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*Institut Charles Sadron  
CNRS UPR 22 - Strasbourg University*



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2007-2011  
June 2011*



*Institut Charles Sadron*  
*CNRS UPR 22*  
*Strasbourg University*

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# Introduction

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The beginning of the reporting period (2007-2011) was marked by an important milestone: the move and the installation of the Institut Charles Sadron (ICS) in its new building, on the Cronenbourg campus, next to other laboratories of the *Pôle Matériaux et Nanosciences Alsace*. With this move a new era has started, featuring better and safer working conditions, novel scientific equipments and platforms as well as a new scientific life including an increasing number of PhD students, post-docs and visitors and further developments of internal collaborations. Many of the actions taken after the move to Cronenbourg were stimulated by a critical analysis of the last AERES report (2008). Following the recommendations of the evaluation panel, a new scientific project was elaborated, taking a real advantage of the multidisciplinary character of the institute. The main objective of the resulting mid-term scientific program was to reinforce the identity of the ICS as an institute for “Chemistry and Physics of Polymers and Self-Assembled Systems”. The document, presenting the detailed objectives of the program and the necessary resources to complete it, was discussed with an external Scientific Advisory Board at the beginning of 2009 (Jean-Louis Barrat, Lyon; Philippe Barrois, Bordeaux; Jacques Penelle, Thiais; François Tournilhac, Paris). Toward the end of 2011, we may say that most of the objectives of the program have been reached, as will be presented in the following.

One of our important concerns was the dramatic decline of the research in polymer chemistry, due to many leaves for retirement. Concerted actions associating the CNRS and the University of Strasbourg have permitted the creation of two new chemistry groups headed by young group leaders : Nicolas Giuseppone (PR at the Uds) leading the SAMS (*Synthèse et Auto-assemblage Moléculaire et Supramoléculaire*) group which explores routes to new classes of supramolecular materials; and Jean-François Lutz (DR at the CNRS) leading the PMC (Precision Macromolecular Chemistry) group which develops novel approaches of polymer synthesis. Both have applied successfully to ERC starting grants which provide their young groups with an important support in terms of equipment and funding for PhD students and post-docs. More recently they have also been involved in the LabEx project “Chemistry of Complex Systems” coordinated by Jean Marie Lehn, which has been positively evaluated and will be funded by the ANR (*Agence Nationale de la Recherche*). On a more technical side, our Platform of Polymer Characterization, which plays an essential role for in-house macromolecular chemistry as well as for external users (from university and industry), was facing a serious threat, with the leave of three engineers and the need for renewing equipments.

Thanks to the Institute of Chemistry (INC-CNRS), the platform is now operated by a new team of efficient young staff, and several novel instruments could be funded by the CPER (*Contrat de Projet Etat-Région*).

A central objective of our mid-term research program was to take better advantage of the rather unique combination of competences in chemistry, physical chemistry, materials science and soft matter physics, present at the Institute. The program identified important scientific challenges and suggested to organize the research along 3 thematic axes selected for their emergent impact, either in terms of applications or with regard to fundamental questions. These axes concern *Polyelectrolytes, Polymers and interfaces and Self-assembled systems*. The first two axes are built on research topics that have a long tradition at the ICS. The third axis, on the other hand, highlights a more recent research interest shared by many groups of the ICS. Scientifically the contents of the axes can be circumscribed as follows:

- **Polyelectrolytes**

Polyelectrolytes are natural or synthetic, water soluble, charged polymers which are widely used in the fields of pharmacy, biology, food processing, water treatment or oil extraction. In most of these applications, the polyelectrolytes are in presence of various components of opposite charge and/or of the same charge. Clearly, the complexity present in these mixtures requires theoretical and experimental studies of model systems, both concerning polyelectrolyte complexes in suspension or multilayers of alternating polyanions and polycations.

- **Polymers and interfaces**

In a number of situations dealing with surface chemistry or surface physics, there are polymer chains adsorbed, grafted or just confined in a very thin layer. Conformation and dynamics of a macromolecule in the vicinity of a surface can differ from those of the bulk. The impact of the surface on the physical-chemical behavior and structure formation still presents many important challenges for fundamental understanding. Theoretical studies and numerical simulations in complement with experimental investigations of surface structure and properties are therefore highly desirable.

**The ten most significant publications of the Institut Charles Sadron (2007-2011)**

***Formation of Helical Mesopores in Organic Polymer Matrices.***

F. X. Simon, N. S. Khelfallah, M. Schmutz, N. Diaz, P. J. Mesini,

**J. Am. Chem. Soc. (2007), 129, 3788-3789.**

They are numerous mesoporous inorganic materials such as silica or alumina. In contrast, mesoporous polymeric materials are scanty. These materials are interesting because they combine the benefits of porosity needed for filtration technology or catalysis and the mechanical properties of polymers conferring tractability, resilience or processability. In this paper we have used self-assembling molecules able to form either nanotubes with monodisperse diameters or helical tapes depending on the concentration. The resolution of the imprint enables the formation of helical pores in the polymeric matrices. This work is one of the projects which has stimulated the TEM Platform to implement up-to-date techniques, namely tomography for this paper. Our results have also triggered collaborations with other laboratories of the *Pôle Matériaux et Nanosciences Alsace*. This work fits in a strategy that takes advantage of self-assembly to prepare genuine functional materials and the process has been patented.

***Why polymer chains in a melt are not random walks.***

J.-P. Wittmer, P. Beckrich, A. Johner, A. N. Semenov, S. P. Obukhov, H. Meyer, J. Baschnagel.

**Europhys. Lett. (2007), 77, 56003, p1-5.**

A cornerstone of modern polymer physics is the concept of chain ideality in polymer melts, i.e., the idea that the conformation of a polymer chain in a melt is solely determined by the connectivity between the monomers, whereas all other interactions may be neglected. This publication challenges this classical view. By theoretical arguments and supporting simulation results from simple polymer models the Letter reveals corrections to chain ideality for the polymer form factor, a quantity accessible by neutron scattering experiments. Despite the increasing evidence compiled by the Theory and Simulation (TSP) group in favor of these corrections during the past years, it is important to demonstrate that the corrections are more than an academic curiosity. As a first step in this direction the TSP group has begun to simulate a chemically realistic model for polyisobutylene (PIB). Concurrently to the simulations, the conformation of PIB is also analyzed by neutron scattering (collaboration with Prof. M. Dadmun, UT Knoxville). Extensions to other polymers, such as polystyrene (internal collaboration with M. Rawiso), are planned. If these studies are successful, it is likely that the discovered corrections to chain ideality will certainly appear in future textbooks on polymer physics.

***Hierarchical functional gradients of pH-responsive self assembled monolayers using dynamic covalent chemistry on surfaces.***

L. Tauk, A. P. Schröder, G. Decher and N. Giuseppone.

**Nature Chemistry (2009), 1, 649-656**

Modulation of pH was used to tune the fast, selective, and reversible attachment of functional amines – with different pKa values – to an aldehyde-coated surface. To illustrate the potential of this technique we have developed dynamic self-assembled monolayers which enable the hierarchical construction of mixed gradients comprised of either small functional molecules or proteins. The control of the (bio)chemical composition at any point on the surface potentially opens up a simple bottom-up method for accessing numerous surface patterns with a broad range of functionalities.

***Epitaxial Growth of Highly Oriented Fibers of Semiconducting Polymers with Shish-Kebab-Like Superstructure***

M. Brinkmann, F. Chandezon, R.B. Pansu, C. Julien-Rabant

**Advanced Functional Materials (2009), 19, 2759-2766**

The discovery of nanostructured and highly oriented shish-kebab fibers for a conjugated semi-conducting polymer (P3HT) is important for different reasons. Firstly, because it is the first occurrence of this peculiar morphology for this class of polymers which could find interesting applications in plastic electronics (e.g. OFETs based on single oriented fibers). Secondly, this result illustrates the unique approach of the SYCOMMOR group: to master and to use physico-chemical methods e.g. heterogeneous nucleation and crystallization mechanisms to generate original nanostructured objects with multi-scale ordering. As such, this result is also a nice illustration of the importance of serendipity in our daily research: The outcome of our research is not always predictable but relies on experienced structural observations.

***Chemistry, Physical Chemistry, and Uses of Molecular Fluorocarbon-Hydrocarbon Diblocks, Triblocks and Related Compounds-Unique "Apolar" Components for Self-Assembled Colloids and Interface Engineering.***

M. P. Krafft, J. G. Riess.

**Chem. Rev. (2009), 109, 1714-1792.**

(Perfluoroalkyl)alkyl diblocks (*F<sub>n</sub>H<sub>m</sub>*): so simple, and yet... they produce exceptionally large organized circular self-assembled domains at the surface of water and on solid substrates. They also form composite films, including, in the case of gemini (perfluoroalkyl)alkyl tetrablocks, organized stacks of nano-objects. *F<sub>n</sub>H<sub>m</sub>* diblocks can act as surfactants, strengthen bilayer membranes, stabilize vesicles and strongly modify their behavior in biological media, and control the phase behavior of phospholipid monolayers. Read more about these astounding molecules and their potential of applications in this review article.

### • Self-assembled systems

Self-assembled systems result from the spontaneous organization which occurs between some well defined molecules thanks to their complementary through weak supramolecular interactions. Self-assembly is programmed by the information contained in the initial molecular or macromolecular individual components which reversibly aggregate in structures of higher dimension and complexity. The main biologic functions of living systems mostly rely on basic principles of supramolecular chemistry and despite their high complexity those are important sources of inspiration for developing new synthetic self-assemblies. Moreover, in nanosciences, the so called « bottom-up » approach is fully related to the control and to the programming of molecular interactions to yield larger objects with new or improved functions, through hierarchical self-assembly. Such approaches require converging efforts in organic synthesis, physical chemistry, theory and simulations, aiming at a better understanding of the thermodynamics and formation kinetics of functional materials based on self assembly and self organization.

The discussions of this mid-term program involved all research groups and resulted in the development of internal collaborations and in a tentative structuring of the research groups along the three axes (see Table 1 of the AERES forms). The collaborating groups have submitted a number of joint proposals to different funding sources (EU, ANR, icFRC foundation, *Université de Strasbourg, Région Alsace*, etc). Although not all of them could obviously be successful, it is worth mentioning that the contractual resources of the ICS have increased from 575 k€ per year (average 2003-2006) to 1 143 k€ per year (average 2007-2010).

In harmony with the structuring effect of the mid-term program, a French-German graduate school was discussed with the University of Freiburg, and a proposal was constructed along three thematic axes which are fairly close to those of the ICS:

- Controlling and directing assembly processes in soft matter systems,
- Designing and improving multi-component soft matter systems,
- Exploring and sensing interfacial properties of soft matter systems.

Therefore the mid-term program of the ICS and program of the graduate school have been reinforcing and enriching each other, especially concerning the internal and external collaborations. Following a positive evaluation by the DFG, the latter initiative has been funded as an *International Research Training Group* (IRTG) entitled “Soft Matter Science: Concepts for the design of functional materials” which was launched in October 2010. The IRTG provides 21 new PhD students with an interdisciplinary and multicultural qualification (see the section on the IRTG, p. 113).

Over the last four years, numerous collaborative projects have also been developed, on the campus of Cronembourg, within the framework of the PMNA which regroups the ICS, the IPCMS (*Institut de Physique et Chimie des Matériaux de Strasbourg*), the InESS (*Institut d'Electronique des Solides et des Systèmes*) and two UMRs of the ECPM (*Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg*). Cooperations are developing through annual scientific meetings, calls for joint proposals and also creation of scientific platforms. The ICS has a strong implication in 3 of these platforms, which are accessible to all the partners: Polymer Characterization, Transmission Electron Microscopy (TEM) and Micro-Nano Mechanics. As mentioned above, the funding of the platforms comes principally from the CPER and is discussed by the council of the PMNA. Besides the chromatography equipment for polymer characterization, a new TEM for soft matter was purchased in 2008 as well as a Nano-indentor for investigating the thermo-mechanical properties of polymer surfaces. Recently the PMNA has also been awarded by the creation of the MICA (Materials Institute Carnot Alsace) which aims at a further development of contractual research with industries, in the branch of Materials Science and Technology (along the different branches of industrial and agricultural activities, only 34 Carnot Institute are subsidized in France). Finally, discussions are currently underway with the Max-Planck Society to create in Strasbourg an *International Max Planck Center on Nanomaterials* with the ICS and the IPCMS as joint partners.

For the period from January 2007 to June 2011, the scientific production of the institute has been abundant and rather equilibrated between the three research axes (taking into account the relative size of the groups). A total of 389 peer-reviewed research papers (ACL) were published, with 97 for *Polyelectrolytes*, 115 for *Polymers and Interfaces* and 177 for *Self Assembled Systems*. In the blue insets are presented 10 publications of high impact which have been selected in such a way that the ensemble gives an overview of the best scientific productions of the institute. The selected papers also point out the development of internal collaborations as, for most of the articles, several groups of the institute are involved as co-authors. In the scientific production of the institute, over the 4 years period, one must also mention the following indicators (listed in Annexe 1) :

- 180 invited talks (INV) at international and national conferences
- 32 books or chapter of books (OS)
- 18 patents (BRE) deposited (and 1 licence transferred) (see also Tables 5.1 and 5.2 of the AERES forms)
- 41 PhD defenses (Table 2.9) and 6 Habilitations (Table 2.10).

Over the four year period, 46 out of the 51 staff scientists of the ICS, have reached the AERES individual criterion of “productivity in science and valorization”. The five others have only published from 3 to 1 ACL, in most cases, because they have been engaged in collective tasks for the benefit of the whole institute.

***The Hierarchical Self-Assembly of Charge Nanocarriers : A highly cooperative Process promoted by visible Light***

E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova and N. Giuseppone

**Angew. Chem. Int. Ed. (2010), 49, 6974-6978**

Triarylamine-based building blocks were shown to respond to visible light exposure by forming cationic radicals which hierarchically self-assemble in molecular wires that in turn combine within larger fibers. In addition to highlighting a unique kind of responsive supramolecular scaffold, such functional properties are of interest for the development of "smart" self-organizing systems that are able to gain in complexity in order to receive, store, and transfer information in space and time. Numerous recent results have now emerged from this seminal paper, in particular by showing that these structures conduct electricity with a metallic behaviour.

***Molecular dynamics simulations as a way to investigate the local physics of contact mechanics: a comparison between experimental data and numerical results***

M. Solar, H. Meyer, C. Gauthier, O. Benzerara, H. Pelletier, R. Schirrer, J. Baschnagel.

**J. Phys. D: Appl. Phys. (2010), 43 455406, p. 1-11**

This paper demonstrates that molecular dynamics (MD) simulations can be used to obtain qualitative agreement of experimental and numerical results, despite the intrinsic differences in time and length scales of both approaches. This finding is very promising: It suggests that the MD simulation can provide information about the molecular mechanism underlying the experimentally observed behavior in contact mechanics. Such local information cannot be obtained from models of continuum mechanics models and will complete the picture found experimentally. This paper was also the first one from the collaboration between two groups on this research topic (TSP and PMTP).

***Spray-on organic/inorganic films: A general method for forming ultrathin coatings by interfacial precipitation reactions.***

M. Lefort &amp; G. Popa, E. Seyrek, R. Szamocki, O. Felix, J. Hemmerlé, L. Vidal, J.-C. Voegel, F. Boulmedais, G. Decher &amp; P. Schaaf.

**Angew. Chem. Int. Ed. (2010). 49, 10110-10113**

Step-by-step deposition processes of two interacting species constitute a powerful way to functionalize surfaces, yet the process is time consuming. Applied to polyanions and polycations it leads to the *Polyelectrolyte Multilayers*. To overcome the inconvenience of the process we introduced a new method of film buildup where both interacting species are sprayed simultaneously on the surface leading to a continuous film growth: the *Simultaneous Spray Coating of Interacting Species* method. The method is very general and is applicable to polyelectrolytes, to polymers interacting through non covalent bonds as well as to inorganic species. It also provides a new tool to investigate polyanion-polycation complexes.

***Scraping and Stapling of End-Grafted DNA Chains by a Bioadhesive Spreading Vesicle to Reveal Chain Internal Friction and Topological Complexity.***

G. Nam, M.L. Hissette, Y. L. Sun, T. Gisler, A. Johner, F. Thalmann, A. P. Schröder, C. M. Marques, N.K. Lee.

**Phys. Rev. Lett. (2010), 105, 088101, p.1-4**

Self-entanglements, a long-sought fleeting state of giant polymer chains, have been revealed by DNA and phospholipid vesicle experiments in the Membrane and Microforce group. Brought first to a flat protein surface, each DNA moves swiftly under the solution random forces until an adhesive lipid vesicle lands somewhere nearby. The bio-functional vesicle adheres strongly to the substrate, wrapping and strapping the DNA to the ground: in a fraction of a second the giant DNA has been stretched and immobilized by hundreds of small stringy ligands. By inspecting the light emitted by the immobilized long chains, ICS scientists and their collaborators from Seoul discovered that some DNA molecules are incapable of stretching under the push of the vesicle wall: the long chain is sometimes in a self-entangled state that is kept imprisoned during the fast fight. Such states happen rarely, even for giant molecules, so that only the happy combination of tight and quick fastening allowed to now succeed where previous attempts to catch self-entanglements had failed.

***Controlled folding of synthetic polymer chains through the formation of positionable covalent bridges.***

B. V. K. J. Schmidt, N. Fechler, J. Falkenhagen, J.-F. Lutz.

**Nature Chemistry (2011), 3, 234-238.**

This article shows the relevance of sequence-controlled synthetic macromolecules for preparing advanced macromolecular origamis. It was shown in this work that reactive alkyne groups can be placed at specific locations in linear polystyrene chains. These reactive linear chains were afterwards involved in intramolecular reactions (e.g. Huisgen cycloaddition or Glaser coupling) in dilute solutions, thus affording different types of covalently folded polymer chains (e.g. P-, Q-, 8- or alpha-shaped origamis). This approach corresponds to a new way of thinking in the field of fundamental polymer chemistry and suggests that sequence-defined macromolecules could be key elements of tomorrow's polymer design.

**Plus a landmark paper :**

In 2008, the following article from the ICS was ranked by ISI as the 8th most cited (2814 citations) among all journal articles published in the field of chemistry in the period of January 1, 1997 to October 31, 2007. On September 1, 2011 the number of citations reached 4754.

***Fuzzy nanoassemblies: Toward layered polymeric multicomposites.***

G. Decher.

**Science (1997), 277, 1232-1237.**

## Introduction

Moreover, the quality and the impact of the scientific production of the ICS was awarded by several distinctions:

- In 2008 Dr Raoul Zana received the Kash L. Mittal Award of the Conference “Surfactants in Solution”.
- In 2008 Dr Martin Brinkmann received the Bronze Medal of the CNRS.
- In 2009 Professor Gero Decher received the Prize Emilia Valori of the French Academy of Sciences
- In 2010 Professor Gero Decher received the Prize Rhodia of the European Colloid and Interface Society.

Concerning the resources of the Institute over the period 2007-2011, Table 3.1 of the AERES forms shows the main sources of funding (UdS, CNRS, international and national institutions) and their recent evolutions. Among the main changes of the recent years was the launching of the ANR and the increasing part of the funding of short term research projects. Tables 4.1-4.3 list the 12 ANR contracts and the 7 EU contracts in which groups of the ICS have been participating either as coordinators or as associated members since 2007 (for a total of 6,14 M€). In addition, Table 5.0 gives some detail on the 13 industrial contracts and 11 subsidized applied research contracts, in which different groups of the ICS have been involved since 2007 (for a total of 2. 25 M€). Such an involvement in collaborative research with industry has certainly contributed to the recent recognition of our institute as a major member of the Material Institute Carnot Alsace (MICA). The additional support obtained from the MICA will result in a further increase of partnerships with industry over the coming years. As regards the balance of expenditures *vs* resources, it has become clear over the past years that the steady increase of costs for infrastructure could not be afforded by the CNRS. We were thus committed to establish an overhead deduction of 25% on every contractual income, except the provisions for wages. Such a deduction is essential to balance the budget of the institute and to face accidental expenses and unexpected but necessary investments. Among those are the investments related to energy savings in our new building which presently exhibits high heat losses, especially due to the 80 extractors of the chemistry laboratories.

Table 2 of the AERES forms is intended to show the evolution of the Human Resources of the research unit between January 2009 and July 2011. For the ICS, the numbers show essentially no change, although the turnover of the research staff was quite important over this period (ca. 23%), with leaves of 1 PR, 3 MCF, 6 CR and 3 DR, almost balanced by recruitments of 2PR, 4MCF, 4 CR and 2DR. Concerning the technical and administrative staff, the numbers show a small (but temporary) increase due to some crucial recruitments for the platforms, which have been made in advance to

allow an overlap between the leaving experts (7) and the arriving young engineers and technicians (9). In this category also, the turnover corresponds to ca. 20% over the 4 years. Let us stress here that such figures could only be obtained through considerable and permanent efforts of the *Direction of the ICS* in arguing with the different boards of the University and of the CNRS to defend the needs of the ICS in terms of human resources. In the evolution reported here, the gender issue has also been among our concerns : it has slightly evolved in the desired direction from 19% of women over all permanent staff in 2007 to 23% in 2011 (clearly, the figures are even better if the post-docs and the PhDs are taken into account!).

Our final remarks will concern the organization and the structure of the institute, in terms of research groups and thematic axes. The present report is organized along the three thematic axes of our mid-term scientific program, with 3 research groups having their center of research interests in the axis *Polyelectrolytes*, 4 research groups in the axis *Polymers and interfaces* and 4 research groups in the axis *Self-assembled systems*. In each of the axes, there are groups of chemists, physicists and physical chemists which have been developing collaborations and the objective of increasing their interactions has been partly reached. In addition, the institute has obtained most of the human resources and equipments required for achieving the mid-term program. Considering now the results obtained, the turnover of the permanent staff and the evolution of the research interests, a new scientific project is being proposed, for which we have not retained the same structure. The reasons for that are explained in the section: “*Overview of the global scientific objectives and actions for the period 2013-2017*” of the document Research Project.

Other important aspects of our research, education and training projects are reported in separate parts of this report:

AERES Forms (Appendix 1)

Publications list (Appendix 2)

Teaching and training activities (Appendix 3)

Continuous education (Appendix 4)

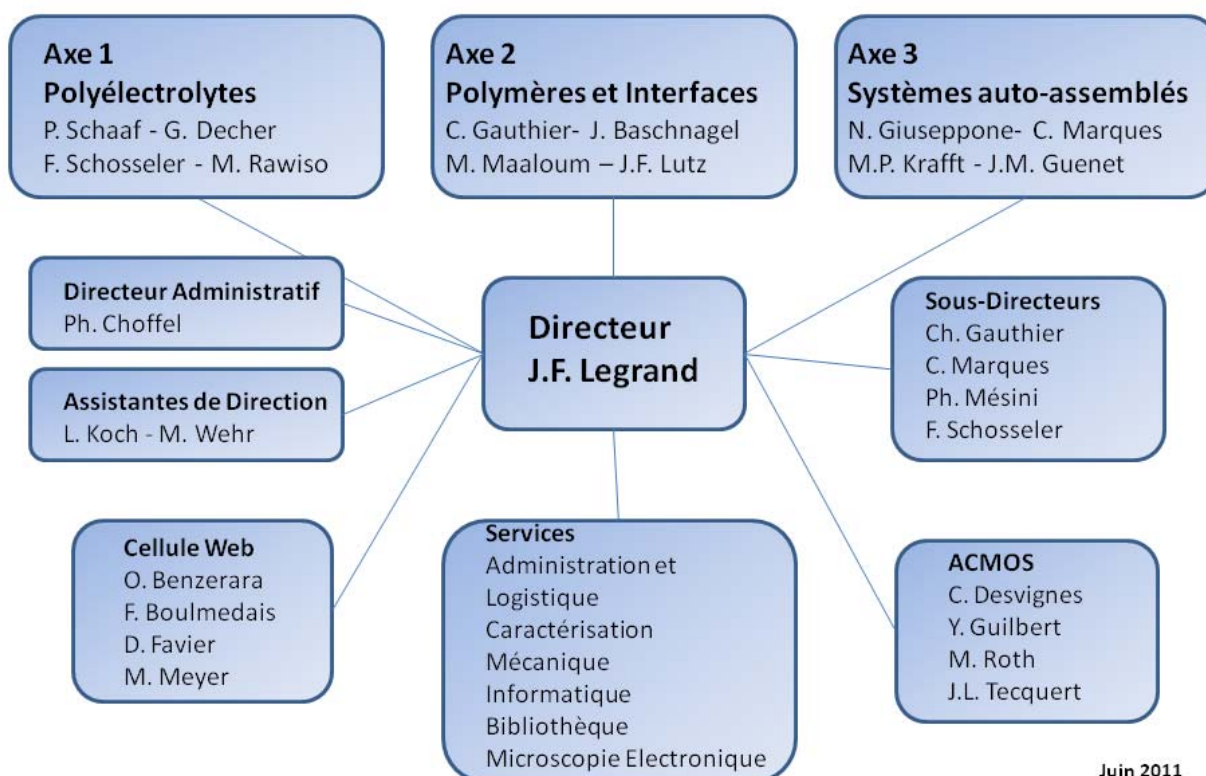
Health and safety (Appendix 5)

Communication: web site, open doors, press release, Organization of conferences and symposia, etc. (Appendix 6)

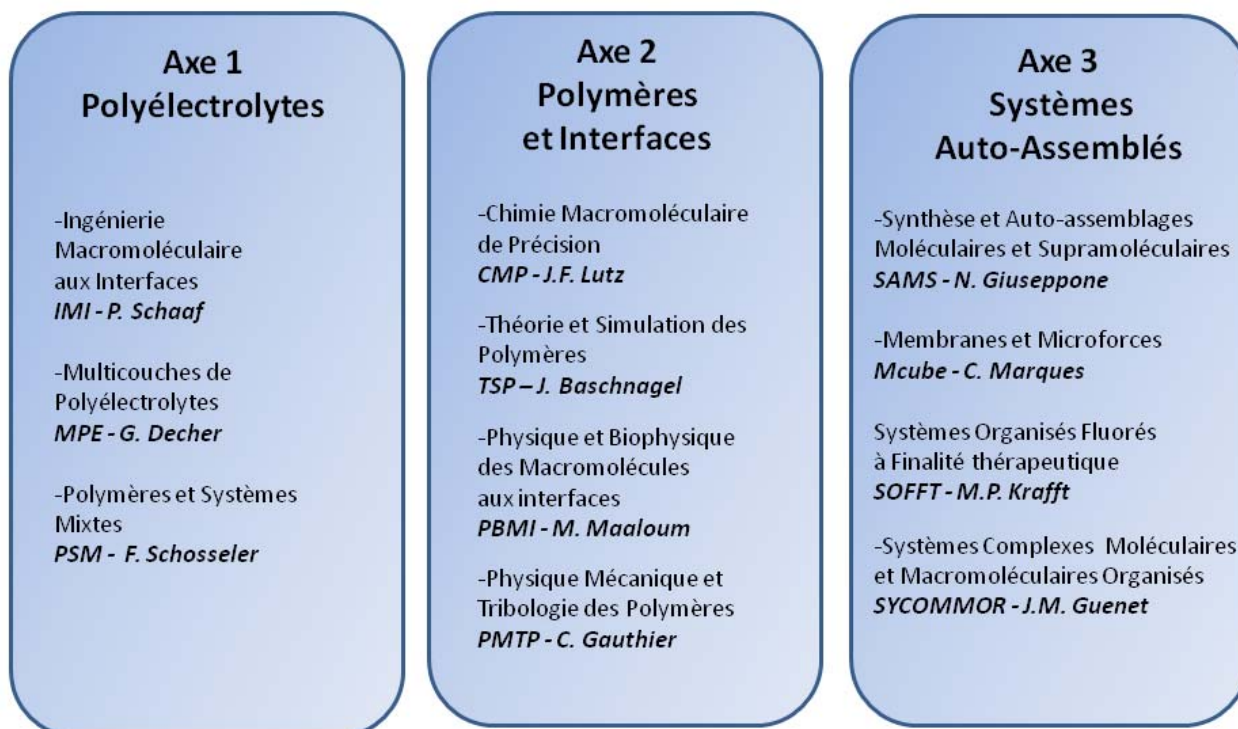
Personal turnover (Appendix 7)

Jean-François Legrand,  
September 5, 2011

## INSTITUT CHARLES SADRON - CNRS UPR 22 ORGANIGRAMME



## ORGANIGRAMME DE L'INSTITUT CHARLES SADRON AXES ET EQUIPES

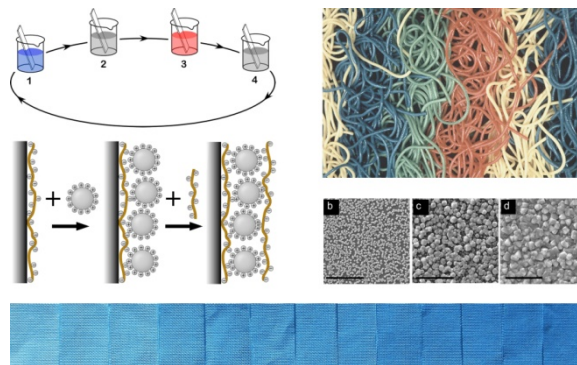


# Axis 1: Polyelectrolytes

MPE Research Group

Head of the Group Gero Decher

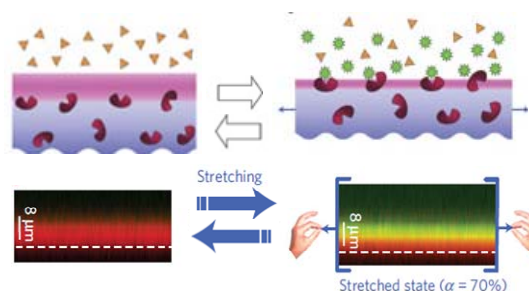
Polyelectrolyte Multilayers



Since about 1990 we are developing the so-called layer-by-layer (LbL) assembly method. This self-assembly method is a bottom-up approach highly suited for the fabrication of nano-organized multimaterial films. It is based on the concept of multiple weak intermolecular interactions, that are mostly electrostatic in nature and combines experimental ease with low cost fabrication and environmental friendliness. Due to the broad range of materials that can be put into multilayers on substrates of almost every shape and every size, it has developed during the last 20 years from a scientific curiosity in fundamental research to an enabling technology, which is in the process of being transformed into a tool for commercial mass production. A large number of independent teams have developed individual research topics based on this method and are publishing now about 1000 articles per year in this field. LbL-films are used to coat objects as small as nanoparticles, as big as cars or as irregular as textiles or fruit. A huge advantage of LbL-assembly is that even films on very different surfaces can be astonishingly similar if prepared at identical deposition conditions. This allows for example to deposit films on surfaces that are difficult to characterize (e.g. paper, textile, fruit, ...) and to learn about their structure by doing x-ray or neutron reflectometry on regular silicon wafers. Due to its general applicability to organic, polymeric inorganic and biological materials and due to its simplicity our nanofabrication process has prompted applied research in domains such as tissue engineering, functionalization of implants, gene delivery and transfection, biosensing, biocatalysis, electroluminescent devices, lithium-ion-batteries, non-linear optics, anti-reflective coatings, corrosion protection, photocatalysis, microreactors, gas and liquid separation, functionalization of nanoparticles, controlled drug release and quite a few others. In addition to LbL-films we are interested in many other kinds of hybrid nanomaterials that are prepared through processes based on self-organization in confined environments.

Head of the Group **Pierre Schaaf**

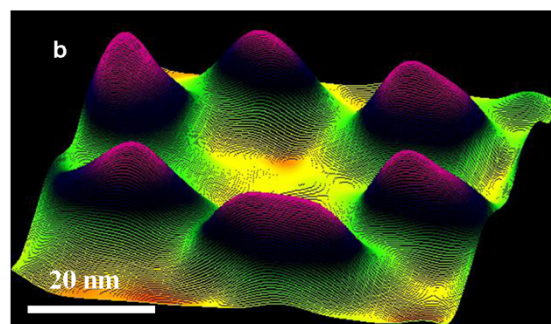
### Macromolecular Engineering at Interfaces



Based on experiences acquired for more than one decade in the field of polyelectrolyte multilayers, the group *Macromolecular Engineering at Interfaces* focuses now on the design of bio-inspired films with special attention towards mecano-transductive coatings and morphogen driven film buildup. At the interface of chemistry and biology, the group is also strongly involved in the development of new biomaterial coatings and of original film architectures for tissue engineering. Another topic developed in the team concerns the oral treatment of diabetes and Lupus, nano-vectorization of insulin and P140 peptide are now developed towards industrial applications.

Head of the Group **François Schosseler**

### Polymers and Mixed Systems



The group focuses its research on the structure and dynamics of mixed systems based on polymers.

Its scientific activity spans a broad spectrum, from synthesis of model components to the study of physical properties of the mixed systems. An emphasis is placed on ternary systems involving electrically charged polymers. The group shares its expertise in scattering techniques with all researchers of the ICS. It is also strongly involved in the scientific support of the Characterization Group.



# Polyelectrolytes

## An overview of the axis

**Permanent staff:** Permanent staff: 2 Professeurs (PR-UdS), 4 Directeurs de Recherche (DR-CNRS), 2 Maîtres de Conférences (MCF-UdS), 5 Chargés de Recherche (CR-CNRS), 2 Assistants Ingénieurs (AI-CNRS), 1 Technicien (T-UdS)

**Involved research groups:** MPE, IMI, PSM

**Keywords:** polymer · chemistry · polyelectrolytes · conjugated polyelectrolytes · multicharged systems · polyelectrolyte multilayers · nano-organized multimaterials · biomaterials · biofunctionalization · smart films



The axis “Polyelectrolytes” assembles researchers of the ICS who study polyelectrolytes (PEs) and multicharged systems, in solutions or at interfaces, and use them to develop distinct applications in drug delivery, gene therapy, sensors, photovoltaic devices and surface coating. It is specifically worldwide recognized in the development of the dipped and sprayed layer-by-layer (LbL) assembly methods that gave rise to novel nanocomposite and smart materials. It is also a major area of multidisciplinary scientific research at the ICS, combining various skills in polymer chemistry, polymer characterization, polymer physics and macromolecular engineering at interfaces. Due to the importance of polyelectrolytes in fundamental aspects of polymer science as well as in materials science, this area of scientific research should remain active at ICS in the next years.

## Polyelectrolyte solutions

PEs are ionic polymers that dissociate into macroions and small mobile counterions when dissolved in a polar solvent such as water. Electrostatic charges of one sign are localized on the macroions whereas an equivalent amount of oppositely charged counterions is either condensed onto the macroions or scattered in the solution. We are dealing with quenched PEs, as the charge distribution along the chemical sequence is static or fixed by chemistry and annealed PEs, as the charge is dynamic or monitored by pH. When dissolved in a good solvent (hydrophilic PEs), their properties are more complex than those of neutral macromolecules mainly because electrostatic interactions are long-ranged (possibly screened by added salts). In a poor solvent (hydrophobic PEs), the complexity results from the competition between the long-range electrostatic repulsions and the short-range attractions associated with the poor solubility. In both cases, further degrees of freedom are brought about by counterions that also play a crucial role with respect to interactions. Increasing attention has been paid to these charged polymers in aqueous solutions. However, the understanding of their properties is far from complete. [1-7]

The main contributions of the axis to this field mainly result from small angle X-ray and neutron scattering studies providing the molecular and dielectric structures

of model flexible PEs in solutions. Various fundamental issues have been addressed:

-Influence of the macroion architecture on the structural properties of hydrophilic PEs. Simple ring-shaped and regularly branched (star and comb-shaped) macroions were considered. [8]

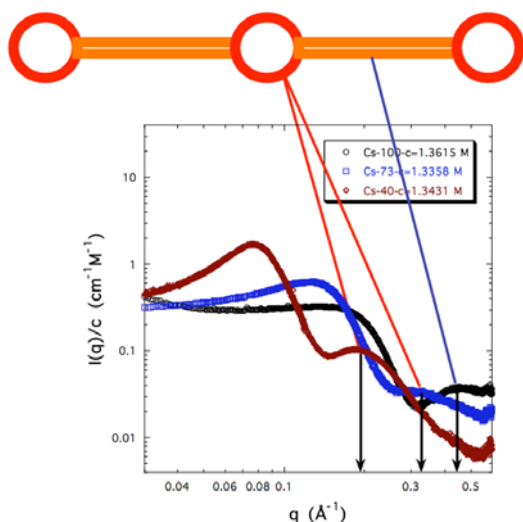
-Influence of the nature and valence of counterions on the structural properties of hydrophilic PEs. Salt free aqueous solutions of sulfonated polystyrene macroions with variable fractions of monovalent ( $\text{Na}^+$ ) and divalent ( $\text{Ca}^{2+}$ ) counterions were investigated and analyzed through scaling theory. The effective charge fraction and its dependence on concentration was estimated by solving the Poisson-Boltzmann equation in the framework of the cell model. [9-10]

-Influence of the hydrophobicity of macroions on the structural properties of quenched PE solutions. High-resolution small angle X-ray scattering experiments provide strong evidences of the existence of pearl necklace average conformations with dense charged aggregates connected by stretched chain parts (Figure 1). Condensed counterions are then localized around the hydrophobic aggregates.

-Influence of the hydrophobicity of counterions on the structural properties of quenched PE solutions. For the less hydrophobic counterions, the structure is found quite similar to that observed with hydrophilic counterions. On the contrary, strong hydrophobic counterions form microdomains that are decorated by macroions. The average conformation of these complexes is like a pearl necklace. It has however a distinct nature of the one due to hydrophobicity distributed along the chemical sequence of the macroions.

-Influence of the hydrophobicity of macroions on the structural properties of annealed PE solutions. The strong coupling between the electronic structure and the average conformation of a conjugated PE has been used to study the first-order discontinuous transition of an annealed PE in poor solvent. The collapse of macroions was demonstrated by using UV-visible absorption spectroscopy. [11]

-Solutions of PEs in ionic liquids (ILs) have also been investigated. Some ILs display density fluctuations on a short spatial scale. In this case, the average conformation of PEs can be easily study by small angle X-ray or neutron scattering and is found to be similar to that of a neutral polymer in a good solvent. PEs in ILs as polymers and copolymers in ILs, are emerging subjects.



**Figure 1.** Form factors of condensed counterions measured from high-resolution small angle X-ray scattering experiments. Macroions of sulfonated polystyrene of different sulfonation ratios are considered: 100% (black curve), 70% (blue curve) and 43% (red curve).

## Multicharged systems

Mixed systems, such as PEs-oppositely charged surfactants, PEs-oppositely charged particles and PE complexes, including polyplexes, have received particular attention because of their numerous applications in cosmetics, paints, drilling muds, and pharmaceutical vectors. Despite the advances of various research groups in the world, some fundamental issues related to these multicharged systems are still shelved. The axis “polyelectrolytes” is mainly interested by those associated with practical applications. Thus, structural studies of some PE complexes in solutions, such as poly(L-Lysine)-DNA complexes and Insulin-poly(diallyl-dimethyl ammonium chloride) complexes, are in progress. A behavior very similar to that of polyampholytes is expected when two PEs of opposite charge are mixed to form a PE complex. Therefore, the first step of such studies aims at obtaining the phase diagrams of these systems. At large enough concentration, solutions phase-separate into a dense complex phase containing both PEs and a very dilute solution. There is also one phase region corresponding to coacervates. The second step aims at investigating the structure of the various phases, using small angle radiation scattering as well as cryomicroscopy. The way used to prepare the systems is important and has to be properly defined. On the other hand, the optical properties of conjugated PEs, involving UV-visible absorption and fluorescence, have recently been probed during their complexation with oppositely charged surfactants. They were correlated with hydrodynamic radius measurements for the first time. The results demonstrate that the use of conjugated PEs in the study of PE complexes should allow further progress, as also suggested by investigations of polyplexes based on conjugated PEs. Specifically, they would be useful in studying the kinetics of PE complex formation. Indeed, several issues are still shelved: reversibility versus irreversibility of PE complexes that depends on molecular weight and PE compactness (branched PEs); complexation of several PEs, e.g., mixtures of polyanions and polycations.

