takes benefit from $\rho_{\text{PSSH}} = \rho_{\text{lyso}}$ to go further in the understanding of the complexation process.

Conformation of a PSS chain within complexes [4]:

The pictures of the two types complexes that can be formed when $[-]/[+]_{\text{intro}} < 5$ (gel or dense globules) suggest that the transition between the two regimes correspond to the overlapping concentration of the chains c^* : when the chains are in semi-dilute regime, the network pre-formed by PSS chains is cross-linked by proteins but when they are in dilute regime, chains collapse with proteins to form globules. In order to check this assumption, the persistence length l_p of the chain within the gel has to be measured to get c^* . c^* is indeed proportional to $1/N^{1/2} l_p^{3/2}$ where N is the number of repetitions units per chain. Experimentally, the system shifts from one regime to another for an N lying between 350 and 600 for [PSS] = 0.1 mol/L with [lyso] = 40g/l and I = 50mM. But if one calculate c^* with $l_p = 50\text{Å}$ (value taken from literature for pure PSS solutions), the system must stay in semi-dilute regime for $N > 30$. The chains should thus be largely shrunk when interacting with proteins.

In order to measure l_p , we have made several mixtures of PSS_H, PSS_D and lysozyme in a solvent that matches both PSS_H and lysozyme with $[PSS_H+PSS_D] = 0.1$ mol/L and $[lyso] = 40$ g/l. The only remaining terms in the scattered intensity are due to the correlations between deuterated PSS monomers $S_{DD}(q)$ that write :

$$S_{DD}(q) = \Phi_D S_{1D}(q) + \Phi_D^2 S_{2DD}(q)$$

where Φ_D is the volume fraction of PSS_D chains, S_{1D} the intra-chains signal and S_{2DD} the structure factor between monomers from distinct chains. As shown in insert of figure 2.a and 2.c, the interpolation at $\Phi_D = 0$ enable a direct measurement of $S_1(q)$:

$$S_{DD}(q)/\Phi_D = S_{1D}(q) + \Phi_D S_{2DD}(q)$$

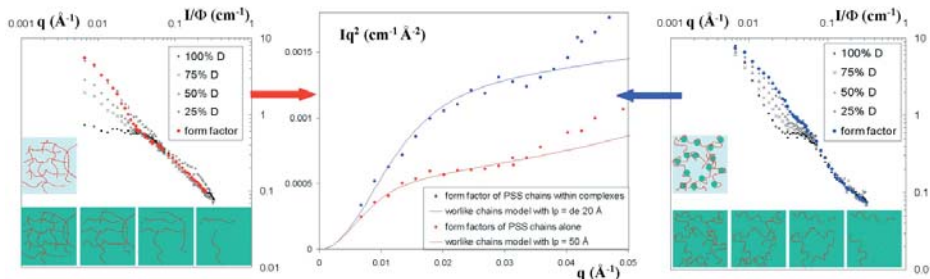


Figure 2. Measurement of form factor within complexes : (a) and (c) experimental value of $I(q)/\Phi_D = f(\Phi_D)$ and interpolation to $\Phi_D = 0$ without proteins (a) or with proteins (c). Insert show the principle of experiment. (b) Comparison of form factor in Kratky plot and scattering modelization with model of wormlike chains.

The measurement made with or without lysozyme are presented in figure 2.a and 2.c. The comparison of the form factor in Kratky plot show a large shrinking of the chains with lysozyme. A fit of the form factor by a wormlike model show that the l_p value of 50Å is recovered without proteins but the l_p is reduced to 20Å when interacting with proteins. Finally, a calculation of c^* with $[PSS] = 0.1$ mol/L and $l_p = 20$ Å show that the transition from dilute to semi-dilute regime should occur for $N \sim 500$ that perfectly matches the value obtained experimentally.

Experimental proof of the counter-ions release during complexation [5].

The counter-ions release is commonly considered as one of the main driving process of the complexation due to the entropic gain associated with the release. Though this is confirmed by simulations, there is not yet an experimental direct proof of such release. We have tested this hypothesis with a 'black or white' experiment by performing SANS measurement on samples that should scatter or not when all species except counterions are matched. This is based on the hairy shell of PSS chains that surrounds the globular complexes in diluted regime as soon as the introduced charge ratio $[-]/[+]_{intro}$ is higher than 1. In case of release,

counterions must be all expelled from the core of the hairy globules but not completely from the shell as there should remain Manning condensation on the free PSS chains. The only samples that should provide a scattering are the ones for which $[-]/[+]_{intro} > 1$ because the counterions decorate the shell (see figure 3). The matching is experimentally performed by replacing the usual Na^+ counterions of hydrogenated PSS chains by deuterated TAM⁺ counterions. Such counterions have a large contrast with a 57% H_2O /43% D_2O solvent that matches both lysozyme and PSS_H chains. Results are presented in figure 3 and unambiguously prove the counterions release : 'naked' samples do not scatter though hairy samples scatter. The counterions scattering is proportional to the one of the chains (obtained with PSS_D chains and hydrogenated TAM⁺, not shown here). This confirms that the counterions decorate the shell

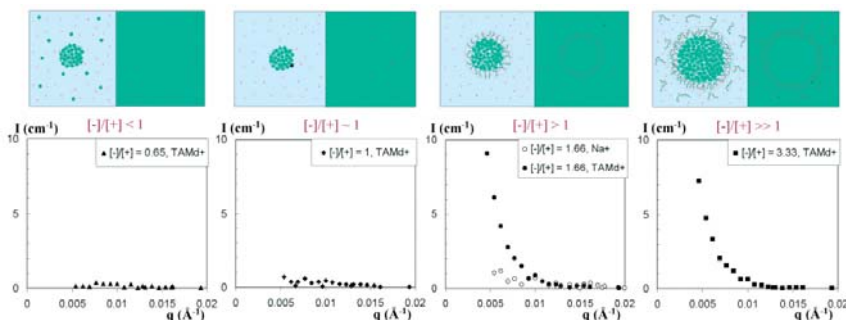


Figure 3. Upper part : Contrast of globular complexes made with lysozyme and hydrogenated PSS chains with deuterated TAM⁺ counter-ions in either a 100% D_2O solvent or in a 57% H_2O /43% D_2O solvent. Lower part : low q SANS scattering in a 57% H_2O /43% D_2O solvent. From left to right : increase of the $[-]/[+]_{intro}$.

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H4. PH-RESPONSIVE INTERFACES GRAFTED WITH POLYELECTROLYTE OR POLYAMPHOLYTE

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Interfaces grafted with polyelectrolytes are of great interest in a wide field of industrial and biological applications as well as in academic research. They are extensively used for the improvement of adhesion, lubrication, tribology, wetting properties or colloidal stabilization. More recently, some strategies are developed for the functionalization of surfaces with polymer brushes to realize smart surfaces with switchable-adaptative-responsive properties and to generate micro-patterned polymer monolayers.¹⁻² Responsive polymer brushes are attractive owing to the change of the conformation of attached chains according to external conditions. As example, neutral polymer chains are sensitive to a good or a bad solvent. For polyelectrolyte chains, the influence of environment on their charge is decisive for the stretching. An important distinction has to be made regarding “strong” polyelectrolyte for which charges are fixed and “weak” polyelectrolyte which are pH-dependent. Polyampholytes bear both positive and negative charges along the chain. With an excess of charge, polyampholyte chains are as stretched as polyelectrolyte chains. With an equal ratio of positive and negative charges, the chains are collapsed due to the attraction between oppositely charged monomers and the expulsion of counterions.³ Stimuli-responsive interfaces investigated here are grafted with polyelectrolyte and polyampholyte. In particular, we are interested in the deformation amplitude of brushes with the variation of pH.

