

5 - SOFT MATTER AND BIOMATERIALS

This report presents a combination of work from the Soft Matter group own research and work from external users; one can see a kind of synergy, since there are common trends, interactions and collaborations with users in the field. The activity involves SANS, Neutron Reflectivity, and to a lower extent Neutron Spin Echo, Light Scattering (in the lab). It covers the field of colloids, self-assembling surfactants, nanoparticles and polymers, our strongest field of expertise.

One, two and many component systems:

A common trend in Soft Matter focus on studies of complex systems, combining two or more components, which can be observed separately due to the wide range of neutron scattering length densities (through deuteration in particular). This is the case for polymers systems mechanically reinforced by nanoparticles fillers, vesicles with membranes stabilised by polymers but also for the rising theme of polyelectrolytes with proteins.

Rheological properties, thin films and biomaterials:

In many of these systems, we are interested in mechanical or rheological properties, prompting structural studies under deformation, in other words Rheo-SANS. Leaving the bulk case, neutrons are also very appropriate for analysing confined systems: chains confined in porous media, or in ultra-thin polymer films. Further down to the two-dimensional case, we used Neutron Reflectivity. After former studies of liquid – air interface of thermo-sensitive polymers solutions (PNIPAM, Methyl Cellulose), and of solid-solid interdiffusion profiles between polymer layers (incl. polymer network, in relation with adhesion), we focus here on layers used to capture DNA oligonucleotides at the surface of biochips.

Modelling and Instrumentation:

Work on Instrument or Methods, new Very Small Angle spectrometer (J. Oberdisse), Time resolved nuclear polarization observed by DNPA. (H. Glättli, thesis E. Leymarié, collaboration with PSI, Switzerland), are detailed in other Chapters, as well as Modelling of the complex associations encountered in nanocomposites (see section 5.2).

POLYMER OBJECTS FROM NOVEL SYNTHESIS ROUTES AND ASSOCIATIONS

New polymer architectures:

Beyond what has been imagined by their creators, new architectures in polymer science have definitely to be characterized and neutron scattering is a tool of excellence in the field.

Copolymers:

A first external work is **highlighted** in this report: it concerns polypeptide-polybutadiene copolymers, which can form vesicles which shape depends on the nature of the aqueous solvent, pH, salt content etc.

Collaboration S. Lecommandoux, F. Checot, LCPO Bordeaux and A. Brûlet, J.P. Cotton, LLB.

Branched polymers:

Several works concern **bottle-brush branched polymers**. Some promising results have already been obtained by grafting living polymer chains of polystyrene (PS) on an already existing backbone of Polyvinylether (PCVE), as done by Schappacher and Deffieux (LPO, Bordeaux).

Macromonomers:

An on going project is the polymerisation of a molecule, Norbornene, on which is grafted a PS chain, which therefore form a “macromonomer” (Y. Gnanou, V. Herroquez, thesis S. Desvergnès). The polymerisation consists in opening a ring (Ring Opening metathesis), the strength of the reaction being able to connect together macromonomers of different nature (e.g. PS branch and polybutadiene branch).



The shape of bottle-brushes crosses over from spherical shape to rod-like and eventually worm-like shape when increasing the ratio of the backbone length (i.e. the degree of polymerisation DP) to the branch length as illustrated in Figure 1 below. The work on PCVE-based grafted bottle-brush showed that, due to the high grafting density of PS, the persistence length is much higher for the backbone of the grafted polymer than for the non-grafted backbone alone. We are also interested in measuring how the lateral polystyrene chains are elongated, using in all those situations appropriate labelling and contrast conditions.

