

# CHEMICAL PHYSICS

The research in the field of chemical physics at LLB involves mostly soft matter, studied by the Small Angle Neutron Scattering (SANS), Neutron Spin Echo (NSE) and Neutron Reflectivity (NR) techniques (with a strong weight on SANS at present), together with Static and Dynamic Light Scattering. The present chapter intends to summarize the work done by LLB researchers, either entirely inside the laboratory or in close collaboration, and covers the field of colloids from polymers to nanoparticles, including surfactants self-assembly. Besides, a considerable number (more than 100) of experiments in chemical physics are performed each year on the LLB spectrometers by external users (see for example the highlight "Structural properties of helical self-assembled polymers with hydrogen bonding" by A. Ramzi *et al.*, Eindhoven University).

## OVERVIEW

The basic systems are often **one component** systems, studied in **volume** by SANS :

**Polymers** (mostly) : Polyelectrolytes, Liquid crystalline polymers, New Polymers,

**Vesicles,**

**Biological** materials : Methyl Cellulose, large proteins (including denatured proteins).

But it is now a common trend in Soft Matter to study more complex systems, **with 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 two important axes : polymer systems mechanically reinforced by nanoparticle fillers, and vesicles with membranes stabilised by polymers, but also for rising themes, such as Polyelectrolytes with charged particles, like proteins. The Dynamic Light Scattering study of protein gels including of latex probes also involves such a mixed system.

In many of these bulk systems, LLB is interested in the **mechanical** or **rheological** properties : this has been the origin for several studies under deformation; **Rheo-SANS** has involved stretching for Liquid Crystalline Polymers and silica reinforced polymers, and shear flow for Liquid Crystalline Polymers, semi-dilute polymer solutions, copolymers, micellar phases and vesicles.

Leaving progressively the bulk case, some LLB researchers have been interested in systems of reduced dimensions such as **chains confined in porous media**, on one hand, and **thin films** on another hand.

Going further down to the two-dimensional case, SANS can be used to characterise interfaces in multi-component systems – as done formerly, and planned for nanocomposites, but in the last two years model systems have rather been studied using **neutron reflectivity**. This is the case for liquid – air interface of thermo-sensitive polymers : PNIPAM and Methyl Cellulose, and for solid-solid **interdiffusion profiles** between a polymer and a **polymer network**, in relation with their **adhesion**.

Studies at these large scales can obviously involve also **dynamics**. The use of **Neutron Spin Echo** to measure Inelastic Scattering has been dedicated to **dynamics of polymer stars**, while Inelastic Light Scattering has been used, at the LLB, for the studies of vesicles, and of **latex spheres in biological gels**.

Finally, work on **Instruments or Methods** is not forgotten. On one hand, a new Very Small Angle spectrometer is under development (*J. Oberdisse, D. Lairez*) : it is composed of a new 2D detector made of a neutron sensitive image plate developed in collaboration with MAR-Research, with a very small-angle collimation, the problem being the reduction of  $\gamma$ -rays background (see Chapter on "Technical and instrumental developments"). On the other hand, many developments have been achieved on induced nuclear polarisation (*E. Leymarié, C. Fermon, H. Glattli*).

## POLYELECTROLYTES

The advantages of neutrons for direct measurements of the form factor of polyelectrolyte chains via the Zero Average Contrast (ZAC) technique have been thoroughly used in the case of totally charged chains (*J.P. Cotton, G. Jannink, F. Boué*). The model polymer is here the Sodium Polystyrene Sulfonate, (PSS)Na. Semi-dilute solutions have been studied in presence of various co-ions, introduced by addition of salts. One of the questions is the relation between the persistence length  $L_p$  which characterises the worm-like conformation of a chain stretched by electrostatic repulsion between monomers, and the electrostatic parameters. The first parameter should give the best estimate of charge screening ; it is expected to be the nominal ionic strength,  $I$ , which controls the Debye screening length  $\kappa^{-1} \sim I^{-1/2}$ . In spite of the most current prediction  $L_p \sim \kappa^{-1} \sim I^{-1/2}$ ,