The synthesis was performed by the “grafting from” method using surface-initiated controlled polymerization to obtain dense polymer brushes with well-defined molecular mass and low polydispersity. First, the halogenated group-functionalized initiator was anchored to the silica surface in self-assembled monolayers. Then, chains were grown from the surface by atom transfer radical polymerization (ATRP). Finally, neutral polymer brushes were converted into polyelectrolyte or polyampholyte brushes by *in situ* chemical reactions.

The swelling of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) polybase brush was investigated as a function of pH and compared to the stretching of poly(2-trimethylaminoethyl methacrylate) (PTMAEMA) quenched brush. PMAA-*st*-PDMAEMA random copolymer of 1:1 molar ratio was investigated as polyampholyte brush. Neutron reflectometry allowed the determination of the monomer volume fraction profile perpendicular to the surface. The swollen thickness was deduced and compared to the values measured by ellipsometry.

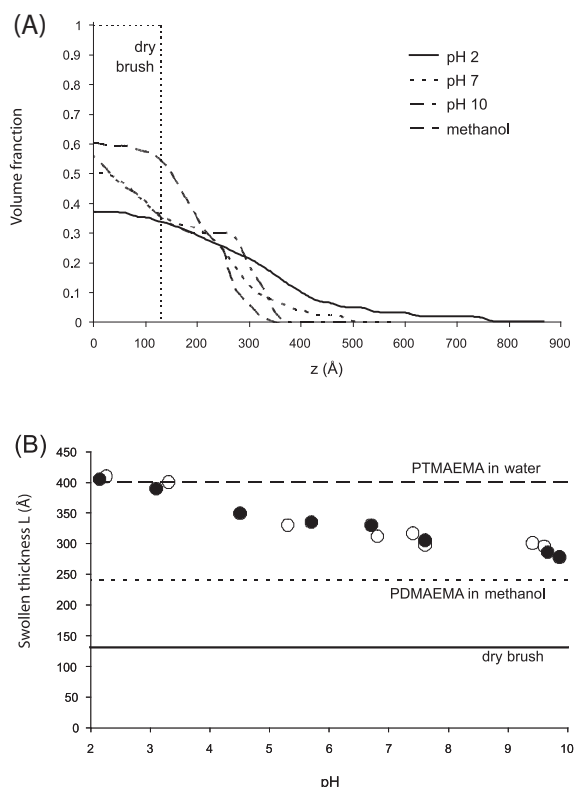


Figure 1. (A) Monomer volume fraction profile of PDMAEMA brush at various pH and in methanol. (B) Swollen thickness of PDMAEMA brush as a function of pH, measured by ellipsometry (○) and neutron reflectivity (●).

Figure 1A shows the monomer volume fraction profile of PDMAEMA brush at pH 2, pH 7 and pH 10 and in methanol. The profile of the dry brush was also given for comparison. The brush was less extended in methanol than in water and was more stretched as pH decreased. The shape of the profiles was analyzed in more detail by fitting the profiles with a parabolic function (predicted for a neutral brush in good solvent) or a Gaussian function (predicted for a polyelectrolyte brush in osmotic regime). The profile of PDMAEMA brush in methanol (respectively at pH 2) could be well adjusted by a parabolic function (respectively a Gaussian shape) as expected. In contrast, the profile at pH 10 was quite far from a Gaussian profile and is closer to a stepwise distribution as predicted for weakly charged polymer brushes.

The swollen thickness can be deduced by computing the normalized first moment of the density profile. These data obtained from neutron reflectivity technique were similar to the values measured by ellipsometry (Figure 1B). There was no hysteresis effect with the pH proving that the brush swelling was completely reversible. The swelling behavior of the pH-responsive brush was between the behavior of a neutral polymer in good solvent and a strong polyelectrolyte brush in osmotic regime, as expected.

We expected the polyampholyte brush to behave as a polyelectrolyte brush at very low and very high pH owing to an excess of charge. It should collapse in the pH range of zero net charge owing to the attraction between oppositely charged units of equal proportion.

The volume fraction profiles of PDMAEMA-*st*-PMAA brush at various pH are shown in Figure 7. The brush was rather stretched at pH 3. It was significantly contracted at pH 7 and the situation was intermediate at pH 10. The chains were not collapsed onto the surface as for a dry brush. The density profile shows a non-monotonic decrease with the distance from the surface. A higher density zone likely due to the attraction between oppositely charged units was observed. This barrier-like zone could hinder the ionization of monomer units close to the surface. It could prevent a collective ionization and reduce the collapse of the polyampholyte brush. In addition, it was found that the amplitude of deformation was higher in the pH range of zero net charge for less dense brushes.

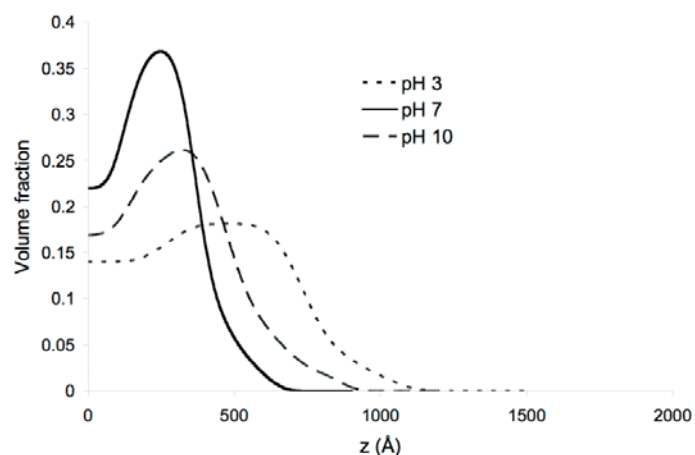


Figure 2. Volume fraction profile of PDMAEMA-*st*-PMAA polyampholyte brush at various pH.

An application of ionic polymer brushes in microfluidic devices is developed. We build microchannels with one-wall covered by the polymer brush. We investigate the electro-osmotic properties by determining the velocity of the flow under an electric field while varying the ionization of the polymer with pH.

We are also interested in the exchange of ions. Scanning Electro Chemical Microscopy (SECM) is used to follow the release of specific ions from the polymer brush. Using selective and sensible microelectrodes, we aim at the detection of protons of the polymer brush.

Neutron reflectivity experiments were performed on EROS with the help of Fabrice Cousin and Alain Menelle.

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H5. A SANS STUDY OF THE ADSORBED ASPHALTENE LAYER IN WATER-IN-HYDROCARBON EMULSIONS

J. JESTIN¹, S. SIMON², T. PALERMO², L. BARRÉ²

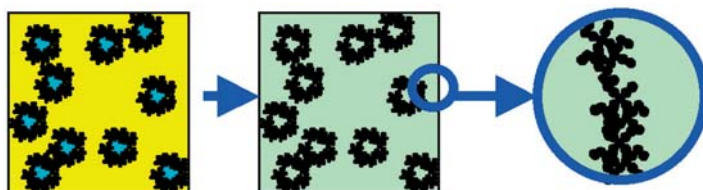
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During oil production, crude oils are typically produced as water in crude oil (w/o) emulsions, which are often very stable. Among the indigenous natural surfactants contained in the crude oils, asphaltenes and resins are known to play an important role in the formation and stability of w/o emulsions [1]. Until now, the stability of the oil/water interface, and particularly the contribution of asphaltene, has been studied mainly from a rheological point of view [2]. Correlations between stability and mechanical properties of the interfaces have been highlighted. Nevertheless, less is the knowledge about the structural organisation of the molecules at the interface and the link between the structure at the local scale and the stabilization mechanisms [3].