## Polyelectrolyte multilayers

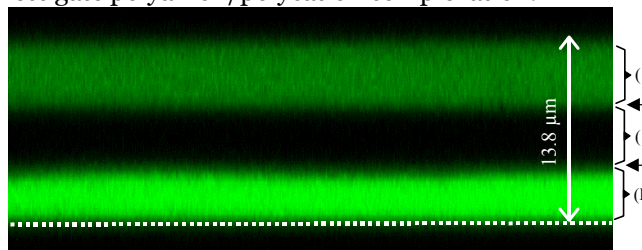
A very important application of PEs that has been developed over the past years at the ICS is the formation of PE multilayers. Starting from a charged solid surface, the multilayer builds up by successive adsorption of oppositely charged PEs. Almost an infinite number of layers can be piled up this way.

From a fundamental point of view, several techniques to build up such PE multilayers have been introduced by the ICS researchers.<sup>[12-18]</sup> Recently, attention has mainly been drawn on spraying techniques. The growth of the films can be linear or exponential. Linearly growing films are observed for polyanion/polycation pairs that interact strongly with each other (exothermic complexation process) whereas when the complexation process is endothermic (it is then entirely driven by entropy) the growth is usually exponential.<sup>[19]</sup> Linearly growing films lead to stratified architectures whereas exponential growth results from the diffusion in and out of the film of at least one of the polyelectrolytes constituting the film during each deposition steps. Such films appear gel-like and are thus much less stratified as linearly growing multilayers. It is also possible to alternate the construction of exponentially and linearly growing films and therefore to build multilayered films with compartment; the linear engrowing multilayer acting as a barrier for the diffusion of PEs but not hindering the diffusion of small ions such as protons (Figure 2<sup>[15]</sup>). In this way, multireservoir films can be obtained and multiple functionalizations of biomaterial coatings as well as for applications in vectorization can be achieved. Actually, only basic rules governing the build up of PE multilayers have been established and numerous fundamental issues remain. For instance, there is no definitive mechanism describing the exponential growth. From this point of view, it would be interesting to compare PE multilayers, i.e. PE complexes at interfaces (2d), with PE complexes in solution (3d). The exchanges between compartments in multireservoirs films are also interesting problems. Finally, films of PE multilayers built by mixtures of polyanions and polycations should also be investigated.

Beside the fundamental aspects of the PE multilayers, they are widespread in applications from surface coating towards biology and medicine. Indeed, the concept of PE multilayers is a particular example of the more general concept of film constructed via layer-by-layer (LbL) self-assembly, allowing to deposit a maximum number of different components on a maximum number of different surfaces in the form of multimaterial multilayer films using a single process. It has become a powerful tool for building PE multilayer films and more complex multicomponent systems with nanoscale precision.

Finally, researcher from ICS have recently developed a new concept of film buildup process that derives from the step-by-step process but overcomes its main inconvenience: the buildup time.<sup>[20,21]</sup> They introduced the concept of *Simultaneous Spray Coating of Interacting Species* where two interacting species (polyanions and polycations) are sprayed simultaneously onto a surface, leading to a continuous film growth. This technique is not only of interest for the

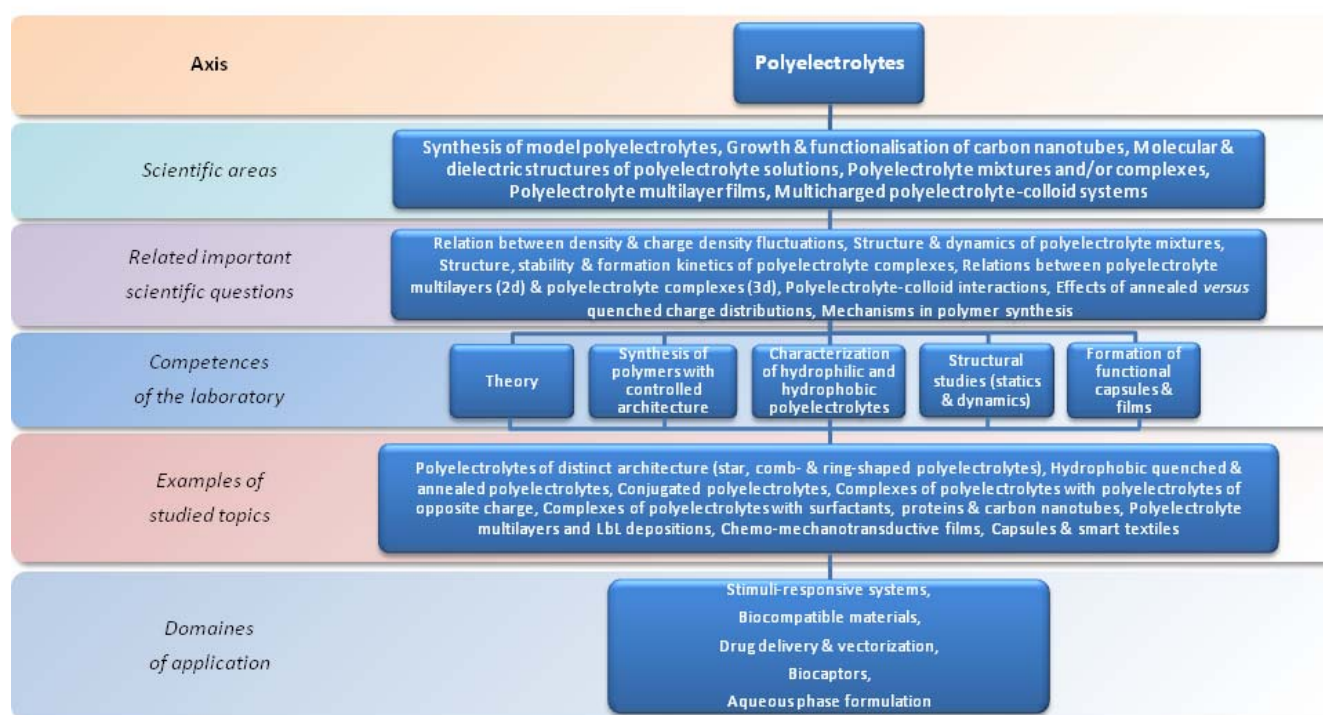
surface coatings but also provide a new tool, to investigate polyanion/polycation complexation.



**Figure 2.** Vertical section image of a  $(\text{PLL}/\text{HA})_{30}/\text{PLL}^{\text{FITC}}/\text{HA}/(\text{PAH}/\text{PSS})_{30}/(\text{PLL}/\text{HA})_{30}/(\text{PAH}/\text{PSS})_{30}/(\text{PLL}/\text{HA})_{30}/\text{PLL}^{\text{FITC}}$  multilayered film architecture in solution (NaCl 0.15 M, pH=5.9) observed by confocal laser scanning microscopy. The horizontal dashed line indicates the position of the glass slide on which the polyelectrolyte multilayers have been deposited. Indications on the right side of the image give the structural interpretation of the section observed.

## Structuring of the axis

The projects along this research axis are mainly performed at the ICS thanks to a combination of competences in polymer chemistry, polymer characterization, polymer physics and macromolecular engineering at interfaces. These competences are distributed within three research teams (MPE, IMI and PSM), each one being specialized in more specific subjects such as polyelectrolyte solutions, polyelectrolyte multilayers, layer-by-layer self-assembled films, chemo-mechanotransductive films, capsules and smart textiles (Figure 3). The experimental techniques used by these teams are: NMR, SEC, FFF, capillary electrophoresis, zeta potential analysis, microcalorimetry, ellipsometry, quartz crystal microbalance (QCM), fluorescence spectroscopy, confocal microscopy, electron microscopy, and small angle scattering (light, X-ray and neutron).



**Figure 3.** Organization chart of the axis highlighting the major areas and questions related to polyelectrolytes. To address them, a number of necessary competences are provided by the involved research groups (MPE, IMI and PSM). Examples of studied objects and targeted applications illustrate both the diversity and coherence of the axis

- [1] Hara, M. (Ed.), *Polyelectrolytes: Science and Technology*; Marcel Dekker; New York **1993**.
- [2] Schmitz, K.S. *Macroions in Solution and Colloidal Suspensions*; VCH; New York 1993.
- [3] Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 51.
- [4] Barrat, J.-L.; Joanny, J.-F. *Adv. Chem. Phys.* **1996**, *94*, 1.
- [5] Radeva, T. (Ed.) *Physical Chemistry of Polyelectrolytes*; Marcel Dekker; New York **2001**.
- [6] Holm, C.; Kekicheff, P.; Podgornik, R. (Eds.), *Electrostatic Effects in Soft Matter and Biophysics*, vol. 46 of NATO Science Series II-Mathematics, Physics and Chemistry; Kluwer Academic Press; Dordrecht **2001**.
- [7] Dobrynin, A.V.; Rubinstein, M. *Prog. Polym. Sci.* **2005**, *30*, 1049.
- [8] Heinrich, M.; Rawiso, M.; Zilliox, J.-G.; Lesieur, P.; Simon, J.-P. *EPJE* **2001**, *4*, 131.
- [9] Combet, J.; Isel, F.; Rawiso, M.; Boué, F. *Macromolecules* **2005**, *38*, 7456.
- [10] Combet, J.; Rawiso, M.; Rochas, C.; Hoffmann, S.; Boué, F. *Macromolecules* **2011**, *44*, 3039.
- [11] Vallat, P.; Catala, J.-M.; Rawiso, M.; Schosseler, F. *EPL* **2008**, *82*, 28009.
- [12] Decher, G. *Science* **1997**, *277*, 1232.
- [13] Lösche, M.; Schmitt J.; Decher, G.; Bouwman, W. G.; Kjaer, K. *Macromolecules* **1998**, *31*, 8893.
- [14] Decher, G.; Schlenoff, J.-B. (Eds), *Multilayers Thin Films: Sequential Assembly of Nanocomposite Materials*; Wiley-VCH; Weinheim 2003.
- [15] Méndez Garza, J.; Schaaf, P.; Muller, S.; Ball, V.; Stoltz, J.-F.; Voegel, J.-C.; Lavalle, P. *Langmuir* **2004**, *20*, 7298.
- [16] Porcel, C. H.; Izquierdo, A.; Ball, V.; Decher, G.; Voegel, J.-C.; Schaaf Langmuir **2005**, *21*, 800.
- [17] Jessel, N.; Oulad-Abdelghani, M.; Meyer, F.; Lavalle, P.; Haïkel, Y.; Schaaf, P.; Voegel, J.C. *PNAS* **2006**, *103*, 8618.



# Polyelectrolyte Multilayers and Nano-Organized Multimaterials (MPE)

Head of the Group *Gero Decher*

**Permanent staff :** Prof. Gero Decher (UdS), Dr. Olivier Félix (Chargé de Recherche CNRS), Jean-Louis Tecquet (Technicien CNRS)

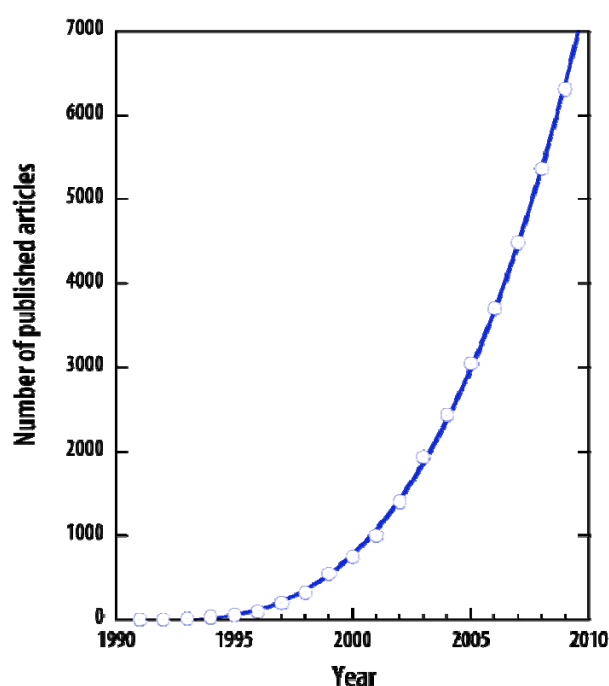
**Non-permanent researchers (2007-2011): 6 post-doctoral associates** (Dr. H. Datta 2008-2010, Dr. El Khouri 2009-2011, Dr. R.D.Jayant 2010-2012, Dr. Y. Ma 2010-2012, Dr. E. Seyrek 2007-2009, Dr. R. Szamocki 2008-2010) **9 PhD students** (R. Blell - defense planned 2012, S. Boudard – defended 2007, N. Cini – defended 2010, D. Dontsova – defended 2011, G. Popa- 2010, J. Sergeeva – defense planned 2012, F. Valenga – 1 year stay, M. Witt - 1 year stay, Z. Zheng - defended 2009) **9 Master students**

**Keywords:** Development of the layer-by-layer assembly method · macromolecules at interfaces · composite biomaterials · (bio)-functional nanoparticles · functional coatings · thin film devices · nanobio-technology · hybrid materials



Our most important activity is our invention and development of the so-called layer-by-layer (LbL) assembly method <sup>[1, 2]</sup>. This self-assembly method is based on the concept of attractive intermolecular interactions between each layer pair, it is mostly electrostatic in nature and combines experimental ease with low cost fabrication and environmental friendliness. LbL-assembly allows to deposit a maximum number of different components on a maximum number of different surfaces in the form of multimaterial multilayer films using a single process. It has, over the last years, become a powerful tool for building polyelectrolyte multilayer films and more complex multicomponent systems with nanoscale precision. Over 200 independent teams are publishing now about 1000 articles per year in this field and LbL-films are used to coat objects as small as nanoparticles, as big as cars or as irregular as textiles or fruit. A huge advantage of LbL-assembly is that even films on very different surfaces can be astonishingly similar if prepared at identical deposition conditions. This allows for example to deposit films on surfaces that are difficult to characterize (e.g. paper, textile, fruit, ...) and to learn about their structure by doing x-ray or neutron reflectometry on regular silicon wafers.

The development of layer-by-layer assembly

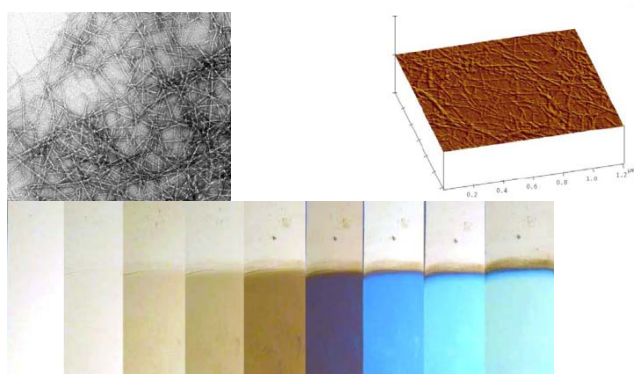


The following activities of our team were selected for the scientific report 2007 - 2011:

- ▶ -The LbL-assembly of highly homogeneous films composed of nanofibrillar materials.
- ▶ -The preparation of new hybrid colloidal systems: Nano-bags.
- ▶ -A structural comparison of “dipped” and “sprayed” LbL-films by neutron reflectometry.
- ▶ A new model approach for cancer therapy: Multifunctional stealth nanoparticles.
- ▶ Nanoscale precipitation coating: LbL-assembly of pure inorganic materials.
- ▶ Step-by-step assembly of self-patterning polyelectrolyte films.
- ▶ Layer-by-layer assembled films for photocatalytic applications.
- ▶ Spray-on organic/inorganic films: A general method for forming nanoscale coatings by interfacial precipitation reactions.

## The Layer-by-layer assembly of highly homogeneous films composed of nanofibrillar materials

In collaboration with the team of Prof. L. Wagberg (KTH, Sweden) we studied the layer-by-layer assembly of cellulosic nanofibrils (MFC) as building blocks. Such fibrils have diameters of a few nanometers and a length of up to several microns (Figure 1), they are obtained in neutral, anionic and cationic form.



**Figure 1.** Transmission electron micrograph of MFCs (upper left) and AFM image of an LbL-film (upper right). Optical interference colors of MFC-LbL-films of different thickness on silicon wafers (bottom).

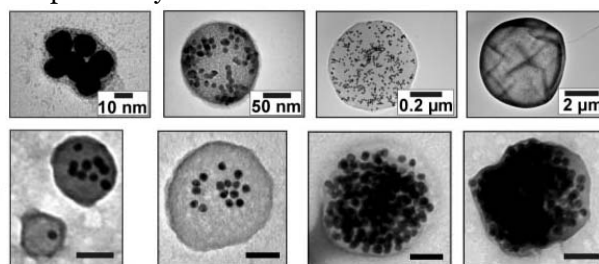
Surprisingly and despite of the fact that the films clearly show that the fibrils form networks with pore sizes that are multiples of the fiber diameter, these films appear macroscopically homogeneous as shown

by thickness dependent interference colors<sup>[3]</sup> (Figure 1).<sup>[3]</sup> The use of such nanoporous films for nanofiltration purposes is currently being explored.

## The preparation of new hybrid colloidal systems: Nano-bags

The control of simple parameters involved in the process of classic bridging flocculation allows the preparation and fine-tuning of a new class of hybrid nanomaterials with respect to size, composition, and morphology. The resulting nano-particle-filled “nano-bags” are obtained in aqueous suspension by mixing three basic components, a polyelectrolyte, a multivalent ion, and nanoparticles in different ratios.

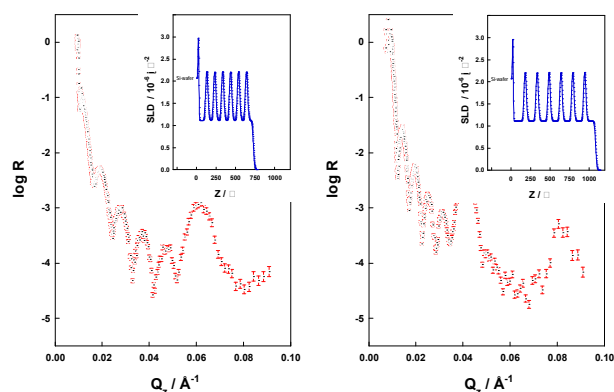
The size range in which nano- and micro-bags can be prepared seems to start at about 25 nm; these are oligo-nanoparticle aggregates whose size is clearly related to the size of the nanoparticles themselves and seems to extend up to about 5  $\mu\text{m}$ . By controlling the stoichiometric balance between the global number of positive and negative charges on the polycation and on the multivalent anion and by controlling the absolute concentrations and the ratios, namely of the polyelectrolyte and the nanoparticles, one has access to a wide range of different nano-bag morphologies and compositions<sup>[4]</sup>. Interestingly, the process of nano-bag formation seems not to be restricted to a single type of nanoparticles since, at least, citrate-stabilized gold and iron oxide nanoparticles showed indistinguishable results in transmission electron microscopy. The outer surface of the nano-particle-filled nano-bags is easily functionalized further through layer-by-layer assembly. The size and the loading of nano-bags are to some extent controlled independently.



**Figure 2.** Transmission electron micrographs of different nano-bags. The top row shows individual nano-bags of different size that are loaded with Au-nanoparticles with a size of 13 nm. The bottom row shows that the degree of loading with Au-nanoparticles can be controlled.

## A structural comparison of dipped and sprayed LbL-films by neutron reflectometry

Earlier on we have pointed out that one of the most interesting aspects of the spray-deposition of LbL-films lies in the fact that spray-assembly can enormously accelerate the deposition time. At the same time we also pointed out that layer-by-layer assembled films prepared by “dipping” or by “spraying” may show considerable differences with respect to their properties. Most importantly, films with the same number of layers prepared from the same solutions by “dipping” or “spraying” differ in thickness, for films composed of the sodium salt of poly(styrene sulfonate) (PSS) and poly(allyl amine hydrochloride) (PAH) we noticed that spray-assembled films only had a thickness of about 70-75% of that observed for classic deposition by “dipping”.



**Figure 3.** Raw neutron reflectometry data (data points), overlaid with the expected reflectometry curves (blue lines) as derived from the theoretical SLD profiles (insets). The theoretical SLD profiles are predicted from the layer sequence, the average thickness per layer pair, the interfacial roughness between layers and the surface roughness of the whole film. The SLDs for non-deuterated and for LbL-films with a maximum of deuteration were determined independently. Note that the match between raw data and expected reflectometry is due to the excellent structural control of LbL spray assembly, none of the structural parameters was numerically fitted to the respective data sets. The difference between the data sets on the left and on the right is the distance between the deuterated layers that results from different layer numbers of non-deuterated polyelectrolytes between the deuterated layers.

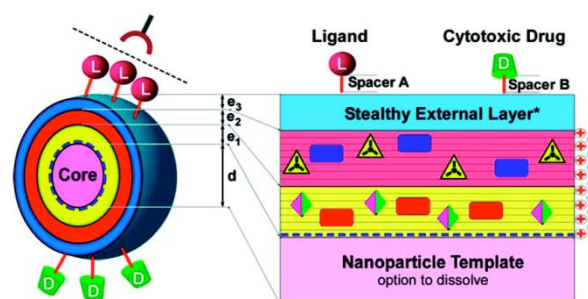
Investigations by atomic force microscopy (AFM) revealed that both kinds of films also differ with respect to surface roughness. These structural differences, whose origin is far from being understood, demanded to investigate if spray deposited films also possess a stratified structure that was observed earlier by us by neutron reflectometry for the case of multilayer films assembled by dipping.

In collaboration with F. Cousin at the Laboratoire Léon Brillouin we investigated LbL-films with several different film architectures by neutron reflectometry<sup>[5]</sup> (Figure 3). The quantitative analysis of the reflectometry data confirmed that LbL-films prepared by “dipping” are different from those prepared by “spraying” and it revealed that spray-assembled LbL-films also possess a “fuzzy” stratified structure as their “dipped” counterparts. Spray-

assembly is such a viable alternative for preparing polyelectrolyte multilayer films of high quality and related hybrid materials.

## A new model approach for cancer therapy: Multifunctional stealth nanoparticles

In collaboration with the team of Prof. K. Ulbrich (Macromolecular Institute, Prague) we developed a highly versatile nanoparticle-based core/shell drug delivery system consisting of cytotoxic stealth carrier particles<sup>[6]</sup>. Their multifunctional shells, mandatory for addressing different diagnostic/treatment requirements, are constructed using a single assembly process in which various different functionalities are incorporated in a modular fashion (Figure 4).



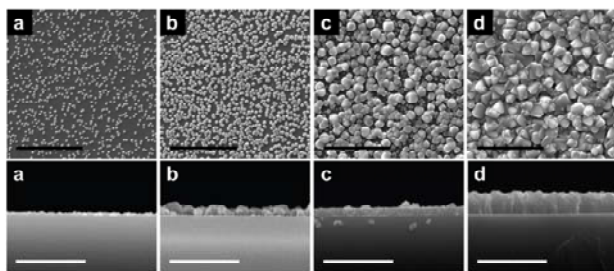
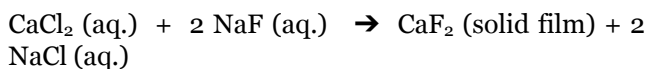
**Figure 4.** Schematic Depiction of Nanoparticles Coated with Multilayer Shells as New Drug Delivery System.

More specifically, a robust electrostatic and covalent layer-by-layer assembly strategy was used as an “engineering approach” toward nanoparticles with multilayer shells that combine all of the following properties: (a) a small size distribution of the nanoparticle carrier, (b) a high stability in physiological media, (c) attachment of a pro-drug in covalent form and thus a low toxicity of the carrier system, (d) the triggered release and activation of the drug only after endocytosis and enzymatic cleavage, and (e) “stealthiness” and thus protection against uptake by macrophages. The use of small, non-aggregated nanoparticles as carriers is required to enhance the accumulation of active drug in the tumor tissue (i.e., enhanced permeability and retention of tumor tissues, EPR). To establish this system as a proof of concept, we use the smallest nanoparticles within the interesting size range of about 25-100 nm for EPR targeting since these are the most difficult to functionalize and because they possess the highest surface area.

In this collaboration we were able to prepare the first nanoparticle-based drug delivery system carrying simultaneously a “stealth” corona and a cytotoxic payload. In addition we could show that the cytotoxic agent was released only by endosomal enzymes. All functions combined are a prerequisite for establishing long circulation times in the bloodstream and a drug release only after endocytosis in the target tissues.

## Nanoscale precipitation coating: LbL-assembly of pure inorganic materials

In collaboration with the teams of J.-C. Voegel and P. Schaaf in Strasbourg we extended the spray-assisted layer-by-layer assembly method toward films of purely inorganic compounds. Instead of spraying polyelectrolyte pairs one simply sprays solutions of complementary inorganic salts in alternating fashion<sup>[7]</sup>. This nanoscale “precipitation coating” technique is based on the step-by-step spraying of solutions of complementary salts that possess a non-negligible difference of the solubility products compared to that of the solid inorganic product that forms a film on the receiving surface by precipitation due to a local supersaturation. Figure 5 shows exemplarily the case of the deposition of CaF<sub>2</sub>-films using a well known precipitation reaction:



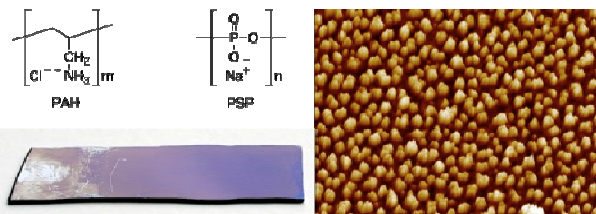
**Figure 5.** Nucleation and growth of CaF<sub>2</sub> crystals on a surface (top row). Side-view of the growth of a dense CaF<sub>2</sub>-film; other components yield other film morphologies.

The “precipitation coating” technique described above is also compatible with the classic LbL-assembly of polyelectrolytes and can be used for the fabrication of multilayer sandwich films.

## Step-by-step assembly of self-patterning polyelectrolyte films

In collaboration with the teams of T. Tulun (ITU Istanbul and V. Ball (University of Strasbourg), we investigated the formation of LbL-films of poly(allyl amine) and poly(sodium phosphate). Besides being self-patterning (Figure 6), such films turned out to be a challenge to the way we think about polyelectrolyte complexation and multilayer formation<sup>[8]</sup>.

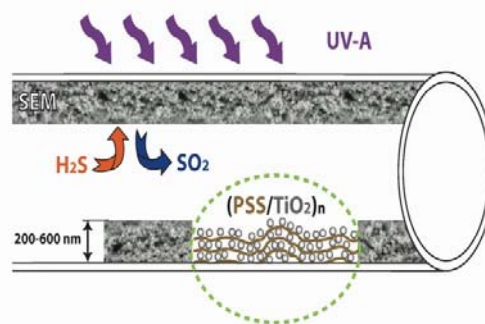
Several observations made with these films cannot be explained with present models for LbL-film formation including: a) films only grow by spraying not by dipping, b) the zeta potential changes slowly positive to negative when depositing hundreds of layers, c) films become smoother or rougher with increasing film thickness depending on polymer concentration or d) the observation of a temporary growth instability at about 75 deposited layers.



**Figure 6.** Polymers used (upper left) and apparently “homogeneous” spray-assembled film sample of these components (lower left). The image on the right (AFM) shows that such films are self-patterning. It turns out that the feature size of the pattern scales linearly with the film thickness, but that the patterns are stable at the same time.

## Layer-by-layer assembled films for photocatalytic applications

In collaboration with an industrial partner and the team of V. Keller and N. Keller (ECPM), we studied LbL-films containing TiO<sub>2</sub> nanoparticles for photocatalytic applications. For this purpose films must be homogeneous and highly transparent over large areas. In addition to the system shown in Figure 7, different nanoparticles and different polyelectrolytes were used to establish structure/property relationships. Films were also prepared on textiles including testing their efficiency for eliminating different gaseous pollutants. Note that controlling film properties on textiles is very difficult due to the limited options for precise characterization on such surfaces.



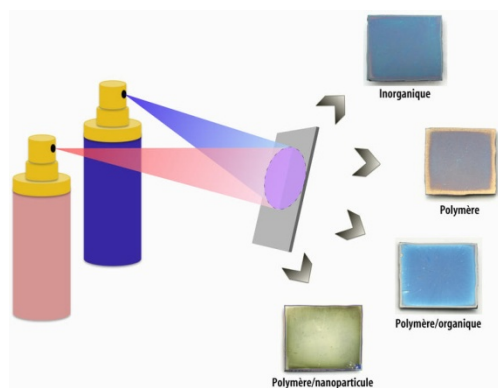
**Figure 7.** Simplified drawing of a reactor for the photocatalytic decomposition of H<sub>2</sub>S. The walls of the cylindrical reactor are coated with LbL-films whose structure is depicted schematically and as SEM image.

The quality of LbL-films obtained here allowed for the first time to determine BET-surface areas of such films and to estimate how much the polymer “matrix” blocks catalytic sites on the nanoparticles. A patent was submitted in early 2011 and the first scientific publication is presently accepted for publication.



## Spray-on organic/inorganic films: A general method for forming nanoscale coatings by interfacial precipitation reaction

In collaboration with the teams of P. Schaaf and J.-C. Voegel in Strasbourg we demonstrated that spray-assisted LbL deposition can be further advanced to lead to a new and general method we termed “simultaneous spray coating of interacting species” [9]. Instead of bringing two spontaneously interacting species into contact step-by-step at an interface to form LbL films, this method is based on the simultaneous spraying of two or more interacting components against a receiving surface. This process results in a fast reaction between the complementary components on a macroscopic surface, hence leading to a continuous and gradual buildup of a coating, the thickness of which is controlled by the spraying time, while the solvent and excess material are removed by drainage. It is applicable to a wide choice of components, some of which do not even form LbL-films when sprayed alternately.



**Figure 8** : Simultaneous spraying as applied to the formation of “Spray-on precipitation coatings”. Images of the films deposited on silicon wafers (40 mm × 40 mm) with colors arising from optical interference. The different films are: (A) Calcium Fluoride, (B) poly(allylamine)/poly(styrene sulfonate) (C) poly(allylamine)/sodium citrate, and (D) poly(allylamine)/gold nanoparticles. The silicon wafers were slowly rotated to improve film homogeneity. Note that some samples show slight edge effects. Please also note that we tried to spray-assemble films such as (B) by simultaneous spraying over many months in the past without any success. The other systems are entirely new.

This article (9) was cited in press releases by C.N.R.S., INSERM, Université de Strasbourg and Angewandte Chemie. After the press release, the topic was featured in many magazines (including Le Monde) and on many websites related to nanoscience.

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- [1] Decher, G., *Science* 277 **1997**, 1232-1237.
- [2] Decher, G., and Schlenoff, J. B., (Eds.) *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*, Wiley-VCH, Weinheim **2003**.
- [3] Wågberg, L., Decher, G., Norgren, M., Lindstrom, T., Ankerfors, M., and Axnas, K., *Langmuir* 24 **2008**, 784-795.
- [4] Schneider, G. F., and Decher, G., *Nano Letters* 8 **2008**, 3598-3604.
- [5] Felix, O., Zheng, Z. Q., Cousin, F., and Decher, G.\*, *C. R. Chimie*. 12 **2009**, 225-234.
- (6) Schneider, G. F., Subr, V., Ulbrich, K., and Decher, G.\*, *Nano Letters* 9 **2009**, 636-642.
- [7] Popa, G., Boulmedais, F., Zhao, P., Hemmerlé, J., Vidal, L., Mathieu, E., Felix, O., Schaaf, P., Decher, G.\*, and Voegel, J. C., *ACS Nano* 4 **2010**, 4792-4798.
- [8] Cini, N., Tulun, T., Decher, G., and Ball, V., *J. Am. Chem. Soc.* 132 **2010**, 8264-8265.
- [9] Lefort, M., Popa, G., Seyrek, E., Szamocki, R., Felix, O., Hemmerlé, J., Vidal, L., Voegel, J.-C., Boulmedais, F., Decher, G., and Schaaf, P., *Angew. Chemie Int. Ed.* 49 **2010**, 10110-10113.

## Self-Evaluation

### Human resources

Permanent members:

Prof. G. Decher (group leader)

Dr. Olivier Félix (CR)

Open position (technician)

Actual non permanent members:

3 postdoctoral fellows (Y. Ma, R. Jayant, D. Dontsova)

2 PhD students (R. Blell, Y. Sergeeva)

1 Master student (Ch. Higy)

Number of post-docs over the period: 6

Number of PhD defenses over the period: 5

Number of master students over the period: 6

### Statement of financial support

ANR "Cartilspray" (2006-2009): Scientific Coordinator J.-C. Voegel, INSERM 977, Strasbourg. (*only consumables*)

ANR "Clickmultilayer" (2007-2010): Scientific Coordinator P. Schaaf, ICS, Strasbourg. (*only consumables*)

ANR "Tailorpack" (2007-2011): Scientific Coordinator Nathalie Gontard, UMR 1208 and INRA, Montpellier.

"DesignCell" (2007-2011): ERA-C project "WoodWisdom". Scientific Coordinator: T. Lindström STFI-Packforsk, Stockholm, Sweden. (1 year postdoc) Industrial contract "RoboSpray" (2008, 6 months) Industrial contract "FiberCat" (2008-2011). (1 PhD thesis).

"SustainComp" (2008-2012): Call FP7-NMP-2007-LARGE-1. Scientific coordinator M. Ankerfors, STFI-Packforsk, Stockholm, Sweden.

ANR "Magarrays". (2009-2012) Scientific Coordinator: Sylvie Begin, IPCMS, Strasbourg. (2 years postdoc)

Pôle de compétitivité / DGE "Ship-In" (2009-2012), Scientific Coordinator: Pascale Bouillé (Vectalys SA)

FRC equipment grant (2010). (40.000,- EUR)

### Statement on scientific collaborations

National collaborations outside the ICS:

J.C. Voegel, Unité INSERM UMR 977, Strasbourg.

Projects: ANR "Cartilspray", ANR "Clickmultilayer".

S. Begin and B. Pichon (IPCMS, Strasbourg). Project "Magarrays".

S. Viville (IGBMC, Strasbourg) and P. Erbacher (Polyplus, Strasbourg). Project "Ship-In".

Valérie Keller and Nicolas Keller, UMR 7515 and ECPM, Strasbourg, France

Natalie Gontard and Carole Guillaume, UMR 1208 and INRA, Montpellier. Project ANR "Tailorpack".

Fabrice Cousin, Laboratoire Léon Brillouin, C.E.A Saclay, Gif-sur-Yvette.

International collaborations:

Lars Wågberg (KTH, Stockholm, Sweden), Lars Berlund (KTH, Stockholm, Sweden), Olli Ikkala (TKK, Helsinki, Finland). Projects "DesignCell" and "SustainComp"

Joseph. B. Schlenoff (University of Florida at Talahassee, USA). Edition of the second volume of the Multilayer Book.

Muhammad Mazhar (Department Of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan).

Tülay Tulun (Istanbul Technical University, Graduate School of Science, Engineering and Technology, Istanbul, Turkey).

Vincent Ball (CRP Henri Tudor, Luxembourg, Luxembourg).

Karel Ulbrich and Vladimir Subr (Institute for Macromolecular Chemistry of the Academy of Sciences of the Czech Republic, Prague, Czech Republic)

Industrial partners:

Clariant AG, BASF AG, Innventia AB

### Statement on scientific production

For the period 2007-2011:

Number of publications: **20**

- 1 Nature Chemistry
- 2 Nano Letters
- 2 Angewandte Chemie
- 1 J. Am. Chem. Soc.
- 1 Advanced Materials
- 1 ACS Nano
- 1 J. Mat. Chem.
- 1 Soft Matter
- 4 Langmuir
- 1 Macromol. Rapid Chem.
- 1 Macromolecules
- 1 Comptes Rendus Chimie
- 1 Biointerphases
- 1 New J. Chem.
- 1 Biomolecular Engineering

Number of citations of articles published 2007-2011 : **314**

Average citations per article : **15.7**

Number of patents 2007-2011 : **5**

Number of citations 2007-2011 of all articles : **6520**

Average number of citations per year : **1430**

Number of invited plenary conference lectures : **9**

Number of invited conference lectures : **28**

Number of invited seminars : **27**

Total number of invited oral presentations : **64**

Number of contributed conference lectures : **2**

Total number of oral presentations : **66**

Since the beginning of the career:

Total number of publications : **130**

Total number of citations : **15200**

Average number of citations per article : **116**

h-index : **52**

m-index : **2**

(Taking the start of the PhD thesis in 1983 as start of career)

Publications with more than 1000 citations : **2**

Publications with more than 500 citations : **5**

Number of patents : **14**

Number of invited plenary conference lectures : 22

Number of invited conference lectures : 108

Number of invited seminars : 84

Total number of invited oral presentations : 214

Number of contributed conference lectures : 34

Total number of oral presentations : 248

9 highly cited publications, one of which is ranked by ISI as 8<sup>th</sup> most cited among all journal articles in the field of chemistry in the period of January 1, 1997 to October 31, 2007.

"Fuzzy nanoassemblies: Toward layered polymeric multicomposites", Decher G., Science 277(5330), 1232-1237 (1997). Total number of citations : 4684  
Distinctions / Awards (2006 - 2011):

2011 Renewal of my nomination as senior member of the IUF

2010 ECIS - Rhodia European Colloid & Interface Prize

2009 Grand Prix of the "Académie des sciences" for nanobiotechnology "Emilia Valori"

2006 Nomination as Senior Member of the "Institut Universitaire de France" (IUF)

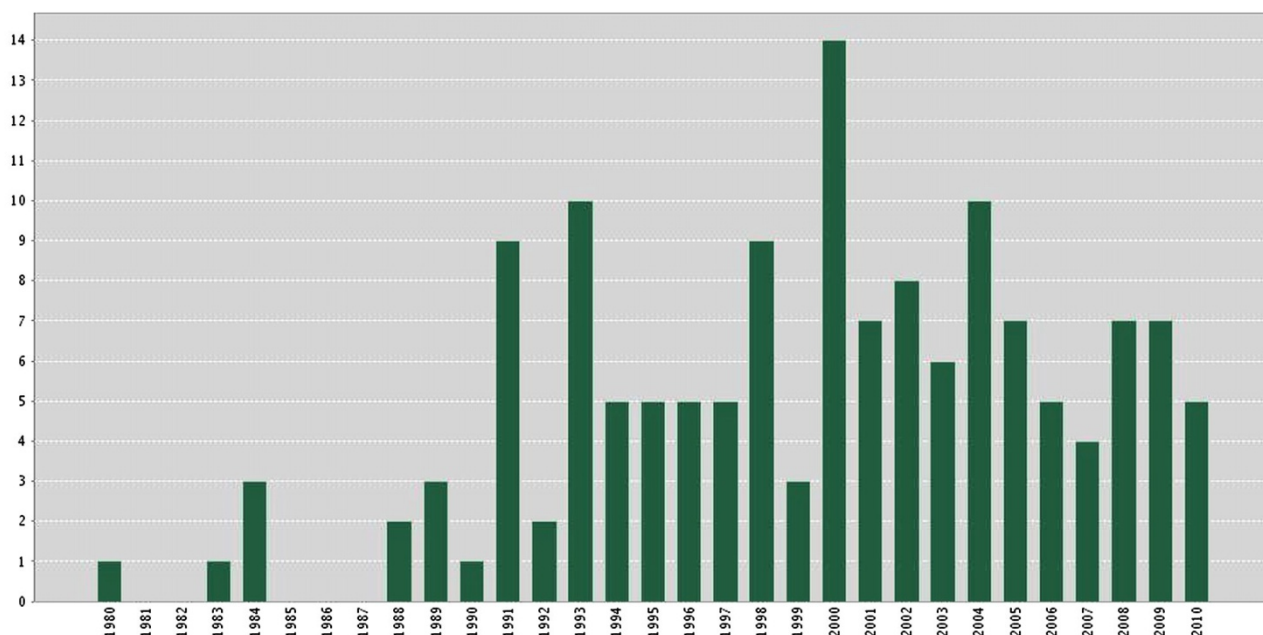


Figure 9 : Publication activity G. Decher since the beginning of the career (July 2011).