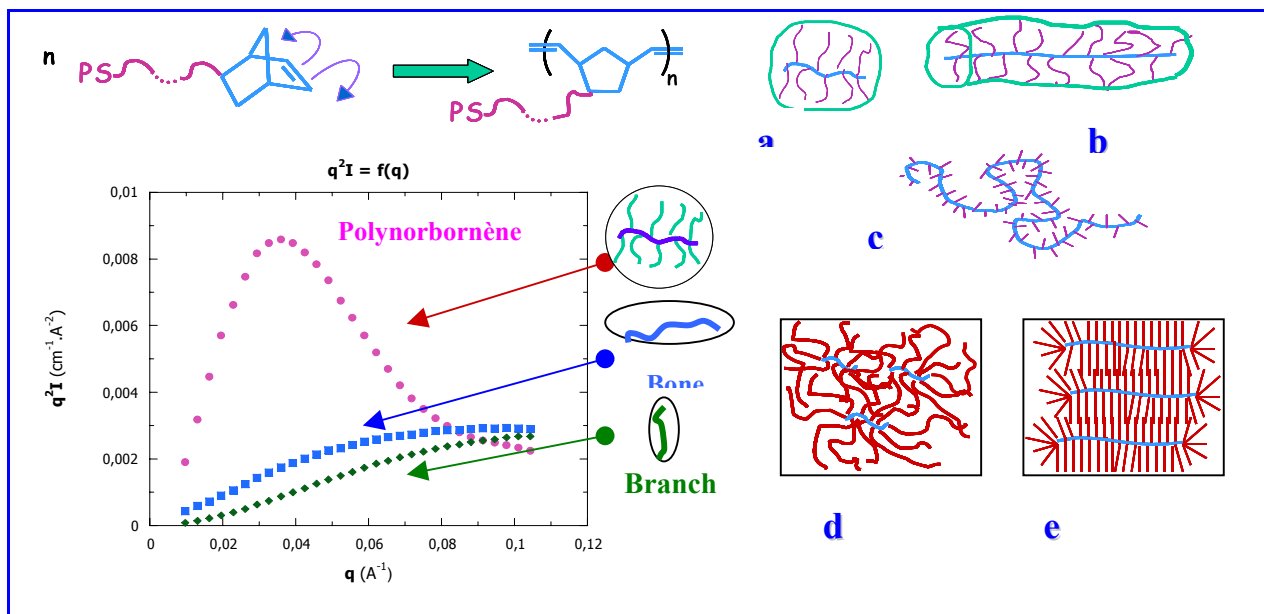


Figure 1. Polymacromonomers. Above, left : a “macromonomer” comprises a polystyrene chain (purple) linked to a Norbornene molecule (blue); this molecule becomes a unit of the backbone after polymerisation by opening the Norbornene ring. Right: depending on the relative length of the backbone (blue) and of the branch chains, the conformation will evolve from a) a sphere to b) a rod and finally to c) a wormlike chain. These objects, depending on their shape, will d) interpenetrate or e) entangle.

Below, left: scattered intensity I (q^2I vs q representation used here) from either the branch or the backbone alone (continuously increasing curve towards a plateau characteristic of a random walk), or from the whole bottle-brush (maximum evidencing the more compact structure similar to the one of a star).

Complex associations and self-assembling systems:

Other complex systems in soft matter take great advantage of the possibilities of labelling using contrast variation, in particular self-assembling surfactants. Instead of pure chemical synthesis, one can create new polymeric objects by association with some molecules, like polyrotaxane introduced through successive rings of cyclodextrines (see “[highlight](#)” M. Van Der Boogaard et al).

Similar systems explored by the Evry associated team (L. Auvray, G. Gueguan), display a scattering law characteristic of a rodlike shape ($I \sim 1/q$). This section is also illustrated by two other highlights:

A first highlight is about an external work on complexation by cryptates of the counterions of the micelles. (see “[highlight](#)” P. Baglioni, C. Gambi and J. Teixeira)

The second highlight concerns an LLB internal work on lipid vesicles extruded through calibrated pores. Variation of the elastic modulus and bending modulus of the membrane (by adding polymer for example) can be followed. (see “[highlight](#)” L. Auvray, thesis S. Guyon, 2002)

Synthesis of nanocomposites and polymer-coated silica particles:

After grafting of chains **on** silica (J.C. Castaing at LLB, 1995), our new route initiate grafting **from** the nanoparticle surface. Polycaprolactone has been “grafted from” silica via Ring Opening Polymerisation (ROP) for the first time (G. Carrot, with Ph. Dubois, Mons, B). Atom Transfer Radical Polymerisation (ATRP) developed also by G. Carrot (first with J.P. Vairon, B. Charleux, Ch. Macromoléculaire, Jussieu) has been applied to platinum nanoparticles (with H. Perez, DRECAM).