We present a new and original method to visualize the interfacial film in liquid-liquid petroleum emulsion by SANS measurements. Though the droplet size is micronic, one structure in the system is a few nanometer, which the water-oil interface, and also some 10 nm asphaltene large fractal-like aggregate present in the oil [4] can be linked to this interface. Neutron scattering is here used at its best, owing to contrast matching of the two liquid phases: by adjusting the scattering length density of the aqueous to the one of the organic phase, we measure the residual scattering contribution of the interface only. Emulsions are water in oil (xylene) mixtures stabilized by asphaltenes, which are the higher molecular mass, the denser, the more polar and aromatic components of crude oils. We showed the possibility to reach to the local structure of the interface (size, composition) and to the linkage of asphaltene aggregate structures between bulk and interface.

To make SANS measurements accurate and meaningful, a specific protocol is used. Asphaltene is dissolved into xylene, and the solution is mixed with water; after the emulsification process (strong stirring), two liquids phases appear, a packed droplet water phase and a supernatant, which separates by decantation. A specific attention was made to know precisely (by weighing) the volumic fractions of oil and water in each phases. It allowed us to measure independently the scattering from the initial asphaltene solution, from the supernatant and from the packed droplet water phase. The oil phase is a mixture of normal and deuterated xylene, the water phase is a mixture of normal and deuterated water. Depending on the deuterated species fractions, we can separate the scattering contribution of the different components of the system. Special care (figure 1) was made in the banks measurements (incoherent scattering and residual asphaltene bulk scattering) to background subtraction to be sure to get the interface scattering.



Scheme 1. The use of neutrons: inner and outer scattering densities are matched, and one look at the scale of the interface.

By matching the asphaltene signal, we can see the water droplets scattering contribution and have an access to the quantity of interface. Systematic experiments were performed by varying the amount of resins (which is related to the size of asphaltenes aggregates), the pH of the aqueous phase, which change the asphaltenes-asphaltenes interactions and the ageing times of the emulsions, to study slowing down effects.

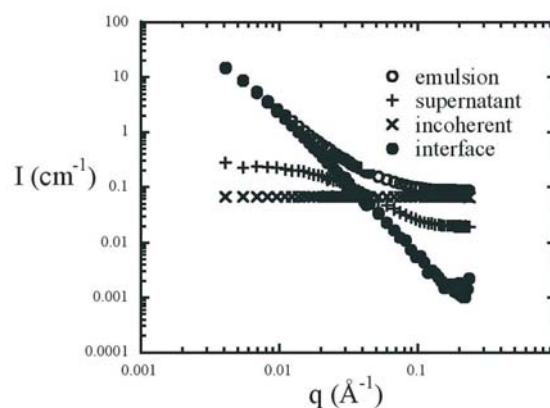


Figure 1. Specific treatment of emulsion measurements in the two liquid phase matching contrast condition to extracted the interface scattering signal after subtraction of the contributions of both incoherent scattering and asphaltene bulk scattering.

From bulk SANS measurements in initial solutions and supernatant, we can deduce radius of gyrations and molecular mass of asphaltene aggregates using the Zimm approximation. We observe a systematic decrease of these quantities after the emulsification process (table 1). This suggested a preferential localisation of the large aggregates in the interface.

Asphaltenes Aggregates	R_g (Å)/ M_w (g.mol ⁻¹) before emulsification (initial solution)	R_g (Å)/ M_w (g.mol ⁻¹) after emulsification (supernatant)
Small	66 / 9.76.10 ⁴	61 / 9.79.10 ⁴
Medium	84 / 1.81.10 ⁵	74 / 1.45.10 ⁵
Large	106 / 3.02.10 ⁵	90 / 2.37.10 ⁵

Table 1. Variation of the size and of the mass of the asphaltene aggregates before and after emulsification.

The interface scattering signal obtained after subtraction of background shows a decrease of the intensity as q^{-2} which is the sign of the scattering of two dimensional objects (figure 2).

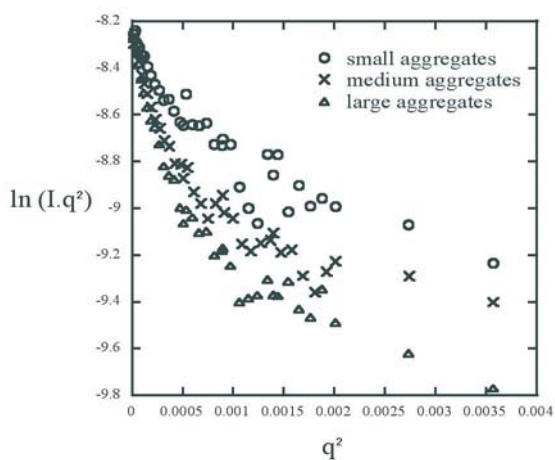


Figure 2. The interface scattering, in a $\log(q^2 I(q))$ versus q^2 plot: the thickness of the interface is given by the slope of the curves assuming a flat disk model.

The signal could be analysed using a simple flat disk model from which we could extract the thickness of the interface. The most important result is that the thickness of the interface is directly correlated to the asphaltene aggregate sizes in bulk: The larger the aggregates in bulk, the thicker the interface. Measurements in asphaltene matching conditions displays a Porod law, as expected, with a specific surface yielding the water droplets radius, in situ. Coupling these values with independent asphaltene adsorb amount in grams per grams of water droplets, using classical adsorption measurement methods, permit to calculate the quantity of molecules in grams per surface unit. The obtained adsorption values are consistent with a structural organization of aggregates as a mono layer at the interface. The stability of the emulsion could be analysed with a simple criterion: the quantity of water resolved after centrifugation and discussed as function of the structural parameter of the interface [5]. The main conclusions could be summarizing as follows: the interface is stabilized by the larger asphaltene aggregates, organized as a monolayer. The thickness of the interface is directly correlated to the asphaltene size in bulk and the larger is the layer the more stable is the emulsion; the lower is the quantity of resolved water after centrifugation. Increasing the pH of the aqueous phase (from neutral to basics values) seems to contribute to the ionization of the polar fraction of the aggregates. This changes the interaction between aggregates inside the layer, which becomes more repulsive, and induced a decreasing of the number of objects per surface unit and in fact, of the emulsion stability.

To conclude, we have demonstrated the capacity of SANS measurement to characterize the structure of liquid-liquid interface in the case of petroleum emulsion and the links between this organization at the local scale and the stability of the emulsions. From a larger point of view, this demonstrates the ability of SANS to study macro emulsions and would be applied to a large panel of experimental systems.

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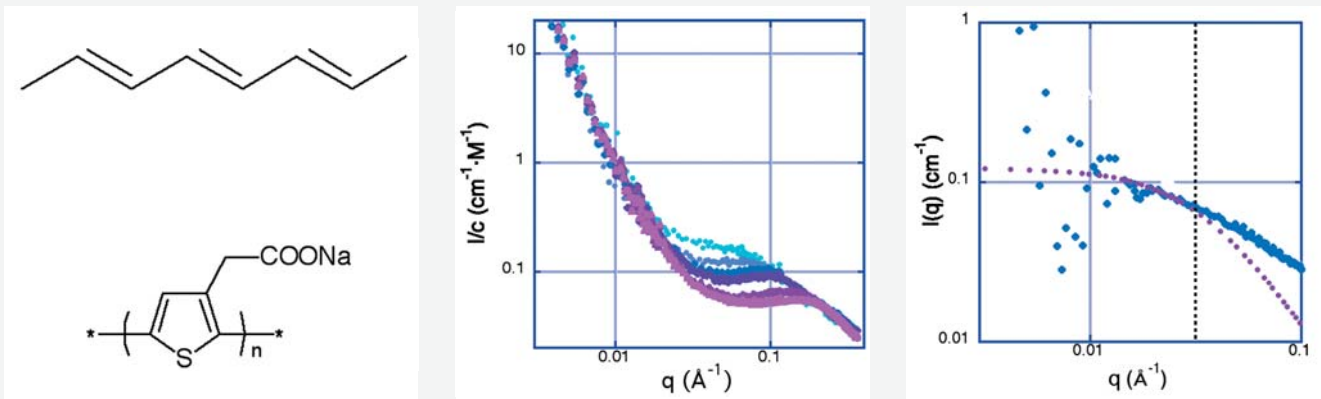
[C1. P. Vallat] Molecular structure of conjugated polyelectrolytes

Conjugated polyelectrolytes are a new class of polyelectrolytes. Their backbone consists of an alternation of simple and double (and/or triple) bonds. Thanks to this conjugation, π -electrons are delocalized along the backbone. Therefore, the polarizability of these chains is strongly enhanced and can even modify the structure of the solutions.