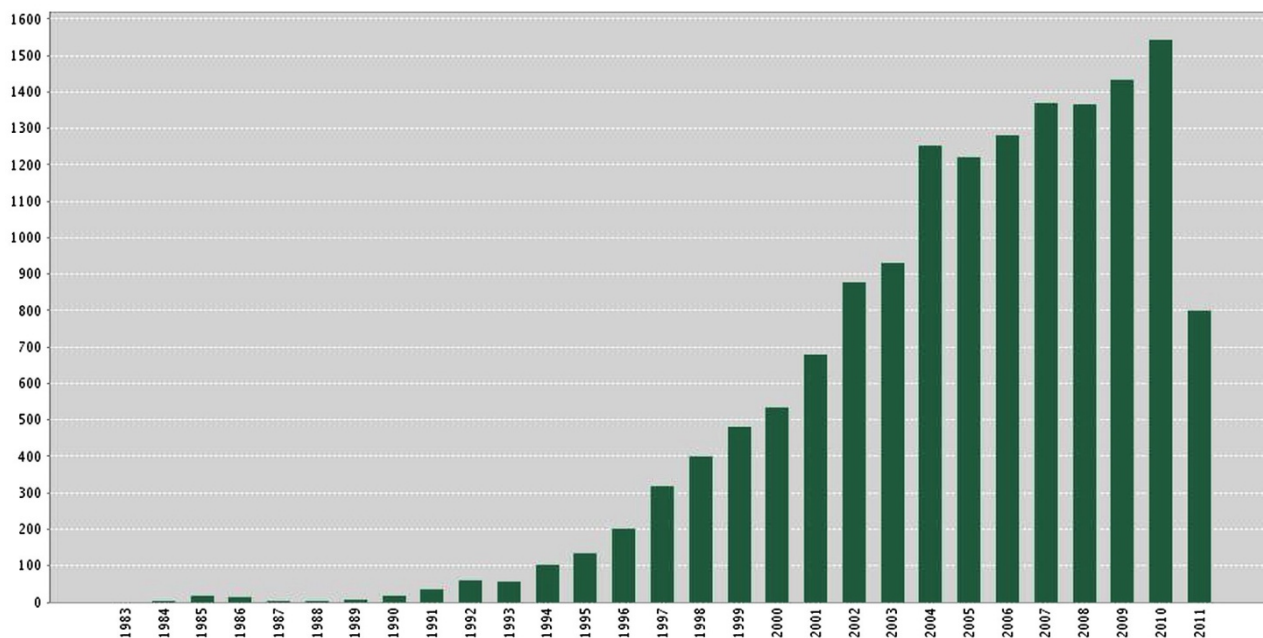


Figure 10. References to our work (ISI-Citations, July 2011)



# Macromolecular Engineering at Interfaces (IMI)

Head of the Group : *Pierre Schaaf*

**Permanent staff:** Prof. Pierre Schaaf (UdS) - Yves Frère (Chargé de Recherche CNRS) - Dr. Fouzia Boulmedais (Chargée de Recherche CNRS) 2006 - Dr. Loic Jierry (Maître de Conférences UdS) 2009 - Eric Gonthier (Technician UDS) 2008

**Non-permanent researchers (2007-2011): 8 post-doctoral associates** (Nathalie Auberval since 2011, Emmanuelle Monchaux since 2009, Audrey Parat since 2008, Prasad Polavarapu 2009-2010, Natalia Bushmarina 2008-2009, Caroline Alhais 2009-2010, Virginia Epure 2007-2008, Imed Montassen 2007-2008) / **11 PhD students** (Cesar Rios defense planned in 2013, Gauthier Rydzek and Gwenaëlle Cado defenses planned in 2012, Mathias Lefort defense planned in 2011, Adeline Callet and Alae El Haitami defended in 2010, Andreas Reisch, Nathalie Reix and Hajare Mjahed defended in 2009, Anne Wawrezinieck and Nicolas Laugel defended in 2007) / **9 Master students**

**Keywords:** polyelectrolytes · multilayers · smart materials · biomaterials · chemo-mechanotransduction · morphogen bio-inspired capsules

The mission of the ICS is to develop Polymer and Self-Assembly based Materials Science. Polyelectrolyte Multilayers films, obtained by the alternate deposition of polyanions and polycations, are typically in the scope of the Institute. They constitute a tremendously versatile tool to answer numerous scientific and societal challenges in fields as diverse as biomaterials, materials for energy, materials for water purification, anti-corrosion coatings or smart materials. With the group of G. Decher, we constitute one of the leading poles, recognized worldwide in this field. Polyelectrolyte multilayers are one of the most active fields in macromolecular physical-chemistry mainly driven by their widespread applications. Yet they are poorly understood from a fundamental point of view. Over the last four years, our group focused essentially on understanding the basic rules governing the buildup of polyelectrolyte multilayers, on extending the layer-by-layer deposition concept to new systems and on developing biomedical applications of multilayers. Our group has also a longstanding activity in capsules and smart textiles, especially towards biomedical vectors.

## Fundamental issues on polyelectrolyte multilayers

In the early 1990<sup>th</sup>, first studies on polyelectrolyte multilayers seemed to indicate that during each deposition step the polyelectrolytes from the solutions interact only with those of the outer layer of the film, leading to stratified architectures with a linear increase of the film thickness. After the discovery of exponentially growing multilayers and of polyelectrolyte exchange (both mainly by our group during the 2001-2006 period), it became clear that this initial picture of polyelectrolyte multilayers was oversimplified and that the deposition process was poorly understood. Major fundamental issues clearly emerged. (Publications pertaining to this section are Refs [1-9]).

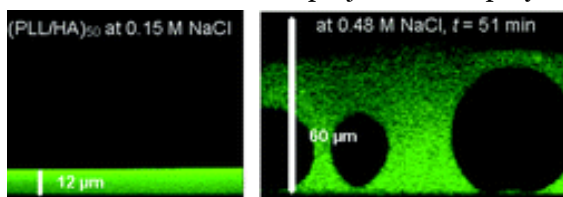
### Multilayer growth regime (linear or exponential)

This is particularly important because the properties of linearly and exponentially growing films are totally different. Our group made significant contributions in this direction. Exponentially growing multilayers are known to result from the diffusion, in and out of the whole film, of at least one of the two constituting polyelectrolytes during each deposition step. Previous studies from our group also showed that the exponential increase of the film thickness takes place only during the initial deposition steps and is then followed by a linear thickness increase. Yet in this linear regime diffusion of the polyelectrolytes "in and out" of the film still takes place. The origin of the change of the buildup regime, from exponential to linear, remained mysterious. We thus addressed this question and found that the thickness increase in the linear regime is independent of the molecular weight of the diffusing polyelectrolyte. We also showed that, during each deposition step, the polyelectrolytes no longer diffuse "in and out" of the whole film but only over a limited upper zone and that then the thickness increment does not depend upon the extension of this zone. We proposed a model based on a limited complex formation during each buildup deposition step to explain the observed features.[8]

### Dynamic processes taking place in exponentially growing multilayers

This issue includes diffusion processes, exchange processes and film evolution by modifications of the surrounding medium. Using fluorescence recovery after photobleaching experiments, we investigated the diffusion behaviour of poly(l-lysine) chains component of poly(l-lysine)/hyaluronic acid (PLL/HA) multilayers. Two populations were found: a mobile one, with a diffusion coefficient of the order of 0.1  $\mu\text{m}^2/\text{s}$  and a population that appears immobile. For chains deposited on top of the film, a third population appeared which is rapidly diffusing ( $D \approx 1 \mu\text{m}^2/\text{s}$ ).[5] We also investigated how exponentially growing films evolve when the ionic strength of the contacting

solution is changed after the film buildup. Again, we addressed this problem for PLL/HA multilayers. When such a film is constructed at a given ionic strength, and is brought later in contact with a solution of higher ionic strength, it swells. But the swelling mechanism remained unknown. We found that by increasing the ionic strength, the swelling of such a film is accompanied by the release of poly(l-lysine). More unexpectedly, we observed that above a critical ionic strength the growth of the film is accompanied by the formation of holes that first grow and later decrease in size. We explained our observations by the dissolution of PLL/HA complexes inside the film. The presence of free PLL and HA chains induces a strong local increase of the osmotic pressure leading to the formation of holes. The holes disappear as the dissolved polyelectrolytes are released from the multilayer (see Figure 1).<sup>[7]</sup> This study was performed within the framework of the ANR blanc project "Cartilspray".



**Figure 1.** Evolution of a poly(l-lysine)/hyaluronic acid multilayer built at 0.15 M NaCl and brought in contact with an aqueous solution at 0.48 M NaCl.

### Buildup and film composition of multilayers constructed from blended polyanion and polycation solutions

In 2003, our group was the first to propose to build polyelectrolyte multilayers from blended polyelectrolyte solutions. This offers new opportunities to finely tune the film properties. We made, for example, use of it to vary the degradability of films in contact with cells allowing to time-schedule the bio-response of a polyelectrolyte multilayer. Yet, tuning the film properties requires knowing the rules governing the film composition with respect to the composition of polyelectrolyte solutions used. These rules remain, even now, largely unknown. We found that there is usually a strongly non-linear relationship between the film and the polyelectrolyte solution composition. In particular when a blended solution of polyanions is used, there is a strong preferred incorporation of one polyanion over the other present simultaneously in the buildup solution. This leads also to non-linear evolutions of the film buildups and of its properties with the solution compositions. Much remains to be done before predictive rules will emerge along this question.<sup>[1, 3]</sup>

Other questions, such as the influence of the nature of the counter ions on the film buildup and on the film permeability, were also addressed.<sup>[2, 4, 9]</sup>

## Step-by-step film deposition processes and new buildup concepts

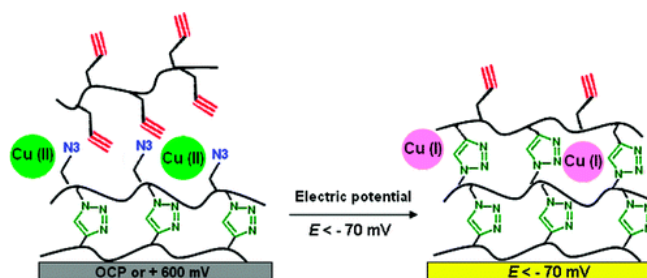
The concept of polyelectrolyte multilayers is a particular example of the more general concept of

films constructed by step-by-step deposition. Our group has worked actively on generalizing the polyelectrolyte multilayer architectures and on developing other buildup strategies belonging or derived from this more general concept of step-by-step film deposition. Some examples are given below. (Publications pertaining to this section are Refs <sup>[10-20]</sup>).

### Step-by-step deposition of "covalent" films

In 2006, Caruso proposed to construct covalently linked multilayers in a step-by-step manner based on the Sharpless click reaction between polyelectrolytes bearing azide and others bearing alkyne groups. The reaction between azides and alkynes, catalyzed by Cu(I), leads to the formation of triazole groups. This technique was extended by several other groups. The Cu(I) is usually generated from Cu(II) in the presence of sodium ascorbate, used as a reductive agent. We investigated several aspects of this buildup.

First, we discovered that Cu(I) strongly interacts with a triple bond resulting in the formation of a rather stable positive complex. This implies that the nature of the polymer, and in particular its charge, has a huge influence of the film growth, polyanions leading to much faster film growth with the number of deposition steps than polycations<sup>[12]</sup>. Next, we investigated the step-by-step film construction through Sharpless click reaction between polymers bearing azide (or alkyne) groups and bifunctional poly(ethylene oxide) linkers bearing alkyne (or azide) groups. This resulted in a new type of architecture presenting a high roughness. The rules governing their buildups were investigated<sup>[11]</sup>. In 2006, J.P. Collman proposed to form Cu(I) by reduction of Cu(II) at an electrode and to induce the click reaction on a self assembled monolayer deposited on the gold electrode. Our group was the first to take over this idea to construct, step-by-step polymer multilayers through electrochemically triggered click-reaction (see Figure 2). This work opens the route towards specific and controlled functionalization of nanoelectrodes<sup>[14]</sup>. This study was performed within the framework of the ANR blanc project "Clickmultilayer"

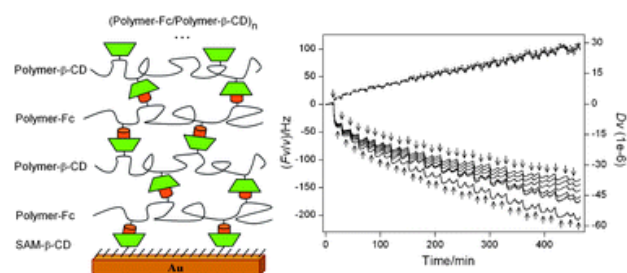


**Figure 2.** Schematic representation of the electrochemically triggered click-multilayer buildup.

### Multilayers based on host-guest interactions: Towards electro-chemically responsive films

Host-guest interactions based on cyclodextrin moieties can be used to form gels or complexes in solution. We demonstrated that these interactions can be used to buildup, in a step-by-step manner, films by alternating poly(N-hydroxypropyl methacrylamide) bearing ferrocene or  $\beta$ -cyclodextrin moieties (see Figure 3). We

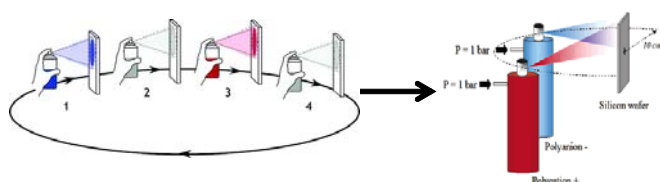
anticipate that the so-made films can be dissolved under the application of an electric potential where ferrocen is oxidized into ferrocenium, having a weak affinity for cyclodextrin. By culturing cells on such films, one should then be able to remove electrochemically a cell monolayer sheet which constitutes a challenge in vessel reconstruction and tissue engineering. This work<sup>[10]</sup> is done in the framework of an ANR blanc project "E-Detachpem" in collaboration with two groups of Grenoble (P. Labbé, UMR 5250 and R. Auzely, CERMAV) and an INSERM group (Jean-Claude Voegel, UMR 977 INSERM) from Strasbourg.



**Figure 3.** (left) Schematic representation multilayers buildup based on host-guest interactions; (right) Corresponding evolution of the quartz crystal microbalance signal (frequency and dissipation) proving the regular film buildup.

### Film by spray-assisted deposition of interacting species

In 2004 in collaboration with G. Decher, we have started to develop the step-by-step film buildup of multilayers by alternate spraying of polyanion and polycation solutions, each deposition followed by a rinsing step. Spray assisted LbL has received, since, considerable attention from the scientific community because it is extremely fast and allows coating wide surfaces. It is thus well adapted to industry. Due to the fact that it is fast, it allowed us to explore fundamental issues related to the exponential growth that were hardly accessible by the usual construction methods<sup>[8]</sup>.



**Figure 4.** Schematic representation of the step-by step and simultaneous spray deposition of polyelectrolyte film. Red (resp. blue) cans represent polyanion (resp. polycation) solutions.

We also extended spray-assisted LbL towards the deposition of inorganic materials<sup>[13]</sup>. By investigating the spray-assisted LbL process, we found that the rinsing step can be omitted without altering fundamentally the film growth. We then discovered that each spraying step can be rendered extremely short. This led us to propose to spray simultaneously the polyanion and polycation solutions which results in a continuous film growth (see Figure 4). This constitutes a real technological rupture with widespread potential applications. From an industrial point of view, it is even simpler and thus more appealing than the LbL process by spraying. We generalized this method to other polyanion/polycation systems, to polyelectrolyte/small multicharged

molecules, to polyelectrolyte/nanoparticle and even to inorganic species (CaCl<sub>2</sub> and NaF leading to the formation of CaF<sub>2</sub>) always leading to the formation of nanometric size coatings<sup>[20]</sup>. Simultaneous spraying of interacting species not only opens new routes for new coatings, it is also a tremendous new opportunity to investigate fundamental questions on polyanion / polycation complexes.

Other new concepts such as that of reactive-spray layer-by-layer were also introduced. It allows to construct mixed organic-inorganic films by generating *in situ* nanoparticles during the film buildup process<sup>[18, 19]</sup>.

## Biological applications of polyelectrolyte multilayers

Polyelectrolyte multilayers can be used in two ways for biological applications: either by rendering surfaces bio-active or by constituting substrates that favor cell adhesion, allowing them to be used in tissue engineering. They are also ideal candidates to investigate the influence of the mechanical properties on cellular adhesion and cell fate. Our group was active in all these three domains. Only two of them will be outlined below. The strength of our group in this field was to work in strong collaboration with the INSERM UMR 977 from Strasbourg and in collaboration with the UMR 7561 from Nancy. (Publications pertaining to this section are Refs. <sup>[15-17, 21-35]</sup>).

### Polyelectrolyte multilayers as tools for biofunctionalization

Our group has a longstanding activity in biofunctionalization of polyelectrolyte multilayers. Over the last four years, we were involved in studies aimed to confer anti-bacterial properties to films. This was done by incorporating liposomes loaded with AgNO<sub>3</sub> solutions into the films.<sup>34</sup> We also explored biofunctionalization of polyelectrolyte multilayers for cell transfection and for stem cells differentiation. To obtain cell transfection, pre-complexed plasmids with linear poly(ethylene imine) and polyelectrolytes functionalized with specific peptides were incorporated in multilayers film at two distinct buildup steps.<sup>[27]</sup> The incorporation of specific peptides towards specific cells enhances the transfection rates. The differentiation of embryonic stem cells into specific directions was performed by incorporating growth factors into polyelectrolyte multilayer films<sup>[23]</sup>.

### Vascular applications of polyelectrolyte multilayers

The replacement of small diameter vessels (diameters smaller than 5 mm) by non-autologous grafts remains a challenge. The problem is that in order to be non-thrombogenic the graft surface needs to be covered by a perfect endothelial cell (EC) monolayer. Yet, endothelial cells poorly adhere on PTFE grafts used for bypass surgery. We showed *in vitro* that PSS/PAH

multilayers can be used to overcome this difficulty by constituting an ideal substrate for surface endothelialization. The use of cryopreserved arteries provides a promising way for small vessel replacement but cryopreservation alters the thrombogenicity of the vessel after implantation. Cryopreserved arteries with deposited PSS/PAH bilayers in the lumen showed a better resistance to thrombus than untreated ones when implanted in rabbits during three months. Moreover, adhesion and spreading of endothelial cells are enhanced so that the internal structure of the vessel closely resembles that of fresh arteries. Our most challenging project is the vessel reconstruction. Vessels are constituted by three main cellular layers from the lumen: endothelial cells, smooth muscle cells and fibroblasts cells. To construct a non-autologous vessel, our strategy is based on the use of stem cells and the detachment of cell layers. In a first step, human smooth muscle cells were grown on an alginate sacrificial gel layer. This alginate gel layer covered by a PSS/PAH multilayer was obtained by spray process. PSS/PAH film, built on alginate gel, favors cell adhesion and their deposition by spray favors cell orientation. After the formation of a cell monolayer, the alginate gel was peeled off from the substrate. The obtained cellularized membrane was rolled around a mandrel. First multi-cellular rolls were recently obtained (see Figure 5). Those information or the work outlined in this section may be found in Refs. [25,30,33,35].



**Figure 5.** Smooth muscle cell sheet obtained after peeling off from the substrate (scheme and the left image) and rolled around a mandrel (right).

## Chemo-mechanotransductive films

The movement of highly organized organisms greatly depends on how they transform mechanical information (forces) into chemical responses and *vice versa*. The processes that govern the transformation of a force into a chemical response are called mechano-transduction. One kind of transduction processes is initiated by proteins that change conformation under mechanical stress. This conformational change then leads to the exhibition of an active site called a cryptic site. Our goal is to create films that mimic, at a macroscopic level, cryptic site proteins or enzymes, namely to allow to induce a cellular or protein adsorption process or to induce a chemical reaction simply by stretching a substrate. It is related to what is called mechano-chemistry, which has received considerable attention over the last three years. Yet, the few materials that were reported up to now led only to intramolecular changes under stress but never induced chemical reactions in their environment. Our

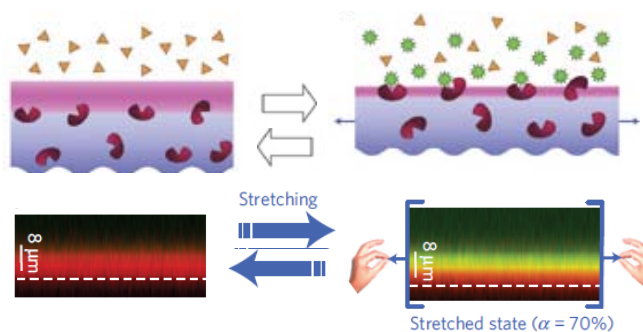
approach is thus totally original and pioneering in this area (Publications pertaining to this sections are Refs. [36-43]).

### Control of protein adsorption and cell adhesion by a mechanical stimulus

The induction of cell adhesion by stretching of the substrate requires first to render the surface non adhesive under and in the absence of stretching. This is a pre-requisite to functionalize the film by incorporation of ligand molecules that are only exhibited under stretching. Up to now we succeeded in creating multilayers that are anti-fouling to proteins and anti-adhesive to cells even under stretching the substrate up to 50% in length. These multilayers are based on polyelectrolytes that bear phosphorylcholine moieties. We are now working on rendering these films cell adhesive only under stretching by incorporation of RGD peptide sequences. We also performed, in collaboration with M-F. Vallat and V. Roucoules from IS2M from Mulhouse, a chemically functionalization silicone sheets, through plasma polymerization, keeping its surface mechanical properties under stretching.<sup>[42, 43].</sup>

### Enzymatically active materials controlled by a mechanical stimulus

One of the major achievements in this field was the development of multilayer architectures that become enzymatically active under stretching, the activation process being reversible, i.e. the activity stops when the film is brought back to its non stretched state (see Figure 6). This constitutes, to our knowledge the first film with chemo-mechanotransduction properties.



**Figure 6.** Schematic representation of the processes taking place during stretching of a chemo-mechano-transductive film containing alkaline phosphate

## Capsules and smart textiles

In order to develop new pharmaceutical vectors and smart textiles, a lot of efforts were put on the encapsulation of hydrophilic or lipophilic active ingredients by various synthesis techniques to obtain hollow or full particles. In collaboration with pharmaceutical industries and with the support of the Region Alsace, our work was dedicated to develop advanced textiles applied in wound care and oral treatments of diabetes and lupus.



### Advanced textiles applied for wound care

In the framework of the “In between” project in collaboration with an industrial company and J-Y Drean (LPMT, Mulhouse), we developed an advanced dressing for chronic scars composed of a new textile functionalized by microparticles. This advanced dressing has to be multi-functional *i*) to regularize the humidity present under the bandage (super absorbent capsules based on poly(acrylic acid)), *ii*) to capture smells (complexing capsules based on cyclodextrines) and *iii*) to liberate active compounds (anti-inflammatory drugs, etc...) under certain pH conditions or in the presence of ions.

### Pharmaceutical vectors for oral treatments of diabetes and lupus

To develop new oral treatments for diabetes and lupus, two projects are funded respectively by the ORAIL project and by a pharmaceutical company. Both projects are based on the development of a pharmaceutical vehicle that contains nanoparticles of bioactive molecules and that is stomach resistant.

In collaboration with the Centre Européen d'étude du Diabète (CEED, Strasbourg), two types of nanoparticles were developed for diabetes treatment *i*) by synthesis of either hollow poly(lactic-co-glycolic) acid (PLGA) particles containing insulin (solvent elimination), or *ii*) by coacervation of chitosan and insulin (polyelectrolyte complexes). These particles were optimized with an average diameter of 150 nm for the passage through the intestinal wall and at an encapsulation rate of about 85% for PLGA vectors. The passage of particles through the intestinal wall was studied *in vitro* using a lineage of specific cells (Caco-2). The developed nanoparticles are adsorbed on cell membranes but are also present within cells, showing their ability to mediate insulin transport. *In vivo* tests were performed by subcutaneous or intra-duodenal administration of nanoparticles on diabetic rats. The injection of PLGA or coacervat nanoparticles induces a decrease in glycemia through both administrations. Encapsulated insulin maintained its activity and did not induce hypoglycemia (glycemia < 0.7 g/l).

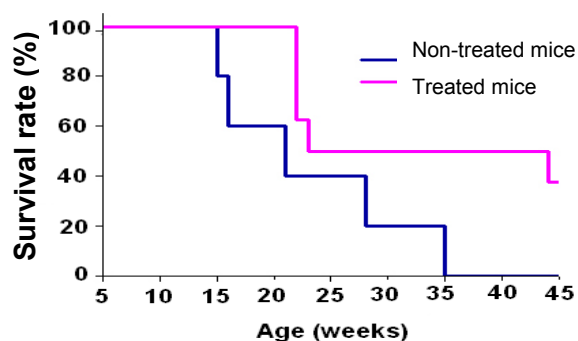


Figure 7. Survival rates of non-treated and treated lupic mice by P140/hyaluronic acid complexes.

In collaboration of Sylvaine Muller (Therapeutic Laboratory of Immunology and Chemistry in Strasbourg), we developed nanoparticles of the P140 peptide by complexation of P140 and hyaluronic acid to treat Lupus. First “*in vivo*” tests on lupic mice showed that the life expectation of lupic mice treated by intra-duodenal injection of P140 particles is increased by a factor of at least two (see Figure 7).<sup>44</sup>

**Collaborations in the axis:** G. Decher, M. Rawiso

**Collaborations with other teams in the ICS:** D. Collin

**National collaborations outside the ICS:** Unité INSERM UMR 977 from Strasbourg headed by J-C Voegel, Dr. B. Frisch (UMR CNRS 7199, Strasbourg), Dr S. Sigrist (CEED, Strasbourg), Prof. S. Muller (IBMC, CNRS UPR 9021, Strasbourg), Prof. M.F. Vallat and Dr V. Roucoules (IS2M, UMR CNRS 7228, Mulhouse), J-Y. Dréan (LPMT, Mulhouse), Prof. P. Menu (UMR CNRS 7561, Nancy), Prof. P. Labbé (UMR CNRS 5250, Grenoble), Prof. R. Auzely (Cermav, UPR 5301, Grenoble).

**International collaborations:** Prof. Schiller (University of Freiburg, Germany) within the IRTG framework, Prof. J. Vorös (ETH Zurich, Switzerland), Prof. A. Fery (University of Bayreuth, Germany), Prof. J. Schlenoff (University of Florida, Tallahassee, USA) who got a chair Gutenberg in our group.

**Industrial partners:** Paul Hartmann (Liepvre, 68), Capsugel (Sélestat, 68), Photon and Polymers (Lutterbach, 68), Société Catalent (Beinheim 67).

**Local networks and affiliations:** Pôle Matériaux et Nanoscience Alsace (PMNA) and International Center for Frontier Research in Chemistry (icFRC - RTRA), pôle de compétitivité Fibre

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- [1] Ball, V.; Bernsmann, F.; Betscha, C.; Maechling, C.; Kauffmann, S.; Sengert, B.; Voegelt, J. C.; Schaaf, P.; Benkirane-Jesselt, N. *Langmuir* **2009**, *25*, 3593.
- [2] El Haitami, A. E.; Martel, D.; Ball, V.; Nguyen, H. C.; Gonthier, E.; Labbe, P.; Voegel, J. C.; Schaaf, P.; Senger, B.; Boulmedais, F. *Langmuir* **2009**, *25*, 2282.
- [3] Francius, G.; Hemmerle, J.; Voegel, J. C.; Schaaf, P.; Senger, B.; Ball, V. *Langmuir* **2007**, *23*, 2602.
- [4] Grieshaber, D.; Voros, J.; Zambelli, T.; Ball, V.; Schaaf, P.; Voegel, J. C.; Boulmedais, F. *Langmuir* **2008**, *24*, 13668.
- [5] Jourdainne, L.; Lecuyer, S.; Arntz, Y.; Picart, C.; Schaaf, P.; Senger, B.; Voegel, J. C.; Lavalley, P.; Charitat, T. *Langmuir* **2008**, *24*, 7842.
- [6] Mjahed, H.; Voegel, J. C.; Chassepot, A.; Senger, B.; Schaaf, P.; Boulmedais, F.; Ball, V. *Journal of Colloid and Interface Science* **2010**, *346*, 163.
- [7] Mjahed, H.; Voegel, J. C.; Senger, B.; Chassepot, A.; Rameau, A.; Ball, V.; Schaaf, P.; Boulmedais, F. *Soft Matter* **2009**, *5*, 2269.
- [8] Porcel, C.; Lavalley, P.; Decher, G.; Senger, B.; Voegel, J. C.; Schaaf, P. *Langmuir* **2007**, *23*, 1898.
- [9] Zahn, R.; Boulmedais, F.; Voros, J.; Schaaf, P.; Zambelli, T. *Journal of Physical Chemistry B* **2010**, *114*, 3759.
- [10] Dubacheva, G. V.; Dumy, P.; Auzely, R.; Schaaf, P.; Boulmedais, F.; Jierry, L.; Coche-Guerente, L.; Labbe, P. *Soft Matter* **2010**, *6*, 3747.

- [11] El Haitami, A. E.; Thomann, J. S.; Jierry, L.; Parat, A.; Voegel, J. C.; Schaaf, P.; Senger, B.; Boulmedais, F.; Frisch, B. *Langmuir* **2010**, *26*, 12351.
- [12] Jierry, L.; Ben Ameer, N.; Thomann, J. S.; Frisch, B.; Gonthier, E.; Voegel, J. C.; Senger, B.; Decher, G.; Felix, O.; Schaaf, P.; Mesini, P.; Boulmedais, F. *Macromolecules* **2010**, *43*, 3994.
- [13] Popa, G.; Boulmedais, F.; Zhao, P.; Hemmerle, J.; Vidal, L.; Mathieu, E.; Felix, O.; Schaaf, P.; Decher, G.; Voegel, J. C. *ACS Nano* **2010**, *4*, 4792.
- [14] Rydzek, G.; Thomann, J. S.; Ben Ameer, N.; Jierry, L.; Mesini, P.; Ponche, A.; Contal, C.; El Haitami, A. E.; Voegel, J. C.; Senger, B.; Schaaf, P.; Frisch, B.; Boulmedais, F. *Langmuir* **2010**, *26*, 2816.
- [15] Volodkin, D.; Arntz, Y.; Schaaf, P.; Moehwald, H.; Voegel, J. C.; Ball, V. *Soft Matter* **2008**, *4*, 122.
- [16] Volodkin, D.; Ball, V.; Schaaf, P.; Voegel, J. C.; Mohwald, H. *Biochimica Et Biophysica Acta-Biomembranes* **2007**, *1768*, 280.
- [17] Volodkin, D. V.; Schaaf, P.; Mohwald, H.; Voegel, J. C.; Ball, V. *Soft Matter* **2009**, *5*, 1394.
- [18] Laugel, N.; Hemmerle, J.; Porcel, C.; Voegel, J. C.; Schaaf, P.; Ball, V. *Langmuir* **2007**, *23*, 3706.
- [19] Laugel, N.; Hemmerle, J.; Ladhari, N.; Arntz, Y.; Gonthier, E.; Haikel, Y.; Voegel, J. C.; Schaaf, P.; Ball, V. *Journal of Colloid and Interface Science* **2008**, *324*, 127.
- [20] Lefort, M.; Popa, G.; Seyrek, E.; Szamocki, R.; Felix, O.; Hemmerle, J.; Vidal, L.; Voegel, J. C.; Boulmedais, F.; Decher, G.; Schaaf, P. *Angew. Chem.-Int. Edit.* **2010**, *49*, 10110.
- [21] Arntz, Y.; Ball, V.; Benkirane-Jessel, N.; Boulmedais, F.; Debry, C.; Dimitrova, M.; Elkaim, R.; Haikel, Y.; Hemmerle, J.; Lavalley, P.; Meyer, F.; Muller, S.; Ogier, J.; Schaaf, P.; Senger, B.; Stanic, V.; Tenenbaum, H.; Vautier, D.; Vodouhe, C.; Volodkin, D.; Voegel, J. C.; Werner, S. *Actualite Chimique* **2007**, *20*.
- [22] Berthelemy, N.; Kerdjoudj, H.; Gaucher, C.; Schaaf, P.; Stoltz, J. F.; Lacolley, P.; Voegel, J. C.; Menu, P. *Advanced Materials* **2008**, *20*, 2674.
- [23] Dierich, A.; Le Guen, E.; Messaddeq, N.; Stoltz, J. F.; Netter, P.; Schaaf, P.; Voegel, J. C.; Benkirane-Jessel, N. *Advanced Materials* **2007**, *19*, 693.
- [24] Grossin, L.; Cortial, D.; Saulnier, B.; Felix, O.; Chassepot, A.; Decher, G.; Netter, P.; Schaaf, P.; Gillet, P.; Mainard, D.; Voegel, J. C.; Benkirane-Jessel, N. *Advanced Materials* **2009**, *21*, 650.
- [25] Kerdjoudj, H.; Boura, C.; Moby, V.; Montagne, K.; Schaaf, P.; Voegel, J. C.; Stoltz, J. F.; Menu, P. *Advanced Functional Materials* **2007**, *17*, 2667.
- [26] Kocgozlu, L.; Lavalley, P.; Koenig, G.; Senger, B.; Haikel, Y.; Schaaf, P.; Voegel, J. C.; Tenenbaum, H.; Vautier, D. *Journal of Cell Science* **2010**, *123*, 29.
- [27] Meyer, F.; Dimitrova, M.; Jedrzejenska, J.; Arntz, Y.; Schaaf, P.; Frisch, B.; Voegel, J. C.; Ogier, J. *Biomaterials* **2008**, *29*, 618.
- [28] Nadiri, A.; Kuchler-Bopp, S.; Mjahed, H.; Hu, B.; Haikel, Y.; Schaaf, P.; Voegel, J. C.; Benkirane-Jessel, N. *Small* **2007**, *3*, 1577.
- [29] Richard, D.; Nguyen, I.; Affolter, C.; Meyer, F.; Schaaf, P.; Voegel, J. C.; Bagnard, D.; Ogier, J. *Small* **2010**, *6*, 2405.
- [30] Rinckenbach, S.; Hemmerle, J.; Dieval, F.; Arntz, Y.; Kretz, J. G.; Durand, B.; Chakfe, N.; Schaaf, P.; Voegel, J. C.; Vautier, D. *Journal of Biomedical Materials Research Part A* **2008**, *84A*, 576.
- [31] Schneider, A.; Vodouhe, C.; Richert, L.; Francius, G.; Le Guen, E.; Schaaf, P.; Voegel, J. C.; Frisch, B.; Picart, C. *Biomacromolecules* **2007**, *8*, 139.
- [32] Schneider, A.; Picart, C.; Senger, B.; Schaaf, P.; Voegel, J. C.; Frisch, B. *Langmuir* **2007**, *23*, 2655.
- [33] Moby, V.; Boura, C.; Kerdjoudj, H.; Voegel, J. C.; Marchal, L.; Dumas, D.; Schaaf, P.; Stoltz, J. F.; Menu, P. *Biomacromolecules* **2007**, *8*, 2156.
- [34] Malcher, M.; Volodkin, D.; Heurtault, B.; Andre, P.; Schaaf, P.; Mohwald, H.; Voegel, J. C.; Sokolowski, A.; Ball, V.; Boulmedais, F.; Frisch, B. *Langmuir* **2008**, *24*, 10209.
- [35] Kerdjoudj, H.; Berthelemy, N.; Rinckenbach, S.; Kearney-Schwartz, A.; Montagne, K.; Schaaf, P.; Lacolley, P.; Stoltz, J. F.; Voegel, J. C.; Menu, P. *Journal of the American College of Cardiology* **2008**, *52*, 1589.
- [36] Reisch, A.; Hemmerle, J.; Chassepot, A.; Lefort, M.; Benkirane-Jessel, N.; Candolfi, E.; Mesini, P.; Letscher-Bru, V.; Voegel, J. C.; Schaaf, P. *Soft Matter* **2010**, *6*, 1503.
- [37] Reisch, A.; Hemmerle, J.; Voegel, J. C.; Gonthier, E.; Decher, G.; Benkirane-Jessel, N.; Chassepot, A.; Mertz, D.; Lavalley, P.; Mesini, P.; Schaaf, P. *Journal of Materials Chemistry* **2008**, *18*, 4242.
- [38] Reisch, A.; Voegel, J. C.; Decher, G.; Schaaf, P.; Mesini, P. J. *Macromolecular Rapid Communications* **2007**, *28*, 2217.
- [39] Reisch, A.; Voegel, J. C.; Gonthier, E.; Decher, G.; Senger, B.; Schaaf, P.; Mesini, P. J. *Langmuir* **2009**, *25*, 3610.
- [40] Mertz, D.; Hemmerle, J.; Boulmedais, F.; Voegel, J. C.; Lavalley, P.; Schaaf, P. *Soft Matter* **2007**, *3*, 1413.
- [41] Mertz, D.; Vogt, C.; Hemmerle, J.; Mutterer, J.; Ball, V.; Voegel, J. C.; Schaaf, P.; Lavalley, P. *Nature Materials* **2009**, *8*, 731.
- [42] Geissler, A.; Vallat, M. F.; Fioux, P.; Thomann, J. S.; Frisch, B.; Voegel, J. C.; Hemmerle, J.; Schaaf, P.; Roucoules, V. *Plasma Processes and Polymers* **2010**, *7*, 64.
- [43] Geissler, A.; Vallat, M. F.; Vidal, L.; Voegel, J. C.; Hemmerle, J.; Schaaf, P.; Roucoules, V. *Langmuir* **2008**, *24*, 4874.
- [44] Danicher, L.; Frère, Y.; Muller, S.; Wawrezinieck, A. *Patent number : FR2931360-A1; WO2009150371-A2, EP22293785-A2.*

## Self-Evaluation

### Human resources

**Permanent members:** Prof. P. Schaaf (group leader), Dr. Y. Frère (CR), Dr. F. Boulmedais (CR), Dr. L. Jierry (MCF), E. Gonthier (Technician)

**Actual non permanent members:** 3 Post-doctoral fellows, 3 PhD students

**Number of post-docs over the period:** 7

**Number of PhD defenses over the period:** 9

**Number of master students over the period:** 9

The group was active in the fields of polyelectrolyte multilayers and capsules. As far as the **capsule activity** is concerned it is strongly oriented towards industrial applications-

### Statement of financial supports

#### 4 ANR blanches

**ANR Cartilspray (2006-2009):** The goal of this ANR was to provide the tools, based on spray assisted polyelectrolyte multilayers, to reconstruct cartilage. We succeeded in creating structured architectures that contained living cells entirely by spraying.

**ANR clickmultilayer (2007-2010):** The goal of this ANR was to investigate the step-by-step buildup of "covalent multilayers" through click-chemistry. This study derived from its original goals with the development of a new concept, namely that of morphogen driven film buildup and the "one-pot" film buildup. (4 papers, 1 in *Angewandte Chemie*).

ANR Edetachpem (2008-2011): The goal of this project is to built ferrocen-cyclodextrin based multilayers that will be used as sacrificial supports for culturing cellular monolayers that can be detached by application of an adequate potential.

ANR Biostretch(2010-2013) : The goal is to develop chemo-mechanotransductive films.

**1 FRC project** (Mechanotransduction) (2009): The goal was to start to work on gels that respond enzymatically to a mechanical stimulus

**1 CNRS prise de risque** : Interface chimie biologie

**3 equipment grants**: 1 CPER and 2 UdS

**2 fundings** from the Région Alsace (In between and ORAIL project DGEs), OSEO, Minefi

#### Statement on scientific collaborations

##### National collaborations outside the ICS:

All our subjects were developed in strong collaboration with the group of J.C. Voegel, Unité INSERM UMR 977 from Strasbourg. This group is specialized in biomaterials.

We have also developed bioactive coatings as well as the click-multilayer project in collaboration with Dr. B. Frisch (UMR CNRS 7199, Strasbourg) who was in charge in polyelectrolyte modifications.

The project of chemo-mechanotransductive films is done in collaboration with Dr. M.F. Vallat and Dr V. Roucoules (IS2M ,UMR CNRS 7228, Mulhouse) who are specialized in surface modifications through polymer plasma.

We work in collaboration with Prof. P. Menu (UMR CNRS 7561, Nancy) as far the vessel reconstruction is concerned.

The ANR Edetachpem is performed in collaboration with the groups of Prof. P. Labbé (UMR CNRS 5250, Grenoble) and Prof. R. Auzely (Cermav, UPR 5301, Grenoble).