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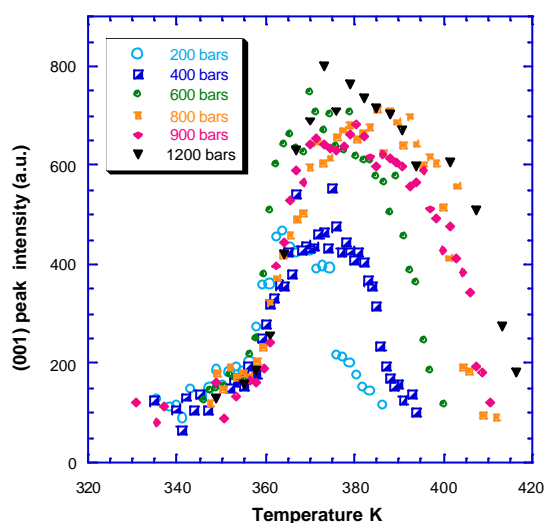
we observed a lower exponent,  $L_p \sim \Gamma^{1/3}$  (J.P. Cotton, G. Jannink, F. Boué). In order to distinguish from another possible law,  $L_p = L_0 + L_e$ , with  $L_e \sim \Gamma^{1/2}$ , where  $L_0$  is the intrinsic length and  $L_e$  the electrostatic contribution, we tried (delicate) measurements at the lowest possible concentration, which confirm the  $1/3$  exponent (with E. Dubois and O. Vidal, *post-docs*). We also varied the valence of added counter-ions. In the case of anions, the result shows that ionic strength remains the best parameter, combined with a weak dependence on the nature of ions (with O. Vidal). In the case of cations, a similar conclusion can be drawn for low ionic strengths. On the reverse, for high ionic strength the chain is no longer worm-like. This is visible at the most for trivalent Lanthanum counter-ions,  $\text{La}^{3+}$ , for which the chain shape can be determined close to the phase separation observed above a given salt/polymer concentration ratio ( $C_s / C_p$ ). This enlightens theories of the separation process, addressing electrostatic bridging between monomers (with E. Dubois). For divalent  $\text{Ca}^{2+}$ , the same trend is observed ; since  $(\text{PSS})_2\text{Ca}$  is soluble, we also measured (using LURE, ESRF and laboratory X rays) the structure factor in absence of added salt. The “polyelectrolyte peak” in such scattering, shows a behaviour surprisingly different from  $(\text{PSS})\text{Na}$  (*coll. with J. Combet and M. Rawiso, Strasbourg*).

**Polyelectrolytes plus proteins.** This system illustrates how SANS is a good tool for mixed systems. We have studied mixtures of negatively charged polystyrene sulfonate with positively charged Hen Egg White Lysozyme (pH 4) ; the phase diagram shows a solubility range, bordered by coacervation lines. In this range we have undergone measurements of the three partial form factors, and extraction of the form factor, over an as wide as possible molecular weight and concentration range (O. Vidal, J. Bonin, F. Boué).

### LIQUID CRYSTALLINE POLYMERS : STATIC AND RHEO -INDUCED EFFECTS

**Liquid crystalline polymers** (LCP) have been an extended matter of study at LLB (J.P. Cotton, P. Keller, L. Noirez, and later F. Boué, A. Brûlet). Several studies still concern the **static** state, in particular the **nematic phase**, which for some of comb-like liquid crystal polymers studied here shows signs of **pre-smectic** fluctuations which depend on the molecular mass. Studies on five narrowly distributed masses show that, in the direction perpendicular to the mesogenic groups, the backbone adopts a random walk conformation, on which, surprisingly, the nematic order has almost no influence. Moreover, the backbone conformation, in the nematic direction, does not remain Gaussian as predicted, but is contracting when decreasing the temperature (J.P. Cotton, A. Brûlet). This is to compare with former results (L. Noirez, *coll. with Germany*). Some studies also explored the effect of **stereo-regularity** on the liquid crystalline state (L. Noirez, *coll. with Austria*).