We study aqueous solutions of a specific conjugated polyelectrolyte: poly(3-thiophene acetic acid)(P3TAA). This macroion is prepared at different degrees of ionization. In a first step, our aim is to study the behavior of these chains in solution when they are completely ionized (with sodium as a counter-ion: P3TNaA) and compare it to the case of saturated polyelectrolytes. While the polyelectrolyte character of the chains can not always overcome the strong polarizability of rigid conjugated polyelectrolytes, the flexible chains of P3TNaA are soluble on a molecular level. It also appears that the behavior of this polyelectrolyte is that of a hydrophilic flexible saturated polyelectrolyte apart from a stronger tendency to self-aggregate (stronger upturns at low q values). However, the heterogeneities are in small quantities and the scaling laws predicted for flexible polyelectrolytes also apply here.

When salt (monovalent cation) is added to the solutions, upturns remain unchanged. Moreover, when the signal of the heterogeneities is subtracted, it appears at high enough ionic strength that the chains behave as neutral polymers with a correlation length ξ_c of 40Å (i.e. $I(q)=1/(1+q^2\xi_c^2)$). This highlights two important facts. **First**, the fact they do not vanish shows heterogeneities are not a polyelectrolyte effect: they differ from what observed for polyions at low ionic strength, or with divalent cations. They exist prior to the polyelectrolyte state, i.e. in the neutral state (degree of ionization zero). **Second**, the fact that they do not increase shows an absence of macroscopic aggregation, even without electrostatic repulsion and in spite of the strong polarizability linked to conjugation. We believe this is due, in this particular example, to the flexibility of the backbone.

[Collaboration : P. Vallat, J.-M. Catala, F. Schosseler, M. Rawiso, Institut Charles Sadron, Strasbourg and LLB]



Left: general scheme of conjugated polymer (top) and molecular structure of P3TNaA (bottom)

Middle: effect of concentration c of salt-free aqueous solutions of P3TNaA; $c=0.08$ (top) to $1 \text{ mol}\cdot\text{L}^{-1}$ (down)

Right: effect of addition of salt on solutions of P3TNaA solutions – upturn subtracted (full diamonds). Comparison with Lorentzian fit (empty diamonds).

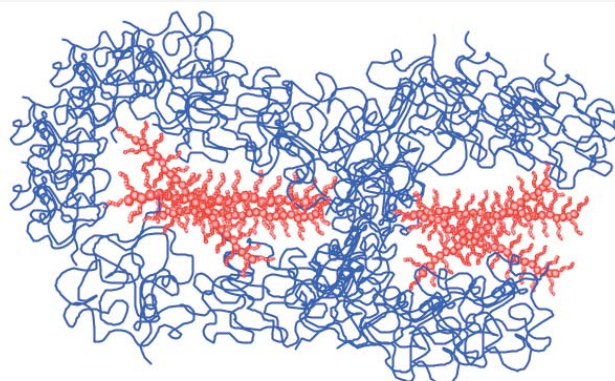
[C2. S. Desvergne] Two polymers made of the same segments which do not mix because of their different architecture

We have mixed deuterated polystyrene linear chains with branched polystyrene chains (“polymacromonomers”), allowing the localisation of the two species by SANS. Deuterated and non deuterated segments can be considered as equivalent here. In spite of this, SANS shows that the linear chains interpenetrate weakly with the branched ones. For the most compact branched architectures, the mixture remains very inhomogeneous at the 10 nm scale, as the result of a kind of depletion, and also in agreement with mean field theory (H. Fredrickson). Our observation can be related with the coexistence of chains of different branching rate in real.

[Collaboration : S. Desvergne (thesis), F. Boué, J. P. Cotton, A. Brûlet, LL; Y. Gnanou, V. Herroque, LCPO Bordeaux]

Blue : linear chains

Red : branched chains



[C3. O. Sandre] Smart hybrid magnetic polymersomes

Novel magnetic nano-composites are obtained by the self-assembly in water of polypeptide-based diblock copolymers polybutadiene-*b*-poly(glutamic acid) combined with either hydrophilic or hydrophobic γ -Fe₂O₃ nanoparticles. These hybrid supramolecular objects are either filled micelles (3-d) or hollow vesicles with a magnetic membrane (2-d). At first, we have used isotropic SANS (PACE spectrometer) to explore the different types of objects formed and prove the formation of closed magnetic membranes (before their visualization by AFM and TEM); the membrane thickness has been calculated using Kratky-Porod plots. [1] Then, the deformation of such polymersomes with a magnetic membrane has been studied as a function of an applied magnetic field intensity by anisotropic SANS on the PAXY spectrometer. Here again, the use of SANS was of great importance to determine the anisotropic deformation of the membrane quantitatively. [2] These magnetic colloids are also able to respond to stimuli such as pH and ionic strength due to the presence of the polypeptide block, forming thus “multi-responsive” nanocapsules. These superparamagnetic hybrid self-assemblies offer attractive potentialities in biomedicine of staying for some time in the blood, due to their dimensions (100-500 nm), of manipulation by an external magnetic field, of local heating by a radio-frequency field for cancer radio-therapy, and of contrast enhancement in Magnetic Resonance Imaging. *Collaboration* : . O. Sandre - R. Perzynski, LI2C Paris 6, F. Chécot- S. Lecommandoux LCPO Bordeaux.

[1]- (a) Lecommandoux, S., Sandre, O., Chécot, F., Perzynski, R. Progress in Solid State Chemistry 34, 2006, p 171. (b) Lecommandoux, S., Sandre, O., Chécot, F., Rodriguez-Hernandez, J., Perzynski, R. Journal of Magnetism and Magnetic Materials 300, 2006, p 71.

[2]- Lecommandoux, S., Sandre, O., Chécot, F., Rodriguez-Hernandez, J., Perzynski, R. Advanced Materials 17, 2005, p 712.