The projects concerning the therapeutic capsules are performed in collaboration with Dr S. Sigrist (CEED, Strasbourg) and Prof. S. Muller (IBMC, CNRS UPR 9021, Strasbourg).

**International collaborations:** Prof. Schiller (University of Freiburg, Germany) within the IRTG framework. This collaboration concerns the development of films that become specifically adhesive to cell under stretching. Professor Schiller engineers fibronectin modules that can be cross-linked on the surface.

We investigate the response of polyelectrolyte multilayers towards electrochemical stimuli with the group of Prof. J. Vorös (ETH Zurich, Switzerland)

We investigate, with Prof. A. Fery (University of Bayreuth, Germany), the mechanical properties of multilayers obtained from blended polyelectrolyte solutions, a subject introduced a few years ago by our group.

Prof. J. Schlenoff (University of Florida, Tallahassee, USA) got recently a chair Gutenberg in our group. We will develop polyanion/polycation materials obtained by ultracentrifugation. These materials

present interesting mechanical properties for biological applications.

**Industrial partners:** Paul Hartmann (Liepvre, 68), Capsugel (Sélestat, 68), Photon and Polymers (Lutterbach, 68), Société Catalent (Beinheim 67).

#### Statement on scientific productions

Publication record (until December 2010): **54 articles**

(1 nature Materials, 1 Angewandte Chemie, 3 Adv Mater, 1 Nano Lett., 1 ACS Nano, 1 Small, 2 Macromolecules, 17 Langmuir, 9 Soft Matter, ....)

Number of patents: **4**

Number of invited talks: **10**

Total number of citations over this period of all the articles from the group: **3717**

Number of citations of the articles published over the period 2007-2010: **659**

Average number of citation per publication published over the period 2007-2010: **12.20**

*h* index of the publications published between 2007 and 2010 : **14**

*h* index of all the publications of the members of the group (no time limit) : **52**

#### Overall statements

**The Polyelectrolyte multilayer** activity is a highly competitive and dynamic field in physical chemistry. Over the period 2007-2010, there were:

1057\* papers published in the field of polyelectrolyte multilayers. These papers were cited 8986\* times with an average citation per paper at 8.5\*.

\*These number were obtained from ISI with the topic "polyelectrolyte multilayers"

Main competitors and their actual human resources in the field are:

##### **Massachusetts Institute of Technology (Boston, USA)**

- group of Prof. P. Hammond: 1 Prof, 17 post doc, 23 PhD students.

- group of Prof. M. Rubner: 2 Prof, 5 post doc, 8 PhD students.

##### **Max Planck Institute of Colloids and Interfaces (Golm, Germany)**

- group of H. Möhwald: 1 Prof., 2 group leaders, 22 PhD students & Post-Docs

##### **Melbourne University (Melbourne, Australia)**

- group of F. Caruso: 1 Prof. 16 PhD, 8 Post-Docs

##### **University of Michigan (Ann Arbor, USA)**

- group of N. Kotov: 1 Prof. 7 PhD, 5 Post-doc

Taking into account these parameters, our group has a great and visible activity in the Polyelectrolyte Multilayers field, despite our small size.



# Polymers and Mixed Systems (PSM)

Head of the Group *François Schosseler*

**Permanent staff :** J.-M. Catala (DR CNRS), M. Duval (CR CNRS), G. Fleith (AI CNRS), J.-P. Lamps (AI CNRS), P. Petit (DR CNRS), M. Rawiso (DR CNRS), F. Schosseler (DR CNRS), J. Selb (CR CNRS)

**Non-permanent researchers : 5 PhD students :** L. Bouzina (2009-2011), I. Echavarri (2008-2011), P. Lorchat (2008- ), D. Salem (2008- ), G. Smolyakov (2009- ), **14 Master and undergraduate students.**

**Keywords:** Controlled polymerization · single-walled carbon nanotube growth and properties · binary and ternary polyelectrolyte systems · conjugated systems · structure and dynamics of soft matter · characterization of macromolecular and colloidal systems

The scientific activity of the *Polymers and Mixed Systems* group is associated with a broad spectrum of competences, from synthesis to the study of physicochemical properties of mixed polymer-based model systems. Its expertise is made available to all researchers of the laboratory through an involvement in: *i*) the counsel to users of scattering and rheology techniques, and of all the techniques of the Polymer Characterization Facility, *ii*) the maintenance and the upgrade of the corresponding instruments, and *iii*) the formation of the ITA staff that is running this instrumentation. Three members of the group have additional collective responsibilities as: supervisor of the Polymer Characterization Facility (J. Selb), elected member in the Comité National de la Recherche Scientifique (CoNRS) (M. Rawiso) or member of the ICS directorial board (F. Schosseler). P. Petit has been an elected member of the Scientific Board of the University Louis Pasteur and its permanent commission, and appointed official representative by the vice-presidency "Recherche et formation doctorale" (2006-2008). M. Rawiso has restructured the Master 2 "Instrumentation et Méthodes d'Analyses Physico-Chimiques" of the physics department of Uds (2010). He also organized with R. Jalabert a common master in between the physics departments of the Université de de Strasbourg (Uds) and the Taras Shevchenko University of Kiev respectively (2010-2011).

Synthesis activities are focused on mechanistic studies of controlled polymerization and on the growth of single-walled carbon nanotubes (SWNT).

The understanding of polymerization mechanisms allows us to control the reactivity and the stability of active centers and to synthesize polymers with well-defined molecular weight, composition and size polydispersity, which facilitates in the next step the study and understanding of the physicochemical properties of the mixed systems built with them.

A similar approach is used for SWNT based nanocomposites. Their full potential can only be obtained if the nanotubes have homogeneous properties. The main difficulty in this field stems from the lack of control in the synthesis of SWNT, which yields samples with a broad distribution of diameters and helicities, and accordingly with a wide variety in their physical and chemical properties. Therefore it is necessary to develop new approaches

to a reproducible synthesis of SWNT with well-defined properties.

The major part of our research concerns polyelectrolyte-based binary or ternary systems. Coulombic electrostatic repulsions allow stretched conformations and solubilization in water of polymers with a hydrophobic backbone. The water solubility can be used to modify the rheological properties of aqueous solutions. The presence of charged groups opens a large variety of applications by allowing complexation with oppositely charged species (drug delivery, multilayer assemblies, chemo- or biosensors, ...).

The structure of binary polyelectrolyte solutions is not fully understood and many open problems remain concerning the average conformation of the chains, their dispersion state and the distribution of counterions in the solution. Many fundamental aspects deserve further investigations. Generally speaking, we are interested in the effects associated with the nature of the backbone (saturated or conjugated), the architecture of the macroions (linear chains, rings, stars, combs), and the valence, hydrophobicity as well as nature of the counterions or added coions.

On ternary systems, we tackle new problems: *i*) the structure of polyelectrolytes (PEs) in an ionic liquid has never been studied and our first results show that the nature of the ionic liquid components has a strong effect on the local and average conformation of the chains, *ii*) the use of conjugated PEs opens new possibilities in the field of PEs/surfactants complexes by allowing the study of very dilute solutions with optical spectroscopy techniques, *iii*) the study of the phase diagram of insulin-poly(diallyl-dimethyl ammonium chloride) (PDADMAC) complexes allows to explore fundamental aspects of the interaction between insulin and oppositely charged PEs, a domain where application-driven experiments aimed at drug delivery have often bypassed the understanding of the complexation mechanisms.

A limited part of our activity deals with neutral systems. A nearly completed study focused on complex chain scission/aggregation effects undergone by PEO solutions when they are submitted to a turbulent flow or to sonication. Another work dealt with depletion interactions in polymer/colloid

mixtures in the little studied regime where the colloids are much smaller than the chains, the so-called protein limit.

The scientific support for the Characterization Service (4 IR, 1 IE, 3 AI, 2 T) and the creation of the Polymer Characterization Facility have demanded a strong involvement by our group to prepare the massive turn-over linked to the retirement of six permanent members. We needed to define which competences should be preserved or acquired, taking into account the middle-term evolution of the scientific project of the laboratory. Also replacement of obsolete equipment and acquisition of new techniques has been done, with funding obtained essentially through grants. The same approach has increased the number of X-ray diffractometers available to internal and external users.

## Synthesis

### Controlled radical polymerization of vinylic monomers

In this area, we have studied the process involving a stable nitroxide radical that leads to a thermoreversible equilibrium between dormant chains (alkoxyamines) and active chains. The aim was twofold, first to make the reaction more useful by generating *in situ* the nitroxide radical of the corresponding alkoxyamine, second to study the controlled radical polymerization of monomers bearing organometallic groups and leading to polymer and copolymer which cannot be realized by other methods.

For the first part, we have carried out kinetics and RPE experiments to clarify the different reactions involved in the pre-reaction. The latter consists in allowing the reaction between a radical initiator and a nitroxide in the presence or the absence of the appropriate monomer. The experimental conditions have thus been optimized as a function of the initiator, of the steric hindrance and the chemical nature of the nitroxide substituents, and of the monomer. The various equilibrium constants have been measured, which allows one to select the temperature appropriate to synthesize polymers and copolymers with well-defined molecular weights.

In the second part, we have synthesized styrenic monomers bearing organometallic groups (Si, Ge, Sn) and studied their controlled polymerization or copolymerization. The reactivity constants have been determined, which allows one to adjust the degree of functionalization and obtain new materials that are useful for inertial confinement fusion experiments with high power megajoule lasers.

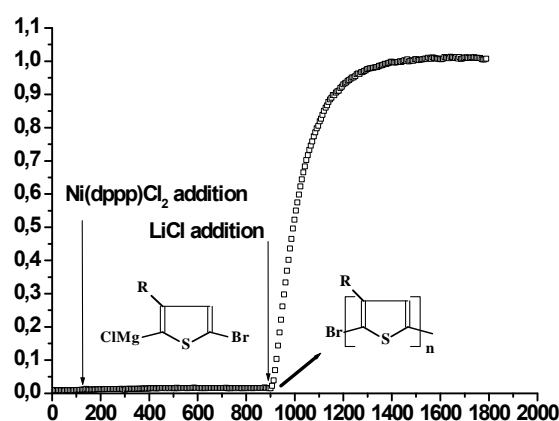
### Controlled polymerization of substituted thiophen monomers

Studies in this domain have been devoted to regioregular conjugated polymers, either

functionalized or not. Usual routes for the synthesis involve an activated monomer and an organometallic catalyst. Most of the published work concerns alkyl-type polymers with a low molecular weight. No detailed kinetic studies have been made to characterize the various reactions as a function of the chemical nature of the substituents, of their steric hindrance, of the catalyst, or of additives that have an effect on the stability of the active centers. However the living character of the active center is crucial to control the characteristics of the polymer formed (molecular weight, polydispersity) and to obtain complex objects with optimized properties. To evaluate the kinetic constants, only spectroscopic techniques permit to follow precisely, in real time, the monomer consumption, even for fast kinetics. For this purpose, an *in situ* UV-visible probe with a very short optical path (< 0.02 cm) has been realized to measure the strong absorption of the polymers in the reaction medium.

This new and powerful technique has shown unexpected phenomena that have been quantified, with the more prominent being:

- the reactivity of the active center depends on the conjugation length and needs the determination of two propagation rate constants to characterize the process;
- particular reactivity ratios leading to block copolymer from a mixture of monomers of the same chemical nature but activated on carbon 5 or 2;
- the addition of a lithium salt in the reaction medium has strong effects on both the kinetic constants of the polymerization (factor 20 on  $k_p$ ) and the reactivity of monomers usually considered as unable to polymerize. As an example monomers activated in position 2 can polymerize only in the presence of added LiCl (Figure 1).



**Figure 1.** Effect of LiCl on the polymerization of the 2-iodo-3-hexyl-5-bromothiophene; evolution of the absorbance versus time ( $\lambda = 448\text{nm}$ ).

This remarkable result has been used to study the polymerization of bulky monomers that usually cannot form chains. The influence of the substituent bulkiness has been quantified by the values of the propagation rates and by the conjugation length of these polymers in solution. Moreover the increase of

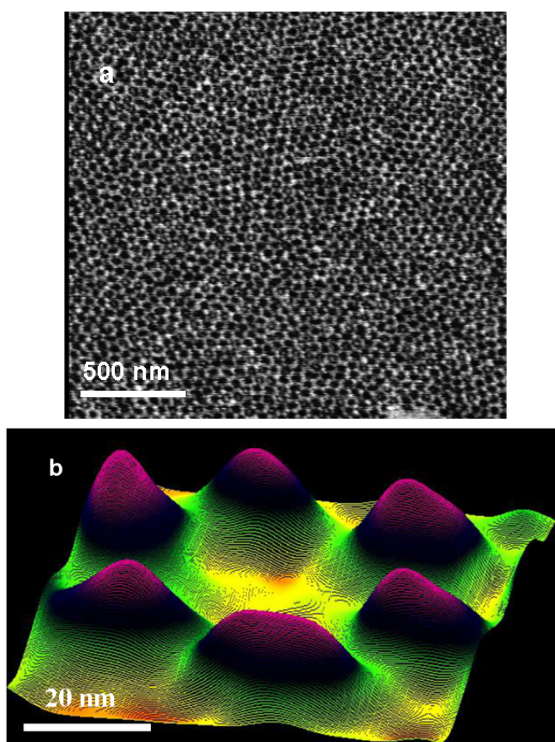
the reactivity implies shorter reaction times, which helps to preserve the stabilities of the active center and of the activated monomers. This feature has been used to obtain high molecular weight chains that are better suited for the study of physicochemical properties, e.g., the conjugation length in solution.

**Growth and functionalization of single walled carbon nanotubes (SWNT)**

To obtain SWNTs with a narrow diameter polydispersity, it is necessary to control the size of the metallic nanoparticles that catalyze their growth but there are other relevant parameters: the interaction of the nanoparticles with the substrate and their crystallinity play also a role that we have studied.

**Surfactant-assisted synthesis of metallic nanoparticles**

In a first approach we have obtained Au or Ag nanoparticles on hexagonal lattices by using hemi-micelles of semi-fluorinated alkanes as a mask-template during evaporation of the metals. The regularity of the lattice of nanoparticles is proved by the analysis of AFM images (Figure 2). We didn't succeed in growing SWNTs using these systems, but, in the case of Au, we have shown their ability to catalyze the oxidation of carbon monoxide into carbon dioxide at low temperature.

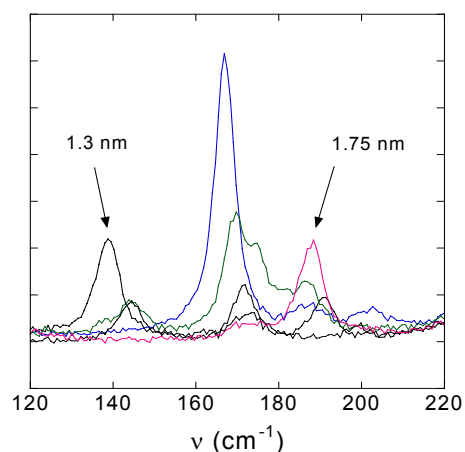


**Figure 2.** a) Hexagonal lattice of supported Au nanoparticles; b) detail.

A second approach has allowed to obtain Fe<sub>2</sub>O<sub>3</sub> nanoparticles with a well-defined height 1.0 ± 0.2 nm by dipping a hydroxylated silicium substrate in an acidic solution containing the metallic salt and the surfactant SDS, the latter being well below its critical micellar concentration (by a factor 10). We are still

working to understand the exact mechanism of this process before publishing these results.

Using these substrates and playing with different parameters (temperature, gas flows, gas composition, reaction duration), we are now able to synthesise dense samples of individual SWNTs with diameters in the range 1.75 nm – 1.3 nm, which is the smallest reported using the CVD technique (Figure 3). This is a major step for homogeneous functionalisation and dispersion of SWNTs in polymer matrices.



**Figure 3.** Raman spectra of the Radial Breathing Modes (RBM) obtained on different areas of a sample. RBM frequencies are inversely proportional to the diameters of SWNTs.

**Role of the catalyst**

► - Interaction with the substrate

A reduction step of the catalyst is always necessary since it is active only in the metallic state. In the related literature, the starting state is very often a thin Ni film. Upon reduction there is a dewetting of the film and nanoparticles form whose size depends on both film thickness and temperature. However there are no published results on the growth of SWNTs from the dewetting of films with subnanometric thickness.

Therefore we have studied the dewetting of thin films as a function of thickness and reduction temperature, but also as a function of the partial pressure of hydrogen, a parameter that has not been investigated yet. By comparing experiments made with an inert gas, we have shown that the dewetting is not simply a thermally induced process, but stems from the formation of Ni hydride, which modifies the free surface energy balance to favor the dewetting. This formation of hydride explains why the scientific community met difficulties to synthesize SWNTs from very thin Ni films.

► - Crystallinity

The influence of catalyst's crystallinity on the growth of multiwalled carbon nanotubes (MWNTs) is only rarely considered in the literature although the nature and the preparation of the catalyst are crucial parameters conditioning its activity. This question

has initiated the PhD by M. Kuras who has shown that the MWNTs allow the identification and the definition of the parameters for the synthesis of Ni oxides with a perovskite structure (C. Petit, supervisor, LSMPC). This work has shown in particular the role played by the crystallinity and the texture of the oxides in the synthesis of MWNTs.

## Polyelectrolytes

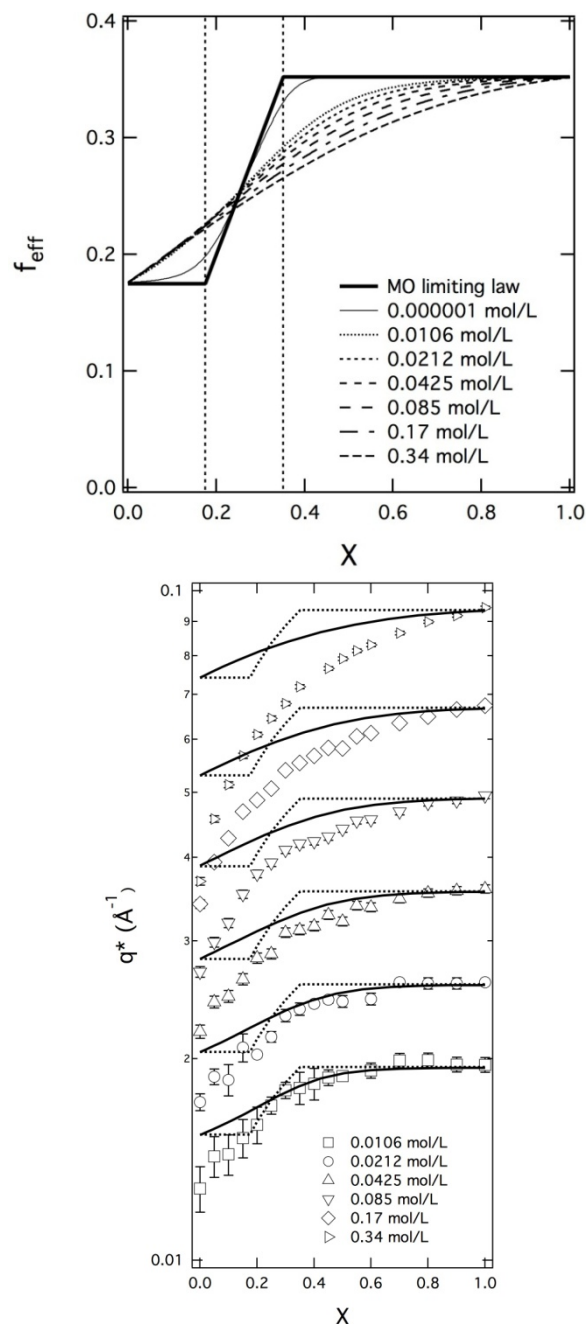
### Polyelectrolytes in the presence of monovalent and divalent counterions

We investigated the role of the counterion valence on the structure of Polyelectrolytes (PE) solutions. Small-angle neutron or X-ray scattering are particularly well suited to probe the relevant length scales of that structure.

In the case of monovalent counterions, the scattered intensity as a function of scattering vector  $q$  exhibit a maximum whose location  $q^*$  mainly depends on the concentration and charge density of the chains. In the case of monovalent counterions, we have shown that scaling laws obtained in the isotropic model of PE solutions (de Gennes/Pfeuty/Dobrynin/Rubinstein) describe the experiments if the chemical charge density of the chains is replaced by the effective charge density that takes into account the condensation of counterions.

To shed new light on this problem we have studied the structure of salt free PE solutions containing monovalent and divalent counterions. We have considered mixtures of sulfonated polystyrene with monovalent ( $\text{Na}^+$ ) and divalent ( $\text{Ca}^{2+}$ ) counterions and measured  $q^*$  as a function of the monomer concentration  $c_p$  and the monovalent / divalent ratio (represented by  $X = n_{\text{NaPSS}} / (n_{\text{NaPSS}} + n_{\text{CaPSS}})$ , where  $n$  is a mole number). The aim was to understand the variation observed in the  $q^*$  value when the average valence of the counterions is gradually increased. We have used synchrotron radiation to improve the quality of the data and varied the monovalent / divalent ratio almost continuously. This has given new results in the ranges of low and large divalent contents. SAXS results were again analyzed through the isotropic model and its scaling laws while replacing the chemical charge fraction of NaPSS and CaPSS, which is given by synthesis, by the effective charge fraction  $f_{\text{eff}}$  which varies with  $X$  in the mixture. We calculated  $f_{\text{eff}}$  by solving the Poisson-Boltzmann (PB) equation in the framework of the cell model for various  $X$  values and different concentrations (Figure 4 top). Severe deviations are found in the effective charge values of mixtures at finite concentrations compared to the classical Manning-Oosawa (MO) prediction (infinite dilution limiting law). We demonstrate that the evolution of  $q^*$  is consistent with the isotropic model and the scaling approach in the low polymer concentration range provided that the divalent content is not too high. In particular, a power law relation  $q^* \propto f_{\text{eff}}^{-0.3}$  can be found which

looks very close to the one observed for weakly charged PEs ( $q^* \propto f_{\text{eff}}^{2/7}$  in good solvent or  $q^* \propto f_{\text{eff}}^{1/3}$  in theta solvent).



**Figure 4.** Top) Effective charge fraction  $f_{\text{eff}}$  as a function of  $X$  for different concentrations  $c_p$ . The values result from the resolution of the PB equation within the cylindrical cell model. The limiting law corresponding to the MO approach is indicated. The two vertical lines located at  $X = b/2l_b = 0.18$  and  $X = b/2l_b = 0.36$  separate three different regimes. In between these two lines,  $f_{\text{eff}}$  is equal to  $X$ ; Bottom) Experimental (symbols) and theoretical (lines) evolutions of  $q^*$  as a function of  $X$  for different concentrations  $c_p$ . Solid lines: PB equation; dashed lines: MO (see text).

Mixtures finally provide a way to adjust the effective charge fraction without changing the chemical nature of the macroions. However this procedure improves the data prediction only in a limited range; it is still not able to fully explain the high polymer concentration range, as well as the high divalent content mixtures (Figure 4 bottom). This is due to the

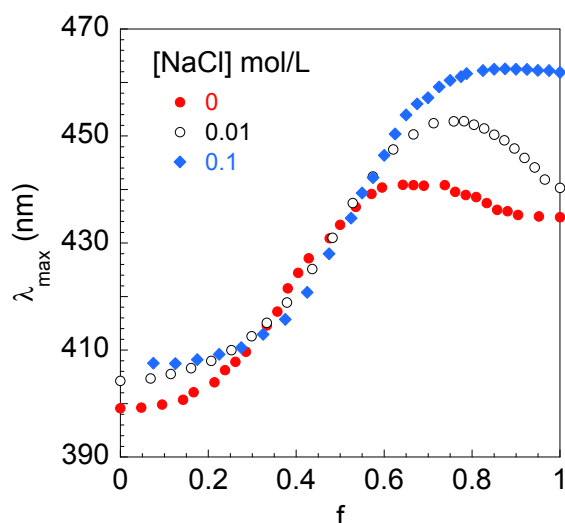


fact that the PB theory is not able to take into account local interactions between monomers and divalent counterions, which go beyond the mean field approach.

### Conformational transitions of conjugated weak polyacids

Polymers with a conjugated backbone exhibit a delocalization of  $\pi$  electrons along the backbone and remarkable optical properties that are related to the average conformation of the chains. The synthesis of conjugated polymers with charged substituents opens interesting possibilities due to their solubility in water.

In the PhD work of P. Vallat (2006) we have defined the conditions for a reproducible synthesis of the poly(3-thiophen acetic acid) (P3TAA) and studied its aqueous solutions as a function of the neutralization degree,  $f$ , of the polyacid and of the concentration,  $C_s$ , of an added salt. The polyacid ( $f = 0$ ) is insoluble in water but the polysalt ( $f = 1$ ) is water-soluble due to the repulsive coulombic interactions. Therefore the UV-visible absorption of the polymer solutions depends on the pH.



**Figure 5.** Evolution of the position  $\lambda_{max}$  of the maximum in the UV-visible absorption as a function of neutralization degree, for different added salt concentration ( $C_{P3TAA} = 1.6$  mM).

Two regimes, with very different behaviours, have been observed (Figure 5):

- When  $f > 0.7$ , the polymer is globally hydrophilic and the evolution of the absorption spectra as a function of  $f$  and  $C_s$  is dominated by coulombic effects on the delocalization of  $\pi$  electrons, which increases as the coulombic interactions decrease: the absorption spectra are red-shifted.

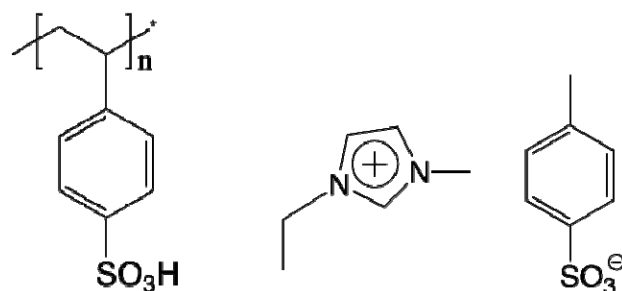
- When  $f < 0.7$ , the hydrophobicity of the backbone plays the dominant role and the evolution of the absorption spectra as a function of  $f$  and  $C_s$  is dominated by conformational effects;  $\pi$  electrons are increasingly localized as the coulombic interactions decrease: the absorption spectra are blue-shifted. The

transition from expanded chain to collapsed coil ( $0.7 > f > 0.3$ ) is followed by a transition from collapsed coil to dense globule ( $0.3 > f > 0.15$ ). The first one corresponds to the first order transition expected for hydrophobic PEs with an annealed distribution of charges. The second one is associated with an increase of H-bonds inside the collapsed coils at low pH and is similar to a coil-helix transition (Ising model).

### Polyelectrolytes in ionic liquids

A ternary system composed of a PE and an ionic liquid (IL) was studied by small and wide angle X-ray scattering (SAXS and WAXS). Poly(4-styrenesulfonic acid) (PSS) was used as PE; 3-methyl-1-ethylimidazolium tosylate (EMIM-Tos), as IL. Related chemical structures are shown in Figure 6. Average conformation of PSS and local structure of IL were investigated by SAXS and WAXS respectively. For comparison, aqueous solutions of PSS with and without low-molecular electrolyte (LME) were also studied by SAXS.

The main result obtained is that PSS in IL behaves like a neutral polymer in a good solvent. Specifically, SAXS curves don't display any electrostatic peak. Moreover, extrapolation of scattering data at zero concentration allows measuring a radius of gyration that is close to the one obtained from aqueous solutions of PSS in the presence of added salt. The local structure of EMIM-Tos is identical in the liquid state with and without PSS. The crystallization temperature of EMIM-Tos is however increased in the presence of PSS.



**Figure 6.** Chemical structures of PSS and EMIM-Tos.

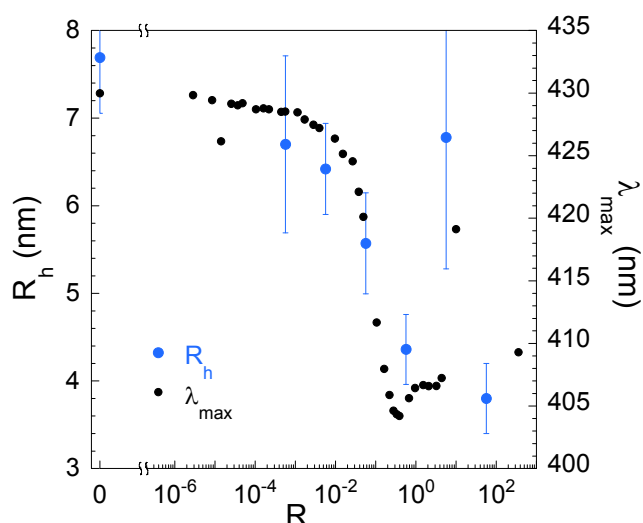
### Optical properties of complexes of conjugated polyelectrolytes with oppositely charged surfactants

The optical properties (UV-visible absorption and fluorescence) of conjugated PEs are very sensitive to the presence of oppositely charged species (surfactants, multivalent ions, proteins, ADN fragments) that affect their average conformation upon complexation.

In the PhD work of I. Echavarrri (2011), we have studied mixtures of P3TAA with oppositely charged surfactants in very dilute buffer solution (pH = 9.3). We have varied the length of the alkyl chain in the alkyl trimethyl ammonium bromide surfactants and the stoichiometric ratio  $R = [\text{surf}]/[\text{monomer unit}]$

( $10^{-5} < R < 100$ ). In contrast with most other conjugated PEs that are aggregated in aqueous solutions, P3TAA chains are molecularly dispersed in solution and we probe essentially optical properties of individual chains during their complexation, a quite unique situation in the literature. We have measured the absorption and the emission of the complexes as well as their hydrodynamic radius as a function of  $R$ .

For the first time we succeeded in correlating a measurement of the collapse of the chains with the evolution of their absorption spectrum (Figure 7). To measure the hydrodynamic radius of the complexes in these very difficult conditions, we have developed new statistical analysis tools for dynamic light scattering experiments.



**Figure 7.** Complexes of conjugated PEs with oppositely charged surfactants: compared evolutions of the hydrodynamic radius  $R_h$  and of the position  $\lambda_{max}$  of the maximum in the UV-visible absorption spectrum, as a function of the stoichiometric ratio  $R = [\text{surfactant}]/[\text{monomer unit}]$  ( $C_{P3TAA} = 0.176 \text{ mM}$ ).

We have shown that the UV-absorption allows to measure the critical aggregation concentration (cac) between PEs and surfactants in very dilute conditions ( $C_p = 0.18 \text{ mM}$ ). The cac values are much smaller than those measured for chains with a saturated backbone and are probably associated with an heterogeneous complexation. In this very dilute regime, the variation of the cac value with the alkyl chain length does not obey the classical behaviour reported in the literature for polymers with a saturated backbone, likely due to the strong hydrophobic character of the conjugated backbone.

After the collapse of the chains, as the complexes become richer in surfactant, a new emission peak, red-shifted by more than 100 nm, appears and the initial fluorescence peak vanishes. This rarely observed phenomenon corresponds likely to the presence of new surfactant/polymer structures that remain to be solved.

### Structure of complexes between polyelectrolytes and multicharged partners

We have also considered multicharged and mixed systems. The following studies were carried out:

- Insulin-poly(diallyl-dimethyl ammonium chloride) (PDADMAC) complexes (coll. A. Laschewsky, Potsdam).
- Structure of polyplexes in solution (coll. V. Stanic and J. Ogier, Biomatériaux et Ingénierie Tissulaire, Strasbourg).

We have studied the changes in conformation of poly(L-Lysine)-DNA complexes according to charge density and DNA concentration.

### Other problems

#### Resolving inconsistencies in the behaviour of poly(ethylen oxide) (PEO) solutions

Published work shows some controversy concerning the solvent quality of water for PEO. Some authors consider water as a good solvent for PEO while others report the presence of aggregates in PEO/water solutions. These contradictions have motivated a study of PEO solutions after magnetic stirring or after a die flow.

This study has shown that water is a good solvent for PEO but that strong flow deformation favor local increase of polymer concentration and the formation of aggregates stabilized by hydrophobic forces due to the presence of the  $\text{CH}_2$  groups on PEO. These aggregates dissolve upon salt addition. Thus the discrepancies reported in the literature can be explained by differences in the preparation protocol.

This peculiar behaviour has been confirmed by submitting PEO solutions to sonication. More quantitative results have been obtained regarding the influence of molecular weight, of polymer concentration, and of sonication duration.

Upon sonication, samples with low molecular weight form aggregates and the resulting solutions contain a mixture of well solvated isolated chains and of low-density aggregates. For a constant sonication duration, the fraction of aggregates is lower for higher polymer concentration, likely due to the increase in the solution viscosity. In a given solution, the increase in the sonication duration increases the fraction of aggregates but the aggregation number is rather insensitive to this parameter. Once formed the aggregates are stable but can be dissolved upon salt addition (0.1 M NaCl). Chains in the latter solutions keep the same molecular weight as before any sonication, which shows that no chain scission occurs upon sonication.

The same experiments repeated with high molecular weight PEO show that sonication induces a decrease in the molecular weight, which is further amplified upon salt addition. Thus, in the case of high molecular weights, the sonication induces a scission of the chains followed by an aggregation of the fragments. We note also a decrease of the dispersity in the molecular weights after the sonication.

These effects of the sonication have the same origin as those observed after strong flow deformation. The aggregates stabilized by the hydrophobic interactions explain the discrepancies observed between published results. They are dissolved by salt addition, which provides an easy check for these artifacts.

### Depletion interaction in mixed polymer-colloid systems

It is known that the addition of non-adsorbing polymers with radius of gyration  $R_g$  to a suspension of colloidal particles of much larger radius  $R$  ( $R_g \ll R$ ) causes phase separation to occur. This behaviour is of technological importance and results from the so-called depletion interaction. We have considered an inverse asymmetry parameter  $\xi = R_g/R \gg 1$  ( $R_g \gg R$ ) that corresponds to the association of non adsorbing long polymers with small colloids, referred to as “protein limit”, and studied the stability of mixed systems involving long polystyrene chains (PS) and soft nanoparticles made of fullerene coated with short PS chains (6 chains of PS grafted on  $C_{60}$  molecule:  $C_{60}(PS)_6$ ). These mixed systems present numerous advantages:  $C_{60}(PS)_6$  nanoparticles are soluble in usual organic solvents of PS; polymer adsorption on nanoparticles can be neglected. Therefore, they allowed focusing on the depletion interaction. The structure of these systems has been investigated through SANS experiments, using the contrast variation method. We studied dilute solutions of hydrogenated nanoparticles  $C_{60}(PS_h)_6$ , having an arm degree of polymerization  $N_a$  close to 25, associated with deuteriated  $PS_d$  chains of degree of polymerization  $N=11\,600$ , in deuteriated tetrahydrofuran  $THF_d$ , a good solvent for PS. The scattering length density of  $THF_d$  is identical to that of  $PS_d$ . SANS measurements therefore lead to the scattering functions of  $C_{60}(PS)_6$  nanoparticles. Distinct matrices of  $PS_d$  in  $THF_d$ , with varying concentrations below and above the critical overlap concentration of  $PS_d$  chains, were prepared, and from each, distinct dilute solutions of  $C_{60}(PS_h)_6$ , with concentration varying from 0.5 to 4%, were considered.

Analysis of SANS experiments via Zimm extrapolation method specifically allowed us to obtain information about the dispersion state and average conformation of  $C_{60}(PS)_6$  nanoparticles. It shows that the addition of long PS chains leads to the existence of an additional attractive interaction between nanoparticles (Figure 8) whereas their average conformation remains unchanged.

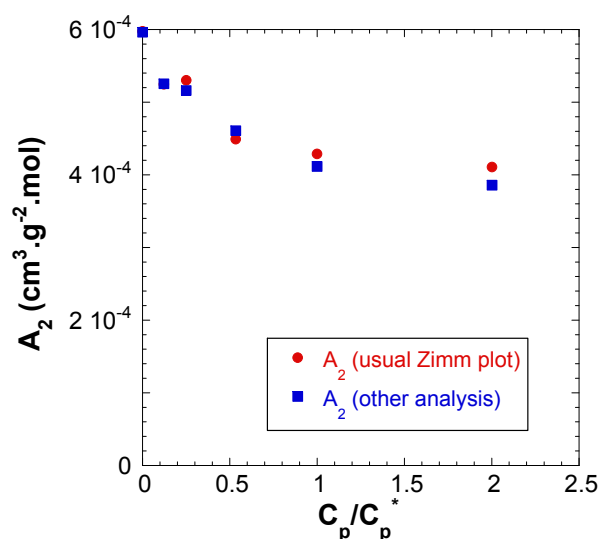


Figure 8. Second virial coefficient of  $C_{60}(PS)_6$  nanoparticles  $A_2$  versus PS concentration

### Structure of dendronized polymers with peripheral poly(ethylene glycol) chains

(coll. S. Méry and B. Heinrich, IPCMS, Strasbourg)

A series of dendronized polymers have been hyperfunctionalized by poly(ethylene glycol) chains. Covering the polymer surface with a high density of ethylene chains naturally induces remarkable properties. The following results have been obtained:

- The conformational study of the polymers in solution by X-rays shows a high compactness of the macromolecules leading to wormlike particles.
- The temperature-induced demixion of the polymers in water (lower critical solution temperature: LCST) is quite sharp and reversible.
- A high and selective affinity of the polymers for silver cations ( $Ag^+$ ) is observed. Its origin is explained from a cage structure with the presence of thio-ether linkages into the dendritic branches. Upon complexation with  $Ag^+$ , the polymer becomes a polyelectrolyte as observed by SANS studies.

### Fluorescent hydrophobic polyelectrolytes

A representative example for the difficulties of characterizing hydrophobic polyelectrolytes is provided by poly(naphthalene sulfonate), PNS. In spite of their long-standing and very numerous applications in many areas (as emulsifier, dispersant, concrete admixture, additives for leather, etc) such polymers are most often badly defined. Actually, there is no fully satisfying way to determine molecular weights and molecular weight distributions of PNS. Indeed, although PNS are readily water-soluble, hydrophobic naphthyl moieties are responsible for aggregation in aqueous solution and adsorption on chromatographic supports. Both phenomena impede a safe characterization when using e.g. light scattering or SEC analysis. In view to overcome these problems, i.e. to find suitable

conditions for which PNS chains are really singly dispersed, we started a study on the behavior of PNS in aqueous media as a function of various parameters that could govern the aggregation process (polymer concentration, ionic strength and nature of added salt, temperature, nature and level of organic co-solvents able to disrupt hydrophobic interactions). In addition to light scattering measurements, fluorescence was the main tool for monitoring hydrophobic interactions, by taking advantage of excimer formation when fluorescent naphthyl groups interact.

## Scientific support for the Characterization Group

To support the scientific project of the ICS, in particular to facilitate a new start in polymer chemistry and to satisfy the needs in the axis *Polyelectrolytes*, it was necessary to anticipate the strong turn-over in the staff of the Polymer Characterization Facility following many retirements, and to update its instruments. More specifically, we had to give the new Polymer Characterization Facility enough human and technical resources to satisfy both routine and research characterization, with the objective to build a reference center for the characterization of water-soluble polymers, starting from the observation that the characterization of hydrophobic or cationic PEs remains a challenge in many cases. Indeed, one specific feature of water-soluble polymers resides in their variety of competing interactions (hydrophobic, coulombic, H-bonds) that confer them interesting properties but hinder their characterization.

The human resources aspect was solved by planned fresh hiring (1 AI in 2009 and 1 IR in 2010) and by reassignment of existing staff (1 AI) to the ICS. Concerning the equipments, several proposals submitted to various funding calls have updated most of the existing equipments and acquired new techniques. These actions have culminated in the creation of the Polymer Characterization Facility, a polyvalent facility grouping all the specific analytical techniques for a complete characterization of polymers at the macromolecular scale, centered on polymer chromatographies coupled on-line with multiple analytical detectors. These chromatographic techniques are either classical, such as Size Exclusion Chromatography (SEC) or less common, such as Asymmetric Flow Field-Flow-Fractionation (A4F). For consistency, several other techniques for the measurements of sizes and charges of macromolecules and colloids have been included in the Polymer Characterization Facility : static and dynamic light scattering, zetametry, as well as capillary electrophoresis.