Our largest effort is now focussed on silica particles: the collaboration with Rhodia Silica Systems aims at the mechanical reinforcement of rubber. Combining chemistry and SANS (A. El Harrak, thesis started in October 2001), we are following step by step the effect of functionalisation and polymerisation on the colloidal stability of the nanoparticle suspension (see Figure 2).

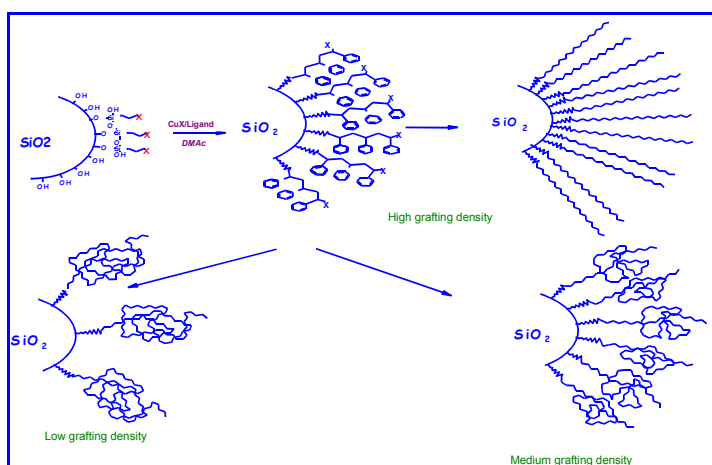


Figure 2. Synthesis of polymer-grafted silica nanoparticles at the surface of which chains are grown ("Grafting from"). The grafting density can be controlled by the polymerisation processes.

SOFT MATTER UNDER CONSTRAINT

Rheology of nanocomposites

Nanocomposites described just above are also studied using rheological measurements and SANS under strain. The effect of stretching has already been studied for nanocomposites polymer/silica materials: they were first made by mixing aqueous suspensions of polymer beads – called polymer latex, with aqueous colloidal silica, drying and letting filmify. *J. Oberdisse*, after careful control, characterisation and modelling of the controlled degree of aggregation, has established the systematic correlation between the structure and the mechanical reinforcement factor (Figure 3).