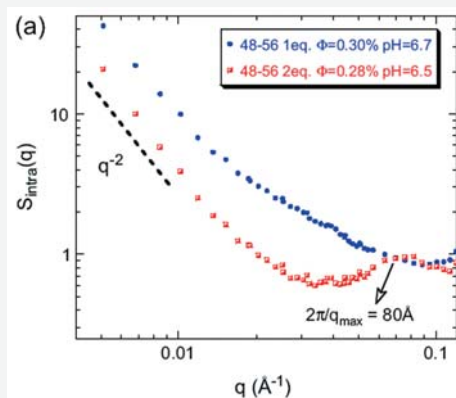
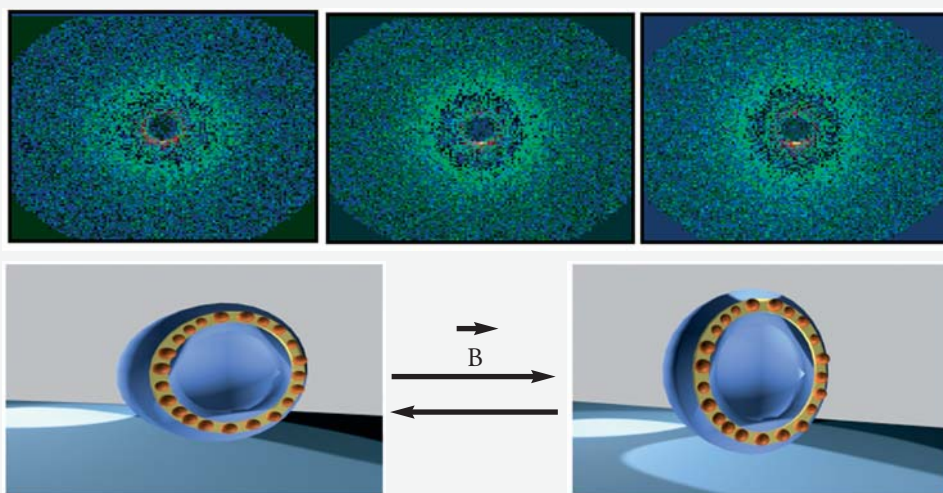


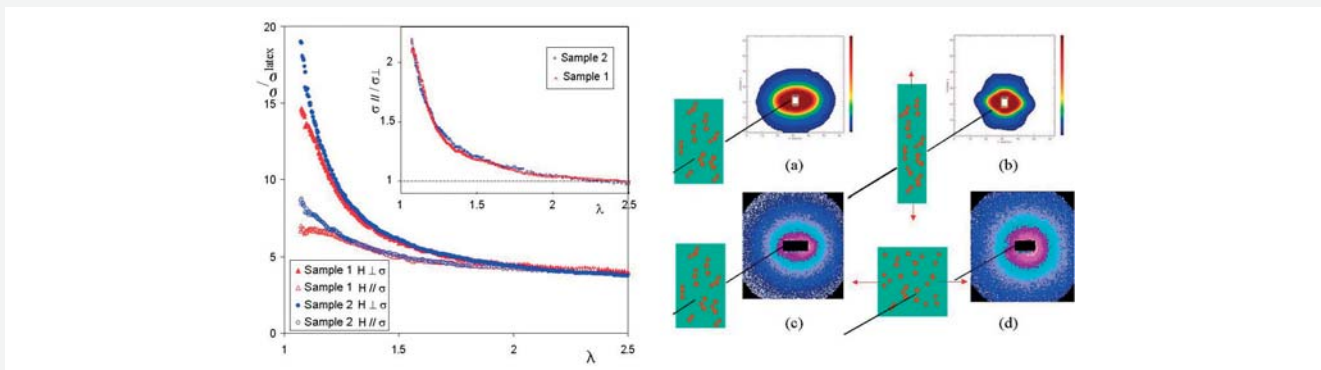
Figure 1 (a) Intra-aggregates' structure factor $S_{\text{intra}}(q)$ for hydrophobic nanoparticles associated to PB₄₈-*b*-PGA₅₆, as measured by SANS. (b) Deformation of hollow magnetic shells of the same polymersomes proven by the anisotropy of the 2D SANS patterns under a magnetic field (oriented horizontally) of variable intensity, and its schematic representation.



[C4. F. Cousin] Anisotropic reinforcement of latex films by magnetic nanoparticles

The mechanical properties of polymeric films can be strongly enhanced by the addition of mineral charges within the polymeric matrix. Recent work from LLB made on films obtained by mixing aqueous solutions of nanoparticles have shown that the mechanical reinforcement is controlled by the size and morphology of aggregates of silica nanoparticles after drying. The morphology of aggregates can be precisely tuned by the pH as it controls the surface charge of nanoparticles and thus electrostatic interactions between nanoparticles during drying. In order to get an additional degree of control on the morphology of the aggregates, we have replaced here the silica nanoparticles by magnetic nanoparticles (γ -Fe₂O₃) of the same diameter (~ 10 nm). The maghemite nanoparticles have firstly be coated by a thin silica layer to get exactly the same surface properties as the silica nanoparticles. We have then obtained homogeneous films latex reinforced by maghemite nanoparticles. When the film is dried without external magnetic field, dipolar magnetic interactions are negligible and the properties of the film are very similar to the one made with silica nanoparticles. When the films are dried under a magnetic field, nanoparticles form chainlike aggregates in the direction of the films. This has a dramatic effect on the mechanical properties of the film : the reinforcement is much higher in the direction parallel to the film than in the direction perpendicular to the film. The reinforcement anisotropy can reach a value of 2 at small deformation ! This is linked to the local structure of chainlike aggregates within the films determined by SANS. When the deformation is parallel to the applied field, aggregates organized themselves though they are broken when the deformation is perpendicular to the film.

[Collaboration : C. Ménager, V. Cabuil, LI2C, Université Paris VI, I. Dubois, J. Jestin, F. Boué, F. Cousin, LLB]



Left: reinforcement as a function of deformation (insert anisotropy of deformation)

Right: SANS experiments : (a) and (c) spectra before deformation, (b) deformation parallel to the field (d) deformation perpendicular to the field

[C5. J. Vinas] Stimuli-sensitive hybrid nano-objects: polymerisation from silica nanoparticles synthesized in aqueous medium.

We are developing new methods in the synthesis of hybrid nano-objects polymer/inorganic particles in aqueous media. We are synthesizing monodispersed nanometric silica particles which are then functionalized through reaction with alkoxy silanes containing an initiator moiety. This new method allowed us to gain in the control of the colloidal stability and to improve the polymerization conditions through a higher amount of initiating sites. Moreover, the polymerisation of thermo- or pH-sensitive monomers will give us an additional degree of liberty in the control of the shape of our objects. These model objects may lead to potential applications as bio-markers, drug delivery systems or diagnostic tools. We use SANS to characterise in details the synthesized particles and the evolution in size of the particles with the change of some reaction parameters and by checking the colloidal stability through the different reaction steps (fonctionnalization, polymerization). Also, by using contrast matching, we can follow the evolution of the polymer layer with polymerization time. The next experiences will also focus on the characterization of the solution properties of our objects by varying the pH or the temperature.

[Collaboration : J. Vinas, D. Gigmes, D. Bertin CROPS, Université de Marseille I, G. Carrot, F. Boué, LLB]