In order to overcome the problems of unusual SEC behaviour frequently observed with many water-soluble polymers, we have investigated more deeply all the parameters that can play a role in the SEC mechanisms depending on the nature of the polymers, e.g., the nature of the columns and the composition of the aqueous eluent.

The A4F is uncommon in France but offers more opportunities, compared to SEC, to characterize 'difficult' aqueous systems. However the A4F is by no means a routine technique but demands the optimization of many parameters to perform satisfyingly for a given sample. Therefore the development of this technique at ICS waited for three years until CPER funds in 2009 permitted the duplication of the analytical detectors and the separate operation of the SEC and A4F analyses.

Our objective to extend analytical potential to all water-soluble polymers, whatever their chemical nature, is not yet fully achieved but significant progress has already been obtained in collaboration with A. Rameau, for the characterization of the polyelectrolytes studied in the above-described projects as well as for some confidential problems brought by our industrial partners.

## Self-Evaluation

The progress in the planned projects has been overall satisfying with a number of original results (see scientific report). New approaches have been developed in polymer synthesis, in the growth of SWNTs, and in dynamic light scattering. Also in the field of methodology, the validity of the coupled analysis of static and dynamic light scattering has been demonstrated on a model system. A new and unplanned study on solutions of polyelectrolytes in ionic liquids started during the fall 2008. Unfortunately too many interesting results are yet unpublished. This is partly due to the fact that most of our projects necessitated new experimental developments. Another reason lies in our strong involvement in collective time-consuming tasks. Our perspectives are mainly following the projects initiated during the period and thus further progress can be expected at lower time cost, which should increase our publication rate. Fresh collaborations within the ICS are also developing with new users of the SAXS equipments.

Our participations in collective tasks have been varied and demanding, at local as well as national levels:

- Research management: ICS directorial board and commissions (F. Schosseler, 2008 - ), elected member of Scientific Council of Université Louis Pasteur and official representative of the vice-presidency "Recherche et formation doctorale" (P. Petit, 2006 - 2008), elected member of CoNRS (M. Rawiso, 2008 - ).

- Instrumentation development: Polymer Characterization Facility (J. Selb) , SAXS (J. Combet, G. Fleith, M. Rawiso).

- Teaching (CNRS staff): licence pro, master pro-2 IMAPC, Master 2 "Matériaux" (option polymers) (J. Selb), "formation permanente" (J. Selb, M. Rawiso), IMAPC master design (M. Rawiso), partnership for a common master with the Taras Shevchenko University, Kiev, Ukraine (M. Rawiso).

Concerning the permanent staff, one scientist and one technician, J.-M. Catala (DR) and J.-P. Lamps (AI), have been integrated and we suffered from the leave of our youngest scientist, J. Combet (MC), who left the group in november 2010 for personal convenience.

The support by technical staff is in progress but still not sufficient for the synthesis of SWNTs.

The number of non-permanent positions has increased at a satisfactory level (about 5 PhD students on the period) compared to the previous evaluation. This corresponds roughly to our needs since our projects demand rather close supervision and interaction. A weekly PSM meeting with an informal progress report by one of the students has been held since fall 2009 and has increased scientific discussion inside our group.

In March 2013, three permanent researchers will be retired. An effort is made to transmit their knowledge before they leave but new hiring of scientists will be critically necessary in the near future if the ICS wants to keep its high expertise in scattering techniques, rheology and chemistry of conjugated polymers. On the period covered by the evaluation we have presented three candidates for a permanent position at CNRS but these attempts were yet unsuccessful.

External financial support was obtained for both equipments and non-permanent researchers. Three projects have gained approval by the ANR (1 as PI, 2 as partners) and one by icFRC. Three PhD theses were funded externally (1 by Région Alsace, 1 by Région Alsace and CNRS, and 1 by Mexican government). One postdoctoral position was funded by the CNRS. Financial support obtained for the Polymer Characterization Facility is described separately.

Numbers associated with scientific production:

Articles: 18

Typical journals: Macromolecules, Langmuir, Soft Matter

Average impact factor of the journals: 4.0

Average number of citations/articles (2007-2010): 4.7

Patents: 0

Invited International Conferences: 3



# Characterization Group

**Permanent staff (all CNRS members):** Joseph Selb (CR1), Jacques Druz (IR2), Catherine Foussat (TCE), Odile Gavet (AI, joined the group early 2011), Yves Guilbert (IR1), Mélanie Legros (IR2, hiring end-2010), Marie-France Peguet (AI), Julie Quillé (AI, hiring end-2009), Alain Rameau (IR1), Cathy Saettel (TCE, shared with SYCOMMOR group), Josiane Widmaier (IE, retirement 2011)

## Background and context

It should be reminded that a *Characterization Common Service* ("Service commun de caractérisation") was created at the Institut Charles Sadron in the 1980's with the goal of pooling several facilities especially devoted to polymer characterization that were previously scattered within many research teams. Thus, the service encompassed all the tools required of determining both chemical and physicochemical parameters of polymers, namely: elemental analysis, optical spectroscopies, NMR, DSC, viscometry, light scattering and Size Exclusion Chromatography (SEC). Note that the last AERES committee reported that the Characterization Service played a key role in supporting the research activity of the Institute. The great benefit of such a service is still more unquestionable nowadays.

However, in the last ICS Scientific Report (2007) we already emphasized that the major problem we would have to face in a near future was the scheduled retirements of 5 permanent CNRS staffs of the Service in 2011-2012 (in addition to previous 4 retirements in 2005-2007). We also stressed that it was necessary to consider how the functioning of the Service could be affected by the following events: the installation in 2008 in the new ICS building; the new scientific environment on the Cronenbourg campus; the renewals in the research teams; the new trends in scientific projects; the technological evolutions in instrumentation.

Over the last years, all these determining points have indeed been taken into account with the objective of maintaining our recognized expertise in the field of polymer characterization. Thus, the main guiding lines of the reorganization project were:

- a multi-annual recruitment plan for 4 Engineers or Technicians,
- the conversion of the Common Service into a Platform in order to be best-viewed by the scientific and industrial communities,
- an extensive renewal of the scientific equipment,
- new financial supports from various research funding organizations.

In this frame, our efforts over the last four years were directed primarily toward the reorganization of human and technical resources of the novel platform. More recently, in a second step, we started to consider the reorganization of the characterization sections not directly housed by the Platform, namely the various spectroscopy facilities.

## Overview of the reorganization plan

Most of the objectives dealing with the Platform have been truly realized during the four-year period, as described hereafter.

### Reorganization of the characterization service

The main feature was the establishment in 2009 of the new *Polymer Characterization Facility*. It must be emphasized that the current scope of the new Platform does not match exactly that of the former Characterization Service. Taking into consideration that the ICS was one of the best-equipped French laboratories for some very specific techniques of macromolecular characterization (SEC, Light Scattering), whereas other general purpose instruments (e.g. NMR, UV, FTIR, DSC ...) are commonly found in many chemistry laboratories, the characterization facilities were divided into two main units (however, until now, J. Selb is still managing both units):

i) The *Polymer Characterization Facility* includes the techniques that are specifically dedicated to the characterization of macromolecules (more especially Size Exclusion Chromatography and Light Scattering). Note that the name "platform" implies that this section is widely open to external analysis needs.

ii) *Other techniques of chemical analysis*, i.e. facilities for spectroscopy (NMR, UV, IR, MALDI), thermal (DSC, TGA) and elemental analysis are not directly housed by the platform, mainly because these facilities are generally used for ICS internal studies only.

### Staff turnover

Two new permanent CNRS staffs were hired: 1 AI ("Assistant-Ingénieur") in December 2009 and 1 IR ("Ingénieur de Recherche") in December 2010. Another AI position was provided by in-house mobility (January 2011).

At first sight, it could be wrongly considered that the characterization group is overstaffed (1 CR, 4 IR, 1 IE, 3 AI and 2 T). However, it must be kept in mind that this is only a transient situation considering that half of the staff will be retired in 2012. Such an anticipated turnover allowed the activity overlap of former and new staffs for a few months, which obviously favors an efficient transfer of scientific knowledge and technical know-how.

### New funding for equipments

In addition to the funds from the ICS budget (on average, 25 k€ / year), the largest financial funding is provided by incomes from analysis works carried out by the SEC laboratory for external academic or industrial demands (around 30-50 k€ / year). For many years, this important financial resource allowed the Characterization Service to continuously rejuvenate its instrumentation. Note that some research teams of the ICS occasionally contribute significantly to facility improvements. Additional incomes are provided by adult education trainings.

To accelerate the modernization process of obsolete equipments and the acquisition of new techniques, it was necessary to find additional sources of funding. Thanks to several proposals submitted in 2008-2011 to various research agencies, we succeeded in 6 equipment grants for a total of 272 k€ awarded by Uds (University of Strasbourg), CPER-RTRA-FRC (Frontier Research in Chemistry), CPER-PMNA ("Pôle Matériaux et Nanosciences Alsace") and C'Nano Grand-Est.

The funding from multiple sources is also one of the basic criteria for a platform. In this way, the range of state-of-the-art facilities has recently been considerably improved. Thus, a lot of new equipments for Size exclusion Chromatography were acquired: 2 x MALS (Multi-Angles Light Scattering), 2 x QELS (Quasi-Elastic Light Scattering), 2 x UV-Vis Photodiode Array (PDA), and 2 Refractive Index detectors, as well as various basic components of SEC systems (pumps, auto-samplers, column ovens).

The new apparatus for the other techniques are: a Fluorimeter, a Laser granulometer, a ZetaSizer-Nano and a rotational Rheometer. As a result, most of the currently available characterization facilities are less than 6 years old, and many of them are still more recent (less than 3 years old). However, the rejuvenation plan should be pursued because some apparatus reach the age limit, e.g. Static and Dynamic Light Scattering (SLS/DLS). To this end, new applications were submitted to the CPER and Uds in 2011.

In the next paragraphs, we give further details about the mission and activities of the platform and of the related analytical services.

## Polymer characterization platform

In order to avoid any confusion about the mission of the technical platform, it must be highlighted that "Characterization" refers here to the characterization of polymers as macromolecules i.e. characterization at the molecular level carried out in solution. Characterizing polymers as bulk materials, i.e. studies on physical, mechanical, and structural properties at macroscopic / microscopic scales, is out of the scope of the platform's expertise.

Even if the name "platform" is recent, it must be emphasized that the SEC Laboratory, the major section of the former Characterization Service, has never been a service simply restricted to the internal use of the ICS. Actually it has already worked as a platform for at least 20 years since it fulfilled the following required criteria: mutualized human, technical and financial resources; response to the needs of other public laboratories; large opening towards the private sector.

To define the evolution of the former Characterization Service towards the novel Platform we considered the following points:

- remedy for aforementioned retirements of highly experienced staffs;
- selection of the competences to be preserved or acquired;
- direct support to the new scientific project of the ICS (in particular, to the axis "polyelectrolytes");
- contribution to a new start in polymer chemistry at ICS;
- improvement of the technical resources to satisfy both routine and advanced characterizations.

### General description of the novel platform

As already mentioned, we succeed in solving the crucial problem of human resources:

- Julie Quillé was recruited as AI in December 2009 in replacement of J. Widmaier (retirement 2011) to take in charge the techniques based on light scattering and electrophoretic mobility, newly included in the platform;
- Mélanie Legros, recruited as IR in December 2010, will be in charge of the platform in 2012, following the retirements of A. Rameau (IR) and J. Selb (CR) who are presently responsible for the SEC Laboratory and the whole characterization group, respectively;
- as previously scheduled, Odile Gavet, AI, rejoined the SEC section in January 2011 by an in-house transfer from the Polymer Chemistry group.

The change in team composition was accompanied by a comprehensive training plan inside and outside the institute (see Training part of the ICS Report)

Concerning the area of competence, we have chosen to focus the activity of the newly-defined Polymer Characterization Facility on the two major historical techniques of the institute, Size Exclusion Chromatography (SEC) and Light Scattering (LS). As before, SEC remains the central part of the activity. A related available technique is the less common Asymmetrical Flow Field-Flow-Fractionation (A4F). For consistency, other techniques for the measurements of sizes and charges of macromolecules and colloidal particles, formerly housed by research teams, were also included in the platform: static and dynamic light scattering, zetametry, and capillary electrophoresis.

SEC facilities are operated by the characterization staff only (A. Rameau, C. Foussat, O. Gavet) to avoid damage caused by inexperienced users and to guarantee the reliability of the experimental results.



The Static / dynamic Light Scattering setup (SLS/DLS ALV) also runs under restricted access only (J. Quillé).

On the other hand, the apparatus for determining size and charge of colloidal particles (Beckman Laser Granulometer, Malvern ZetaSizer) that are less sensitive to misuses are in open-access with intranet reservation schedules, under the supervision of J. Quillé who ensures training for new users (this mission was insured by J. Widmaier until 2010)

Capillary Viscometry also runs under open-access (C. Foussat).

With currently 6 different SEC facilities (4 in organic solvents and 2 in aqueous solvents) 4 of which work with multidetection, and the A4F system, the platform offers a comprehensive and diversified set of polymer chromatography capabilities that few French laboratories have in-house. The only weakness in the field is the lack of high temperature installations for characterizing polyolefins. On the other hand, the systematic use of SEC-MALS coupling is our strength in the field.

The wide range of SEC capabilities and our expertise is well acknowledged as evidenced by the network of lasting collaborations, which has been established with numerous public laboratories and private companies (see outside relationships section).

#### Current trends in polymer characterization

Note that there is a significantly increased number of internal analysis requests following the installation of the new PMC team.

As a general rule for SEC analyses, our aim is to go beyond the conventional results that are often restricted by common users to the simple values of  $M_w$ ,  $M_n$  and polydispersity index. For this purpose, the combination of MALS detector, viscosimeter detector and less conventional detectors such as QELS and PDA provide valuable information on the structure and conformation of polymers.

One of our major concerns is to fulfill the new characterization needs in aqueous media. A striking observation for many years is the continuously growing interest in water-soluble polymers because the range of present or potential applications of such polymers has been strongly broadened. The current trend in this field, both outside and inside the ICS (e.g. in the IMI, PCM, PSM or SAMS teams), is to use some naturally occurring polymers eventually chemically modified, or to synthesize sophisticated polymeric structures designed for smart materials. Unfortunately, the specific features that confer interesting properties to such polymers lead also to serious drawbacks in their characterization. One has to face frequently encountered problems arising from various interactions (hydrophobic, ionic, polar, H-bonding), such as aggregate formation and adsorption on the chromatographic material. For this reason, SEC analyses in aqueous media are far to be as straightforward as for SEC in organic solvents. Unusual SEC behaviour is frequently observed with many water-soluble polymers, in particular with cationic and amphiphilic polymers.

In the 2007 Scientific Report, we stated that a challenge for the forthcoming years was to be able to fully characterize any water-soluble polymer whatever its chemical nature. According to this statement, we launched actions with the (ambitious?) objective of building a reference center for the characterization of water-soluble polymers. The more significant technical breakthrough was the acquisition, in early 2010, of a second aqueous SEC facility fully equipped with a combination of sophisticated detectors (MALS, QELS, PDA). Thus, for SEC analyses in aqueous media, two complete state-of-the-art facilities are now available. In this way it is easier to vary the numerous parameters that could intervene in the SEC process, namely, the type of columns, nature and concentration of the added salt, pH, nature and content of an organic co-solvent, etc. Such thorough investigations are most often required for tuning experimental conditions in order to overcome the recurring problems that hinder seriously their characterization.

Our objective to extend the analyses capacity to all water-soluble polymers, whatever their chemical nature, is not yet fully achieved but significant advances have already been obtained in the framework of the ICS projects of PSM and IMI teams, as well as for problems brought by our industrial partners.

To characterize "difficult" aqueous systems, an available tool in the platform is A4F which is uncommon in France but offers more opportunities, compared to SEC. However, the A4F is not yet a routine technique because, for a given sample, it requires time-consuming attempts to optimize many parameters. Another present drawback is that the FFF setup shares LC elements and detectors with one of the SEC facilities, which restricts its working time.

Capillary electrophoresis, not yet fully exploited at the ICS, is another tool that has to be developed (J. Quillé in replacement of J. Widmaier) to support studies of the polyelectrolytes axis.

#### Outside relationships

The activities of the SEC Service is far to be limited to the ICS. On average, studies for the ICS represent roughly only 1/3 of the analyses. Numerous external requests originate from several public research laboratories of Strasbourg (DMO-IPCMS, ISIS, three UMRs of the Faculty of Pharmacy, LIPHT, Institut de Chimie) or other French University-CNRS laboratories (Lorient, IS2M and LCOB in Mulhouse, and more occasionally IMP Lyon, University of Tours, PCI Le Mans, LCPO Bordeaux).

A lot of work is also carried out for regional and national industrial companies (e.g. Capsugel, Amcor, Pierre Fabre, Clariant, PCAS, BIC, Sankyo, FCI, Syral, Bic, Seppic, Essilor, L'Oréal, OM Pharma, ...) and as subcontractor for "CRITT Matériaux Alsace". These works may consist in simple routine analyses, but also frequently require studies in greater depth, as for example for demands dealing with the REACH regulation. Note that the analyses for companies are not carried out to the detriment of our own studies. On the contrary, the interest of the industrial

relationships is twofold. First they provide a significant financial support, but also an incentive to develop new analytical procedures specifically adapted to the problem to be solved. Sometimes, deeper collaborations led to research contacts (e.g. Clariant, L'Oréal, PCAS). Analysis costs for public and private partners were agreed by the CNRS.

Note that the platform also plays the role of a portal to redirect external requests to the relevant experts within the ICS or elsewhere, when the submitted characterization problems are out the competences of the platform.

### Quality management

To be in accordance with the running rules of CNRS platforms, a "quality in research" plan has recently been launched. It is still in its beginning phase and efforts on this topic will be intensified in the next few months. In this respect, it is intended to benefit from the experience acquired by other laboratories already involved in this quality approach (e.g. CERMAV)

### Teaching and training

Members of the platform have been involved in educational activity for many years.

- Daily feedback to students regarding the interpretation of analysis results (all members)
- Courses on polymer characterization for 2 Masters and 1 "Licence Professionnelle" studies, University of Strasbourg (J. Selb)
- Practical works on SEC, Light Scattering, Viscosity, for Master students (A. Rameau, J. Selb, C. Foussat)
- Training-period (in between 1-5 months) for students at different university levels (supervisors: J. Selb, A. Rameau, M. Legros)
- Introductory or advanced training courses of Adult Education managed by the "Service de formation continue" of the University of Strasbourg (J. Selb and A. Rameau). This comprises:
  - i) one annual 4-days training on Multidetector Size Exclusion Chromatography, in collaboration with M Rawiso;
  - ii) several 3-days training on the same topic within companies: EMFI (2009), Sanofi-Aventis (2010), L'Oréal (2011);
  - iii) two new trainings on "Water-Soluble Polymers" (ICS and Capsugel, 2011) in collaboration with P. Lutz.

## Services of chemical analysis

Beside the novel Polymer Characterization Facility, a wide range of indispensable analytical facilities is available in the characterization department of the ICS, mainly various spectroscopy and thermal analysis tools:

- spectroscopies: NMR, UV-Vis-near IR, IRTF (with ATR), Fluorescence, MALDI-TOF
- thermal analysis: DSC, micro-DSC and TGA
- elemental analysis (CHNS-O)

These basic techniques, not formally included in the Polymer Characterization Facility, are relevant for both small molecules and macromolecules, i.e. are of prime importance for all the research teams of the ICS, especially for the chemistry (SAMS, PMC) and physico-chemistry groups (PSM, SYCOMMOR, IMI). However, contrary to the platform, these facilities are much less used for external needs because most of them are commonly available in any chemistry laboratory. On the other hand, for the studies on polymers conducted at the ICS, it is clear that these analytical techniques remain tightly linked to that of the Platform.

Apparatus are generally rather recent, except UV-visible spectrometers whose updating has to be considered very shortly in the near future.

Most of the facilities are in open-access according to intranet reservation schedules. The characterization staffs, Y. Guilbert (NMR), J. Druz (UV, IRTF), J. Selb (Fluorescence) ensure user training and technical maintenance.

Some other apparatus are only operated by the characterization staff, C. Saettel (DSC), Y. Guilbert (TGA and MALDI-TOF), and a limited number of expert-users.

The elemental analysis section (M.F. Peguet) is the oldest common service at the ICS. Its activity is in decline over the last years and is now restricted to a single CHNS-O analyzer that fulfills basic analytical needs of the ICS and neighboring DMO-IPCMS.

The replacement of two IRs currently in charge of spectroscopy techniques is now a problem to be urgently solved (retirements in 2012 and 2014). At least, one new member should be recruited to manage the whole spectroscopy facilities that are obviously vital for the ICS. This would be necessarily accompanied by the reinforcement of in-house trainings with the goal to have a few new experts able to maintain the good running of each apparatus.

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**Financial support from grants:** UdS (30 k€ in 2008, 30 k€ in 2009), CPER-RTRA-FRC (129 k€ in 2009), CPER-PMNA (50 k€ in 2009), C'Nano Grand-Est (15 k€ in 2010, 18 k€ in 2011)

**Income from external analysis requests:** 30-40 k€ / year

# Axis 2: Polymers and Interfaces

PMC Research Group



Head of the Group **Jean-François Lutz**

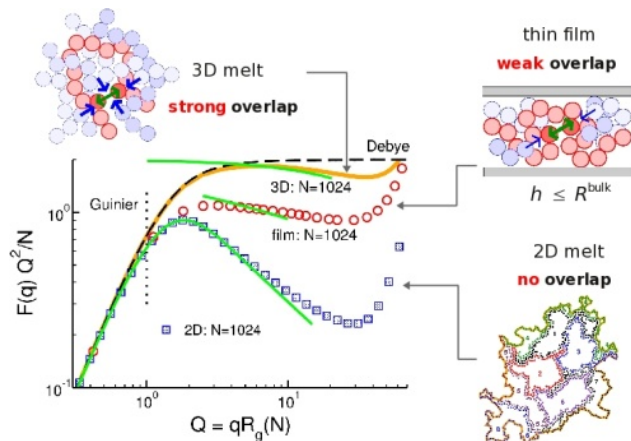
## Design and Synthesis of Tailor-Made Synthetic Polymers.

The Precision Macromolecular Chemistry group covers many aspects of polymer synthesis and materials design. In particular, our team explores challenging topics in polymer science such as the synthesis of sequence-defined macromolecules, the development of single-chain technologies or the preparation of metal/organic hybrid polymers. These high-risk areas of research may have a strong influence on future materials design and technologies.

TSP Research Group

Head of the Group **Jörg Baschnagel**

## Theory and Simulation of Polymers

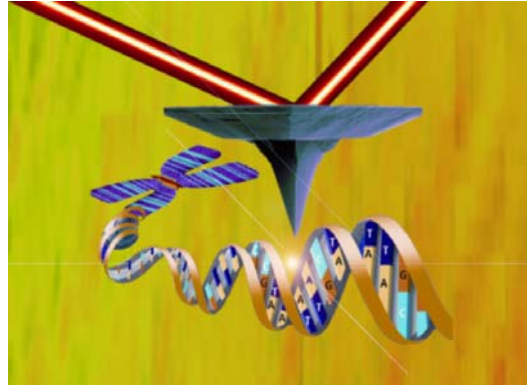


We deploy theoretical and simulation methods to explore structure, conformation and dynamics in polymer systems. During the past four years we mainly made contributions to the axes *Polymers and interfaces* and *Self-assembled systems*. The contributions to *Polymers and interfaces* include the discussion of deviations from classical behaviour in bulk and spatially confined polymer melts (see the Figure above where  $F(q)$  denotes the form factor of a chain), the dynamics of semiflexible chains, polymers and colloids, lubrication properties of polymer brushes, and the relaxation and mechanical behaviour of glassy polymer films. The contributions to *Self-assembled systems* include the study of structure and structure formation in polymers with strongly associating groups, of the impact of chirality on self-assembling polymer systems, and of the kinetics of living polymerization. A further research direction involves the study of structure-property relations of biofilaments.

PMBI Research Group

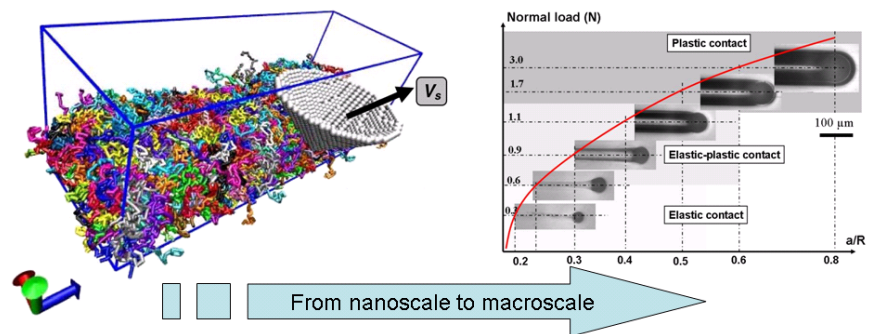
Head of the Group Mounir Maaloum

Physics and Biophysics of  
Macromolecules



Our research comprises the broad field of "Soft Matter" with a special interest in biopolymers such as nucleic acids (DNA, RNA) and proteins and synthetic polymers with different architecture (linear, ring, branched). We presently focus on their behaviour at surfaces. This is important because the structure, properties, and reactivity of matter at a surface can be very different from that in the bulk. Activities in our group involve the manipulation of single molecules by adsorption, self-assembly, and application of pico- and nano-Newton forces with atomic force microscopy (AFM) in solution and controlled environment. The questions of the mobility of these molecules, how and why the conformation and the relaxation are different from the bulk, and how to manipulate their interactions and structures form the basis of many significant scientific problems to whose solution we would like to contribute in the areas from physics to biology.

PMTP Research Group



Head of the Group Christian Gauthier

Physical-Mechanics and  
Tribology of Polymers

The group focuses its research essentially on the mechanical properties of polymeric surfaces, the mechanisms of damage of these surfaces, and the mechanical properties of surfaces of soft matter. Researchers of this group mainly come from Mechanical and Materials Sciences. The group uses this unique and original position in the French research community to try to link physical and chemical properties of surfaces and sub-surfaces, with the tribological behaviour of polymeric surfaces.

The major originalities of the group emerge from the experimental instrumentation that permits both *in-situ* visualisation and scale crossing (nanoscale to macroscale).

# Polymers and Interfaces

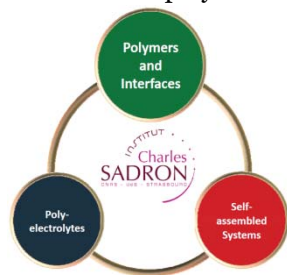
## An overview of the axis

**Permanent staff:** 4 Professors UdS, 6 Directeur de Recherche CNRS, 4 Maîtres de Conférences UdS, 6 Chargés de Recherche CNRS, 2 Ingénieur de Recherche CNRS, 1 Ingénieur d'Etudes CNRS, 1 Technician

**Involved research groups:** Mcube, PBMI, PMC, PMTP, Sycommor, TSP

**Keywords:** macromolecular synthesis · polymer and bio-physics · surface forces and imaging · polymer morphology · contact mechanics, adhesion and friction

A central research area of the ICS has always been the broad field of polymer science. The axis “Polymers and Interfaces” rests on this tradition and encompasses polymer chemistry, physics and engineering. Its research activities often involve synthetic or bio-macromolecules near interfaces, where we address fundamental questions and also work on technical developments of the pertinent characterization techniques. These techniques as well as some of the research projects are directly relevant to applications, e.g., in materials science, optoelectronics or medicine.



polydispersity, architecture<sup>[6]</sup> and microstructure, cf. Figure 1).<sup>[7]</sup> Various polymerization techniques are explored, such as, ionic polymerization, polymer catalysis,<sup>[8]</sup> controlled radical polymerization, iterative synthesis, ligation chemistry and different types of macromolecular shapes (e.g., graft copolymers, macromolecular brushes, loops) can be synthesized.

These structures are very relevant for the research of the axis. In particular, tailor-made single chains (e.g., rigid macromolecules, branched architectures, folded topologies) are interesting objects for single chain physics. In this respect, active collaborations with the PBMI group (M. Maaloum) were intensified during the period 2007-2010. This constructive feedback between polymer synthesis and single chain physics allows detailed investigation of crucial phenomena such as chain conformation (*vide infra*), macromolecular complexation or chain manipulation. In addition, polymer materials, such as colloidal thin films (Y. Holl),<sup>[9]</sup> surface-attached hydrogels (P. Lutz) or surface brushes (J.-F. Lutz)<sup>[10]</sup> are prepared by the PMC group. In particular, an emphasis is put on smart materials allowing control of surface parameters, such as, wettability, elastic modulus, adhesion or bio-recognition. All these fundamental aspects are studied in close collaboration with experts from tribology (M. Maaloum, C. Gauthier). Ultimately, these active collaborations should result in the design of new generations of smart polymer surfaces.

In addition, we have also developed a versatile process to coat a substrate (metallic, organic, inorganic, etc.) by a polymer film (natural or synthetic, various architectures, etc.), which is stable in solvent flow or in humid atmosphere (P. Kékicheff).<sup>[11]</sup> This technique has many potential applications, such as, anti-corrosion coatings, lab-on-chip systems, etc.

## Polymers and interfaces

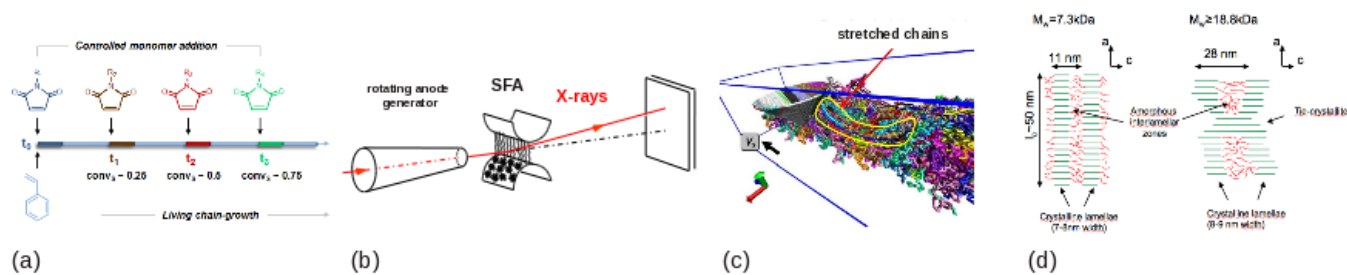
Certainly, polymer science has achieved a high level of maturity. This is demonstrated by excellent textbooks in the field (see e.g. [1,2]). However, this impressive compilation of knowledge does not imply that there are no further intellectual challenges. Quite the opposite. A recent perspective<sup>[3]</sup> even qualifies the field as “more vibrant” than ever. This is due to the fact that polymers are among the most pervasive materials in our society. Their multiple and tunable properties, obtained e.g. by adjusting macromolecular structure and architecture or by blending polymers with other components, allow them to serve in varied applications. This versatility in applications naturally spurs fundamental research on macromolecular synthesis, characterization techniques, and structure-property relations,<sup>[3,4]</sup> in particular of macromolecules at interfaces.<sup>[5]</sup> In the following, we give a few examples of our contributions to this field of research.

### Macromolecular synthesis

In polymer chemistry important progress has been made in our ability to design tailor-made polymer materials, like single polymer chains, colloids, networks, metal-organic hybrids, modified surfaces, to name only a few. The PMC group has its focus of research in this field. An important strength of the group is the synthesis of well-defined macromolecules with controlled molecular structures (i.e., chain length,

### Characterization and platforms

Research in polymer chemistry requires the ability to characterize the resulting molecular structure and key material properties. In this respect, invaluable support is provided by the highly competent characterization platform of the ICS (SEC-GPC, DSC, NMR, etc.). This characterization furnishes essential feedback, eventually enabling advances in macromolecular design.



**Figure 1.** Examples from the research of the axis. (a) Concept of sequential atom transfer radical copolymerization of styrene and various N-substituted maleimides (PMC group). (b) Combination of the SFA and X-rays scattering (P. Kékicheff). (c) MD simulation of nanoscratch tests on a glassy polymer film (PMTP and TSP groups). (d) Schematic representation of the microstructure in semicrystalline P3HT as a function of molecular weight (M. Brinkmann).

In addition to this platform further powerful tools, such as, electron microscopy or AFM, are readily accessible for characterization and are also deployed for original research. For example, advances in the development of AFM in aqueous solution has opened the possibility to investigate the structure of macromolecules at high resolution (below 1 nm) and force-driven conformational changes of synthetic and biopolymers as a function of environmental conditions (e.g. of pH). By this technique the helix-coil transition of a single homopolypeptide has recently been studied, providing evidence for a novel two-step transition (coil to helix to extended coil) at large pH.<sup>[12]</sup>

A further achievement on the experimental side is the combination of two techniques, such as AFM and *in-situ* fluorescence measurements (M. Maaloum). Very promising is also the ongoing realization of the tandem of the surface force apparatus (SFA) and *in-situ* X-ray scattering (P. Kékicheff), which will allow to explore the correlation between structure and effective forces of spatially confined soft matter materials at the nanoscale (see Figure 1). This new development will pay dividends in the future, in particular because it is currently ported to the large-scale synchrotron facility of the E.S.R.F (LEMAX project coordinated by P. Kékicheff with colleagues from the IPCMS, Strasbourg, and the IS2M, Mulhouse).

The aforementioned advanced AFM technique has been integrated (and the SFA will be upon completion) into a pool of characterization tools through the recently created platform on nanomechanics and micromechanics (C. Gauthier with colleagues from the ICS and INSA Strasbourg). Additionally, the platform comprises a host of powerful techniques to explore the surface mechanics and tribology of polymer films (nanoindenter, nanoscratch with built-in AFM, wear tests, profilometry with and without contact). The purpose of the platform is to make these techniques available to other researchers from the Cronenbourg campus or private companies (as a part of the platform for the Institut Carnot “MICA”) and thus to facilitate transfer of knowledge towards the materials science community.

### Some further results from “Polymers and interfaces”

In many applications polymers are utilized in confined geometry, e.g., as protective coatings or in polymer optoelectronics. Understanding the properties of confined polymers is thus of particular significance.<sup>[5]</sup>

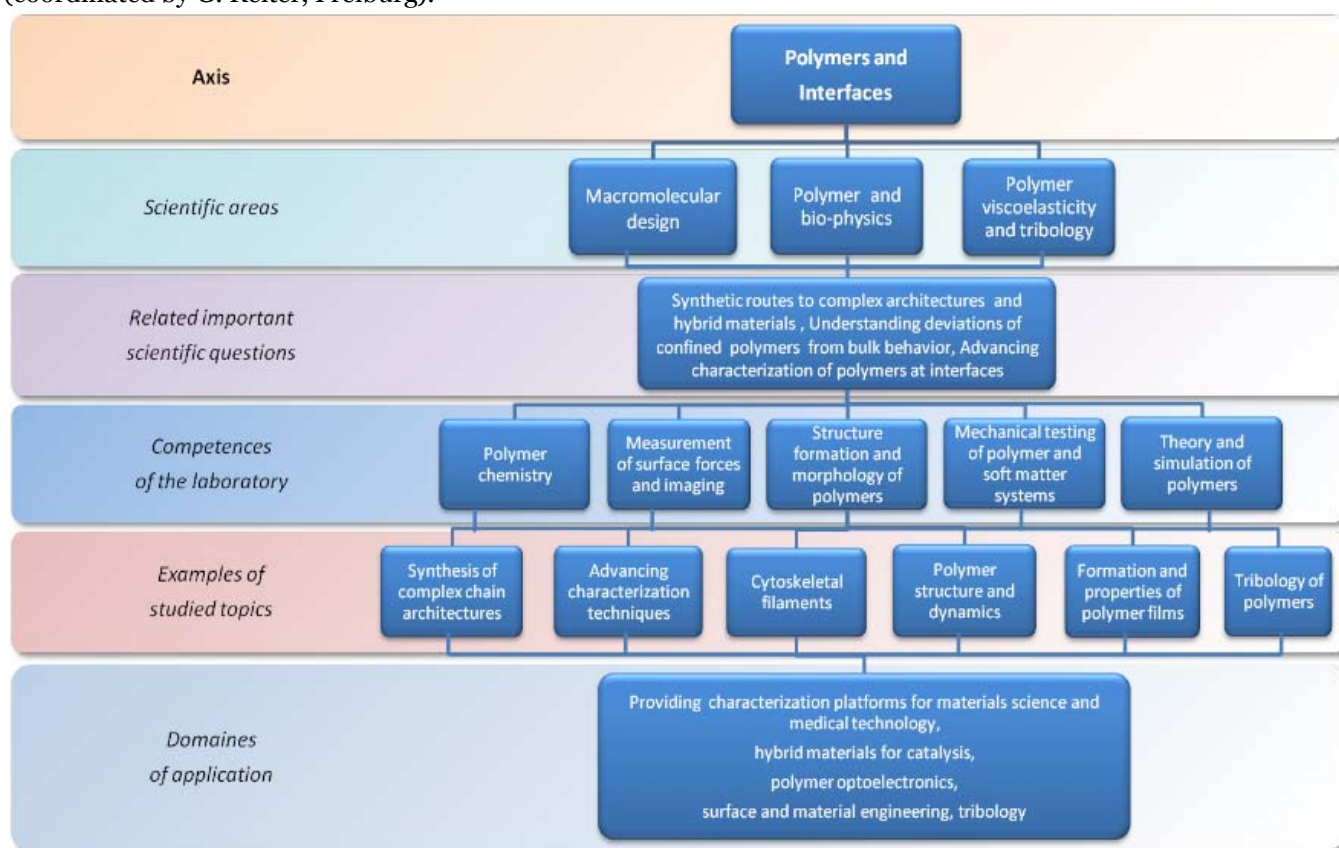
Even the simplest situation of a film of linear flexible homopolymers still has important open questions regarding the chain conformations. The classical view assumes the chains to remain unperturbed (“ideal”) in direction parallel to the film interface. In the past years, the joint work of theory and simulation indicates that this classical view needs to be amended. Due to long-range correlations chain conformations in polymer melts are perturbed from ideal behaviour even in the bulk<sup>[13]</sup> and these deviations are more pronounced in confined geometry (e.g., films<sup>[14]</sup> or pores<sup>[15]</sup>). This work on static properties is a prerequisite for studies of the polymer dynamics, a problem which we are beginning to address.<sup>[16]</sup>

At the macroscopic level, the response of an amorphous polymer surface to scratching is of great practical importance. Scrutiny of this behaviour is possible experimentally through *in-situ* measurement of the groove left by the scratching tip on the polymer surface.<sup>[17]</sup> These studies suggest that the simplest viable model to describe the experimental observations must take into account three ingredients, the elastic properties of the polymer below the yield point, its strain hardening behaviour above it, and a local friction coefficient between the polymer and the tip.<sup>[18]</sup> Certainly, this description remains empirical. A step towards a more microscopic modeling was undertaken by a collaboration between the PMTP and TSP groups (PhD thesis of M. Solar). In this feasibility study, a molecular-dynamics (MD) simulation tool for indentation and scratch tests was developed. Overall good qualitative accord between simulation and experiment was found,<sup>[19]</sup> suggesting that the simulated system is large enough to be considered as a representative volume element in the sense of continuum mechanics and that the study should be extended to explore the molecular mechanisms responsible for the scratch resistance of polymer surfaces (see Figure 1).

Not only amorphous, but also semicrystalline polymers are important in many applications. For instance, polymeric semiconductors, like poly(3-hexylthiophene) (P3HT), are used for the elaboration of low-cost and large-area organic electronic devices. For these materials, it is essential to understand the correlation between charge mobility and structural order as a function of genuine polymer features, such as molecular weight. A prerequisite to this is to precisely characterize the morphology of P3HT in the semicrystalline state. In this respect, important results have been obtained from electron microscopy of epitaxially crystallized P3HT (triggered by a crystallizable solvent),<sup>[20]</sup> revealing the crucial impact of molecular weight on the crystallinity of the thin polymer film (see Figure 1).<sup>[21]</sup> This work is currently developed further and is also planned to be extended within a (still pending) European ITN “C2E” project (coordinated by G. Reiter, Freiburg).

