4 - PHYSICAL CHEMISTRY AND SOFT MATTER

Scientific activity in soft matter at LLB has two main features: research about new materials, either from chemical synthesis or by combining existing species in composite systems, and a call for a thorough understanding of some specific model systems. In both approaches, LLB is devoted to academic research that bears primers of applications planned aftermath.

Conformation of new macromolecular architectures: from synthesis to structure

SANS was developped at LLB in conjunction with the problems of polymer chain arrangement and conformation. Though the most important aspects are solved, the problem is interesting for new species recently synthesized from the large numbers of novel routes for model architectures of polymers. One aim of LLB is to offer chemists our knowledge for rapid and precise structural investigations.

Synthesized since a few months, polymers which are **both conjugated and polyelectrolytes** (J.M. Cathala, M. Rawiso, thesis of P. Vallat, I. Ch. Sadron) offer a new toolbox: precise identification of form and structure factors shows how to tune the balance between van der Waals attraction due to high polarisability and electrostatic repulsion due to high polyion charge.

Well defined **bottlebrushlike polymacromonomers** can be precisely modelized in terms of shape change as a function of polymerisation degree (from star to rod-like), compactness and interpenetration, in relation with their rheology and mechanical properties (thesis of S. Desvergne in collaboration with LPO, Bordeaux, see highlight).

Not implying synthesis, and classical - but not solved, is the question about the role and localization of metallic counterions and co-ions in **polyelectrolyte** solutions. Here the interesting approach is to use X rays, which “see” the metallic ions, in complement with neutrons which “see” the organic polyion part owing to labelling (M. Rawiso, J. Combet, F. Boué).

New tricks in self-assembling systems: copolymers and others

Self-assembly involves a composite structure of the object, the different parts of which can be “switched on or off” by varying their scattering length, a privilege of neutron scattering.

For example organic long **molecular threads** formed **spontaneously** in solution looks impressively well ordered, as seen on a Electronic microscopy picture below. SANS is used to measure their axial diameter which is one key of their association: this is measured using deuteration of the side-parts (M. Mesini, ICS Strasbourg, see Figure).