**LCP and rheo-SANS.** But most of the recent work on LCP has been dedicated to **deformation** effects. Results of the PhD thesis of V. Fourmaux-Demange (with J.P. Cotton, A. Brûlet, F. Boué), dedicated to detailed studies of chain conformation under **stretching** (coupled with rheology measurements), have been published extensively these last two years. The behaviour in the “isotropic” phase should be close to any amorphous polymer; however, on the one hand, the degree of entanglement is very low, on the second hand, rheometry as well as rheo-SANS suggest additional links leading to clusters of chains. In the nematic phase, there exists a clear difference in the orientation response, probably associated with the nematic domains. In all cases, the relaxation processes are different from amorphous polymers. L. Noirez studied **shear-induced** effects, with V. Casteletto (*post-doc*), showing that pre-smectic fluctuations can counteract the chain flow-alignment, and now with C. Pujolle (*PhD*), coupling chain conformation observations, optical observations and rheology (*coll. with ESPCI*). Hence, last year, the most striking result came from these three combined techniques : starting from the isotropic phase, a **shear-induced transition** towards a nematic state, has been chosen as our internal “highlight”. This last field is rich enough to deserve extensions in the next couple of years. Pressure is also interesting (G. Pepy) : it can increase a lot the smectic ordering of a side-chain liquid crystal polymer, and extend its range to higher temperatures (PA-CN reentrant phase, studied using a new sapphire window high pressure cell up to 1200 bar) (see Figure 1). The shape of the smectic domain versus temperature and pressure looks very different from that of reentrant (non polymer) liquid crystals.



**Figure 1.** Maximum intensity of the 001 smectic reflection versus temperature, at various pressures. The convergence of the intensity values at low temperature indicates that the Nre-SAd remains unaffected by the external pressure.

## RHEOLOGY OF POLYMERS : RHEO-SANS.

Other systems implying mostly polymers have been studied with Rheo-SANS (in situ SANS measurements under applied strain).

**Copolymers.** Though copolymers are widely studied (including now on LLB instruments the groups of *B. Hamley* and *K. Mortensen*, *Risö*), we believe that a careful description of the crystalline phase has been established for the first time in a close collaboration with the University of Pau (*A. Lapp*, coll. with *J. Peyrelasse*, thesis of *C. Perreur*). The method used comes from an analogy with the rotating-crystal method used in WAXS (Wide Angle X-ray Scattering). Comparison with the diffraction spots obtained under shear orientation of a copolymer (Pluronic) micellar crystalline phase makes clear that the scattering is due to an ensemble of different crystalline domains of all orientations, but all with their  $\langle 111 \rangle$  aligned axis along the flow. This analysis definitely establishes the existence of a unique type of crystal of cubic B.C.C structure (see Figure 2).



**Figure 2.** Scattering map for a Tetronic 908 (4 branches star polyPOE co POP) solution at 30% in  $D_2O$  ( $T = 47^\circ C$ ) oriented by a shear rate  $\dot{\gamma} = 371 \text{ s}^{-1}$  (left hand side) compared with theoretical figures for body centered cubic lattice.

**Semi-dilute polymer solutions**, under shear, have been studied (*F. Boué*, thesis of *I. Morfin*, in coll. with *P. Lindner*, *ILL*), because they show surprising shear-induced concentration fluctuations. These effects had yet been studied only using light radiation : eye (induced turbidity was first detected 20 years ago), static wide angle light scattering (WALS), dichroism, polarised light, and during the beginning of our SANS studies, small angle light scattering (SALS) and microscopy. However, all these observations had to be done close to the bad solvent regime, in other words below or close to the theta temperature  $\Theta$  which separates the good solvent from the bad solvent regime. The reason was that the sizes had to be large enough for light (0.1 to 10  $\mu m$ ). SANS probing smaller sizes, and being quite sensitive too, allowed us to see the onset of enhancement much above  $\Theta$ . It turned out that far above  $\Theta$ , fluctuations are simply enhanced along the flow, and do not correspond to a phase separation. Such “first stage” is encountered for polystyrene (PS) in DiOctylPhthalate (DOP) above its theta temperature ( $22^\circ C$ ), as well as for PS in DiEthylPhthalate (as seen for the first time),