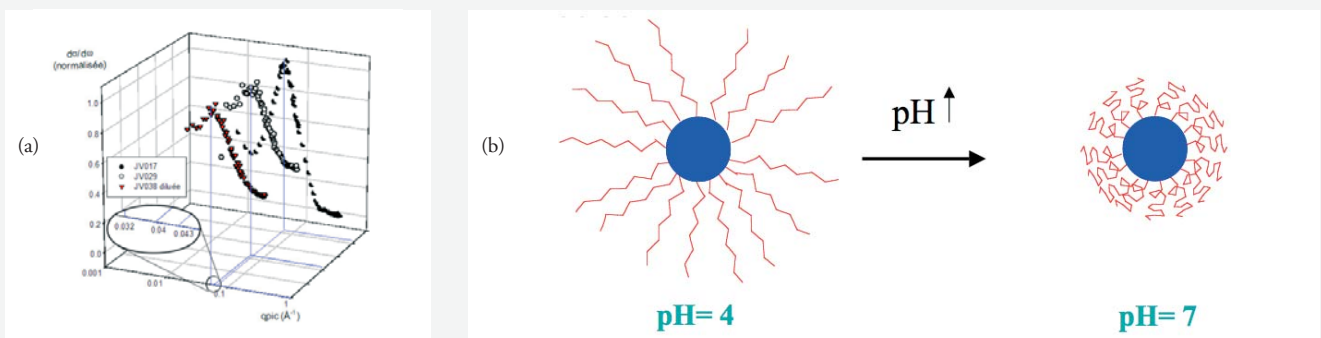
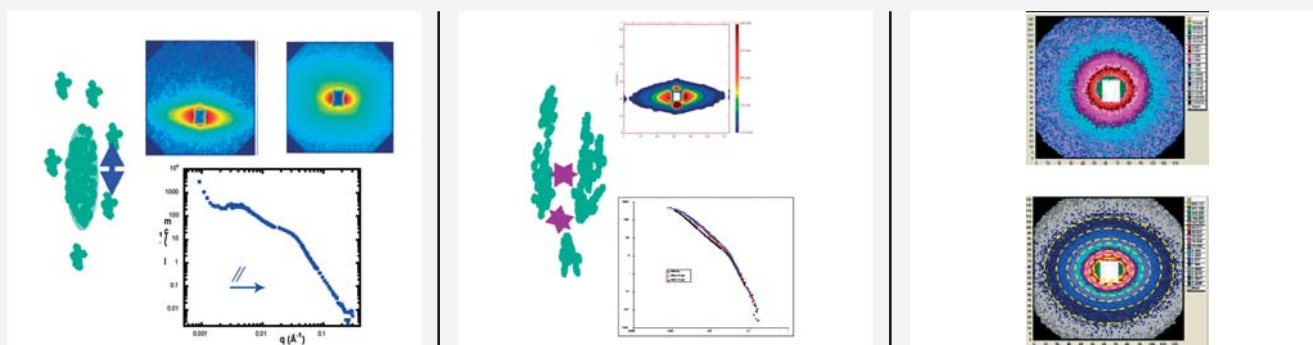


Figure 1. (a) SANS measurements of different particle sols. (b) Reversible changes in chains conformation depending on pH (stimuli-responsive polymers)

[C6. J. Jestin] Dispersions of polymer grafted nanoparticles in a same polymer matrix : the effect of deformation

Recently nanoparticles with grafted chains were synthesized owing to grafting from controlled radical polymerization in polar organic solvent. After purification, we obtain a stable sol, with silica cores of the same size as in the original sol, and characterize the polymer layer around the silica core using contrast matching [1]. We then disperse these particles in a polymer matrix of the same polymer as the grafted one. We observe that they **re-aggregate**, in different ways depending on the synthesis. Observation under deformation permits to refine the differences between two cases: left, coexistence of large deformable compact aggregates (responsible for a elongated scattering pattern) with small aggregates responsible for a correlation peak in $I(q)$ along the parallel ($//$) direction; middle: large deformable fractal-like aggregates (elongated scattering pattern, $I(q)$ curves shifted along q). We can also observe the polymer corona among matrix chains of different labelling. We conclude from the patterns anisotropy (silica core, right above, corona, below) that the corona is interpenetrated with the matrix chains, and deformed with a similar ratio.

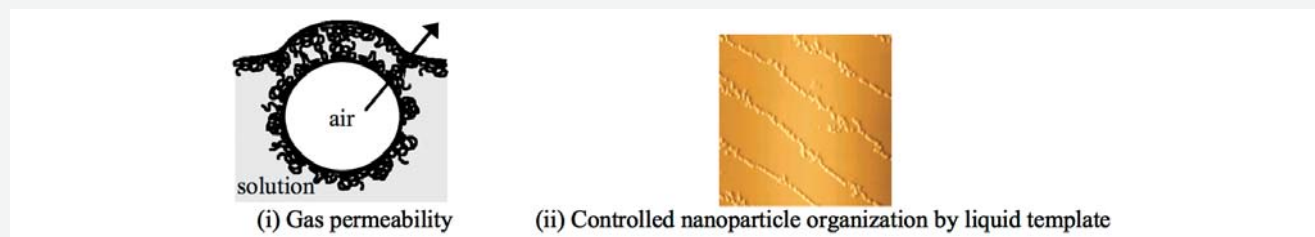
[Collaboration : A. El Harrak, S. Lorrain, G. Carrot, J. Oberdisse, J. Jestin, F. Boué, LLB]



[1] G. Carrot, A. El Harrak, J. Oberdisse, J. Jestin, F. Boué, *Soft Matter*, in press

[C7 & C8 L.T. Lee] Interfacial and thin-film properties of complex systems

This project aims to correlate interfacial structures of complex systems (polymer-surfactant-nanoparticle) with their thin film properties that are of relevance in potential applications. Neutron reflectivity used in conjunction with isotopic substitution provides a unique route to obtain structural and compositional information of surface layers in multicomponent systems. Here, we show two examples where structural and compositional information of adsorbed mixed layers are correlated with: (i) soap film stability and gas permeability, and (ii) thin-film dewetting as liquid template for nanoparticle organization on solid substrates.

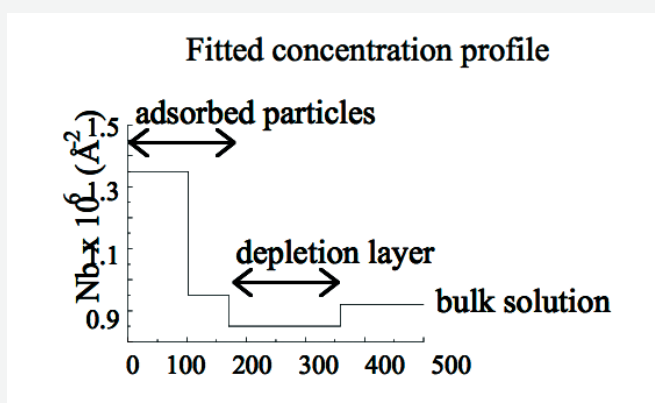
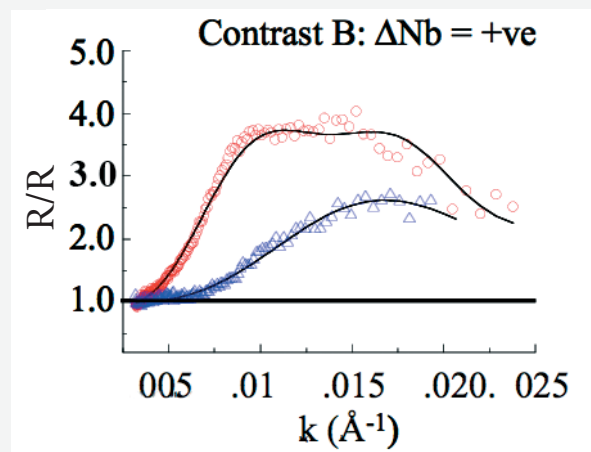
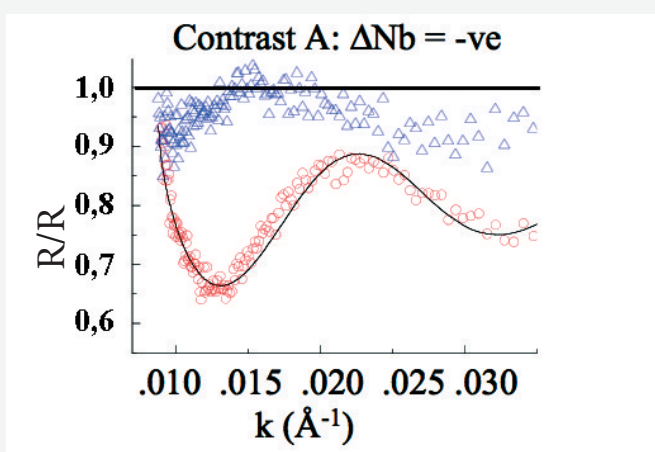


(i) Gas permeability of polymer-surfactant layers The structural properties of adsorbed poly(N-isopropylacrylamide) (PNIPAM) and mixed PNIPAM-SDS layers are correlated to gas permeation behavior of thin foam films. The gas permeability coefficient (K) of the liquid film is evaluated from the rate of diminishing size of microbubbles ($d \sim 250$ nm) formed on the surface of the solution. Irrespective of film thickness and physical appearance, the gas permeability of a film stabilized by PNIPAM alone is low ($K \approx 0.045$ cm/s) compared to that stabilized by SDS alone ($K \approx 0.10$ cm/s). This is explained by the characteristic concentration profile of the adsorbed polymer layer: a monomer-rich proximal zone ($\phi_p \sim 1$) and a solvent-rich central zone. The closed-packed structure of monomers in the proximal zone thus acts as an efficient barrier to gas permeation - an explanation supported by the non-dependence of the proximal zone and of K on polymer chain length. For polymer-surfactant mixtures, K increases with surfactant/polymer ratio in the adsorbed layer up to $K \approx 0.14$ cm/s. Mixed layers therefore show reduced efficiency as gas barrier, a result attributed to mutual decrease in the structural order of the adsorbed species.