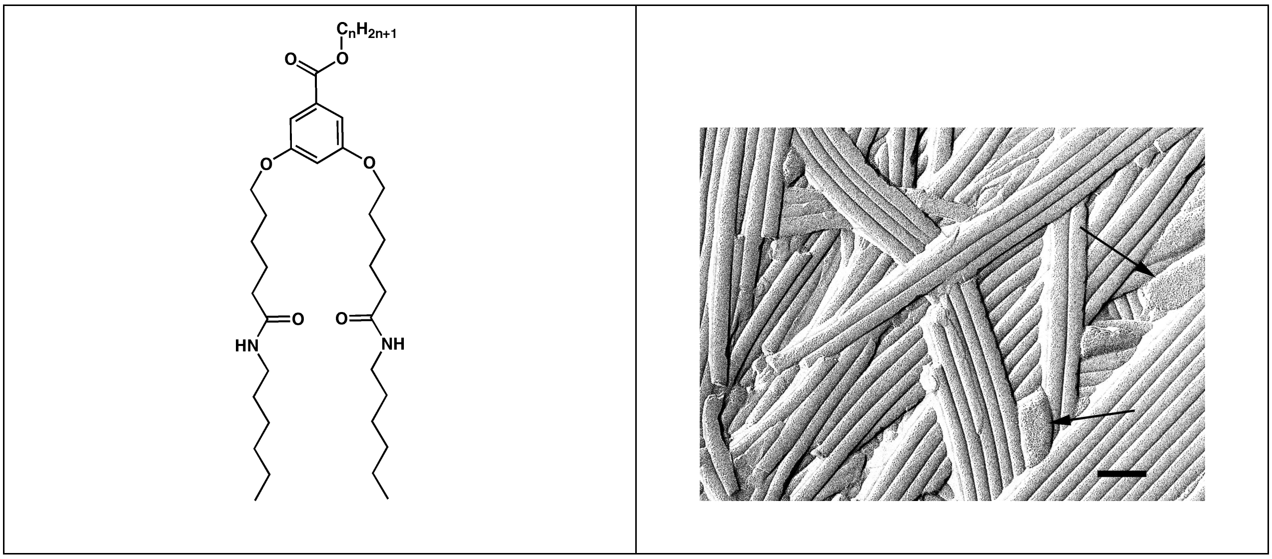

Figure. Organic long molecular threads formed **spontaneously** (from the molecules pictured on the left hand side) in solution as seen here by electronic microscopy are also studied by SANS in order to understand the effect on the axial diameter of a given part of the molecules, which is labelled.

Such **supramolecular association** (as named by J.M. Lehn) can also extend to **macromolecules**. The ability to self-assemble **in water** for elementary bricks including a polymer part has been directly monitored in terms of length and mass of the rods (see Highlight by L. Bouteiller et al), owing to the high contrast with D20 solvent.

Hydrophobic interactions are also source of association: copolymers, for example can be nicely combined with specific associations of the other block: a Bordeaux team has synthesized a polypeptide block which brings a (relatively unusual) rod-like feature, and lead to "**polymerosomes**" structures (Lecommandoux et al., LPO Bordeaux, see Figure below). The vesicle-like shape could be resolved only using SANS.

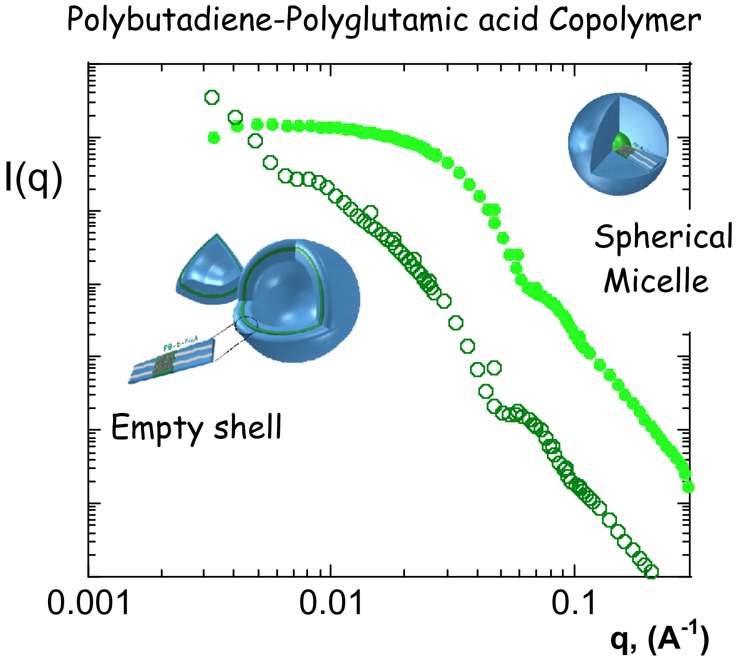

Figure. Scattering from polymerosomes.

Another example of mixed self-assembled systems is **surfactant phases containing copolymers** with hydrophobic blocks. Copolymers can modify the physical properties of various surfactant phases; this is a wide investigation field of the Rhodia Cranbury unit. Using labelled surfactants allows distinguishing them from the polymer. The effect of the chain confinement is also important here, and a balance between the two effects must be studied, which includes the case of homopolymers with surfactants (C. Ligoure, L. Ramos, Montpellier).

Other composite polymers with hydrophobic moieties attached in another way (e.g. pending), have associative properties also often studied. These moieties are labelable. The novelty is that they can be made **thermo-sensitive**, as for PNIPAM, leading to environment adaptative gels (Hourdet, ESPCI): microscopic regions of collapsed chains are immediately visible.