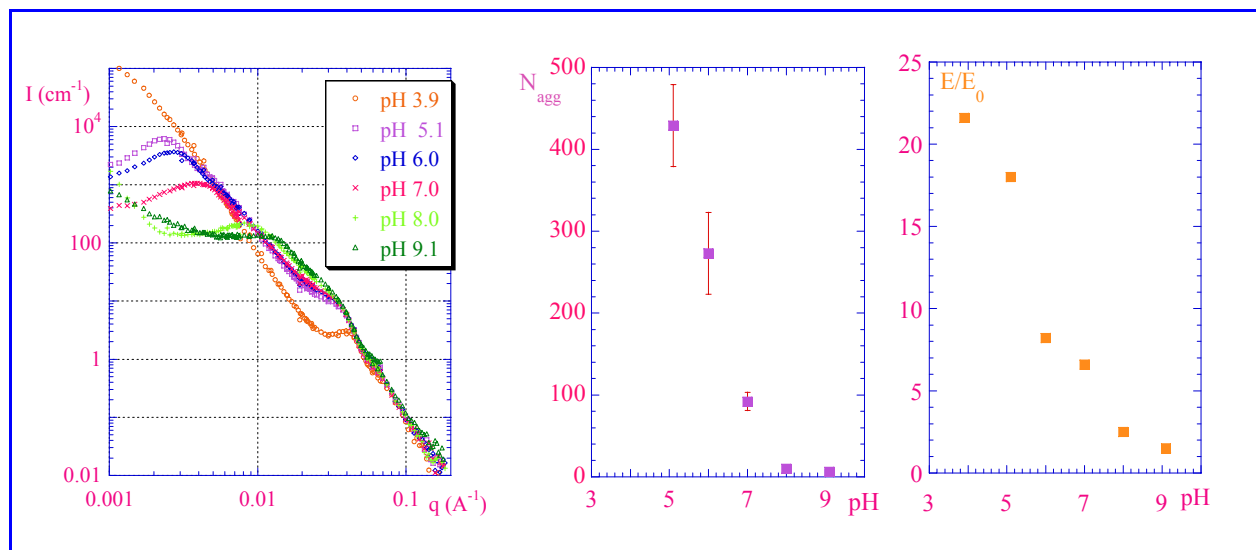


Figure 3. Reinforcement in nanocomposites. Left : Plot of SANS scattered intensity $I(q)$ vs q in log-log scales, for nanocomposites latex-silica filmified from silica plus latex suspensions at different pH (between 3.9 and 9.1, see different colours). Centre : Aggregation numbers extracted from the analysis of the scattered intensity (abscissa of the maximum), vs pH of synthesis. Right : Reinforcement of Young modulus as a function of pH.

The increase of the Young modulus can be very high (100) for large aggregates, indicating steric interactions. The effect of deformation has been modelled.



The effect of in situ silica precipitation in PolyDiMethylSiloxane (PDMS) networks has been studied in coll. with ICSI, Mulhouse (B. Haidar, P. Ziegler, thesis O. Spyckerelle).

Rheo-SANS studies of polymers:

In situ shear is also well developed in polymers. It concerns polymer solutions in two cases:

First, copolymers (B. Hamley, K. Mortensen, Cranbury-Rhodia team, and Pau team (J. Peyrelasse, J. François, thesis C. Perreur) with A. Lapp).

Second, shear-induced concentration fluctuations in Semi-dilute polymer solutions (thesis I. Morfin, with P. Lindner, ILL, and F. Boué,) coupling SANS with SALS measurements (with T. Hashimoto, Kyoto). This last study showed the progressive arise of fluctuations gently enhanced along the flow in a first stage (good solvent), then coupled to phase separation close to the bad solvent regime in a second stage, which make them visible by eye. In good solvent, we measured the form factor of a sheared single chain in solution in the Couette, at very high shear ($\dot{\gamma} \cdot \tau > 5$).

Results are compared to recent theories of partial disengagement from the tube, the only possibility to explain the shear plateau observed.

Rheology of liquid-crystalline polymers and shear-induced nematic transition:

The shear-induced nematic re-entrant transition has been found for the first time and characterized in two series of comb-like liquid crystalline polymers (LCP): phase diagrams and “plateau” constraints were determined as a function of temperature and compared to theory and related results in giant micelles.

The most striking results come from combined observation of chain conformation by SANS under shear, optical birefringence and rheology (coll. with ESPCI). Starting from the isotropic phase, a shear induced transition has been observed towards a nematic state, which is different from the static one obtained by magnetic field orientation, since both the backbone and mesogens are parallel to velocity (Figure 4).

For one kind of LCP polymer, striking oscillations are observed in rheology, coming either from complex viscous flows and elastic domains or from sliding-adhesion phenomena at the Couette cell walls.