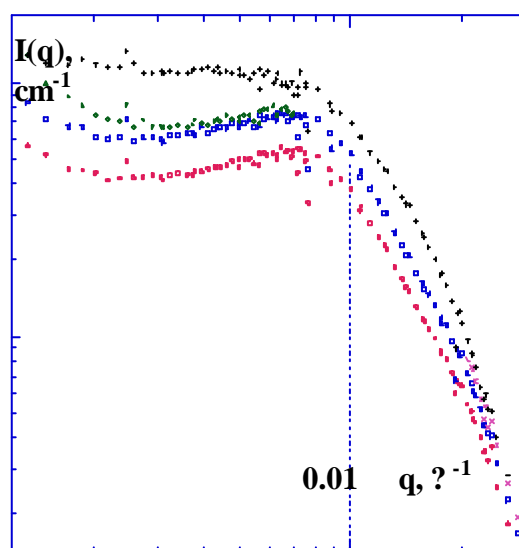
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which is a good solvent at any temperature above crystallisation. When getting closer to  $\Theta$  (i.e. for DOP), results are sensitive to the vicinity of the phase separation line (cloud point  $T_c < \Theta$ ). One proof is that the scattering does not depend only upon the Weissenberg number  $W_i = \gamma \cdot \tau$ , but also upon  $T - T_c$ . Using  $W_i$  corrects results from the temperature dependence of the terminal time. This would be enough if it was a purely mechanical effect. But the larger and larger fluctuations couple with the stress, and result in a kind of shear-induced phase separation, which we called "second stage". To understand better the evolution of this second stage, we coupled **SANS with SALS** measurements, which has been the opportunity of a collaboration with *T. Hashimoto, Kyoto*. The theoretical predictions do not seem to agree neither with the first stage nor with the second one, which is highly non-linear, and thus requires numerical simulations.

### NANOCOMPOSITES

The effect of stretching is also studied for nanocomposite polymer materials : these were first made by mixing aqueous suspensions of polymer beads – called polymer latex, with aqueous colloidal silica, drying and letting filmify. This technique has been re-examined in detail (*J. Oberdisse*); we have also tried other ways like in situ silica precipitation in PolyDiMethylSiloxane (PDMS) networks, developed in coll. with ICSI, Mulhouse (*B. Haidar, P. Ziegler, thesis of O. Spyckerelle*), and finally silica particles grafted with polymer chains. After few trials of grafting PDMS chains to the surface (as previously done by *J.C. Castaing at LLB*), a different route of initiating the polymerisation from the surface ("grafting from") has been started recently (*G. Carrot*). Firstly, Atom Transfer Radical Polymerisation (ATRP) has been successfully developed by *G. Carrot* while in post-doc (with *J.P. Vairon, B. Charleux, Chimie Macromoléculaire, Jussieu*). Secondly, PolyCaproLactone has been "grafted from" silica via Ring Opening Metathesis (ROM) for the first time (*G. Carrot, coll. with Ph. Dubois, Mons*). Thirdly, a collaboration with Rhodia Silica Systems including chemistry, rheology and SANS

has been initiated (*A. El Harrak, PhD thesis, planned October 2001*). On the other hand, "grafting from" has been developed this year on functionalised platinum particles (with *Xavier, DEA, in coll. with H. Perez, DRECAM*).



**Figure 3.** Scattering from a polymer film, reinforced with silica of different volume fractions  $\phi$  : the peak indicates the distance between silica clusters, and therefore their aggregation number, constant with  $\phi$ . This indicates that we can control the separation process between the silica spheres and the polymer beads, hence control the dispersion.

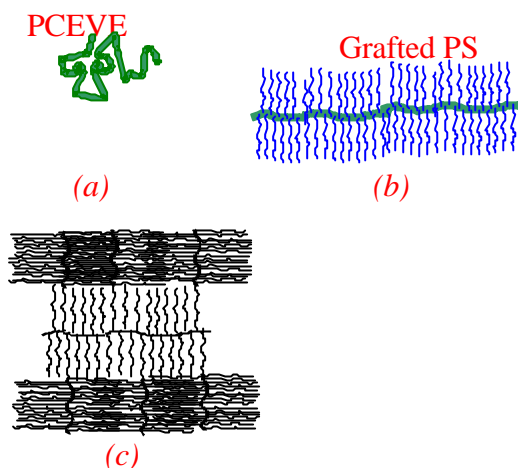
### STUDIES ON NEW POLYMERS

We are currently focusing more efforts on **new polymers** synthesised via novel routes, in coll. with the LCMO in Bordeaux (*A. Brûlet, J.P. Cotton, with S. Lecommandoux, R. Borsali*) : for preparing stiff polymers (also called bottle-brushes), different controlled polymerizations are combined (*Schappacher, Deffieux*), cationic for the polyvinyl ether backbone and anionic for the PS-Li living branches, which are finally grafted on the backbone (1% of the mass).

This gives well controlled architectures of extremely high branching density with equal branch length. Recent SANS and X-ray experiments show that their shape 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 polymerization DP) to the branch length. Besides, the persistence length appeared much higher for the graft copolymer than for the precursor PCEVE (see Figure 4), due to the high grafting density of PS. We are also interested in measuring how the lateral polystyrene chains are elongated. Further SANS experiments with appropriate labeling and contrast conditions will be performed in order to determine behaviors of the PECE backbone and of polystyrene lateral chains.