PH sensitive moieties are another route to adaptative response. Corresponding materials are often gels, and SANS gives the solvent (e.g. water) localization inside the gel, hence its kinetics, and its mechanical properties.

Reflectivity can also be useful, in relation with "adaptative adhesion". One measures the penetration profile of a polymer brush into a pH sensitive gel layer (Geoghegan et al., highlight). Adhesion can also be studied by reflectivity through interpenetration of two different polymers layers (Schach et al., highlight).

Nanocomposites: particles plus polymers.

The dispersion of nanoparticles in a bulk polymer matrix has also many applications, permitting the best use of nanoparticles, or improvement of polymer properties, such as mechanical reinforcement. In all cases the use of contrast matching via partial deuteration of the solvent allows to see either the mineral part, or the organic part.

Nanoparticles can be made compatible with polymer by grafting: in LLB, contrast matching has been thoroughly used to follow the growth kinetics of polymer chains from the surface of silica nanoparticles (the so-called **“grafting from”** method - G. Carrot, thesis of A. El Harrak, with J. Oberdisse and J. Jestin, LLB, see highlight). The polymer grafted silica nanoparticles are subsequently dispersed inside a polymer matrix, as can be followed by SANS.

Stabilization of silica **particles** is also done using copolymers, like in water for cosmetics (ESPCI, UMR Lafuma, contract with **Dior**), or using small molecules, like for fumed silica modification dispersed in an Epoxy resin (J.F. Gérard, INSA Lyon, E. Bugnicourt, thesis grant by **Wacker**).

A third way is to immobilize the nanoparticles inside a gel: in particular ferrofluids nanoparticles (8nm, stable in water) have been introduced inside natural alginate hydrogels (R. Perzynski, V. Cabuil, A. Bée, S. Roger). In such **ferrogels** the coupling can lead to modification of the magnetic suspension and its dynamics, as well as to macroscopic properties of the gel under magnetic field. Ferrofluid particles have also been introduced in the polymerosomes described above (O. Sandre, S. Lecommandoux).

In nanoparticle synthesis routes, the “mixed” nature of the system can be inherent to the chemical route, like in the use of copolymers for the growth of mineral particles (C. Gérardin Montpellier) or at first stages of the **growth of metallic particles** where some organic ligands wrap the metallic initiator (M. Kahn, K. Phillipot, C. Amiens, A. Maisonat, B. Chaudret, Lab. Chimie de Coordination, Toulouse). In both cases we use contrast to follow the particle initial growth together with the organic medium organisation.

To close this section, let us recall **GI-SANS** measurements (see instrumentation section): in such case, instead of bulk dispersion, nanoparticles are dispatched on a surface.

Biotechnology

Biotechnological systems, for food, medicine can display simple situations in our field of competence: for example, the “ball + chain” association is present in the case of water soluble **polymers associated with proteins**. We are studying at LLB the case of synthetic polyelectrolytes (Sodium polystyrene sulfonate, PSSNa) mixed with lysozyme (F. Cousin, thesis of J. Gummel). This internal work is linked with similar studies of external users: C. Tribet, at ESPCI, uses hydrophobic moieties grafted on the chains, which can interact with the protein hydrophobic sequences; M. Axelos and I. Schmidt, at INRA (see highlight), use a pectin as the polyelectrolyte, and the protein is a napine, found in wheat. We then reach the field of **food research**; we unravel very similar structures for the two LLB and INRA systems, whereas the possibility of deuterating PSSNa makes a deeper analysis possible and useful in both cases. Deuteration has also been developed now by C. Tribet. All this work is also included in the CNRS-INRA GDR *Autoassemblages des molécules végétales* (biophysical aspect of plant growth, see below). The cases of polyelectroyte plus surfactant complexes (D. Langevin, Orsay), as well as arabic gum (acacia; C. Sanchez, D. Renard) give also very close structures.

In **biomedical** aspects, physico -chemistry can also be important:

- association between **polycations and DNA** bears many resemblances with the case just evoked; this work is developed at Evry by L. Auvray, associate researcher of the lab.