L. Noirez with V. Castelletto, postdoc, thesis C. Pujolle, 2002.

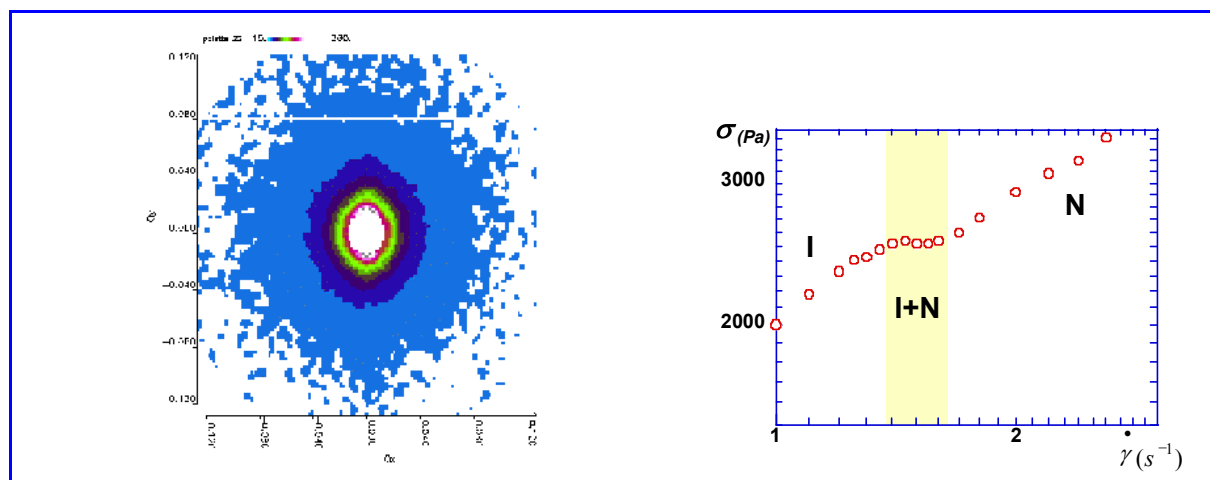


Figure 4. Liquid Crystalline Polymer chain under shear. Left : S.A.N.S from LCP inside a Couette cell, in the plane (\vec{v}, \vec{z}) where \vec{z} is the neutral axis of the shear (PAXY SANS spectrometer at LLB, wavelength 8\AA , sample-detector distance 2m). The velocity axis is horizontal. The elliptical shapes are due to the anisotropy of the chain form factor at $T > T_{NI}$ in the shear induced nematic phase; the large symmetry axis of the chain is parallel to velocity. Right : Mechanical response of a liquid crystalline polymer melt to a simple shear : stress vs shear rate at $\Delta T = 5^\circ\text{C}$ above $T_{NI} = 110^\circ\text{C}$, the nematic-isotropic transition temperature. The yellow zone enlightens the stress plateau corresponding to the coexistence of isotropic and shear induced nematic phase. For each point, a delay of 1000s was applied before measurement in order to reach a steady regime.

Liquid crystalline polymers have been also studied under pressure, using neutron high penetrability through many materials. Using a special pressure cell, the different phases of LCP can be observed.

G. Pépy, L. Noirez.



Confined polymers, thin films and porous media:

Confinement, finally, was also studied. Chains trapped in a **Vycor porous glass** are visible inside the nanochannels, since Vycor can be masked by using a D_2O/H_2O mixture also suitable for Zero Average Contrast (ZAC) investigation of the polyelectrolyte chain form factor (L. Auveray, coll. J. Lal, Argonne). Chains dynamics under these conditions are under studies.

Concerning thin films of polymers, measurements of the form factor of chains confined in a **layer as thin as 10 nm**, (Cotton, Brûlet, Boué) are planned for completion of previous studies in the field.

Fuel cell operation observed in situ by SANS:

A last important study under sollicitation, completely oriented towards technology application, is the study of a **Nafion** (sulfonated Teflon) **fuel cell** under working conditions (see **"highlight"** by G. Gebel et al).

PHYSICOCHEMISTRY OF BIOLOGICAL OBJECTS

Biology related chemical physics problems, finally come as the rising field of activity in soft matter. A first type of biomaterials concerns complex molecules that can be extracted from living systems, e.g. for agro-industry, like Methylated Cellulose, a water-soluble derivative of cellulose. Its complex solution phase diagram (gel formation/phase separation due to temperature balance between methyl groups hydrophobicity and H bonds) has been explored on a very large q range, using SANS, Static, Dynamic and Small Angle Light Scattering (M. Delsanti, SCM), and finally Neutron Reflectivity at air interface, correlated with tensiometry measurements done at INRA Nantes.