Other hyperbranched polymers (as shown in Fig. 4c) are already envisaged.



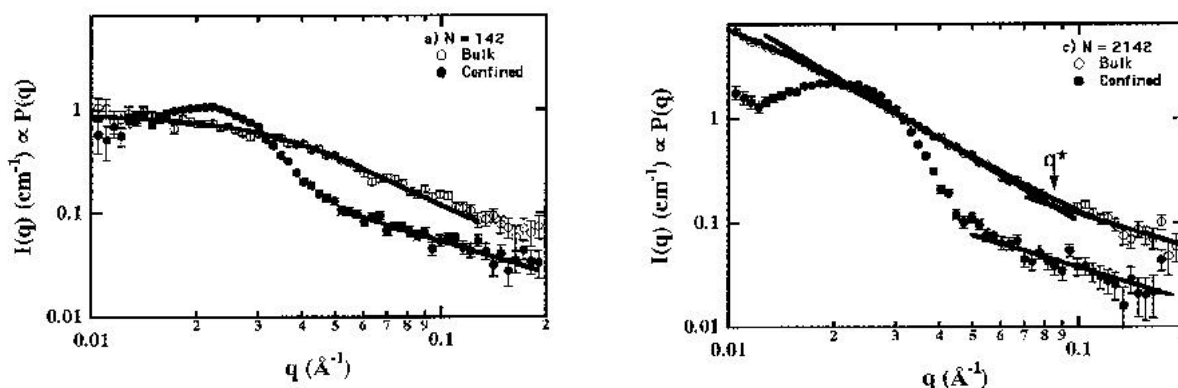


**Figure 4.** Schematic representation of PCEVE polymer chain (a), and the same chain grafted with polystyrene (b)  $\text{PS}_{\text{DP}=30}$ - $\text{PCEVE}_{\text{DP}=1042}$ . The persistence length increases from 13 Å up to 106 Å. Hyperbranched objects (c) can be built step by step by using controlled living polymerizations.

## CONFINED POLYMERS

SANS is also well suited to studies in confined environment, as illustrated by two different works. A first one (*J.P. Cotton, A. Brûlet, A. Menelle, F. Boué*) uses SANS at its limits, by measuring the chain form factor in a thin film as thin as 10 nm ! One can distinguish three  $q$  ranges : in the low  $q$  range, the scattering is very sensitive to film preparation (cf. problems reported by Jones, Russel et al.) ; in the medium  $q$  range, the chain conformation is the usual one (as found by the same other authors); finally, in the large  $q$  range, we have detected some differences in the apparent persistence length, which remain to be understood.

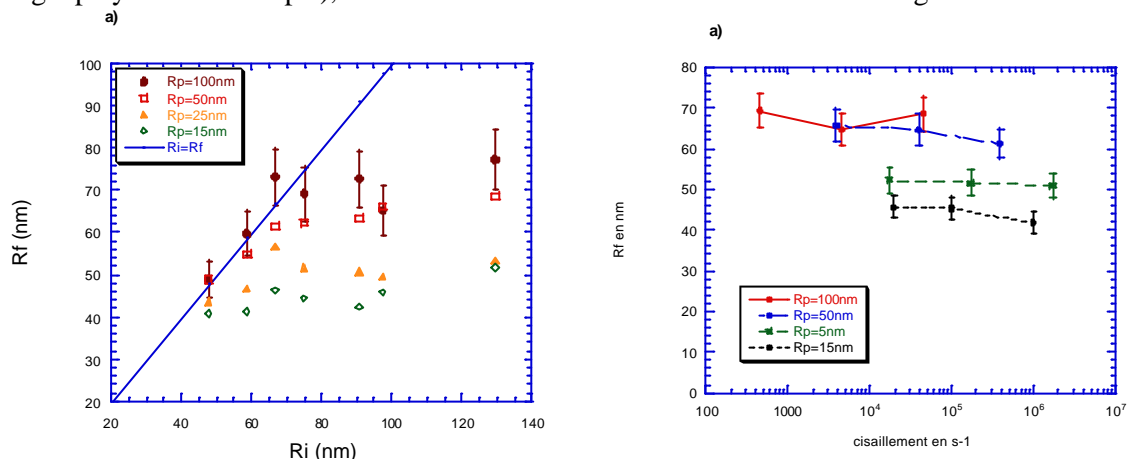
A second work looks at chains trapped in a Vycor porous glass made of kinds of channels of several nm diameter; the signal of the Vycor can be masked by using a deuterated/non deuterated mixture, which is also suitable for ZAC (Zero Average Contrast) investigation of the chain form factor, for amorphous polymers (PDMS) as well as for polyelectrolytes (*L. Auvray, coll. J. Lal, Argonne*). They find that the chains are more stretched in confined geometry than the bulk, as evidenced by the  $1/q$  scattering region. They are also sufficiently extended as to highlight the large-scale disordered structure of Vycor; this effect increases with molecular weight. In addition, we have determined  $S(q)$  for both the bulk and confined states. The asymptotic behaviour of the observed interchain structure factor is  $1/q^2$  for free and  $1/q$  for confined chains and is a consequence of the local rod-like structure of the chains (see Figure 5). While the observed increase in chain rigidity may be the dominant factor, since the weakly charged Vycor surface is unlikely to significantly reduce the bound counterion fraction around the highly charged (fully-sulfonated) backbone.