[Collaboration: L.T. Lee, LLB; G. Andreatta, J.-J. Benattar, SPEC-CEA, Saclay]

(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.

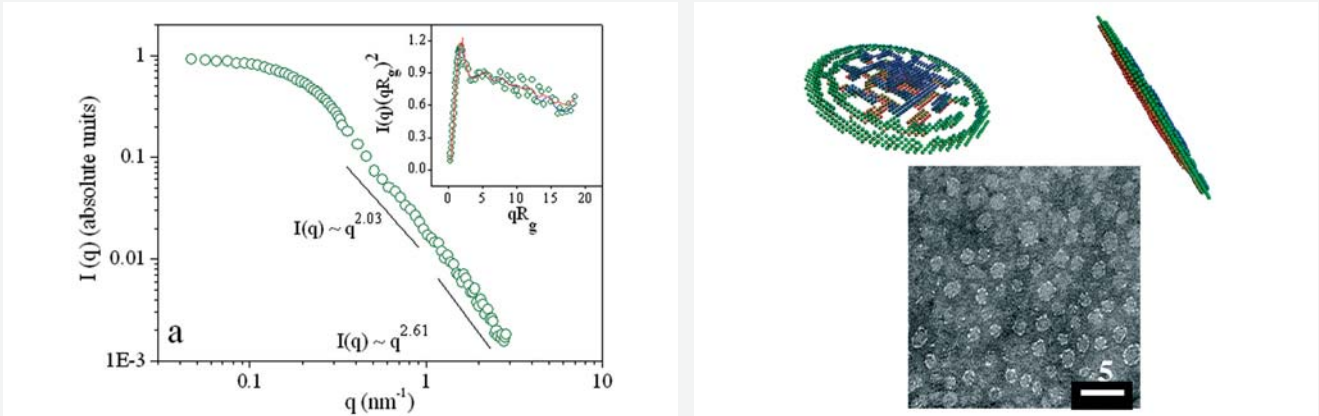
In this representation, all deviations from $R/R_F = 1$ are due only to the adsorbed layer. ΔN_b = difference in scattering length density between nanoparticle and solvent. Polymer solution (circle), polymer+surfactant solution (triangle).

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].

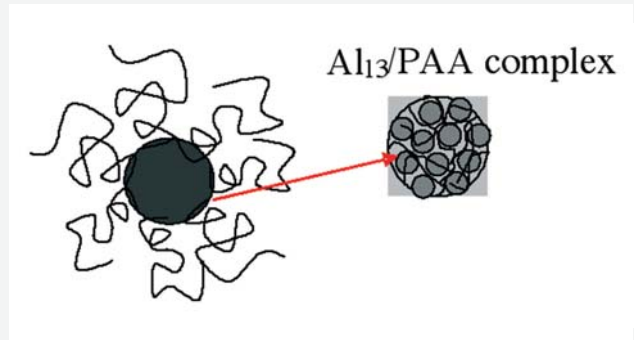
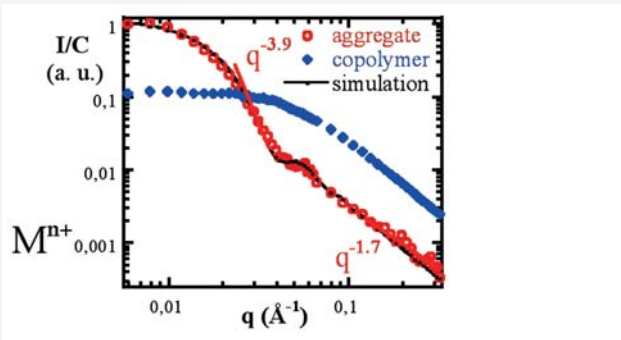
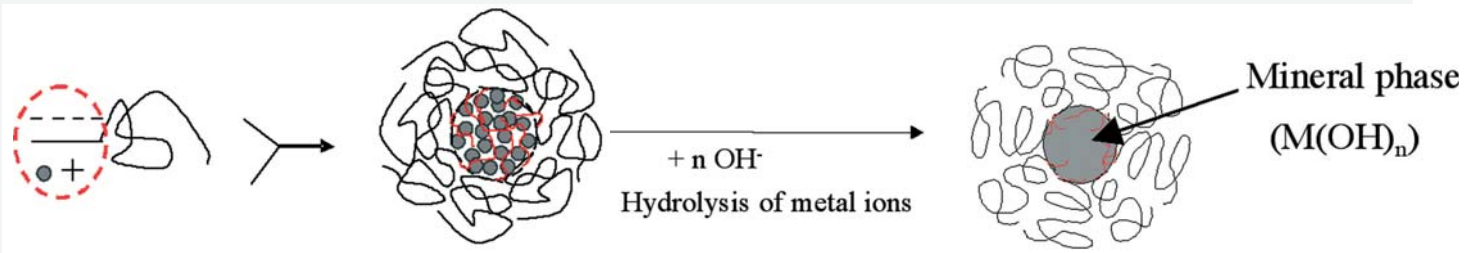
Anionic-neutral double hydrophilic block copolymers are used to control the growth and morphology of inorganic particles and directly prepare sterically stabilized suspensions of metal hydroxides. Metal hydroxides are obtained by hydrolysis of metal cations in the presence of the copolymers. The metal-complexing 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).

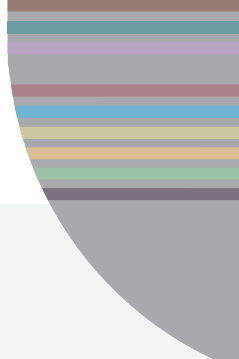
The micelles are then used as *adjustable supramolecular precursors* for the formation of metal hydroxide particles. Hydrolysis of metal ions in the micellar core leads to *mineralization* of the colloids. The size of the stabilized particles can be tuned by adjusting the copolymer-to-metal ratio, the 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.