## Structuring of the axis

The purpose of preceding section was not to be an exhaustive description of our research, but rather to give an introductory overview exemplifying the breadth of the available competences and scientific activities. The competences include macromolecular chemistry, polymer and bio-physics, measurement of surface forces and diverse imaging techniques, control and analysis of polymer morphology, and mechanical testing of soft matter systems (Figure 2). These competences are found in 5 research groups (PMC, PBMI, TSP, PMTP, Mcube, Sycommor), which address fundamental and applied problems in polymer science (see “Examples of studied topics” and “Domains of application” in Figure 2).



**Figure 2.** Organization chart of the axis highlighting the major scientific areas and questions. To address them several competences exist in the involved research groups. Examples of studied objects and possible applications are indicated.

- [1] M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, **2003**, Oxford.
- [2] *Comprehensive Polymer Science*, 2<sup>nd</sup> edition, K. Matyjaszewski, M. Möller (Eds), Elsevier, **2011**.
- [3] C. K. Ober et al., *Macromolecules* **2009**, *42*, 465.
- [4] G. H. Fredrickson, *Nature Materials* **2008**, *7*, 261.
- [5] S. Granick et al., *J. Polym. Sci. B* **2003**, *41*, 2755.
- [6] J.-F. Lahitte et al., *Polymer* **47**, 1063 (2006).
- [7] J.-F. Lutz, H. G. Börner, *Macromol. Rapid Commun.* **2011**, *32*, 107; H. Harris et al., *Macromol. Symp.* **2010**, *291-292*, 43.
- [8] P. Kuhn et al., *Dalton Trans.* **2007**, 515.
- [9] C. Arnold et al., *J. Phys. Chem. B* **2010**, *114*, 9135.

- [10] E. Wischerhoff et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 6974.
- [11] Patent P.C.T. n° EP2009/05435.
- [12] M. Maaloum et al., *Phys. Rev. Lett.* **2011** (submitted).
- [13] J. Wittmer et al., *Macromolecules* **2010**, *43*, 1621; A. N. Semenov, *ibid.*, 9139.
- [14] A. N. Semenov, A. Johner, *Eur. Phys. J. E* **2003**, *12*, 469.
- [15] N.-K. Lee et al., *Europhys. Lett.* **2011**, *93*, 48002.
- [16] J. Wittmer et al., *Phys. Rev. Lett.* **2010**, *105*, 037802.
- [17] E. Charraut et al., *J. Polym. Sci. Phys. B.* **2008**, *46*, 1337.
- [18] H. Pelletier et al., *Wear* **2010**, *268*, 1157.
- [19] M. Solar et al., *J. Phys. D: Appl. Phys.* **2010**, *43*, 455406.
- [20] M. Brinkmann, P. Rannou, *Adv. Funct. Mat.* **2007**, *17*, 101.
- [21] M. Brinkmann, P. Rannou, *Macromolecules* **2009**, *42*, 1125.





# Precision Macromolecular Chemistry (PMC)

Head of the Group *Jean-François Lutz*

**Permanent staff:** Dr. habil. Jean-François Lutz (Directeur de Recherche CNRS – hired at the ICS in November 2010), Prof. Yves Holl (UdS), Dr. Pierre Lutz (Directeur de Recherche CNRS), Dr. Paul Baxter (Chargé de Recherche CNRS), Laurence Oswald (Technician CNRS – hired at the ICS in November 2010), Alexandre Collard (Technician CNRS).

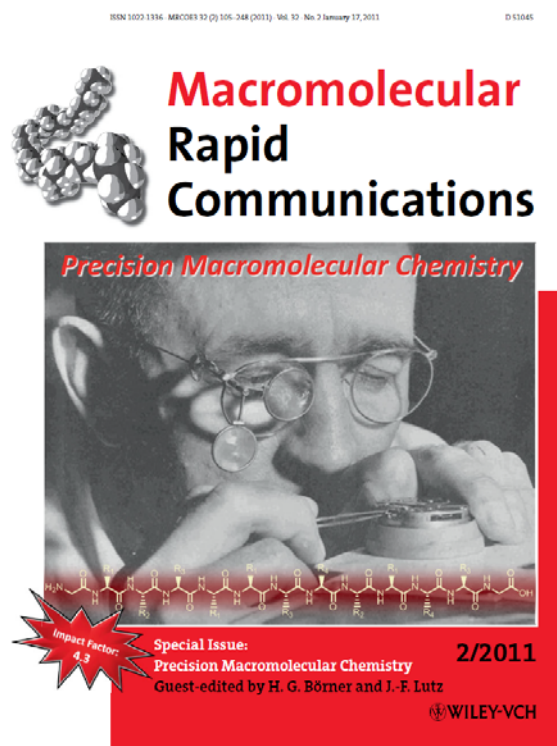
**Non-permanent researchers (status June 2011):** **1 non-permanent assistant professor** (Dr. Nezha Badi), **2 post-docs** (Mirela Zamfir, Matthias Welker), **7 graduate students** (Anna Meszynska, Inès Souilem, Sylvain Grégoire, Gladys Pozza, Maximilian Vielhauer, Mohamed Maaouni, Guillaume Klein), **4 undergraduate students**.

**Keywords:** macromolecular synthesis · polymer microstructure · polymer architecture · stimuli-responsive materials · colloids

## History and concepts

The research group *Precision Macromolecular Chemistry* (PMC) is the youngest working group in the Institut Charles Sadron. This team was created in November 2010 and merged the existing know-how of the research group *Polymer Chemistry* with outside competences. In particular, two permanent CNRS staffs were recruited in November 2010 (Jean-François Lutz as group leader and Laurence Oswald as technician) to strengthen the development of the PMC group. The installation of the group was also supported by the University of Strasbourg (i.e. an assistant professor will be hired in May 2011), the *International Center for Frontier Research in Chemistry* (in form of a FRC installation grant) and the European Union. In the latter case, a prestigious starting grant of the European Research Council (ERC) was awarded to Jean-François Lutz in November 2010. The PMC group was also recently included in the *Center for Chemistry of Complex Systems* (LABEX CSC) directed by Jean-Marie Lehn.

The main scientific objective of the PMC group is to explore the frontiers of synthetic polymer chemistry. In particular, our aim is to go beyond the current state-of-the-art in the field. In that regard, the name of our group reflects our scientific philosophy (Figure 1).<sup>[1-3]</sup> Indeed, the term “precision” has been associated in recent years to certain aspects of polymer synthesis, which are generally difficult to control without accurate and adequate chemical tools.<sup>[4]</sup> For instance, crucial macromolecular parameters, such as polydispersity, tacticity, monomer sequences and folding, are still not fully mastered in current polymer science. In this context, the aim of the PMC group is to develop new avenues for macromolecular design. In particular, three principal topics are central in our research: *i*) controlling the molecular structure of synthetic polymers, *ii*) investigating the supramolecular organization of polymers (i.e. folding, self-assembly) and *iii*) using macromolecular design for generating advanced properties. These topics will be discussed in the next paragraphs.



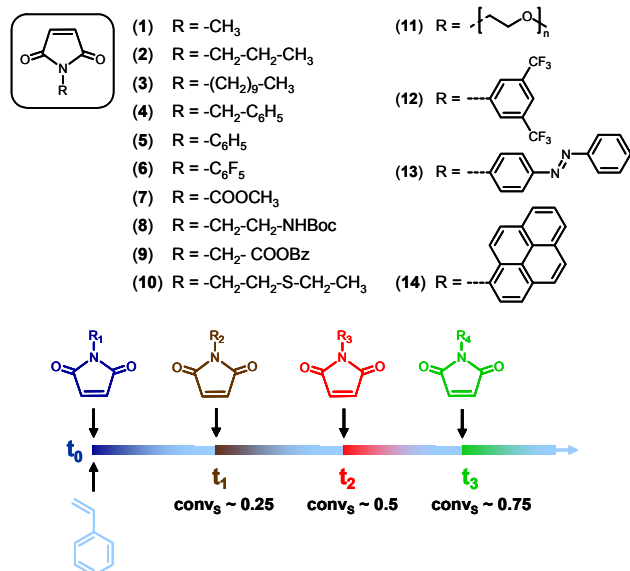
**Figure 1.** Cover of the special issue of *Macromolecular Rapid Communications* on *Precision Macromolecular Chemistry* published in January 2011 (guest-edited by Hans G. Börner and Jean-François Lutz).<sup>[4]</sup>

## Control of the molecular structure of polymers

As mentioned above, controlling the molecular structure of synthetic macromolecules is an important aspect of our research.<sup>[5]</sup> Therefore, the PMC groups studies various chemical tools (e.g. living polymerizations, iterative synthesis, ligation chemistry) for controlling the microstructure (i.e. sequences and tacticity) or the architecture (i.e. topology) of synthetic polymers.

### Sequence-control in polymer synthesis

The control over comonomer sequences in synthetic polymerization processes remains one of the last major fundamental challenges in polymer chemistry.<sup>[6-7]</sup> Indeed, contemporary synthetic methods do not allow precise control over polymer microstructures. In this context, our team studied various approaches for controlling sequence-distribution in synthetic polymerizations.



**Figure 2.** Concept of the sequential atom transfer radical copolymerization of styrene and various N-substituted maleimides.

For example, we recently reported a simple method for controlling comonomer sequence distributions in a radical chain-growth polymerization (Figure 2).<sup>[8]</sup> This concept relies on the atom transfer radical copolymerization (ATRP) of functional N-substituted maleimides with styrene. This copolymerization is a controlled radical process, which combines two unique kinetic features: (i) all the polymers chains are growing simultaneously and (ii) the cross-propagation of the comonomers is highly-favored as compared to homopolymerization. Thus, discrete amounts of N-substituted maleimides (e.g. 1Eq. as compared to initiator) are consumed extremely fast in the copolymerization process and are therefore locally incorporated in narrow regions of the growing polystyrene chains. Furthermore, the position of the N-substituted maleimides in the polystyrene chains can be kinetically-controlled by adding them at desired times during the course of the polymerization. Thus, the styrene/N-substituted maleimides copolymerization platform constitutes a real step forward in the field of radical chain-growth polymerization. Indeed, this technique can be applied to a wide variety of functional MIs and can therefore be exploited to create tailor-made microstructures.<sup>[8]</sup>

### Synthetic polymers with defined architectures

The control over macromolecular topology is a strong competence of the PMC group. Indeed, several examples of block-, graft-, star- copolymers and

macromolecular networks have been reported by Jean-François Lutz or Pierre J. Lutz over the last few years.<sup>[9-10]</sup> In particular, cationic polymerizations, living anionic polymerizations, controlled radical polymerizations and polymer modifications strategies are studied in our group for the synthesis of advanced polymer architectures. Moreover, polymer catalysis is a subject, which has been extensively studied by Pierre J. Lutz over the last years.

Among all these examples, the chain-growth polymerization of oligo(ethylene oxide)-based macromonomers remains an internationally-acknowledged strength of our research group. This topic was started at the ICS in the early 1980s but remains timely today.<sup>[11]</sup> Indeed, oligo(ethylene oxide)-based macromonomers allow synthesis of water-soluble macromolecular architectures such as graft copolymers or networks. Importantly, the aqueous properties of these macromolecules can be tuned by polymer design. For instance, it was recently discovered that oligo(ethylene oxide)-based graft copolymers exhibit a controllable lower critical solution temperature (LCST) in aqueous medium.<sup>[12]</sup> This important aspect is discussed in detail in the last paragraph of this report.

### Folding and self-assembly of synthetic polymer chains

Although our research group has a strong focus on polymer chemistry, our scientific vision is not limited to molecular design. Indeed, our team is also interested in supramolecular events, such as polymer folding or polymer self-assembly. Some of these aspects are discussed below.

#### Macromolecular folding

In general, synthetic polymer chains, prepared by synthetic polymerization processes, do not contain precisely addressable sites, which can be used for controlling their intramolecular folding. The only precisely localizable functions in chain-growth polymers are usually the chain ends or, in the case of block copolymers, the spacers between the segments. Polymer chain ends can be utilized to promote intramolecular covalent cyclization. However, this approach only leads to simple cyclic topologies. In that regard, the sequence-controlled polymers described in the first paragraph of this report open new avenues for synthesizing foldable linear macromolecules. For example, we recently demonstrated that controllable covalent bridges can be prepared using the styrene/N-substituted maleimides copolymerization platform.<sup>[3]</sup> In this approach, small amounts of TMS- or TIPS-protected N-propargyl maleimide were added during the course of styrene homopolymerization. Thus, various types of linear polystyrene precursors containing localized alkyne functions were synthesized. These reactive linear chains were afterwards involved in intramolecular reactions (e.g. Huisgen cycloaddition or Glaser coupling) in dilute solutions, thus affording different types of covalently

folded polymer chains. For example, P-, Q-, 8- and  $\alpha$ -shaped macromolecular origamis were prepared. In all cases, FT-IR and SEC analysis indicated the successful formation of localized intramolecular covalent bridges.<sup>[3]</sup>

### Self-assembly, micellization, colloids

The preparation of polymer-based colloidal dispersions in water is an important aspect of our research. Indeed, polymer-based colloids have gained a huge importance for a wide-range of practical applications in biosciences, cosmetics, food industry and health-care. Hence, two main routes for preparing aqueous polymer dispersions are studied in our group: *i*) emulsion polymerization, and *ii*) the self-organization of well-defined macromolecular building-blocks. In the former case, the scientific expertise of Yves Holl is certainly crucial for the PMC group.<sup>[13-14]</sup> Indeed, various projects related to colloid synthesis and colloidal thin films were developed during the last few years in our group. In particular, our team recently investigated, in close collaboration with the *Ecole de Chimie des Polymères et des Matériaux* (ECPM) in Strasbourg, optimal experimental conditions for synthesizing monodisperse miniemulsions. For instance, a custom-made mixer, developed at the ECPM, was studied for optimal colloidal preparation. This instrument led to very promising preliminary results. Furthermore, the formation and the properties of dried latex thin films were studied using AFM and tribology. In these particular cases, collaborations with Mounir Maaloum and Christian Gauthier (i.e. within the axis *Polymer and Interfaces*) were essential.

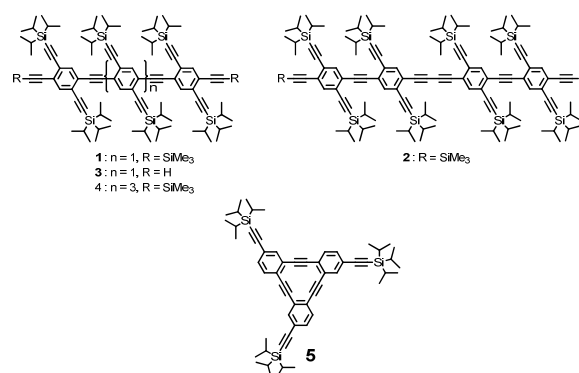
## Tuning properties via advanced macromolecular design

The range of applications of synthetic polymer materials has considerably broadened within the last few decades. Besides commodity applications, synthetic macromolecules have been recently extensively explored in numerous specialty areas as diverse as nanoelectronics, data storage devices, alternative energy resources, cosmetics, healthcare and biotechnology. However, these new technologies require high-performance properties, which are often not attainable with standard polymer materials. In this context, the PMC group developed recently advanced macromolecular structures with tailored properties.

### Metal/organic hybrid polymers

Our group investigates the synthesis and the physicochemical properties of structurally new classes of supramolecular hybrid inorganic/organic materials, anticipated to be of primary importance for future nanotechnology and materials science applications. For instance, we study: *i*) the self-assembly of nanostructured metallopolymers: nanosensors, nanofilters and host-guest systems, (*ii*) the generation

of new smart supramolecular magnetic/electronic wires and networks, *iii*) sterically isolated conjugated nanostructures: new supramolecular fluorophores, polyradical and electron reservoirs, *iv*) dehydroannulenes as novel molecular electronic materials. *v*) the development of polypyridine-bridged metal chalconide nanoparticles for photovoltaic applications.

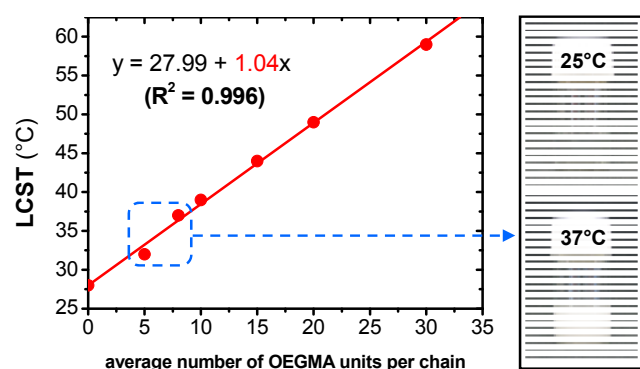


**Figure 3.** Molecular structure of sterically protected tetraphenyleneethynylene cruciform oligomers.

As part of our research effort toward the construction of nanosized conjugated ligands for the creation of multifunctional hybrid polymers, we have prepared a series of tetraphenyleneethynylene cruciform oligomers with sterically bulky triisopropylsilyl (TIPS) substituents covalently attached the main backbone (Figure 3).<sup>[15]</sup> Oligomers **1** and **5** were found to be electrochemically active undergoing two, one-electron reductions which were strikingly similar despite their very different (linear vs cyclic) topologies, suggesting that their electrochemical properties are determined more by the presence and number of the benzene rings, which are 3 in each case. Spectroscopic studies showed that it was possible to fine-tune the optical bandgap ( $E_g^{opt}$ ) upon increasing the conjugation length of the oligomeron from **1** to **4**, with the pentamer approaching the effective conjugation length for the linear systems. The latter studies also revealed that intermolecular associations between the oligomers were absent in dilute solution, verifying that the steric isolation resulted in single molecule properties. In particular, **1** and **3** exhibited very high thermal stability, photostability, and high quantum yields ( $\Phi$ ).<sup>[15]</sup> These conjugated fluorophores thus exhibit physicochemical properties characteristic of single molecules, unperturbed by effects resulting from intermolecular aggregation and associations. They therefore function as ideal models for studying the effect of steric isolation at a molecular level on their electronic and spectroscopic properties, and should in particular serve as promising candidates for the creation of conjugated polymers with enhanced emission characteristics. The above results suggest that these systems may be excellent candidates for the construction of new light absorbing materials with potential photonics and solar energy applications.

### Smart biocompatible polymers

Although some polymers such as poly(ethylene glycol) (PEG) or poly(lactide-co-glycolide) (PLGA) have been successfully exploited in numerous commercial bio-applications for many years, several novel areas of biosciences and biotechnology (e.g. bioseparation, diagnostics, gene- or protein- therapy, controlled release, implants) certainly require “smarter” macromolecules with more sophisticated properties. For instance, synthetic macromolecules undergoing rapid conformational change in response to an external stimulus, such as pH, temperature, ionic strength or irradiation (i.e. stimuli-responsive polymers), became lately very important in applied biological science.



**Figure 4.** Properties of PEG-based biocompatible polymers with a tunable thermoresponsive behaviour in aqueous milieu.

Our research group described, for example, the synthesis of thermoresponsive copolymers by controlled radical copolymerization of 2-(2-methoxyethoxy)ethyl methacrylate (MEO<sub>2</sub>MA) with oligo(ethylene glycol) methyl ether methacrylates (OEGMA). These copolymers combine the advantages of PEG (i.e. biocompatibility) and thermoresponsive polymers (i.e. LCST behaviour in water) in a single macromolecular structure (Figure 4). Moreover, they have inherent advantages as compared to traditional PNIPAM such as: *i*) an excellent bio-repellency below LCST (i.e. anti-fouling behaviour), *ii*) reversible phase transitions (i.e. no marked hysteresis), and *iii*) bio-inert properties (i.e. no specific interactions with biological materials). Furthermore, most of these oligo(ethylene glycol) (meth)acrylates are commercial products and are therefore readily available for materials science. Moreover, these monomers can be polymerized using straightforward controlled radical polymerization techniques such ATRP or reversible addition-fragmentation chain-transfer (RAFT) polymerization. These modern polymerization approaches offer broad possibilities of macromolecular engineering. Therefore, OEGMA-based polymers can be easily attached to a wide variety of materials, including planar substrates, networks, porous monoliths, colloidal particles or biological objects. Thus, the controlled radical polymerization of OEGMAs constitutes a unique platform for preparing thermoresponsive materials as diverse as polymer-enzyme bio-hybrids, injectable hydrogels, capsules for drug-release, modified magnetic particles for *in vivo*

utilization, cell-culture substrates, antibacterial surfaces, or stationary phases for bioseparation.

**Collaborations in the axis:** M. Maaloum, C. Gauthier

**Collaborations with other teams in the ICS:** N. Giuseppone, J.-M. Guenet, M. Brinkmann, G. Decher (planned), P. Schaaf (planned)

**Collaborations outside the ICS:** Mitsuo Sawamoto (University of Kyoto), Peter Seeberger (MPIKG Potsdam), Frank Caruso (University of Melbourne), Patrick Theato (University of Hamburg), Ullrich S. Schubert (University of Jena), Frances Heaney (NUI Maynooth), Hans G. Börner (Humboldt University), Christopher Barner-Kowollik (Karlsruhe Institute of Technology), Frédéric Chandezon (CEA Grenoble), Fritz E. Kühn (TUM, Munich), Carsten Rudolph (LMU Munich), Manfred Schmidt (University of Mainz), Stephan Mecking (University of Konstanz), René Muller (ECPM), Michel Bouquay (ECPM), Christophe Serra (ECPM).

**Local network:** Excellence laboratory (LABEX) Center for Chemistry of Complex Systems (CSC). International Center for Frontier Research in Chemistry (FRC - RTRA).

- [1] N. Giuseppone, J.-F. Lutz, *Nature* **2011**, *473*, 40-41.
- [2] J.-F. Lutz, *Nature Chem.* **2010**, *2*, 84-85.
- [3] B. V. K. J. Schmidt, N. Fehler, J. Falkenhagen, J.-F. Lutz, *Nature Chem.* **2011**, *3*, 236-240.
- [4] J.-F. Lutz, H. G. Börner, Special issue: Precision Macromolecular Chemistry, *Macromol. Rapid Commun.* **2011**, *32*, 107-244.
- [5] Y. Holl, *Actualite Chimique* **2008**, *319*, 14.
- [6] N. Badi, J.-F. Lutz, *Chem. Soc. Rev.* **2009**, *38*, 3383-3390.
- [7] S. Pfeifer, Z. Zarafshani, N. Badi, J.-F. Lutz, *J. Am. Chem. Soc.* **2009**, *131*, 9195-9197.
- [8] J.-F. Lutz, B. V. K. J. Schmidt, S. Pfeifer, *Macromol. Rapid Commun.* **2011**, *32*, 127-135.
- [9] H. Harris, B. Nohra, O. Gavati, P. J. Lutz, *Macromol. Symp.* **2010**, *291-292*, 43-49.
- [10] F. Pelascini, S. Plentz-Meneghetti, P. J. Lutz, V. Krukoni, K. Williams, *Macromol. Res.* **2010**, *18*, 449-457.
- [11] P. J. Lutz, *Polym. Bull.* **2007**, *58*, 161-171.
- [12] J.-F. Lutz, *Adv. Mater.* **2011**, *23*, 2237-2243.
- [13] C. Arnold, F. Thalmann, C. Marques, P. Marie, Y. Holl, *J. Phys. Chem. B* **2010**, *114*, 9135-9147.
- [14] C. Arnold, G. Klein, M. Maaloum, M. Ernstsson, A. Larsson, P. Marie, Y. Holl, *Colloids Surf., A* **2011**, *374*, 58-68.
- [15] A. Al Ouahabi, P. N. W. Baxter, J. P. Gisselbrecht, A. De Cian, L. Brelot, N. Kyritsakas-Gruber, *J. Org. Chem.* **2009**, *74*, 4675-4689.

## Self-Evaluation

### Creation of the group and human resources

In 2008, the main criticisms of the AERES committee regarding the polymer chemistry group of the ICS were the following ones: *i*) Overall, the team is too small in size for the ICS, *ii*) the number of students and post-docs is not sufficient and *iii*) several permanent researchers are reaching the age limit and will soon leave in retirement. Thus, the committee strongly encouraged an action for hiring new permanent researchers.

Based on these comments, the situation was dramatically improved. First of all, Jean-François Lutz was hired as a new head of the group in November 2010. Jean-François Lutz is ranked among the most cited polymer chemists worldwide (rank #30 at the international level and rank #1 in France, according to the last update of Essential Science Indicators). This recruitment will certainly revitalize the research on polymer synthesis at the ICS. Moreover, 3 other permanent team members were or will be soon recruited: Nezha Badi (Maître de Conférence Uds), Delphine Chang-Seng (Chargée de Recherche CNRS) and Laurence Oswald (Technician CNRS). Altogether, this new task force should bring a new research dynamism in the team. For instance, the number of students has already increased significantly since November 2010.

In conclusion, we believe that the management of human resources was extremely positive. Our group now fulfills all the AERES criteria.

### Statement on financial supports

The financial situation of the group was dramatically improved during the last 8 months. First of all, a prestigious ERC starting grant of 1.2 M€ was awarded to Jean-François Lutz in November 2010 for supporting his research on sequence-defined polymers. An additional grant of 25000 € was awarded to Jean-François Lutz by the International Center for Frontier Research in Chemistry (FRC) for supporting his research on single-chain technologies. The recent integration of the group in the excellence network of Jean-Marie Lehn (LABEX CSC) will certainly bring soon some financial input. In addition, 3 ANR proposals and 3 PhD applications have already been submitted in 2011.

Therefore, our group reached an almost self-standing financial status. It is therefore obvious that we took very seriously the comments of the AERES committee into account.

### Statement on scientific collaborations

International collaborations have never been a significant weakness of our team. All senior researchers of our team are known internationally and have a network of national, European and international collaborations (see detailed list at the end of the previous page). This situation has been preserved during the last 4 years. For example, we had active research cooperations during that timeframe with world-leading teams in Germany, Japan and Australia.

### Statement on scientific productions

Scientific productivity and visibility was one of the weaknesses of the polymer chemistry team in 2008, according to the AERES evaluation. This aspect was dramatically improved recently. For example, more than 15 publications were submitted and/or published by our team for the sole year 2011. Some of these publications were published or accepted in high impact journals such as Nature, Nature Chemistry or Angewandte Chemie International Edition. Furthermore, one special issue of *Macromolecular Rapid Communications* on Precision Macromolecular Chemistry and one volume of *Advances in Polymer Science* on Bioactive Surfaces were edited by our group. A thematic issue of the RSC journal *Polymer Chemistry* on New Method of Polymer Synthesis is also planned for early 2012.

Overall, we believe that the productivity and the visibility of our work have been significantly improved. Based on citations records, the PMC group is now ranked as #1 in polymer chemistry in France (Essential Science Indicators, May 2011).

### Overall statement

Altogether, the research on polymer chemistry was strongly revitalized in our institute. The new PMC group was specifically created in response to the AERES criticisms. This new research team is *i*) supported financially by several research grants, *ii*) rejuvenated by the recruitment of new permanent researchers, post-docs and graduate students, and *iii*) scientifically active and known internationally. Therefore, our self-evaluation is very positive for the overall period 2008-2011.



# Theory and Simulation of Polymers (TSP)

Head of the group *Jörg Baschnagel*

**Permanent staff :** Prof. Jörg Baschnagel (UdS), Dr. Albert Johner (Directeur de Recherche CNRS), Dr. Alexander Semenov (Directeur de Recherche CNRS), Dr. Joachim Wittmer (Directeur de Recherche CNRS); Dr. Jean Farago (Maître de Conférences UdS), Dr. Igor Kulić (Chargé de Recherche CNRS since 2009), Dr. Hendrik Meyer (Chargé de Recherche CNRS); Dr. Olivier Benzerara (Ingénieur de Recherche CNRS).

**Non-permanent researchers (2007-2011): 4 post-doctoral associates** (Dr. A. Cavallo 2007-2008, Dr. T. Kreer 2006-2009, Dr. I. Nyrkova 2007-2011, Dr. F. Ziebert 2010-) / **13 PhD students** (P. Beckrich – defended 2007, F. Crevel – defended 2007, M. Durand – defended 2010, A. Galuschko – defended 2010, E. Maresov – defended 2009, S. Peter – defended 2007, M. Solar – defended 2010, S. Frey – defense planned 2012 (cotutelle), G.-M. Nam – defense planned 2012 (cotutelle), P. Polińska – defense planned 2013, N. Schulmann – defense planned 2012, A. Shevts – defense planned 2013, J. Zabel – defense planned 2013) / **12 Master students**

**Keywords:** theoretical and computational polymer physics · soft matter physics · systems inspired by biology

## Geometrically confined polymer systems

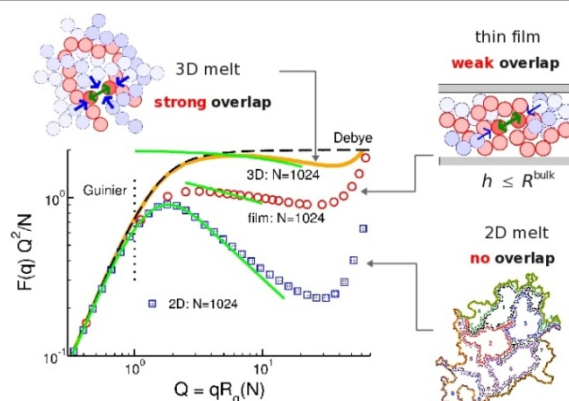
Long-range correlations in the structure of concentrated polymer solutions and melt

Structural properties of the bulk

The classical view on the equilibrium structure of concentrated solutions or melts of flexible polymer chains supposes that all spatial correlations are short-range: They vanish for length scales larger than a few monomers.

Our recent theoretical work has amended this classical view. In collaboration with S. Obukhov (Gainesville) we found that correlation functions of density fluctuations<sup>[1]</sup> or bond orientations<sup>[2,3]</sup> display long-range power decays, both for single-chain and collective quantities. At the single chain level, this implies corrections to ideal (Gaussian) behaviour. The molecular origin of these deviations from chain ideality is related to the interplay of chain connectivity and the incompressibility of the melt. This interplay leads to an effective repulsion between chain segments due to a correlation hole effect.<sup>[1-3]</sup>

These theoretical advances prompted us to perform extensive computer simulations to seek for the predicted corrections from classical behavior. Since the corrections should manifest themselves best for (nearly) incompressible systems of long flexible chains, the simulations employed generic polymer models (bead-spring models, bond-fluctuation lattice model). These studies led to the implementation<sup>[4]</sup> of new algorithms (connectivity-altering Monte Carlo moves) as well as variants of the simulation models (models with finite monomer excluded volume) and also stimulated further theoretical developments for the description of the simulation results.



**Figure 1.** Kratky plot of the form factor for 3D melts, thin films, and (self-avoiding) 2D melts. The symbols represent simulation results for a bead-spring chains of length  $N=1024$ . The lines are the theoretical predictions (3D melt<sup>[1]</sup>, thin films<sup>[5]</sup>, 2D melt<sup>[6]</sup>). The sketches illustrate the decrease of the overlap between the chains when going from 3D to very thin films; this decrease increases the effective repulsion between chain segments due to a correlation hole effect. Strictly 2D melts (of self-avoiding chains) are different due to chain segregation (no overlap).

This joint effort between theory and simulation has allowed us to verify quantitatively many of the theoretical predictions for the chain conformations in the melt (e.g. for the form factor; see Figure 1), at least for highly flexible generic polymer models.

Of course, it is important to explore also real polymers in order to ascertain to what extent the corrections to classical behavior could influence experimental results. As a step in this direction we have begun to study a chemically realistic model for polyisobutylene (PIB) (thesis: J. Zabel; project ANR blanc 2009). Concurrently to the simulations, the conformation of PIB has also been measured by neutron scattering (collaboration with M. Dadmun, Knoxville). A comparison between experiment and theory is currently carried out.

### Extensions to confined polymer systems

Theory suggests the corrections to classical behavior to become more pronounced in strong spatial confinement, e.g. for polymer melts in thin films<sup>[5]</sup> or narrow pores<sup>[7]</sup> (provided the chains still overlap; see

below). We have extended our simulation efforts in this direction. A first analysis<sup>[8]</sup> of the chain conformations in thin films provided some evidence in favor of the theoretical predictions, but must be considered as preliminary because the studied chain lengths were still fairly modest. In the meantime, we have simulated much longer chains, not only in a film geometry, but also in pores of various diameters. A detailed analysis and comparison with the theory will be carried out in the near future.

Chains that do not overlap, but are segregated, display qualitatively different behavior.<sup>[5]</sup> We explored this case for the example of a two-dimensional (self-avoiding) polymer melt. The analysis of conformational properties revealed strong deviations from chain ideality due to the compactness of the chains and the irregularity (fractality) of their border.<sup>[6]</sup> The fractality of the chain border also influences the polymer dynamics and leads to a relaxation mechanism which is faster than Rouse-like motion.<sup>[9]</sup>

### Polymer films at low temperatures: Glass transition and modeling of nanoindentation

#### Cooling toward the glass transition

Numerous experiments have found deviations from bulk behaviour when a polymer film is cooled through its glass transition. One of the most discussed examples of such deviations is the thickness ( $h$ ) dependence of the glass transition temperature,  $T_g(h)$ , of the films. We contributed to this research by molecular dynamics (MD) simulation of supported and freely standing polymer films (generic bead-spring model). The simulations were used to obtain a tomography of the local dynamics in the films, monitored, e.g., through the segmental mode of dielectric relaxation (collaboration with experimental colleagues from Leuven).<sup>[10]</sup> This analysis revealed a smooth gradient of enhanced dynamics near the interfaces (free interface or interface to the smooth substrate) to bulk-like behaviour in the center of the film. The gradient grows on cooling and gives rise, on average, to faster than bulk dynamics, leading to a depression of  $T_g(h)$  in the films, in good agreement with (some) experimental results. This mobility gradient is also an important ingredient of a diffusion model which we developed to describe the simulation results for the solvent evaporation from a polymer film close to its  $T_g$ .<sup>[11]</sup>

#### Modeling of nanoindentation

Scratch resistance is an important mechanical property for surfaces of materials. For polymer surfaces this resistance can be improved by decreasing the local friction or obtaining good recovery after scratching. Scrutiny of the contact mechanics through nanoindentation tests and finite-element modeling is one of the thrust in the PMTP group at the ICS (headed by C. Gauthier).

In collaboration with this group we developed a simulation tool to model nanoindentation in a glassy polymer film by a conical tip (thesis: M. Solar). Following typical experimental protocols (displacement or load control) force-indentation curves on loading and unloading were measured at various temperatures and indentation rates. We found good (qualitative) accord between simulation and experiment,<sup>[12]</sup> suggesting that this feasibility study should be extended to explore the molecular mechanisms determining the scratch resistance of polymer surfaces. We plan to do so in the future.

### Other confined polymer systems

#### Semiflexible macromolecules

Many biological polymers are either rigid (e.g., double-stranded DNA, actin, microtubules) or able to form rigid filaments by self-assembly (e.g., peptide fibrils or fibers). Rigid or semiflexible macromolecules thus constitute an important and extensively studied class of soft materials.

An important model for semiflexible polymers is the wormlike chain (WLC) model characterized by a single parameter, the persistence length. We (collaboration with I. Nyrkova) developed a theory<sup>[13]</sup> for the dynamic light scattering of dilute solutions of the (uniaxial) WLC model and a biaxial extension thereof, characterized by two persistence lengths resulting from an anisotropic cross section of the chain (different stiffnesses are associated with the short and long sides of the cross section). Relevant realizations of the biaxial model include ribbonlike polymers or fibrils. The theory reveals that biaxiality may yield a significant broadening of the relaxation spectrum.<sup>[13]</sup> A nonmonotonous  $q$ -dependence of the dynamic structure factor is found, whose relaxation is also strongly influenced by longitudinal motions of the macromolecules.

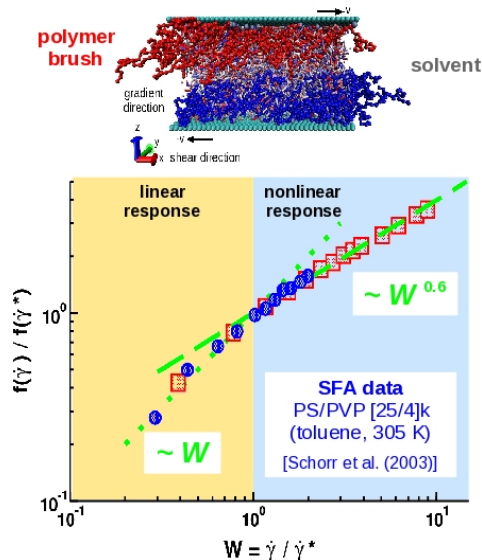
These bulk studies are complemented by work on the dynamics of a single WLC in confined geometry, in narrow pores<sup>[14]</sup> and on a substrate<sup>[15]</sup> hindering free motion through a (disordered or order) array of impenetrable obstacles (thesis: G. Nam; collaboration with N.-K. Lee, Seoul). By theory and Brownian dynamics simulations (of a bead-spring model) it was shown that the confinement leads to deviations from the free chain motion of the bulk. For long chains and strong confinement (i.e., for pore diameters or distances between obstacles much smaller than the persistence length) an intermediate time regime is found where the transverse chain fluctuations are relaxed and longitudinal fluctuations determine the chain motion alone, leading to a  $t^{1/2}$  increase of the mean-square displacement of a monomer.<sup>[14,15]</sup>

#### Grafted chains

In collaboration with the Mcube group at the ICS (headed by C. Marques), T. Gisler (Konstanz) and N.-K. Lee (Seoul) we analyzed the stretching of end-grafted DNA caused by the spreading front of a bioadhesive vesicle (thesis: G. Nam).<sup>[16]</sup> Two chain



conformations were identified experimentally, so-called *tadworms* (DNA fully confined below the membrane) and *tadpoles* (DNA with a stretched part below the membrane and a coiled part outside). A rationale of these distinct conformations is suggested in terms of the presence (*tadworms*) or absence (*tadpoles*) of self-entanglements of the stretching DNA chain (see report of Mcube for further details).



**Figure 2.** Scaling plot of the friction force versus the Weissenberg number ( $W$ ) for two opposing polymer brushes in contact that are subject to a shear force. The squares show simulation results of a bead-spring model (with explicit solvent) and the circles are results from SFA experiments as indicated in the Figure. A crossover from linear to nonlinear response occurs for  $W=1$ . The sublinear increase of the shear force ( $\sim W^{0.6}$ ) in the nonlinear regime can be explained by scaling theory<sup>[17]</sup>

We also explored by MD simulations and scaling theory the shear response of two polymer brushes in contact (thesis: A. Galuschko; ANR blanc 2006, post-doc: T. Kreer). While for small shear rates extremely small resistance to lateral shear is found, a sublinear increase of the frictional force can be observed at large shear rates.<sup>[17]</sup> Our numerical results indicate that the sublinear, non-Newtonian behaviour is related to tilting and stretching of the grafted chains in shear direction and a concomitant decrease of the overlap between the opposing brushes. A scaling theory estimating the viscous dissipation in the overlap region gives good agreement with our numerical results and recent experiments (see Figure 2).

### Polymers and colloids

It is known that a certain amount of free polymer added to a colloidal suspension can enhance its stability. This so-called *depletion stabilization* is not well understood. To elucidate its origin a universal, asymptotically exact theoretical approach has been developed.<sup>[18]</sup> The theory predicts that colloidal particles in a semidilute polymer solution may be kinetically stabilized by a long-range polymer-induced repulsion due to the depletion of chain ends in the middle between two colloidal particles.

When treating the statistical behaviour of (long) ideal polymers near an impenetrable wall or a colloidal particle, the Dirichlet boundary condition is commonly used. This condition implies that the end and total monomer concentrations vanish at the wall. Together with I. Erukhimovich (Moscow) and J.-F. Joanny (Paris) a first-principles statistical mechanical approach was employed to derive the Dirichlet condition and corrections to it.<sup>[19]</sup> The theory suggests that the corrections can become substantial in the case of nano-colloids (the so-called protein limit).