**Figure 5.** SANS from polyelectrolytes in ZAC condition in **bulk and confined geometry**. Low (a,  $N_w = 142$  units) and large (b,  $N_w = 2142$  units) molecular weight at  $0.306 \text{ g cm}^{-3}$ . Bulk data have been fitted to the Sharp and Bloomfield model for wormlike chains for  $q l_p < 2$ . Also shown in (b) are  $q^{-2}$  and  $q^{-1}$  regions in the SANS which crossover at  $q^*$ .

## SURFACTANT ASSEMBLIES : VESICLES

Recent work on surfactants has been focussed on lipids vesicles. The lipid bilayer forming such bags can be compared with the phospho-lipid membrane enveloping of a cell. One aim of the work has been to make small vesicles (radius :  $30 \text{ nm} < R < 150 \text{ nm}$ ) in aqueous suspension, by extruding larger vesicles through 6 to  $10 \text{ }\mu\text{m}$  thick polycarbonate films of controlled pore size ( $10 \text{ nm} < R_{\text{pore}} < 200 \text{ nm}$ ). When the pore radius is smaller than the one of vesicles, the vesicles break into smaller ones of final radius  $R_f$  smaller than their initial radius  $R_i$ . SANS and DLS measurements have shown that  $R_f$  depends on  $R_{\text{pore}}$ , but not on the flow rate (which determines the shear rate) (see Figure 6). Breaking is due to bending effects rather than to shear stresses on the membrane. Variation of the elastic modulus and bending modulus has been realized (by adding a polymer for example), in order to understand their relation with breaking.



**Figure 6.** a) Radius of vesicles after extrusion ( $R_f$ ) versus their initial radius ( $R_i$ ), for various values of the pore size ( $R_p$ ) b)  $R_f$  versus shear rate.

## BIOMATERIALS

A first type of biomaterial is industrially extracted from living systems, e.g. for food or agro-industry, like cellulose from vegetal. One of its water soluble derivatives is Methylated Cellulose. It is a central polymer in the science of modified natural polymers, with many applications. It presents, among other cellulose derivatives, a peculiar phase diagram : not only it forms gels when  $C$  is increased, via association of the methyl groups, but also it phase separates when  $T$  is increased (Lower Critical Separation Temperature  $\sim 40^\circ\text{C}$ ) due to temperature sensitive balance between methyl groups hydrophobicity and H bonds. The final texture can therefore be quenched by gelation, with kinetics aspects ; it was important to study it precisely on a very large  $q$  range (S. Guillot, PhD thesis, co-direction D. Lairez – M. Axelos, INRA Nantes) using SANS, Static Light Scattering (SLS), Dynamic Light Scattering (DLS), and Small Angle Light Scattering (SALS, coll. with M. Delsanti, CEA/SCM). The phase separation is not completed, since it does not lead to a Porod law (variation in  $q^4$  characteristic of sharp interfaces). The second half of the work deals with interfacial properties, studied using tensiometry in Nantes and also neutron reflectivity (see below).