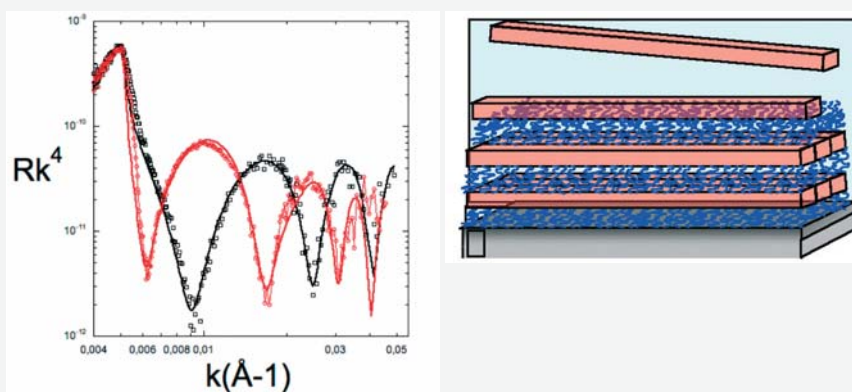
[C11. B. Jean] Cellulose whiskers-based multilayers

Layer-by-layer assembly is used here to prepare multilayer films composed of colloidal cellulose whiskers (negatively charged rod-like nanocrystals with cross dimensions between 2 and 25 nm, depending on the biological origin, and lengths between 0,3 and several mm) and a polycation, Poly-allylamine hydrochloride (PAH). They provide tools for understanding biopolymers interactions in primary cell walls and designing biocompatible materials.

Neutron Reflectivity experiments and AFM imaging allowed us to characterize the multilayers and results show that cellulose layers with a high packing density and low roughness can be obtained. A linear growth of the film with the number of layers was observed and oriented layers were prepared using ordered cellulose nanocrystals suspensions. Moreover, the possible replacement of PAH interlayers by positively charged nanoparticles such as chitin nanocrystals (rods) or mineral platelets (discs) was also evidenced.

[Collaboration : B. Jean CERMAV-Grenoble and F. Cousin LLB]

Figure 1. Neutron reflectivity curves of a polyelectrolyte (blue in the drawing below) -cellulose whiskers (red) multi-layer *before* (black squares) and *after* (red circles) adsorption. Continuous lines are fits to a multilayer model.

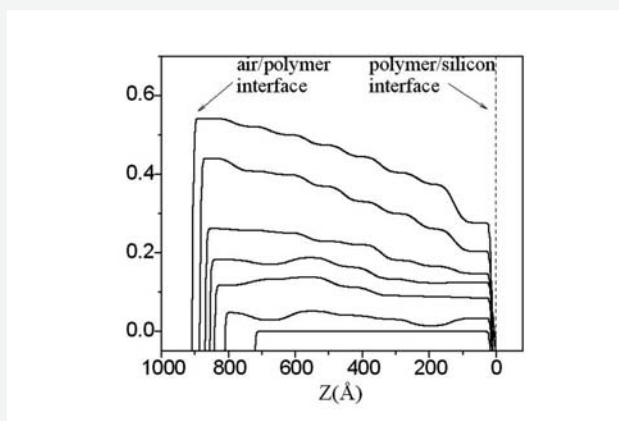


[C12. J. Daillant] Effect of solvent-polymer interaction in swelling dynamics of ultra-thin polyacrylamide films : A neutron and x-ray reflectivity study

The swelling dynamics of the ultra-thin polyacrylamide (PAM) spin-coated films in saturated vapour of D₂O and H₂O were studied using neutron and x-ray reflectivity. A uniform scattering length density (SLD) profile represents the dry PAM films, whereas the SLD profiles corresponding to the swelled films were characterized with a decreasing solvent concentration along the film thickness from top surface to the film/substrate interface. The profile of D₂O fraction in the film (725 Å) at different exposure times is shown in the figure below. The diffusion mechanism of D₂O into the films was found to be a non-Fickian process, as the D₂O diffusion coefficient was observed to be decreasing as a function of film thickness. The thickness dependent structural changes in the dry polymer films were suggested from the increased density of thinner films. The diffusion coefficient of polymer chains in the solvent on the contrary was independent of film thickness. A different nature of D₂O-PAM interaction (stronger) as compared to H₂O-PAM interaction was found to play a crucial role on the diffusion of polymer, where the diffusion coefficient of the chains was an order of magnitude higher in D₂O as compared to that in the H₂O. A lower value of the excluded-volume parameter in case of D₂O also indicates stronger monomer-solvent interaction [1].

[1] submitted to Macromolecules (2006)

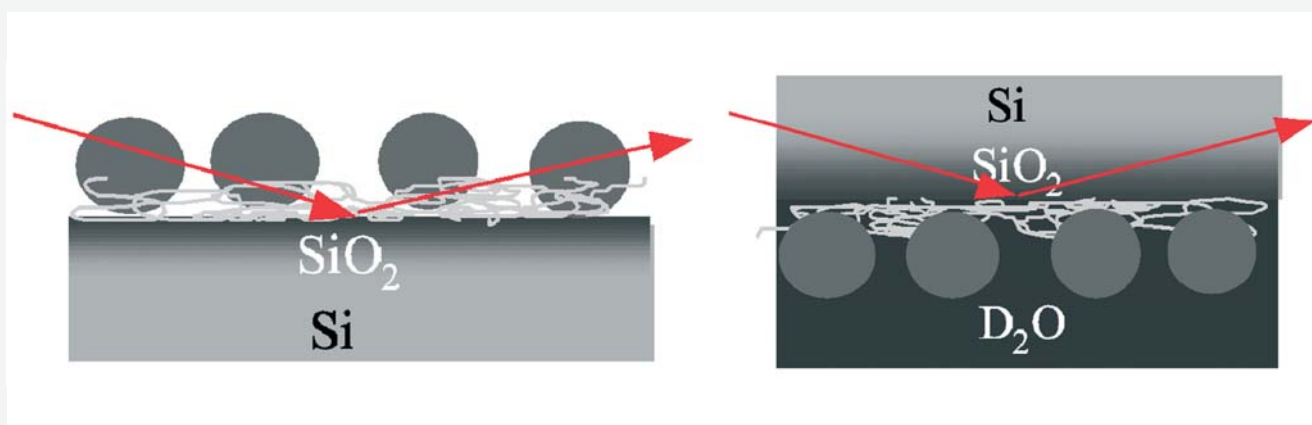
[Collaboration : M. Mukherjee, A. Singh, Saha Institute of Nuclear Physics, India, J. Daillant, LIONS, CEA-Saclay, A. Menelle, F. Cousin; LLB]



[C13. G. Chaboussant] **Study of adsorbed nanoparticles at a solid-liquid interface by neutron surface scattering.**

Using neutron surface scattering techniques like grazing incidence neutron small angle neutron scattering (GISANS) and Specular Neutron Reflectivity (SNR) we have characterised the adsorption process of SiO_2 nanospheres (of radius 8-13 nm) at a silicon-water interface for different preparation process and chemical conditions. The silica nanospheres are dispersed in aqueous media and two different size of spheres have been tested. Prior to adsorption on the surface the spheres have been characterized in bulk solution by classical SANS and a classical extinctions of the form factor of spherical particles is observed. It reveals a very narrow size dispersion. In particular, it is possible to measure the lateral correlation length of a single layer of grafted beads and to derive information on the configuration of the grafted beads at the solid surface. GISANS measurements provide a clear cut answer through the measurement of the structure surface factor which is found to be reminiscent of a repulsive liquid, with correlation peaks coherent with the surface fraction obtain from SNR. The repulsion process between the spheres occurs during grafting. This is linked to the electrostatic process of adsorption on the negative spheres on the positively charged silicon wafer. Once a sphere has adsorbed on the surface, it locally inverses the charge surface and prevents adsorption of others spheres in its vicinity through electrostatic repulsions with a repulsion range dependent on the salinity but not on spheres radius. In effect, the surface electrical charges on the spheres prevent them from forming a dense adsorbed layer at the solid surface. The typical distance of the adsorbed beads is 50% larger than the diameter of the beads.

[Collaboration: F. Cousin, J. Jestin, G. Chaboussant, S. Gautrot, F. Ott (LLB)]



Left: Large spheres adsorbed at the surface (air-solid interface). Right: Small spheres adsorbed at the surface (solid-liquid interface). The greyscale corresponds to the scattering length density (SLD) of the species.