## Self-assembled systems

The group did not only contribute to the axis “*Polymers and Interfaces*”, but also to the axis “*Self-Assembled Systems*”. Self-assembly in soft matter systems is controlled by distinct and often competing factors, among which prominent examples are the amphiphilicity of the building blocks (e.g., copolymers, surfactants) and the anisotropy of chain shape or interactions (e.g., anisotropic rigidity, chirality). These factors do not only yield specific (mesoscopic) structures, but can also lead to unusual structure formation and relaxation processes. Some aspects of these effects are illustrated by the examples below.

### Strongly associating polymer systems

In collaboration with experimental colleagues from Grenoble (M. Rinaudo, R. Auzely-Velty, A. Charlot) the dynamics of associating polymer solutions above the reversible gelation point was studied.<sup>[20]</sup> Each polymer consists of a soluble backbone and a small fraction of strongly interacting stickers (polysaccharides with adamantyl and beta cyclodextrin moieties). The theory elucidates essential features of the rheological behaviour of these systems, including the strong temperature dependence of the characteristic frequency, an extremely strong effect of added free stickers on the dynamics, and the key role played by the randomness of the sticker distribution along the chain, causing marked deviations from Maxwellian viscoelastic behaviour.<sup>[20]</sup>

### Copolymers and similar systems

Finding ways to control the formation of well defined polymer globules or stable aggregates can provide a basis for the development of functional polymeric materials, perhaps with functionalities similar to those found in nature (e.g., as for native folded proteins that are in a stable compact state). In the thesis of E. Maresov a theory of finite-sized aggregates and domain structures in dilute solutions of amphiphilic macromolecules (homopolymers or copolymers) was developed.<sup>[21]</sup> The theory studies a polymer model with two types of chemical groups (insoluble H and soluble P) in the regime where the polymer tends to phase separate. By changing model parameters, like energy or bond length, it was shown that the surface tension at the polymer/solvent interface can be decreased down to zero (or even

below). A low value of the surface tension impedes macroscopic aggregation and favors formation of finite aggregates (so-called mesoglobules).<sup>[21]</sup> The theory thus provides a framework for the explanation of colloidally stable equally sized spherical aggregates observed in solutions of some thermoresponsive homopolymers.

Due to their strong amphiphilic character semifluorinated alkanes, like  $F(CF_2)_{12}(CH_2)_{12}H$  (F12H12), are the molecular analogue of incompatible diblock copolymers. The dynamics of F12H12 that undergoes two condensed phase transitions was investigated (together with experimental colleagues from Germany and Greece).<sup>[22]</sup> A coexistence of solid and amorphous regions in the submicrometer range at thermal equilibrium as revealed by the SAXS was rationalized by a two-stage mechanism for melting of the smectic phase (II) of F12H12.

### Chiral surfactant systems

Surfactant membranes can also occur in unusual forms of twisted strips, helical tapes, tubules or cylinders. Their shape and internal structure is defined by directional interactions (like hydrogen bonds) between the surfactants and by the presence of chiral centers. In collaboration with I. Nyrkova we reanalyzed a (classical) bilayer model proposed to explain experimental results on twisted membrane structures. However, in order to account for these results we found that it is necessary to generalize the model in two directions:<sup>[23]</sup> Multilamellar ribbons and a crystalline state (L-beta) of the bilayers must be taken into account. Then, the predicted multilayer crystalline structure of self-assembling twisted ribbons was found to be consistent with recent experimental results on gemini surfactants. The theory also yields the dependence of the twisted ribbon width and pitch on the degree of chirality (more precisely, on the enantiomeric excess). This dependence is in reasonable agreement with data based on TEM images.<sup>[23]</sup>

### Living polymers

Living polymers are macromolecules that can reversibly change their polymerization degree. Such reversible (equilibrium) polymerization is typical of many systems, such as cylindrical wormlike surfactant micelles, self-assembling dynamic supramolecular structures, etc. An example for living polymers that are out-of-equilibrium are cytoskeletal filaments like actin and microtubules which assemble by hydrolysis of ATP (adenosine triphosphate).

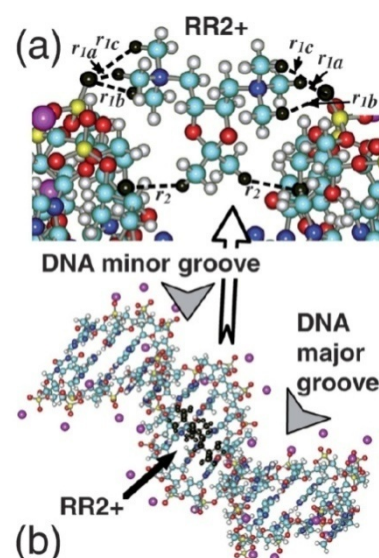
By simulation and theory we explored structural and dynamic features of model systems for living polymers. The simulations focused on corrections to the classical behaviour caused by the interplay of chain connectivity and the incompressibility of the melt, in analogy to those discussed in the section on long-range correlations in melts. They confirm theoretical predictions, suggesting deviations from the classical exponential chain-length distribution

(MWD) and a nonextensive correction to the chemical potential of a chain.<sup>[24]</sup>

The role of correlation effects for the dynamics of living polymers were explored theoretically in collaboration with I. Nyrkova.<sup>[25,26]</sup> In contrast to commonly employed classical models the theory reveals that the stress relaxation of long living polymers is defined by dynamical correlation effects between chain scissions and recombinations: multiple self-recombinations are much more frequent than recombinations with other chains.<sup>[25]</sup> This leads to a strong slowing down of the terminal relaxation process and to nonexponential stress relaxation. Furthermore, living polymerization often requires a transformation of a unimer from an inactive to an active state, typically associated with a large activation energy. For large activation energy living polymerization is a sharp thermodynamic transition, but this sharpness has an important impact on the polymerization kinetics.<sup>[26]</sup> It leads to transient regimes where the MWD is strongly nonexponential and involves two nonlinear modes. This transient regime is long-lived because the terminal relaxation time of MWD increases exponentially with the activation energy.

## Systems inspired by biology

There are also some studies which do not lend themselves to be easily incorporated into the categories of the three axes at the ICS. These studies deal with systems inspired by biology. In the future, we expect to have more activity in this field, also due to the arrival of I. Kulić (CNRS recruitment 2009).



**Figure 3.** Optimized positions of one RR2+ dication near the double-strand poly-AT DNA fragment (the system is neutralized by 28 additional Na<sup>+</sup> cations); the dications are strongly adsorbed in the DNA minor groove. Part (b): View of the molecular arrangement in (a) from above.<sup>[27]</sup>

### Chiral recognition in DNA condensation

In collaboration with I. Nyrkova a theory has been developed,<sup>[27]</sup> which provides a rational basis for a strong chiral discrimination effect recently observed in the collapse of long DNA molecules induced by conformationally rigid divalent enantiomeric cations (SS and RR enantiomers). The theory shows that the DNA binding ability of a di-cation and its compaction activity is anti-correlated: the compaction activity of the less strongly bound SS di-cation is much higher than that of the RR enantiomer (cf. Figure 3). DNA compaction is found to be largely due to bridging by di-cations between neighboring DNA molecules.<sup>[27]</sup> The bridging competes with the adsorption of di-cations onto the DNA surface. The RR molecules tend to replace the SS enantiomers adsorbed on the DNA so that SS compaction ability is significantly reduced in the presence of RR isomers. This provides a basis to explain stereoisomeric selectivity and antagonistic effects in DNA compaction.

### Elasticity of cisplatin-bound DNA

Cisplatin is very successful antitumor drug. It is therapeutically active upon binding to DNA and locally kinks it. In a collaboration with experimental colleagues from Seoul and S. Obukhov it was demonstrated that the degree of platination of a single DNA molecule can be estimated from elasticity measurements.<sup>[28]</sup> To extract this information from the experiment it is necessary to describe cisplatin-bound DNA by two separate persistence lengths provided by the random flight model and an aligned kink model for the low- and high-tension regimes.

### Cytoskeletal filaments

#### Torsional switching in actin

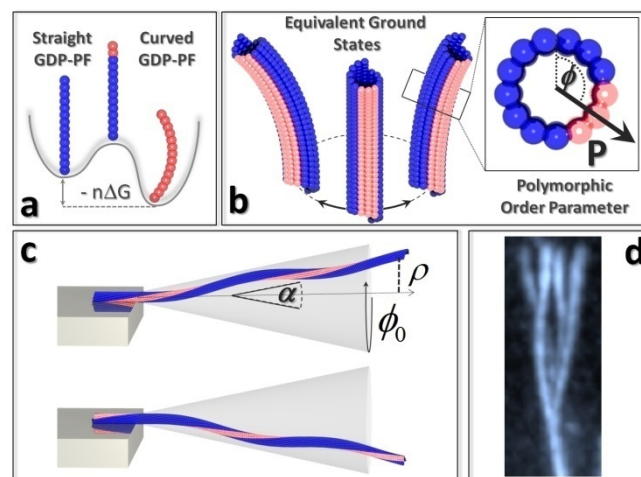
Actin is a globular protein that can assemble (on ATP activation) into helical filaments. In a joint effort with Z. Dogic (U Brandeis, USA) we were able to circularize single actin molecules by confining them to interfaces and observe ring supercoiling dynamics, a new manifestation of actin's torsional polymorphism.<sup>[29]</sup> It was found that when exposed to fluorescence excitation light, rhodamine-phalloidin-labeled actin filaments undergo a change in their natural twist. This photomechanical transition induces a localized small-wavelength supercoiling transition of absorbed actin rings.<sup>[29]</sup>

Upon completion of the photoinduced reaction, the twist of neighboring monomers in an actin filament changes by approximately  $0.26^\circ$ . The implications of actin's polymorphism on cellular structures like actin bundles and the cortical actin network are important future directions of this recently initiated work.

### Polymorphic dynamics of microtubules

Microtubules are the stiffest cytoskeletal component. They consist of elementary building blocks, the tubulin dimers, which polymerize head to tail into linear protofilaments (PFs). PFs themselves associate side by side to form the hollow tube structure known

as the microtubule (MT). Based on the novel hypothesis that the tubulin dimer unit is a conformationally bistable molecule, rapidly fluctuating between a discrete curved and a straight state, we have developed a model for the (polymorphic) dynamics of the MT lattice (see Figure 4).<sup>[30]</sup> It was shown that tubulin bistability consistently explains unusual dynamic fluctuations, the apparent length-stiffness relation of grafted MTs, and the curved-helical appearance of MTs in general. Within our "polymorphic tube model" we made the prediction that, when clamped by one end, MTs undergo an unusual zero energy motion ("Goldstone mode"). Based on all available experimental data and the theory we finally concluded that MTs must exist in highly cooperative energy-degenerate helical states that have likely important implications for the mechanics of living cells.<sup>[30]</sup> The initial suggestion of MT helical polymorphism created a starting point for an activity of G. Nam who is presently performing simulations and analyzing new experiments (by F. Pampaloni and I. Kulić) within the framework of his doctoral thesis.



**Figure 4.** Polymorphic tube model: (a) The tubulin dimer fluctuates between two states : straight / curved. (b) Tubulin switching on one microtubule side leads to spontaneous breaking of symmetry. Combined with the built-in lattice twist a microtubule forms a polymorphic helix. The polymorphic order parameter  $P$  with phase angle  $\phi$  describes the distribution of tubulin states in the cross section. (c) Polymorphic wobbling - the zero-energy motion of the phase angle at each cross-section. It is responsible for the rotation on a cone with opening angle  $\alpha$  when clamped by the end. (d) Anomalous fluctuations of partially surface grafted microtubules from experiment (Nam, Pampaloni and Kulić, in preparation).

**Collaborations in the axis:** C. Gauthier, M. Maaloum.

**Collaborations with other teams in the ICS:** N. Giuseppone, C. Marques, M. Rawiso, T. Schmatko, F. Thalmann.

**Collaborations outside the ICS:** E. Bartsch (Freiburg), K. Binder (Mainz), A. Blumen (Freiburg), S.-H. Chong (Okazaki), Z. Dogic (Waltham), I. Erukhimovich (Moscow), C. Friedrich (Freiburg), M. Fuchs (Konstanz), H. Mohrbach (Metz), S. Napolitano (Leuven), S. Obukhov (Gainesville), N.-K. Lee (Seoul), K. Shin (Seoul), A. V. Subbotin (Moscow), O. Vitrac (Paris), M. Wübbenhorst (Leuven), H. Xu (Metz).

**Active national network:** ANR blanc 2009 FqSimPIB, ANR blanc 2011 VizBioNano (pending)

**Active European network:** IRTG Soft Matter Science (Freiburg/Strasbourg/Mulhouse/Basel)

- [1] P. Beckrich et al., *Macromolecules* **2007**, *40*, 3805.  
 [2] J. Wittmer et al., *Macromolecules* **2010**, *43*, 1621.  
 [3] A. N. Semenov, *Macromolecules* **2010**, *43*, 9139.  
 [4] J. Wittmer et al., *J. Chem. Phys.* **2009**, *131*, 064901.  
 [5] A. N. Semenov, A. Johner, *Eur. Phys. J. E* **2003**, *12*, 469.  
 [6] H. Meyer et al., *J. Chem. Phys.* **2010**, *132*, 184904.  
 [7] N.-K. Lee et al., *Europhys. Lett.* **2011**, *93*, 48002.  
 [8] H. Meyer et al., *Eur. Phys. J. - ST* **2007**, *141*, 167  
 [9] J. Wittmer et al., *Phys. Rev. Lett.* **2010**, *105*, 037802.  
 [10] S. Napolitano et al., *Macromolecules* **2008**, *41*, 7729.  
 [11] S. Peter et al., *J. Chem. Phys.* **2009**, *131*, 014903.  
 [12] M. Solar et al., *J. Phys. D: Appl. Phys.* **2010**, *43*, 455406.  
 [13] I. A. Nyrkova, A. N. Semenov, *Phys. Rev. E* **2007**, *76*, 011802.  
 [14] G. Nam et al., *Eur. Phys. J. E* **2010**, *32*, 119.  
 [15] G. Nam et al., *J. Chem. Phys.* **2010**, *133*, 044908.  
 [16] G. Nam et al., *Phys. Rev. Lett.* **2010**, *105*, 088101.  
 [17] A. Galuschko et al., *Langmuir* **2010**, *26*, 6418.  
 [18] A. N. Semenov, *Macromolecules* **2008**, *41*, 2243.  
 [19] I. Erukhimovich et al., *Eur. Phys. J. E* **2010**, *31*, 115.  
 [20] A. N. Semenov et al., *Rheol. Acta* **2007**, *46*, 541.  
 [21] E. Maresov, A. N. Semenov, *Macromolecules* **2008**, *41*, 9439.  
 [22] E. Nunez et al., *J. Phys. Chem. B* **2008**, *112*, 6542.  
 [23] I. A. Nyrkova, A. N. Semenov, *Soft Matter* **2010**, *6*, 501.  
 [24] J. Wittmer et al., *Eur. Phys. J. E* **2010**, *31*, 229.  
 [25] I. A. Nyrkova, A. N. Semenov, *Europhys. Lett.* **2007**, *79*, 66007.  
 [26] I. A. Nyrkova, A. N. Semenov, *Eur. Phys. J. E* **2007**, *24*, 167.  
 [27] I. A. Nyrkova, A. N. Semenov, *Soft Matter* **2009**, *5*, 989.  
 [28] N.-K. Lee et al., *Phys. Rev. Lett.* **2008**, *101*, 248101.  
 [29] T. Sanchez et al., *Phys. Rev. Lett.* **2010**, *104*, 098103.  
 [30] H. Mohrbach et al., *Phys. Rev. Lett.* **2010**, *105*, 268102.

## Self-Evaluation

The 2008 AERES report identified the following points on which the group should improve:

- 1) There should be a stronger involvement in doctoral and post-doctoral training.
- 2) The interaction with the other activities of the ICS should be reinforced.

There should be more collaborations with experimental groups.

- 3) In the following paragraphs we comment on how we have addressed this criticism during the past years.

### Statement on human resources and financial support

From 2007 to 2011 the group had two CNRS recruitments, O. Benzerara (Ingénieur de Recherche 2007) and I. Kulić (Chargé de Recherche 2009).

#### Ad 1): Doctoral and post-doctoral training

From 2007 to 2011 we supervised 13 PhD theses:

**P. Beckrich:** *Correlation properties of linear polymers in the bulk and near interfaces* (2004-2007)

Advisors: A. Johner, A. N. Semenov

Funding: MESR

Current position: high-school teacher in physics (professeur agrégé) at the Lycée d'Aulnay sous bois (Paris)

**F. Crevel:** *Static and dynamics properties of living polymers in the bulk and thin films* (2004-2007)

Advisors: J. Wittmer

Funding: MESR

Current position: SNCF (Lyon)

**M. Durand:** *Molecular dynamics simulations of oligomer diffusion in polymer melts* (2008-2010)

Advisors: H. Meyer, O. Vitra (INRA, Massy)

Funding: CNRS/INRA (CPR COPOLA)

Current position: training in numerical engineering for radiology

**A. Galuschko:** *Molecular dynamics simulations sheared polymer brushes* (2007-2010)

Advisors: J. Baschnagel, J. Wittmer

Funding: ANR blanc SPBRUSH (2006-2009; coordinator: J. Baschnagel)

Current position: post-doc (Göttingen)

**E. Maresov:** *Statistical physics of self-assembling structures in amphiphilic polymer systems* (2005-2009)

Advisors: A. N. Semenov

Funding: MESR

Current position: post-doc (Pittsburgh)

**S. Peter:** *Structure and structural relaxation of glass-forming polymer films* (2005-2007)

Advisors: H. Meyer, J. Baschnagel

Funding: RTN POLYFILM (2004-2008; coordinator: M. Geoghegan, Sheffield)

Current position: risk management (Vienna)

**M. Solar:** *Molecular dynamics simulations of the normal and tangential contact between a nanoindenter and an amorphous polymer film* (2006-2010)

Advisors: H. Meyer, C. Gauthier (mechanical engineering group)

Funding: Région Alsace

Current position: post-doc (Groningen)

**S. Frey:** *Shear relaxation function and related quantities in glass-forming polymer melts* (2009-)

Advisors: J. Baschnagel, H. Meyer

Funding: MESR (IRTG Konstanz-Strasbourg-Grenoble)

**G.-M. Nam:** *Anomalous elasticity and dynamics of biofilaments* (2009-)

Advisors: A. Johner, I. Kulić; N. K. Lee (Seoul, Korea)

Funding: cotutelle UdS/Seoul

**P. Polinska:** *Rheology of transient self-assemble networks from microemulsions and telechelic polymers* (2010-)

Advisors: J. Wittmer

Funding: Région Alsace (IRTG Freiburg-Strasbourg)

**N. Schulmann:** *Elastic and plastic properties of fibre systems* (2008-)

Advisors: J. Wittmer, T. Charitat (Mcube group)

Funding: Région Alsace

**A. Shvets:** *Colloidal stabilization by unattached homopolymers and copolymers* (2010-)

Advisors: A. N. Semenov

Funding: UdS (IRTG Freiburg-Strasbourg)

**J. Zabel:** *Form factor of poly(isobutylene): molecular modeling for comparison with neutron scattering experiments* (2010-)

Advisors: J. Baschnagel, J. Wittmer

Funding: ANR blanc FqSimPIB (2009-2013; coordinator: J. Baschnagel)

*Comment:* Compared to the previous report period (2003-2007) the number of PhD theses has not

substantially increased (11 in 2003-2007; 13 here). However, contrary to the previous period, all current PhD theses are obtained from external grants (i.e., not from the annual distribution of MESR stipends to the local *Ecole Doctorale*).

In addition to PhD students, the group has also collaborated with post-docs:

**A. Cavallo:** *Corrections to chain ideality in polymer melts and thin films*

Funding: CNRS post-doc (2007-2008; coordinator: J. Wittmer)

Current position: lecturer at the University of Salerno

**T. Kreer:** *Influence of long-range interactions in sheared polymer brushes*

Funding: ANR blanc *SPBRUSH* (2006-2009; coordinator: J. Baschnagel)

Current position: temporary researcher position at the IPF (Dresden)

**I. A. Nyrkova:** *Self-organization in heterogeneous polymer and self-assembling systems*

Funding: DR2 grant CNRS (2007-2009), ANR blanc *DYNABLOCKS* (2009-2011; coordinator: N. Giuseppone)

**F. Ziebert:** *Modeling of late stages of spin-coating / Actin and microtubules*

Funding: IRTG Freiburg-Strasbourg (2010-)

#### Statement on scientific collaborations

##### **Ad 2) Interactions with other ICS activities**

The collaboration with the Mcube group has been intensified (joint supervision of the PhD thesis of N. Schulmann; joint publications, e.g. A2-ACL-94, A3-ACL-5). In the future, this collaboration will still be extended through the work of I. Kulić (micromanipulation of biopolymers) and also involve the group of N. Giuseppone.

Through the thesis of M. Solar we started a collaboration with the PMTP group (headed by C. Gauthier) on the molecular modeling of scratch and nanoindentation tests of glassy polymer films. This collaboration will be continued in the future.

Further future projects involve a collaboration between A. N. Semenov/I. Nyrkova and the SAMS group (N. Giuseppone) on the light-responsive self-organizing supramolecular structures as well as between A. Johner/I. Kulić and T. Schmatko/P. Muller/M. Maaloum on plasmids adsorbed on charged surfaces. With M. Maaloum (coordinator) A. Johner and J. Wittmer submitted an ANR blanc (pending) on *in-situ* visualization of the transport of ring biopolymers on nanostructured surfaces.

##### **Ad 3) Collaborations with experimental groups outside the ICS**

Several of our publications during the last four years were written with experimental groups outside the ICS. Examples involve A2-ACL-21, A2-ACL-55, A2-ACL-94, or A3-ACL-142.

Recently, we extended these interactions, for instance, through the thesis of J. Zabel (collaboration

with M. Dadmun, Knoxville, USA and M. Rawiso, ICS) and in particular through the IRTG Freiburg-Strasbourg (Project A1: C. Friedrich, experiment; J. Wittmer, simulation. Project B3: E. Bartsch, experiment; H. Meyer, simulation. Project B4: E. Bartsch, experiment; A. N. Semenov, theory.)

#### Statement on scientific productions

In the period of 2007 to 2010 we published 63 articles in peer-reviewed journals. Their impact can be estimated by following Wikipédia's definition of the Impact Factor (IF). For instance, the IF of 2010 is defined as the ratio  $A/B$ , where

$B$  = total number of articles of the group published in 2008 and 2009;

$A$  = number of citations in 2010 of all these articles published in 2008 and 2009.

An analysis from the Web of Knowledge gives ("Total" = total number of articles in year X):

Year	2007	2008	2009	2010
Total	23	11	8	21
IF	3.8	2.38	2.24	1.84

*Comment:* The high IF of 2007 can be traced back to a well cited review article published in 2005 (on the glass transition). The IFs of 2008 and 2009 appear to be more representative of the group; they reflect roughly the IFs of journals we publish in (e.g., *Physical Review E*). The IF of 2010 is particularly low, partly due to the fewer numbers of articles in 2008 and 2009, many of which are fairly specialized. In the next years, we expect our IF to increase again, mainly due to the seven *Physical Review Letters* published in 2010 and 2011.

The permanent group members presented our research through talks (46) and posters (8) at national and international conferences. Twenty-seven of the talks were invited. Examples involve invited talks by A. N. Semenov on mesoglobule structures in solutions of amphiphilic polymers (International Conference *POLYFILM*, Sheffield, 2008), by H. Meyer on two-dimensional polymer melts (Conference on Computational Physics, Trondheim, 2010), or by J. Baschnagel on the glass transition in polymer films (APS March Meeting, Portland, 2010).

#### Further professional activities

##### **Teaching activities**

In addition to the regular teaching duties of J. Baschnagel and J. Farago the group has been involved in the following training related activities:

- J. Wittmer organizes the group seminars. These seminars also include presentations by young researchers of the ICS, who have to give talks as a part of their PhD requirement.
- Every fall semester A. Johner (and T. Charitat, Mcube group) taught a course on the statistical mechanics of polymers and membranes in the

Master II programme on *Condensed Matter and Nanophysics*.

- In the same Master programme O. Benzerara (Ingénieur de Recherche CNRS) supervised projects of students doing a practical on numerical modeling in condensed matter physics (4 students in 2009/2010; 6 students in 2010/2011).
- Members of the group taught courses in summer schools. Examples involve lectures on block copolymers (A. N. Semenov; Utrecht 2007, 2010) and on molecular simulations in condensed matter and polymer physics (J. Baschnagel; Azzefoun, 2007; Les Houches 2011).
- In the framework of the IRTG Konstanz-Strasbourg-Grenoble (2001-2010) student workshops were organized in 2007 and 2008 (J. Baschnagel).
- Within the IRTG Freiburg-Strasbourg (2010-2015) a summer school on Soft Matter Science was organized in July 2011 (C. Vergnat, G. Reiter, Freiburg; J. Baschnagel).

#### **Organized workshops, seminars, ...**

From 2007 to 2011 members of the group have been involved in the organization of seminars, workshops, etc. A nonexhaustive list includes:

- J. Wittmer organizes the monthly seminars of the *Consortium of Theoretical Physics of Strasbourg*. He is also a member of the Steering Committee of the Consortium, together with colleagues from neighbor institutes (IPCMS, IPHC) and C. Marques (Mcube group)  
<http://www-ics.u-strasbg.fr/~etsp/seminar/theostras.php>
- Satellite symposium on *Polymers* of the DeGennesDays, Paris, 15-17/5/2008, organized by F. Lequeux (Paris) and J. Baschnagel
- Workshop Challenges and Potential of Polymer Physics, 4-6/5/2011, Schluchsee (Germany) organized by G. Reiter (Freiburg), T. Thurn-Albrecht (Halle), J. Baschnagel  
<http://www.softmattergraduate.uni-freiburg.de>

#### **Coordination of scientific projects**

From 2007 to 2011 members of the group have been involved in the coordination of scientific projects. A nonexhaustive list includes:

- CNRS/Kosef (*Adhesion in polymers and membrane*, 2008) and MAE/NRF (Micro-manipulation and Imaging of cisplatin-DNA and related adducts, 2009-); coordinators: N.-K. Lee, Seoul, Korea; A. Johner
- International Research Training Group (IRTG; Konstanz-Strasbourg-Grenoble) *Soft Condensed Matter Physics of Model Systems* (2001-2010); coordinators: G. Maret, Konstanz, Germany; J. Baschnagel
- IRTG (Freiburg-Strasbourg; Basel, Mulhouse) *Soft Matter Science: Concepts for the Design of Functional Materials* (2010-2015); coordinators: G. Reiter, Freiburg, Germany; J. Baschnagel

#### **Computer resources**

The group has currently good access to local computer resources (about 300 cores) which are managed by O. Benzerara.

In the framework of the CPER agreement (France, Région Alsace, CNRS) a computing cluster for parallelized applications (infiniteband network and around 300 cores reserved for ICS needs) was purchased for all laboratories on the CNRS Cronenbourg campus of the PMNA ("Pôle Matériaux et Nanosciences d'Alsace"). Olivier Benzerara is collaborating with the staff at the IPCMS on the administration and future development of the cluster. The group also uses extensively the natural superconductivity center GENCI-IDRIS.

Olivier Benzerara contributed to the call "Grand emprunt/Equipex" as part of a project led by GENCI ("Equip@Meso"). At the local level, the project shall provide numerical resources for the research groups in the Alsace and their collaborators from outside. This project has been validated (grade A, 10M Euros) and should be operational in 2012. Currently, we collaborate on the choice of the hardware for novel usage in soft matter science (GPU, NUMA, hybrid hardware, ...).

#### **Visiting scientists**

From 2007 to 2011 the group hosted a number of visiting scientists. A nonexhaustive list includes I. Erukhimovich (Moscow), H. Mohrbach (Metz), S. Obukhov (Gainesville), N.-K. Lee (Seoul), A. V. Subbotin (Moscow), O. Vitrac (Paris), and H. Xu (Metz).

#### **Overall statement**

Following the recommendations of the 2008 AERES report the group has strengthened its involvement in training in polymer science, e.g. through organization of seminars, workshops or schools and through lecturing (summer schools/ Master courses). Furthermore, the group has reinforced its collaborations with experimental groups inside and outside the ICS. About 20% of our publications from 2007 to 2011 were signed with experimental colleagues. We expect this percentage to persist in the future, e.g. due to the collaborations within the IRTG Freiburg-Strasbourg and the research of I. Kulić who has both a theoretical and experimental activity.

While the research of the group has had a "transversale" role – it has contributed to two of the existing axes, *Polymers and Interfaces* as well as *Self-Assembled Systems* – in the period covered by the report, there are also projects which involve internal collaborations between theory and simulation. A major one is on corrections to classical behaviour in bulk and confined polymer melts. We intend to pursue this internal collaboration in the future, presumably with a focus on polymer dynamics.

# Physics and Biophysics of Macromolecules at Interfaces (PBMI)

Head of the Group *Mounir MAALOUM*

**Permanent staff:** Prof. Mounir Maaloum (UdS), Dr. Pierre Muller (Chargé de Recherche CNRS), Dr. Pascal Marie (Chargé de Recherche CNRS), Christophe Contal (Technician UdS)

**Non-permanent researchers:** 4 *PhD students* (4 defended): Axel Gromer (2008), A. Pefferkorn (2009), Eric Charault (2007, co-direction), Céline Arnold (2010, co-direction) / 6 *Master students*.

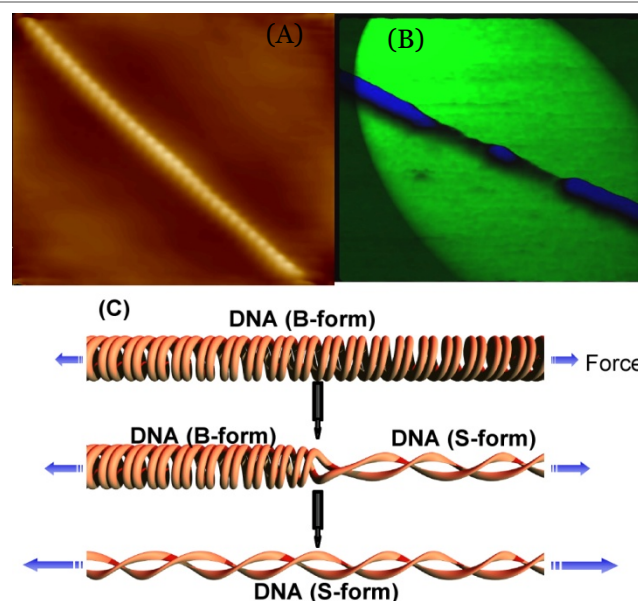
**Keywords:** biophysics · nucleic acids · proteins · polymers at interfaces · physics of single molecules · atomic force microscopy · structure and dynamics of systems of biological interest

## Physics of single biological macromolecules

Our first axis of research has focused on mechanical and structural properties of single biological macromolecules at interfaces. Almost two decades ago, techniques called “micromanipulation of single molecules” (atomic force microscopy, optical tweezers, magnetic tweezers, ...) were developed to study the properties of a single entity. In this work, the elasticity of molecules is studied either as an end in itself or as a probe to inform us about the state of the system at scales too small for observation by optical microscopy. The evolution of the system may be followed with good time and spatial resolution under conditions close to physiological conditions. This type of study is particularly interesting when a measure of a large ensemble of molecules would not give a significant result.

### DNA under stretching

Measurements of force versus extension on isolated double-stranded DNA molecules revealed a force plateau<sup>[1,2]</sup>. This unusual stretching phenomenon in DNA suggests that the long molecules may be extended from the usual B-form into a new conformation. Different models have been proposed to describe the nature of DNA in its stretched form, S-DNA. In this context, we have shown that a non-canonical S-DNA structure (i.e. different from the B-DNA double helix form discovered by Watson & Crick, with diameter of 2.4 nm and helix pitch of 3.4 nm) appears when DNA is stretched in a molecular combing experiment (Figure 1). We provide strong evidence for the existence of a first-order transition between B and S forms<sup>[3]</sup>. The structural analysis of the deformations induced by the stretching force using AFM show that this new conformation corresponds to the tilt and lateral shift of base pairs, reducing the DNA diameter (1.2 nm) and increasing the length of the double helix pitch (18 nm). This new structure could have an interest in biology since many proteins that interact with DNA also strongly distort its structure.

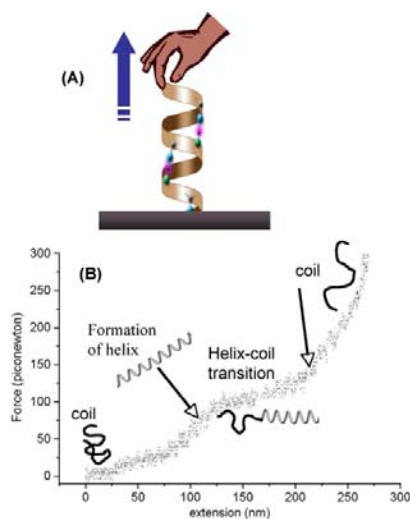


**Figure 1.** A) Double stranded DNA molecules at small extension. The periodicity of DNA helix of 3.4 nm is clearly visible. B) Combed DNA showing the coexistence between two forms of DNA, B-DNA and S-DNA. C) DNA structure model for different applied forces.

### Probing polypeptide using AFM-based force spectroscopy

In this context, we studied the effect of an external force on the helix-coil transition of homopolypeptides, a polymer consisting of a single type of amino acid residues. The variation of environmental conditions, such as pH, lead polypeptide chains to adopt dramatic configurational changes from randomly coiled forms to ordered structures associated with  $\alpha$ -helices. Force *versus* extension curves of homopolypeptides (poly-L-lysine) are obtained using a home made AFM-based force spectroscopy. Two possible transitions were observed during extension of poly-L-lysine depending on pH conditions. Our experimental results have shown that there exists a characteristic force profile of the transition during extension<sup>[4]</sup>. Unconstrained chains are in a coil state for pH below 10, and form  $\alpha$ -helices at higher pH. We have shown that, just below the helix state, i.e. at pH=10 (polypeptide chain is in a disordered state (coil), but close to the transition), the force *versus* end-to-end distance curve exhibits two plateaus associated with the coexistence of helical and coil domains. The lower plateau is due to a tension

induced onset of coil-to-helix transition. The transition allows the polypeptide to compensate for the loss of entropy imposed by the extension by forming hydrogen bonds ( $\alpha$ -helix). The higher plateau corresponds to the melting of the helices back into coils by overextension.



**Figure 2.** (A) Schematic presentation of stretching of a single polypeptide chain. (B) Curve of force versus end-to-end distance when the polypeptide chain is in a disordered state (coil), but close to the transition. Force profile exhibits two plateaus associated to two coexistences between two conformations: helix and coil.

## Physics of polymers at interfaces

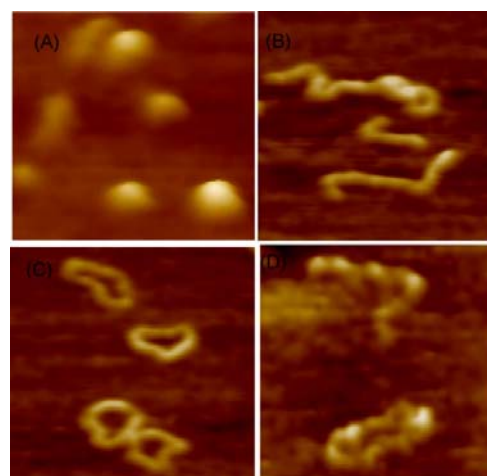
The second axis of our research concerns the study of conformational and mechanical properties of natural and synthetic polymers in a confined space in two dimensions.

### Charged synthetic polymers at interfaces

An important part of this work was to study the conformational change of hydrophobic polyelectrolyte chains (partially sulfonated polystyrene, PSS), linear or ring-shaped, in two-dimensions using AFM in solution. These experiments have measured the persistence length of PSS as a function of ionic strength of the solution. In parallel, AFM imaging allowed to visualize these polymer chains after adsorption onto a surface. These measurements nevertheless pose the question of correspondence between the conformation of PSS in the bulk and the conformation on surface. PSS chains were adsorbed on two types of surfaces: mica, and phospholipid bilayers made of mixed neutral and cationic lipids. We showed that the chains with a low charge density (32%) are collapsed in spherical globules while highly charged chains (67% and 92%) are fully extended. At an intermediate fraction of charge (60%), a pearl necklace conformation has been observed as predicted by theory<sup>[5]</sup>.

End-to-end distances and contour lengths of the extended chains were measured<sup>[5]</sup>. We showed that for fully charged polymers (100%) using the worm-like

chain model (WLC) the conformation of the chains corresponds to 2D thermodynamic equilibrium with a persistence length of the chain of 12 nm, which is comparable to that in 3D in very dilute solutions. Statistical analysis shows also that the persistence length of these chains depends on the surface where they adsorb. On lipid bilayers, highly ordered monolayers of polymers are formed upon increase of the proportion of cationic phospholipids<sup>[5]</sup>. These results show that highly charged PSS chains behave in a similar manner than the stiffer, hydrophilic DNA when adsorbed on surfaces. It could lead to the design of new types of nanostructured surfaces using polyelectrolyte molecules synthesized with specific properties.

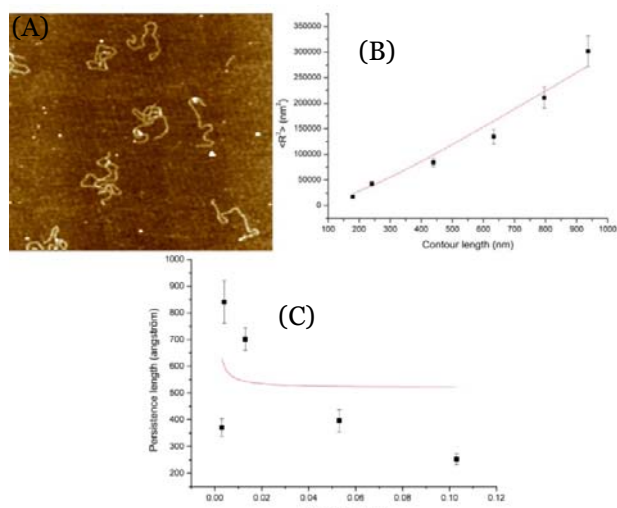


**Figure 3.** AFM images of PSS in solution. (A) PSS chains with 40% of fraction of charges. The chains adopt a globular conformation. (B) Fully charged PSS chains. The chains are extended on the surface. (C) PSS chains in form of ring (100%). (D) At intermediate fraction of charge (67%) a pearl necklace conformation is clearly visible (image size: 100 nm x 100 nm).

### DNA molecules at interfaces: conformational and mechanical properties

Using atomic force microscopy in solution, we performed measurements of the persistence length of DNA molecules at interfaces. We found very good agreement between the worm-like chain model and experimental data<sup>[6]</sup>. However, the measured persistence length values in solution differ from those found by several authors using the same technique but in air. In order to determine the contribution of the electrostatic persistence length to the total persistence length of DNA, we varied the salt concentration. We have shown that there is a large discrepancy between the Odijk, Skolnick and Fixman theory and our measurements<sup>[4]</sup>. This discrepancy can be explained either by the effect of divalent ions or by the possible omission in the theory of the dependence of non-electrostatic persistence length on salt concentration. In fact, divalent ions can interact specifically with DNA bases causing the instability of the double helix, which contradicts the previously accepted role of cations in stabilizing DNA. These interactions involve a change in the intrinsic mechanical bending of the DNA chain.





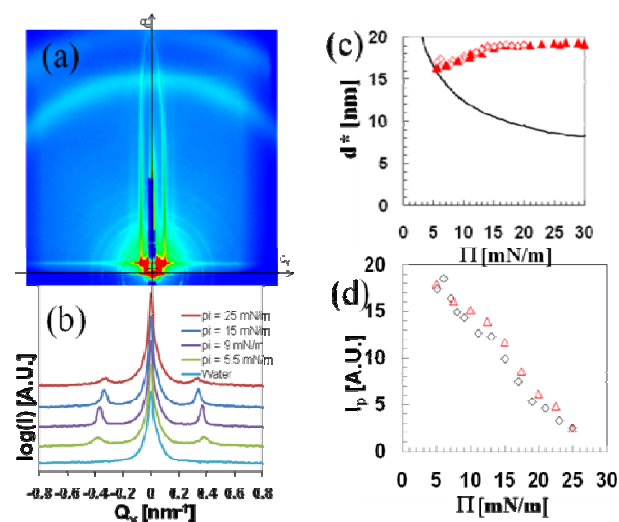
**Figure 4.** A) AFM image of double stranded DNA molecules in solution. B) Graph obtained when we plot the mean square value of the end-to-end distance as a function of the contour length. The fit (solid line) corresponds to the worm like chain model in 2 dimensions with the *persistence length* as fitting parameter. C) Values of the persistence length for different ionic strength of the solution. The full line corresponds to the Poisson-Boltzmann theory for a uniformly charged cylinder. The Figure shows clearly a large discrepancy between experimental data and theory.