- gels studies for **capillary electrophoresis** of DNA thermosensitive copolymers have been made by J. L. Viovy et al., at Institut Curie, Paris. They have a polyacrylamide backbone with grafted small chains of poly(N-isopropylacrylamide) or poly(N,N-dimethylacrylamide), which make them undergo a transition between a high and a low viscosity state. DNPA studies (thesis of V. Barbier, 2002, thesis price GFP 2003) show that the high viscosity state at high temperature retains some micellar aggregates which damage the separation properties, due to hydrophobic interactions with DNA.

- specific silicone gels for **artificial eye crystalline** display systematic solvent localisation heterogeneity in relation with the high softness required for the ophtalmologic application in cataract disease (with J. Hilborn et al., E.F.P.L. Lausanne, now at Uppsala).

Finally, let us quote the case of **biochips**. Here it is possible to use reflectivity to characterize the polymer layer used to bear the detecting macromolecule (oligonucleotide for example). Special copolymers have been developed by Biomérieux ad characterized at the laboratory (F. Cousin, LLB, coll. with B. Cabane).

Films, foams, emulsions.

The polymer concentration profile of **polymers grafted** on a inorganic substrate is studied by **reflectivity**, as highlighted in the contribution of C. Devaux, J.P. Chapel, and F. Cousin, and of Geoghegan et al. Another surface grafting by L. Billon et al., Pau, is studied by reflectivity (wafer grafting of wafers). In the latter case, a SANS study is planned, on chain grafted on silica particles. There can be a link between reflectivity and SANS studies at this level.

Such relation between SANS and reflectivity is also present in the study of a special state of matter, the foams. This has been initiated at the lab in collaboration with M. Axelos, INRA. Two other groups are now working on it, R. Delanay, A. Renaud, and J. Etrillard (UMR A. Renaud Rennes; see Figure below) and C. Dame (th. CEA) with S. Faure (Cadarache - Marcoule, CEA) for **nuclear decontaminating foams**: interestingly, the SANS spectra scattered by a dry foam are very much like the reflectivity spectra by a thin film. This allows studying the films inside the foam, which can be different from an individual one.

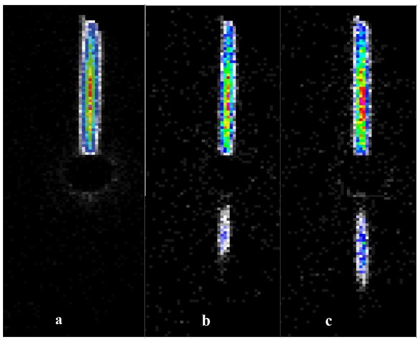

Figure. Neutron scattering by a single foam film (Rennes-INRA-LLB team)

A medium similar to foam is emulsion: studying **asphaltene water in oil emulsions** has been undergone by D. Langevin (L.P.S. Orsay) and L. Barré, C. Argyllier, T. Palermo, of Institut Français du Pétrole. This is the basis of a IFP-LLB contract (2004 post-doc grant of J. Jestin, now hired at LLB).

Soft matter under Constraint.

SANS shows a large versatility to various sample environment more complex than simple liquid or solid samples in a simple cell. A first widely developed at LLB field is the study under deformation.
In-situ shear ("Rheo -SANS") has been developed via the use of several shear cells, with various original geometries (Couette cell, cone-plate shear cell, (velocity, velocity gradient) cell), which can be made transparent to neutrons.
The main current field of shear investigation at LLB is the rheological response of different melts including **liquid crystal polymers** (LCPs), by L. Noirez and Hakima Mendil (thesis student; former studies were done by C. Pujolle-Robic (PhD) and S. Lerouge, post-doctoral position). LCP'S are interesting since they display in addition to the flow instabilities encountered for melts (extrusion defects, slip effects and other yet unsolved problems), some properties related to the long range ordering of liquid crystals. One of the most spectacular features of these non-linear LCPs' properties is the appearance within the isotropic phase, of a non-equilibrium phase induced above a critical shear rate. Strikingly, the characteristic times deduced from Small Angle Neutron Scattering under flow, from viscoelasticity and from rheo-birefringence disagree with conventional rheological models for linear amorphous polymers (Rouse, reptation). This suggests novel correlation scales at a supramolecular level, which should be generalized in a generic analysis of non-linear behaviours in non-newtonian fluids, underlining in particular the analogy between melts and lyotropic systems.