Other types of biomaterials are directly involved in biology. This the case of fibronectin, a protein important in the Extra Cellular Matrix (ECM); its shape in solution, a kind of necklace of successive spheres, has been studied both in the native state and in a reversible denatured state (D. Lairez, coll. J. Pelta, Univ. Cergy - Pontoise). It was interesting to study gels formed by this protein, gelled materials being involved in the ECM, and moreover, in order to understand the motion of cells in the ECM, the local mechanical properties, and their response to enzymatic degradation. In a first step, for the sake of simplicity, a smaller scale has been studied : latex beads have been introduced in simple gels like gelatine, and their motion studied by DLS. It is planned to cover these beads by enzymes able to degrade the gel (protein gels, with latex additions (G. Fadda, thesis, with D. Lairez and J. Pelta)).

Finally, a new bio-chips project is starting on interfaces (see below)

### INTERFACES

Neutron reflectivity (NR) has been developed very early in LLB. It can be used, as in a very recent work, to characterise the different layers of bio-chips (*L. T. Lee, F. Boué, A. Menelle, F. Cousin (military service); coll. with B. Cabane, Paris; C. Pichot and A. Te, UMR Biomérieux-CNRS*).

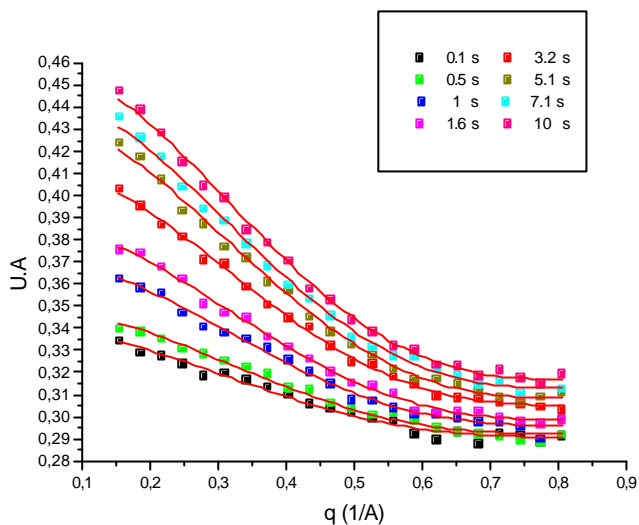
But one of the LLB expertises is the study of polymers at the **liquid-air interface**. This involved recently thermo-sensitive polymers, e.g. the case of PNIPAM solutions, which phase separates at a LCST of 32°C (*B. Jean, thesis, L.T. Lee, coll. with B. Cabane*); the interaction with surfactants and the eventual association between polymers and micelles has been studied in volume (SANS) and at the interface, which explains the interfacial surface tension and the existence of a complex interface with layers of different species (see “highlight” in the former 1997-98 report). A few measurements have also been done on Methyl Cellulose : they correlate well with the bulk phase separation behaviour, and are currently discussed at the light of tensiometry data (*S. Guillot, thesis, D. Lairez, M. Axelos, L.T. Lee*)

The structure of another type of interface, of the **solid-solid** type, has also been cross-checked with **mechanical properties** : a thin layer of deuterated polystyrene, cross-linked or not, is created on a wafer by spin-coating. A second layer of cross-linked polystyrene, made by spin-coating or solvent casting, is deposited on top of the first one. Such sandwich is annealed for a given time, which permits interdiffusion of the two layers. Former experiments on this system gave access to various tracer diffusion, self-diffusion, mutual diffusion coefficients for different rates of cross-links of the layers. These results were obtained by NR for short sizes, as well as by Ion Beam Analysis (ERDA in particular) for larger sizes, both techniques being sensitive to the presence of deuterium (*with M. Geoghegan*).