Thesis S. Guillot 2001, D. Lairez, M. Axelos, L.T. Lee.

Biochips

Biochips correspond to a second type of biomaterial, closer to biotechnology. Our collaboration with Biomérieux (L. T. Lee, F. Boué, A. Menelle, F. Cousin, with B. Cabane, Paris, and C. Pichot and A. Teretz, UMR Biomérieux-CNRS) shows the potentiality of Neutron reflectivity to characterise successive layers in bio-chips: first the silanisation step, second bounding of proteins or of polymer used to link a third layer of DNA oligonucleotides used to capture the DNA targets in the solution deposited on the chip. The whole system realised with the Biomérieux UMR, mimics a biochip.

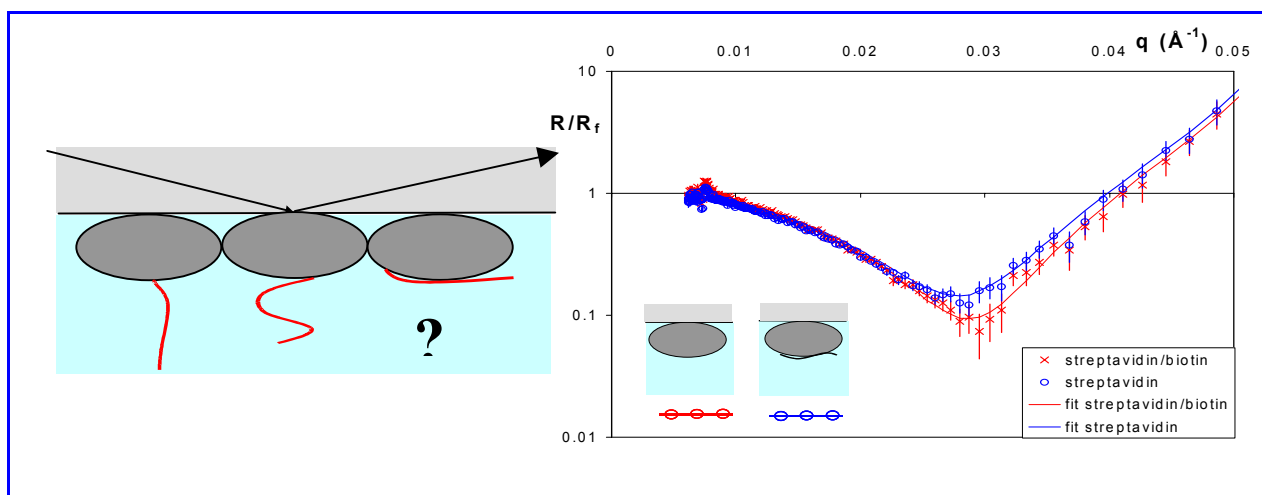


Figure 5. Neutron reflectivity R vs q (represented as divided by the Fresnel reflectivity for a single interface) of a silicon wafer silanised and coated with a layer of streptavidin, on which a biotine layer will in turn adhere.

Polyelectrolytes and DNA:

A **natural polysaccharide**, hyaluronane, has also been studied on a purely physicochemical point of view, to serve as a **model semirigid Polyelectrolyte**. In this case where the intrinsic persistence length is large, the OSF law for the electrostatic part of the chain rigidity is observed for the first time in a covalent polymer (OSF stands for Odijk, Skolnick and Fixman).