Some external groups such as the Pau group (J. Peyrelasse et al.) in collaboration with A. Lapp also study shear effects, looking at the induced modification of structure formed by **associative polymers**.

Stretching of complex polymer films is also under study in several cases:

- monitoring **particles displacement** under stretching - in order to understand mechanical **reinforcement**, in nanocomposites films obtained by mixing our polymer grafted silica nanoparticles described above with the same polymer (thesis of A. El Harrak; this has been made formerly by J. Oberdisse for nanocomposites films obtained by mixing silica nanoparticles and latex nanoparticles).

- relaxation after a **step deformation** of melt made of **bottlebrush** polymacromonomers mixed with linear chains (S. Desvergne et al., highlight), allowing to understand the corresponding dynamics and their rheological properties.

- **glass transition** of polymers **under stretching**, by C. Alba - Simoniesco, Orsay, in coll. with F. Lequeux, ESPCI (SANS and inelastic neutron scattering, time of flight , MIBEMOL)

- **latex polymer films** (Y. Rharbi, Lab. de Rhéologie Grenoble) are actually biaxially stretched (in other words crashed along the third direction). This is linked with the study of interpenetration of polymer latex particles during filmification or coalescence, and their possible properties modification (like glass transition). From the point of view of polymer interpenetration, such bulk study meets the surface study made by neutron reflectivity quoted above.

- **ion conducting nafion membranes** have been studied by L. Rutabat (SFN thesis price 2004) thoroughly at rest but also in stretched state, which give additionnal information of the cylinders and fibres hierarchy of structure (see highlight), in particular owing to contrast matching.

National and European programs and Industrial collaborations

Another aim of LLB is to build **direct contracting** with different industries: we quoted above the cases of Rhodia Complex fluids Lab of Cranbury, US, as well as the Rhodia research unit of Aubervilliers (grafting polymer from silica particles), Institut Français du Pétrole, Biomérieux, CEA (foams for decontamination, special surfactant (F. Testard et al., thesis of J. Prevost, SCM, Saclay -Marcoule), dispersion of uranium by specific ligands (thesis of J. Causse Montpellier). It is important to understand that **at the same time, many other industrial applications are developed via the work of external users**.

LLB is implied in several programs. The national network “Groupe de Recherche” («**GDR»**) **«ABV**», Autoassembly of Biomolécules Végétales” (BULEON Alain, INRA Nantes) is now launched (in parallel, a European NoE proposal Biopan will be re-submitted for a second round). This «GDR» establishes a bridge between CNRS and INRA teams working on plant growth, at the level of Plant walls, Polyphénols, and Albumen (wheat, starch, protein corpuscles), and interfacial properties. The national «GDR» «**PolyFUM** » (Dr Gunther Reiter), merged with the European RTN **Polyfilm**, studies thin films: our contribution has been to show that the conformation of polymers in film thinner than the chain equilibrium size is still a random walk at semi-local scale. We now observe the slowing down of the dynamics of polymers chain grafted at the surface of a silica particle. A European NOE on networks has been submitted but must be resubmitted (Gert Heinrich, M. Geoghegan, U. Sommer). A Marie Curie project on reinforcement is under curent proposition by J. Oberdisse. The GDR project on **foams** (MOUSSE, Michèle ADLER LPMDI, Université de Marne la Vallée) will be a good opportunity to make useful our in situ studies of the film thickness in foams.