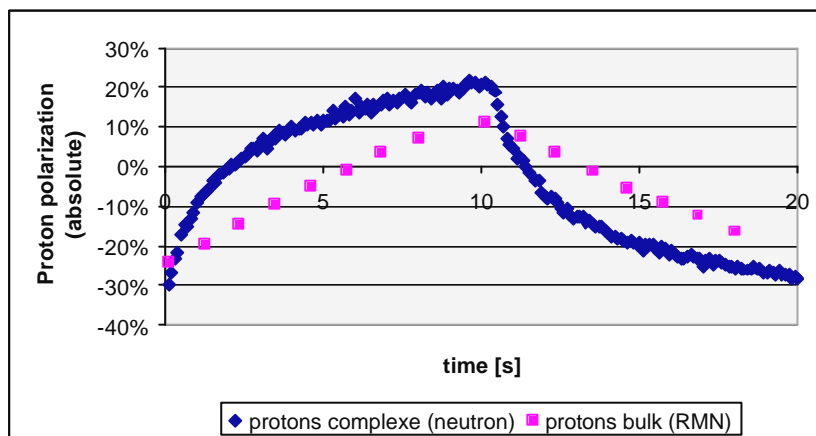
We then created an interface as similar as possible to the one studied by NR, confined this time between two thick polystyrene plates ; we finally measured the interface strength as a function of the annealing time, using the "razor blade" test of Brown et al. The aim is to correlate interdiffusion and adhesion. Different regimes were observed depending on the degree of interpenetration. If both layers are networks, equilibrium interpenetration is the number of units between two cross-links,  $N_c$ . If one layer is an uncross-linked polymer (“melt”, with number of units  $N$ ), a controlling parameter is the ratio  $N/N_c$ . When  $N/N_c > 1$ , interpenetration is limited to  $\sim$  one network mesh,  $\sim N_c^{1/2}$ . However the mechanical strength of the interface may show surprising behaviours. This has been enlightened by coupling again NR with ERDA and other Ion Beam techniques : this permitted to reconstitute the crack path. Since one of the layers was deuterated, it was possible to know inside which layer, or between which layers, had the crack propagated. Other analysis such as profilometry have been used (*G. Bacri, thesis, with F. Boué, A. Menelle, M. Geoghegan, Leeds, F. Abel, GPS- Jussieu, C. Creton, ESPCI*).

### DYNAMIC NUCLEAR POLARIZATION

Time resolved nuclear polarization has been observed by SANS (*H. Glättli, thesis of E. Leymarié, collaboration with PSI, Switzerland*). Dynamic nuclear polarization (by «solid effect » as named by A. Abragam) of some nuclei in the vicinity of paramagnetic centers (of reduced concentration) polarized by NMR, has an obviously strong interest in SANS when applied to H nuclei : it modifies their scattering cross-section and thus permits tuned labeling instead of deuteration chemistry. For a better understanding of this mechanism, the group of *H. Glättli (LLB – SPEC)* has studied spatial inhomogeneity of polarization in the first instants after applying the polarizing field. The data acquisition was time- resolved in 200 frames of 0.1 s, synchronized with a flipping each 10 seconds of the dynamic polarization orientation. The paramagnetic center was a Chrome V complex diluted in a 90% deuterated solvent. The scattering can be fitted by the form factor of two concentric spheres around each Chrome complex (Figure 7). It is clear that proton polarization close to the paramagnetic impurity increases much faster than the one of the bulk proton (Figure 8).



**Figure 7 :** Time evolution of the SANS signal during the negative polarization of protons, fitted by the form factor of two concentric spheres (measured at D22, ILL).



**Figure 8 :** Dynamic proton polarization as a function of their spatial localization. The polarization in the Cr-complex (blue line) is measured by time resolved SANS, while that of the bulk protons is given by NMR –pink dots).

## NUMERICAL SIMULATIONS

It would be particularly useful for SANS to have some ways of modeling the shapes and arrays in many materials : this is a unique way of calculating precisely their scattering and compare to complex models. We hope to be able to develop it in the future. A seed for this activity is the work of J. Oberdisse. A first part concerns nanocomposites (*J. Oberdisse, Y. Rharbi, F. Boué*) : the shapes and arrays of silica clusters of one to several hundreds of particles have been modeled following different mechanisms of aggregation. Then, the motion of these clusters during stretching has been simulated. Their center of mass is moved affinely to the macroscopic elongation, as long as two particles do not hit. This occurs because stretching produces shrinking along the transverse directions. When hitting onsets, different local rearrangement have been tested. The choice of a mutual local shear permitting the two objects to avoid each other gives a simulated scattering with the same features as observed experimentally : namely, butterfly patterns are observed in a 2d contours map, but with four maxima.

The second work has been initiated during the post-doc stay of *J. Oberdisse* in Italy (*coll. with G. Marucci and G. Ianniruberto, Napoli*). The influence of trapped entanglement on the stress has been calculated. The polymer chains are cross-linked, but also entangled with each other : each one can be simulated as a Gaussian chain passing through some “slip link” between two cross-links. Beautifully, the analytical result of *Ball, Doi, Warner and Edwards* is recovered! This work is under development (influence of limited extensibility of one chain between cross-links).