The electrostatic part of persistence length L_e is seen to vary as the **square** of the Debye screening length (κ^{-1} , which varies with ionic strength I as $\kappa^{-1} \sim I^{-1/2}$). This is in contrast with direct measurements of the form factor of polyelectrolyte chains in semi-dilute solutions (Zero Average Contrast technique) for



flexible totally charged chains (Sodium Polystyrene Sulfonate, NaPSS), which showed that the total persistence length L_p varied as κ^{-1} , or even at a lower power (expressed as a function of I , this was giving $L_p \sim I^{-1/3}$, instead of $L_p \sim \kappa^{-1} \sim I^{-1/2}$). (see **“highlight”** of E. Buhler and F. Boué)

The latter variation was confirmed (E. Dubois O. Vidal, post-docs) at the lowest concentration possible and in presence of multivalent co-ions, introduced by addition of salts. At high concentration, multivalent cations bridge the chains; actually even the structure factor, which displays interactions between chains, is surprisingly different from the (PSS)Na one (collaboration with J. Combet and M. Rawiso).

To finish with polyelectrolyte solutions, let us quote finally studies of DNA strands, in particular the presence of plectonemes (see **“highlight”** by J. van der Maarel et al, Leyden, with A. Lapp).

Proteins mixed with polyelectrolytes:

A last biotechnology-oriented study illustrates how SANS is a good tool for mixed systems (O. Vidal, F. Cousin, F. Boué). We have studied mixtures of negatively charged polystyrene sulfonate with positively charged Hen Egg White Lysozyme (pH 4). In the demixed regions of the phase diagram, we observe different morphologies (turbid suspension, solid precipitates, gel) to which we can associate a corresponding structure of aggregates viewed by SANS : closely joined protein in compact aggregates, or looser ones. The phase diagram shows also a solubility range, in which the association is strongly different, related to protein partial unfolding (see figure 6).

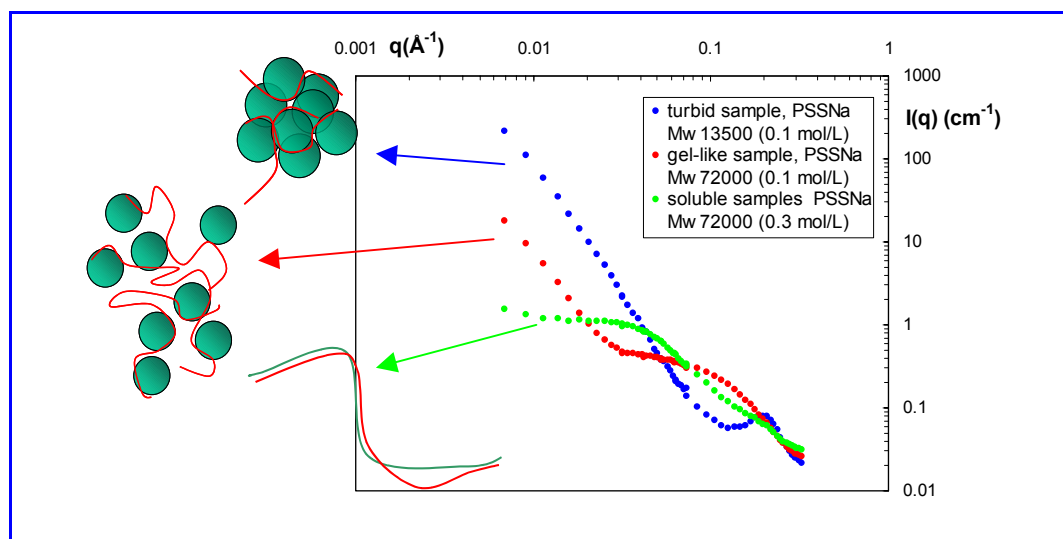


Figure 6. Complexes of polyelectrolytes (sodium polystyrene sulfonate, NaPSS) associated with proteins (lysozyme) : the drawings represent compact aggregates, loose aggregates, and the case where the protein is unfolded, as can be drawn from the aspect of the scattering curves.

We reach here the border with the biology Chapter, where are described related works such as the structure of lignin films probed by neutron reflectivity (B. Cathala), SANS studies of protein denaturation, as well as the diffusion of enzymes through a biopolymer gel, gelatine (G. Fadda, thesis, D. Lairez, and J. Pelta, Univ. Cergy – Pontoise).