### Diblock copolymer at interfaces

Using Langmuir-Schaefer methods, we analysed the behaviour of a model hydrophobic surface (polystyrene) by coating a monolayer of a polystyrene-block-poly acrylic acid (PS-b-PAA) by water droplet contact angle measurements. While it is indeed possible to achieve hydrophilization of a hydrophobic surface using this method, it should be mentioned that this only happens at the highest possible deposition surface pressure, and needs a careful treatment after Langmuir-Schaefer deposition to get reliable results. At lower surface pressure for deposition, the treated surface displays a huge hysteresis between advancing and receding contact angle, which could be explained by the presence of patterns at the surface, probably caused by surface micelles. The surfaces treated at the highest surface pressure are much smoother.

These observations of surface micelles at low deposition pressure and their absence at higher pressure on the solid surface lead us to wonder about the origin of those surface micelles. To elucidate this question, we used grazing incidence small-angle X ray scattering (GISAXS) directly at the air-water interface within a Langmuir trough at NSLS synchrotron at Brookhaven on line X22B.

Thanks to this technique, we were able to show that the PS-b-PAA monolayer displays an interference signal at intermediate surface pressure due to long range ordering of surface micelles.<sup>[5-11]</sup> Moreover, we found that those surface micelles do reorganize upon monolayer compression (whereas bulk micelles of PS-b-PAA are frozen). This surprising fact can be understood by the much smaller energy difference between surface micelles and isolated copolymers at the air-water interface, which leads to a faster reorganization of the micelles. At high pressure, the surface micelles disappear to form a uniform polymer brush.



**Figure 5.** a) GISAXS image of PS-PAA monolayer at 6 mN/m. b) Evolution of the interference peak in function of the surface pressure. c) Evolution of the distance between micelles. Full line: expected behaviour for frozen micelles. d) Evolution of the peak intensity per copolymer chain showing a loss of the order for a pressure greater than 30 mN/m.

- [1] S.B. Smith, Y. Cui, C. Bustamante, *Science* **1996**, *271*, 795–799
- [2] P. Cluzel, A. Lebrun, C. Heller, R. Lavery, J-L. Viovy, D. Chatenay, F. Caron, *Science* **1996**, *271*, 792–794
- [3] M. Maaloum, A-F. Beker, and P. Muller, *Phys. Rev. E*, **2011** *83*, 031903.
- [4] M. Maaloum, R. Lévy, P. Muller, *submitted (2011)*.
- [5] J A. Gromer, M. Rawiso and M. Maaloum, *Langmuir* **2008**, *24* (16), 8950-8953.
- [6] J S. Mantelli, P. Muller, S. Harlepp and M. Maaloum, *Soft Matter*, **2011**, *7*, 3412-3416.
- [7] M. Jacquin, *et al. Macromolecules*, **2007**, *40*, 2672-2682
- [8] M. Jacquin *et al. J. Coll. Int. Sc.*, **2007**, *316*, 897–911
- [9] M. Jacquin *et al.*, *Langmuir*, **2007**, *23*, 9939 – 9948
- [10] P. Muller, G. Sudre and O. Théodoly, *Langmuir*, **2008**, *24*, 9541 – 9550
- [11] O. Théodoly, M. Jacquin, P. Muller and Sophie Chhun, *Langmuir*, **2009**, *25*, 781-793
- [12] O. Théodoly, A. Checco et P. Muller *EuroPhys. Lett.* , **2010**, *90* 28004
- [13] M. Jacquin, P. Muller, H. Cottet and O. Théodoly, *Langmuir*, **2010**, *26* (24), 18681–18693

## Self-Evaluation

In early 2010 we have set up a new research group named “Physics and Biophysics of Macromolecules at Interfaces” (PBMI) composed of 4 permanent members (one Professor, two CRs and 1 technician). The set up of this new group is established following the retirement of several members of the former team (E. Pefferkorn, R. Zana, F. Candau). Also two researchers in the former team have integrated other groups. The team has therefore initiated a reorientation of its research activity comprising the broad field of “Soft Matter” with a special interest in the physics of polymers and biopolymers, such as nucleic acids and proteins, at interfaces and at the single molecular level.

The 2008 evaluation of the AERES has stated the following points on which the team should improve:

1. *The production of the former group over the last 4 years is still relatively fragmented, probably reflecting its history.*

2. The volume and the number of publications are insufficient in proportion to the resources mobilized.  
3. The impact factor has been decreasing steadily since 2004.

In the following statements, we comment on how our group has addressed these criticisms in the past years.

#### Statement on human resources

During the 2007-2011 period, the PBMI group has recruited 4 PhD students (for 2 HDRs) and 6 Master students. The PhD students have performed their defense. Three of them have found post doc positions and one of them is researcher-dentist.

#### Statement on financial supports

☞ ANR blanc MultiSelf (2011) (600 k€, 2011-2015) (Partner)

☞ We have obtained 50 k€ from the Alsace region (2011) for the development of scanning probe techniques.

☞ We have also obtained two Ukrainian Master student grants from Strasbourg-Kiev Master cooperation (2011).

#### Statement on scientific collaborations

**Internal Collaborations in the ICS:** We are tightly collaborating with the SAMS group (N. Giuseppone, E. Moulin, G. Fuks), the PMC group (J-F. Lutz) and the TSP group (A. Johner, J. Wittmer, A. Semenov).

During the past years, our team has enhanced the use of AFM techniques like force spectroscopy and imaging mode in liquid. These techniques have become indispensable characterization techniques for all research teams within ICS and for research teams outside the ICS.

**Collaborations in Strasbourg:** We have collaborated B. Doudin (IPCMS) on Multi-functional memory elements using supramolecular self-constructing interconnects (ANR project) and S. Harlepp (IPCMS) on the study of DNA-protein complexes using single molecule manipulation (AFM and optical tweezers).

**National and international collaborations:** Thanks to the IRTG network between Strasbourg and Freiburg, we started collaboration with E. Bartsch (Albert-Ludwigs-Universität Freiburg, Germany) and A. Semenov (ICS) on the stabilization of colloids by unattached homo- and copolymers. Other international interactions were developed during the past years with Rhodia-Bristol (Pennsylvania, USA) on diblock copolymers at interfaces. Recently, we have established links with H. Hörber (Bristol, UK) on the photonic force microscopy applied to biology.

#### Statement on scientific productions

In the period of 2007-2011 we published 21 articles in peer-reviewed journals. Here are some indicators from the ISI Web of knowledge on the scientific production of the PBMI team on the 2007-2011 period.

☞ Number of articles – **21**

☞ Journals – Macromolecules/Soft Matter/Langmuir/Physical Review/Angewandte Chemie International Edition/Journal of Polymer Science/Dental Research.

☞ Average impact factor of the journals

Year	2007	2008	2009	2010
Average impact factor	3,675	3,751	3,898	5,439

☞ Average number of citations per article (published in the group on the period 2007-2010) – **6,47**

*Comment:* Following the recommendation of 2008 AERES report the average impact factor of journals increases each year. This great evolution of the impact factor of the journals can only reflect the quality of research in our group.

#### Further professional activities

In addition to the regular teaching duties of M. Maaloum the team has been involved in the following professional activities:

- P. Muller taught courses in the “Licence” life sciences.

- M. Maaloum taught courses in summer and thematic schools (European school “Physics of living matter”, Strasbourg, Scanning probe spectroscopy in biology, Summer school “Chirality in Biology”, “Transport in complex systems”, Saarbrücken, Germany).

- We have taken in charge new courses in physics of soft matter, biophysics and biomaterials in Dental Faculty in Strasbourg.

- M. Maaloum: consultant of the company Capsugel Alsace for two years (2009-2010).

#### Overall statement

Following the recommendation of the 2008 AERES report the group has regenerated and established a new team focusing its work on a smaller number of themes, with as the principal axes: polymers at interfaces. Research in the team has focused in recent years on problems in biophysics with direct relevance for biology, where the team has successfully exploited its expertise in applying physical techniques to the study the self-assembled systems at surfaces and interfaces.

Despite its size, the group is very active and benefits from strong internal collaborations. All groups of the ICS benefit from the expertise of the PBMI team in scanning probe techniques (three AFM instruments, in spectroscopy and imaging modes with controlled environment).

In addition to the further investigation of polymers at interfaces, the group is starting a number of new projects for the future, which are all challenging, novel, biologically interesting, and in some cases completely different from its activities thus far. Examples are *i*) identification the role of Tau proteins in DNA protection in the Alzheimer disease *ii*) the combination of single molecule near-field force techniques with conductivity measurements to be able to combine force information with electronic property in self-assembled systems. This last experiment is technically very challenging, but the group has exactly the right (and unique) expertise that is required to bring the experiment to a successful end.

We are confident that the research plans of the team will produce successful and innovative results in the future, keeping up the high impact factor in journals and standard of scientific achievement.

# Physics-Mechanics and Tribology of Polymers (PMTP)

Head of the Group *Christian Gauthier*

**Permanent staff:** Damien Favier (Instrumental Engineer CNRS) Prof. Christian Gauthier (Full Professor UdS), Dr. Vincent Le Houérou (Assistant Professor UdS), Dr. Hervé Pelletier (HdR 2011) (Assistant Professor INSA Strasbourg) 2006, Dr. Anne Rubin (Assistant Professor UdS) 2009, Dr. Robert Schirrer (Research Director, retirement 2010), Dr Thierry Roland (Assistant Professor INSA Strasbourg), XX Characterization Engineer CNRS >2011

**Non-permanent researchers (2007-2011): 5 Post-doctoral associates:** Thibaud Chatel (2009-2010), Eric Charrault (2007-2008), Anne-Lise Durier (2008-2009), Leandro Jacomine (2010-2012), Mathieu Solar (2009-2010)  
**6 PhD students:** Thibaud Chatel, (100% C. Gauthier, defended November 2010), Eric Charrault (50% C. Gauthier – 50% P. Marie, defended December 2007), Eleonora Grespan (V. Le Houérou 50%, G. Reiter 50%, since 2011), Joseph Lejeune (C. Gauthier & H. Pelletier 50%, R. Mulhaupt 50%, since November 2010), Muhamad Mansha (100% C. Gauthier, defended autumn 2011), Mathieu Solar (50% C. Gauthier – 50% H. Meyer, defended May 2010)  
**Master students:** three M2 Matériaux (duration, 3 months), three M2 Ingénierie & Technologie (duration, 5 months), six M1 Matériaux (duration, 2 months)  
**Bachelor students:** three training period (less than one month)

**Keywords:** Contact mechanics · damage · scratching · indentation · friction · coating · micro and nano scales

## Presentation

The group studying the physical mechanics of solid polymers and tribology currently focuses the research essentially on *i*) the mechanical properties of polymeric surfaces (friction, scratching, indentation, wear), *ii*) the mechanisms of damage (cracking, crazing, blistering of coating, creeping and self healing of imprint), and *iii*) the mechanical properties of soft matter (dynamic interfacial adhesion, high friction coefficients).

During the last four years, we have collaborated with many groups inside and outside the institute to develop some original analysis of the surface behaviour of various polymeric systems: physics of confined polymers (J. Baschnagel & H. Meyer, ICS), tribology of PEEK coating (P. Kekicheff & P. Marie, ICS), relationship between adhesion and friction (P. Marie, ICS), surface properties of latex (Y. Holl, ICS), scratch behaviour of photoreticulated coating (C. Crouxte-Barghorn, DPG-UHA), experiments of contact mechanics (M.C. Baietto, LaMCoS, INSA Lyon),...

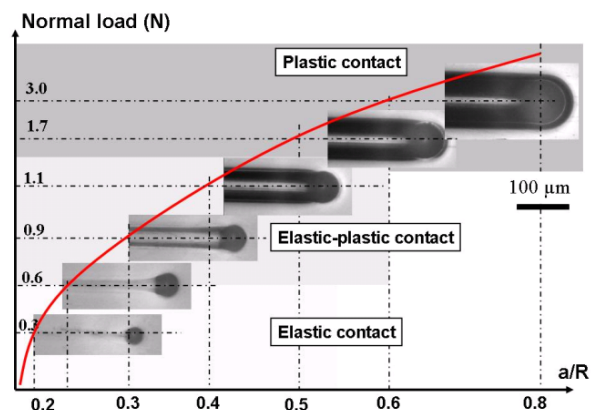
The research of the last four years is easily ordered in three areas. For each of them the following presentation will give some highlights.

## Scratching analysis

### Competition between true local friction and geometrical contact strain

Using our experimental scratch device, we are able to observe *in situ* and as a function of the experimental parameters (normal load, tip geometry, temperature, sliding velocity) the evolution of mechanical behaviours during scratch experiments on amorphous polymeric surfaces, as depicted in Figure 1<sup>[1]</sup>.

Our different studies on various polymeric surfaces have shown that these tests are controlled by the imposed elastic-plastic strain, in terms of the maximum value and size, but also its localization through depth beneath the moving tip. Using finite element modeling<sup>[2,3]</sup>, we have shown for different rheological parameters the influence of the local friction coefficient, as shown in Figure 2.<sup>[4,5]</sup>



**Figure 1.** Mechanical transition from elastic sliding to fully plastic scratching observed during experiments with increasing applied normal load for PMMA and friction coefficient  $\mu=0.2$ .

We have proposed a generalized function, describing the evolution of the representative strain during indentation and scratch experiments, depending on the geometrical strain defined as the ratio between the contact radius and the radius of the tip ( $a/R$ ) and the local friction.<sup>[6]</sup> Note that the geometries of the contact and the residual groove left on the polymeric surface are directly related to this defined representative strain.<sup>[5,7]</sup>

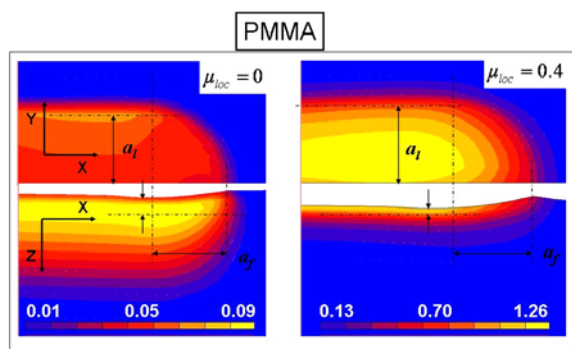


Figure 2. Equivalent plastic strain maps as computed by simulation for  $a/R=0.2$  with  $\mu_{loc}=0$  and  $\mu_{loc}=0.4$  in PMMA.

### Scratch damage of uncoated material

By coupling experimental observations and advanced finite elements modeling, we have investigated the scratch behaviour of a thermoset solid polymer exhibiting brittle behaviour. The 3D crack pattern, formed at the rear part of the contact and in the residual groove, due to the high tension stress during the scratch tests, has been analyzed using fluorescence confocal microscopy (Figure 3). Using our finite element modeling, the distributions of the normal contact pressure and the interfacial shear stresses in the contact area at the sample/indenter interface have been computed and used as input data for the 3D crack network analysis based on combined 3D localized multigrid and X-FEM/level set techniques.

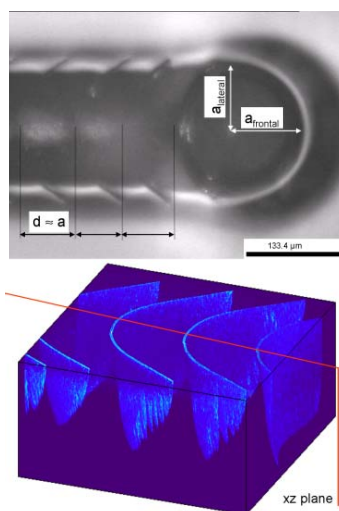


Figure 3. In-situ photograph of CR39 damage. Cracking appears near the rear edge of the contact area,  $a/R = 0.8$  (left). 3D crack pattern reconstruction from confocal microscopy. The surface fracture is roughly a part of a cylinder (right).

The fracture process responsible for the crack pattern formation was identified as a complex 3D unloading/reloading process, predominantly driven by mode I. Furthermore, a failure strength around 90 MPa was estimated (Figure 4 and 5). It is the value reached by the computed tensile stresses at the rear edge of the contact area for a distance between the last crack and its rear equal to the measured distance between two consecutive actual cracks.<sup>[8]</sup>

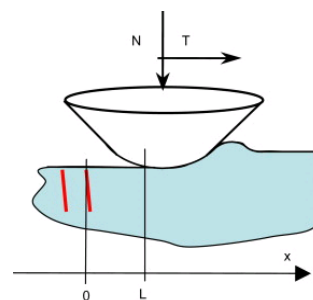


Figure 4. Reloading length  $L$  between the crack mouth of the last crack of the network and the rear edge of the contact area.

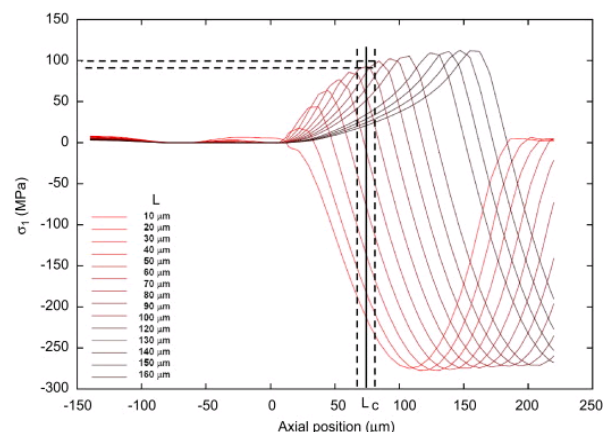


Figure 5. Computed  $\sigma_1$  profiles along  $z=0$  versus the axial axis  $x$  for different values of  $L$  ranging from 10 to 160  $\mu\text{m}$  between the last crack and the rear edge of the contact area.

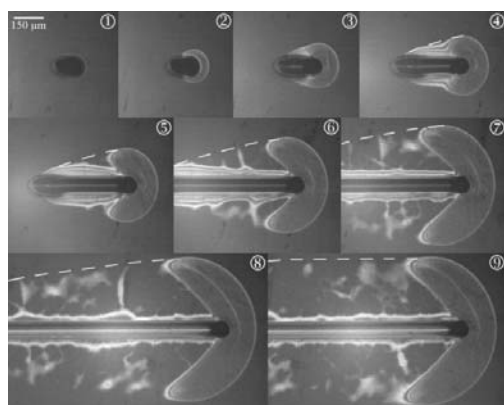
### Scratch damage of coating

The scratch resistance of coatings is a key feature of surface durability. As a consequence, the damage of such a system has to be explored. In particular, the substrate/thin film adhesion must be well controlled and measurable.

Using our experimental scratch device, allowing *in-situ* observation of the scratch, the fracturing of some thin coatings deposited on various substrates were investigated under different conditions of temperature and scratching speed. A collection of fracture mechanisms were observed,<sup>[9]</sup> depending on these two variables. A global energy balance model<sup>[10]</sup> of the stable blistering process (see Figure 6) which is obtained for some experimental conditions permits one to determine the adhesion of the system. The adhesion can be measured by following the delaminated area (quantified by image analysis) as a function of the scratching distance during blistering.

The adhesion corresponding to different substrate/thin film systems was derived using the global energy balance model and thanks to Finite Element (FE) modeling.

The study of similar films with different thicknesses proved that some confinement effect occurs and led to discuss the results with regard to the probe properties, size and roughness.



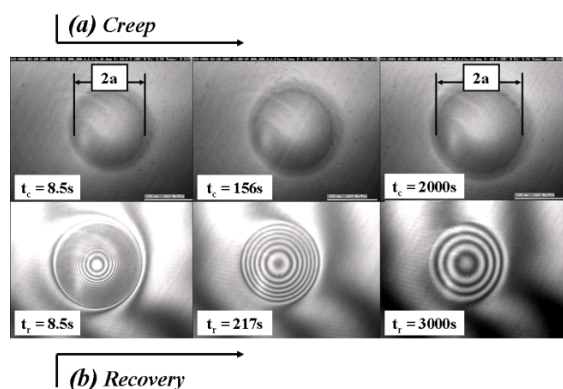
**Figure 6.** Full sequence of the crescent blister growth during scratching of the material with 10 μm/s scratching speed and a temperature of 90 °C. The labels ① to ⑩ chronologically number the pictures. The dashed lines indicate the part of the thin film which has stuck back onto the substrate.

### Creeping and recovering of the imprint

We have developed, for the first time, the analysis of the creep and the recovery occurring in an amorphous polymer during indentation and scratching (Figure 7), characteristic of the self healing performances of the material. The influence of the temperature, initial imposed strain and creep duration were analyzed. In the case of indentation, the evolution of the true contact area versus the time was studied and we demonstrated a non-linear behavior of the amorphous polymer during both creep and recovery phases. The results are confronted to the viscoelastic model of Lee and Radok and the non-linear viscoplasticity is only found for reasonable initial mean contact. The creep tests realized permit to show two non-linear relationships: the first is a non-linear viscoelastic behavior, identified by its difference in viscoelastic model of a contact, but whose evolution is linear with the logarithm of time, and the second is a non-linear behavior evolving non-linearly with the logarithm of time.

The study of the recovery permits to obtain information on the healing behavior of a residual imprint. When the creep phase is linear and follows the model of Lee and Radok, the recovery obtained is linear, whatever the applied holding time. For a non-linear behavior during the loading phase, it is possible to obtain a complete healing or non-linear with the onset of permanent strain.<sup>[1]</sup>

In case of scratching, the sliding speed plays the role of the loading time and the friction coefficient is an important parameter. Friction coefficient, mean contact strain, and sliding speed have the same influence on the possibility for the groove left on the surface to recover. The viscoelastic bulk behavior is identified from compressive relaxation test and an attempt was made to simulate these mechanisms using FE simulations. One of the major results is that the self healing may appear, even if the matter is yielded during the contact. Two conditions are identified: the size of this volume yielded must be smaller than the contact radius and not located at the surface but in the subsurface volume.

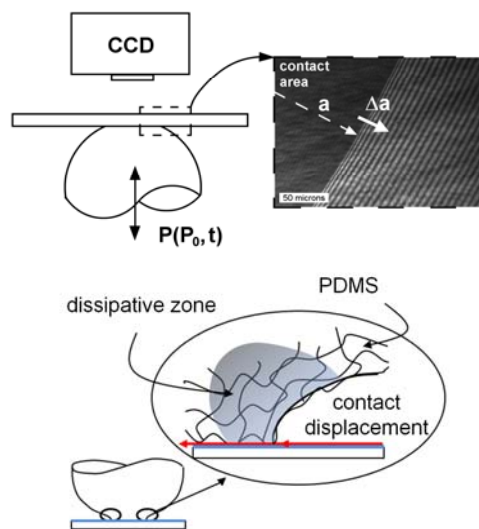


**Figure 7.** In situ observations of the contact area (a) during the creep and (b) of the residual imprint during self-healing as a function of (a) the creep time and (b) the recovery time, during indentation of a spherical probe head into a PMMA surface

## Adhesion and friction

### Adhesion and friction of soft matter

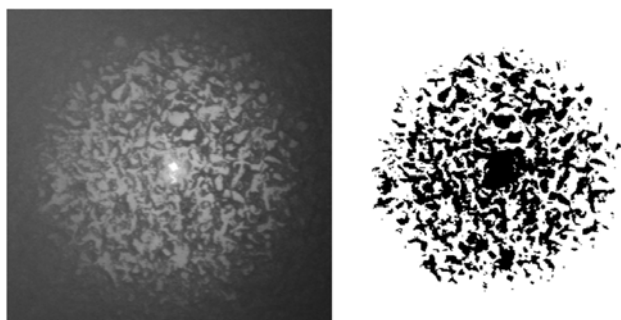
The major difficulty in the analysis of adhesive contact between viscoelastic solids is to separate the surface and bulk energy dissipations. The JKR test is one of the most popular adhesion tests that involves the contact between a sphere and a flat surface. It consists in measuring the energy release rate that is required to decrease the contact area between the two bodies.



**Figure 8. Top:** Experimental “dynamic JKR” device. The applied load  $P$  and the radius of contact  $a$  are measured. **Bottom:** The circled zones indicate where the energy dissipation occurs during the unloading of a PDMS lens in contact with PDMS deposited on a rigid substrate as the crack advances.

We built an original “dynamic JKR” apparatus (see Figure 8) to analyze the energy dissipated (surface and volume) during a visco-elastic adhesive JKR contact between a flat surface and an elastomeric sphere submitted to an oscillating normal load. The evolution of the adhesion hysteresis as a function of temperature and frequency shows results in accordance with bulk properties.<sup>[12]</sup> The profiles of the near contact are assessed through image analysis of interferometric fringes and validate the previous discussion. The size of the dissipative zone was explored through different considerations<sup>[13]</sup>: *i*) activation energy involved in the

deformation and *ii*) independence of results of the height of the spherical cap in contact. It appears clearly that the dissipative zone is restricted to the very close vicinity of the contact, according to theoretical results published recently. This better understanding of adhesive viscoelastic contacts permits to consider the rough sliding contact of soft matter. A particular effort was provided to set up image an analysis in order to quantify the characteristics of the contact area as a function of temperature, sliding speed and bulk material properties (see Figure 9). Even though trends have already been, this work is still in progress.

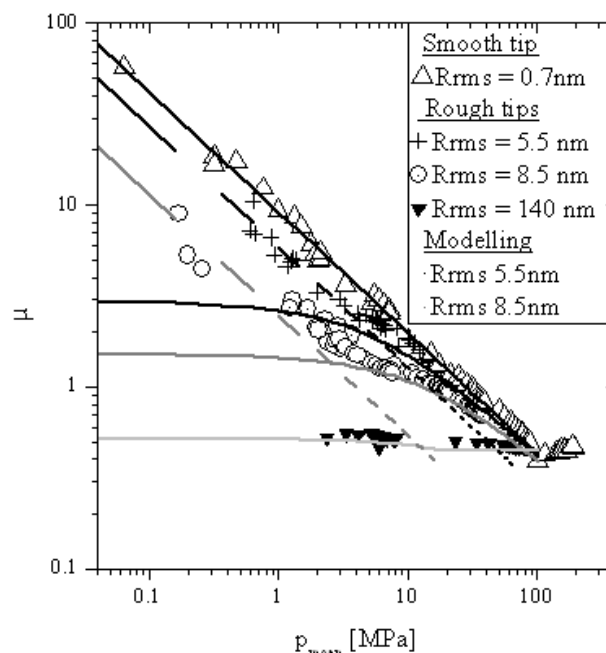


**Figure 9.** In-situ visualisation of the rough sliding contact of soft matter (PDMS) and its treated corresponding image.

### Friction of solid polymer

During the sliding friction between a rigid tip and a glassy polymer energy dissipation occurs in the polymer bulk and at the surface due to local interfacial scission. The interfacial rheological behavior of the polymer depends on the mean contact pressure (i.e. the macroscopic contact scale) and on the tip roughness (i.e. the local scale). In order to decorrelate these parameters an important experimental study was performed on glassy polycarbonate surfaces with spherical indenters. Figure 10 shows the intrinsic true friction coefficient  $\mu$  versus the mean contact pressure  $p_{\text{mean}}$ . Results show first that below the yield stress ( $p_{\text{mean}} < 100 \text{ MPa}$ ) the intrinsic friction coefficient follows a master curve for smooth indenters ( $\Delta$ ). In a second step roughened indenters were realized using chemical etching (fluorhydric acid) which allows monitoring the nanoroughnesses parameters. From 5.5 rms nm to 140 rms nm the friction coefficient  $\mu$  progressively falls to a plastic-like constant value (fig. 10 – ( $\Delta$ )  $R_{\text{rms}} = 0.7 \text{ nm}$ ; (+)  $R_{\text{rms}} = 5.5 \text{ nm}$ ; ( $\circ$ )  $R_{\text{rms}} = 8.5 \text{ nm}$ ; ( $\blacktriangledown$ )  $R_{\text{rms}} = 140 \text{ nm}$ ). This gives the basics to study confined polymer layers.

To explain these experimental results an original modeling was developed (Figure 10 – color lines). Considering our statistical nano-roughness geometries, two domains emerged. Discrete contacts occur at low mean contact pressure ( $p_{\text{mean}} < 4 \text{ MPa}$ ) whereas continuous contact occurs at intermediate pressures ( $4 \text{ MPa} < p_{\text{mean}} < 100 \text{ MPa}$ ). The latter is characterized by a mixtures law between macroscopic mean contact pressure and local pressure due to the nano-roughnesses. As far as we know, this modeling is a premiere.<sup>[14]</sup>



**Figure 10:** Experimental friction coefficient  $\mu$  versus mean contact pressure  $p_{\text{mean}}$ . Curves obtained during sliding and scratching tests with spherical lenses on rejuvenated PC surface ( $v=30 \mu\text{m/s}$ ,  $T=30^\circ\text{C}$ ) – ( $\Delta$ )  $R_{\text{rms}} = 0.7 \text{ nm}$ ; (+)  $R_{\text{rms}} = 5.5 \text{ nm}$ ; ( $\circ$ )  $R_{\text{rms}} = 8.5 \text{ nm}$ ; ( $\blacktriangledown$ )  $R_{\text{rms}} = 140 \text{ nm}$ .

## Molecular analysis of the nanocontact

Mechanical analysis of normal and tangential contact, using Molecular Dynamics (MD) simulations have been made (Figure 11). MD simulations have the advantage of a microscopic thermodynamic formulation, which is more appropriate to study the local physics of a phenomenon, i.e. in our case the rheology of the material confined under the tip.

During this work done in collaboration with the TSP group, conical indentation on amorphous polymer surfaces was simulated at various conditions and the results are qualitatively compared with experimental data coming from tests on epoxies of various glass temperatures, and show good agreement.<sup>[15]</sup> Subsequently, scratch tests with a conical tip on amorphous polymer surfaces were simulated at various temperatures, roughnesses of the tip, interactions between the tip and particles of the polymer film and last, various scratch velocities. The local friction coefficient for the different investigated contact conditions was calculated by studying the apparent friction and the contact asymmetry. The results are in good agreement with experimental data coming from tests on classical polymer surfaces at micron scale.<sup>[16]</sup>

Bond orientation, chain configurations and the stress field were also analysed during tangential contact using MD simulations. The study of the second Legendre polynomial in small domains (allocated around the tip) gives the bond orientation inside the

polymer film during the sliding of the tip. Moreover, the study of the gyration tensor in small layers inside the polymer film reveals the configuration of the polymer chains around a fixed axis of inertia. Last, the “structural dynamics” of polymer films was investigated at the interface between the tip and the polymer film. This work argues in favor of Briscoe’s hypothesis of a small sheared layer surrounding the moving tip during a scratch test.

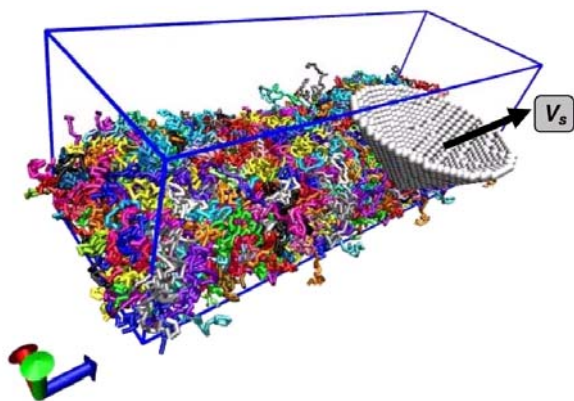


Figure 11. Molecular Dynamics simulation of a nanoscratch test with a rough conical tip on a polymer film

A comparison between MD simulation and a Continuum Mechanics (CM) approach was also made. One-dimensional mechanical behavior of a polymer box sample is studied using the MD simulations. The results are in good agreement with experimental data, and mechanical properties are computed from the MD simulations. This one-dimensional mechanical behavior was implemented in simulations with continuum mechanics approach through an elasto-viscoelasto-viscoplastic constitutive law. The mechanical response of a polymer film during an indentation test modeled with the MD simulations is then compared to the one modeled by the FE simulations using the previous constitutive law. The comparison between the MD and CM simulations was promising, though not perfect. Furthermore, the comparison provides guidelines to transpose the results of MD simulations (LJ units) to CM simulations (SI units).

## Instrumental development and licence transfer

One of the specificities of the group is to develop original devices which allow us to record mechanical information without being model dependent.

To study the creep and recovery behavior of polymer surfaces, i.e. to analyse the self-healing of the imprints left on the surface and of the grooves left after the contact phase, we have updated our “microvisioscratch” and added a new set-up and new driving mode (Figure 12). This device allows *in-situ* observations of the contact area during tests and determination of

the true contact geometry, without the need of any intermediate model. After the creep phase, the indenter takes off the surface and a glass blade slides over the residual imprint. The resulting interference fringes permit to analyse the depth of the imprint. So the volume of the residual imprint during recovery phase can be described as a function of recovery time.

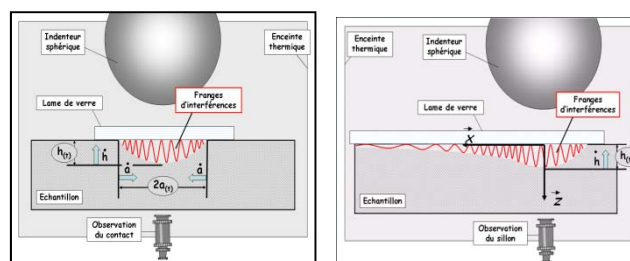
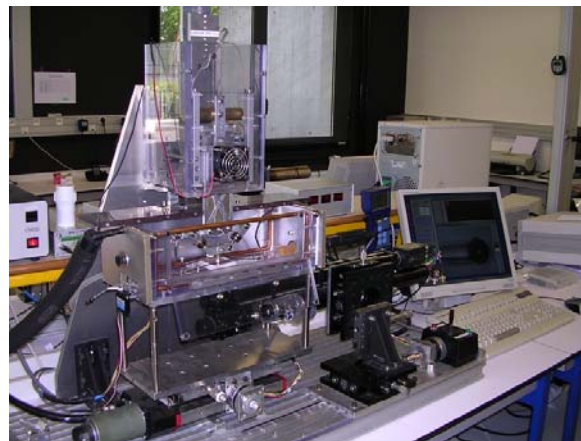


Figure 12. Set-up added on our Microvisioscratch device to analyse the self-healing of surfaces.

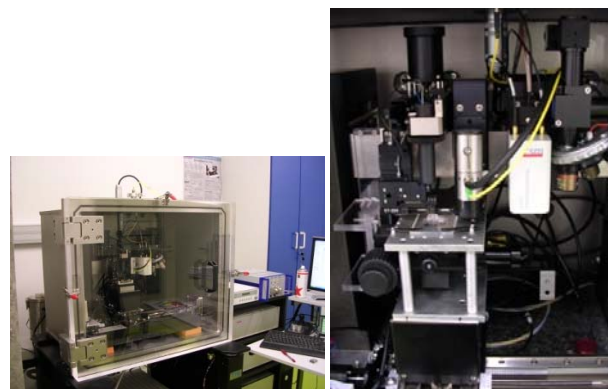


Figure 13. Nanoscratch nanoindenter tester including the first *in-situ* vision set-up based on a licence of know-how.

Our “microvisioscratch” has been patented. The major feature of the system is to show through transparent sample the true contact area. In 2008 a non exclusive license of know-how has been signed between the CNRS and the society CSM Instruments, the leader of the tribology device builders.<sup>[17]</sup> Currently we test the commercial version of our *in-situ* vision, included in our new nanoindenter nanoscratch tester (Figure 13). This test phase authorises us to obtain some new results as we now have the possibility to record simultaneously the load, the depth and the contact area, with the possibility of new loading process.

**Collaborations within the axis:** J. Baschnagel, H. Meyer, Y. Holl, P. Marie,

**Collaborations with other teams in the ICS:** P. Kekicheff, T. Charitat

**Collaborations outside the ICS:** O. Etienne (Dental Faculty of Strasbourg), C. Crouxte-Barghorn (LPIM-UHA), M.C. Baietto (LaMCoS, INSA Lyon), B. Semail (L2EP, Lille), M.-F. Vallat, V. Roucoules, L. Vonna (IS2M-UHA), X. Boddaert (Centre de Microélectronique de Provence - Georges Charpak, Gardanne)

**International collaborations:** G. Reiter (FRIAS Freiburg – Germany), R. Mulhaupt (FRIAS Freiburg – Germany), M. Moreno (CRP Gabriel Lippmann, Luxembourg), H. Fouckhardt, E. Hein (Technische Universität Kaiserslautern, Germany), M. Barletta (Università degli Studi di Roma Tor Vergata, Roma, ITALY)

**Local network:** French Tribology Society, GdR 2796 Dynamique Interfaciale des Milieux Confinés sous Contrainte Mécanique (2004-2008),

**Active European Network:** IRTG (four PhD as co-advisors or collaborators)

**Financial supports and grants:** PEPS (2009) - PPF INSA Strasbourg/ULP-ICS (2005-2008) - ANR MatetPro (Myrheca) – UdS (Starting grants Scientific Council) – CPER Nanomat – Grant for risk-taking program "Physics, Chemistry & Biology" – Funding project PMNA Young Researcher (promised 2011)

**Industrial collaborations:** ANR MatetPro (Myrheca) with SOCOMOR, EADS and AIRBUS (France) - PostDoc funded by Arcelor Mittal (Belgium) - PhD sponsored by Arkema (GRL Pau) – Rescoll (Bordeaux) - Polymer glazing project (labelized June 2011 by the competitive poles of "Future Vehicules", "Materialia" and "Plastipolis")

- [1] H. Pelletier, C. Gauthier, R. Schirrer, Journal of Engineering Tribology 2008, 222 (3), Pp. 221-230
- [2] H. Pelletier, C. Gauthier, R. Schirrer, Tribology Letters, 2008, 32, (2), Pp. 109-116
- [3] H. Pelletier, C. Gauthier, R. Schirrer, Materials Letters 2009 63 (20), Pp. 1671-1673
- [4] H. Pelletier, C. Gauthier, R. Schirrer, Wear Vol. 268, Issue 9-10, 2010, Pp 1157-1169
- [5] H. Pelletier, C. Gauthier, R. Schirrer, Tribology International 2010 43 (4), Pp. 796-809
- [6] H. Pelletier, C. Gauthier, R. Schirrer, Journal Of Materials Research, 2009, 24 (3), Pp. 1184-1196
- [7] H. Pelletier, A.-L. Durier, C. Gauthier, R. Schirrer Tribology International 2008 41 (11), Pp. 975-984
- [8] M.C Baietto, J. Rannou, A. Gravouil, H. Pelletier, C. Gauthier, R. Schirrer, In Press, Tribology International (2010) Doi:10.1016/J.Triboint.2010.04.014
- [9] V. Le Houerou, C. Robert, C. Gauthier, R. Schirrer, Wear, 265 [3-4] (2008), Pp. 507-515.
- [10] V. Le Houerou, C. Gauthier, R. Schirrer, Journal Of Materials Science, 43 (2008), Pp. 5747-5754.
- [11] T. Chatel, C. Gauthier, H. Pelletier, V. Le Houerou, D. Favier, R. Schirrer Accepted To Journal Of Physics D: Applied Physics (2011)
- [12] E. Charrault, C. Gauthier, P. Marie, R. Schirrer, Langmuir 25(10): 5847-5854.
- [13] V. Le Houerou, E. Charrault, C. Gauthier, R. Schirrer, Submitted To Tribology Letters (2011).
- [14] A. Rubin, C. Gauthier, R. Schirrer Submitted To Journal Of Physics D: Applied Physics (2011)
- [15] M. Solar, H. Meyer, C. Gauthier, O. Benzerara, H. Pelletier, R. Schirrer And J. Baschnagel Journal Of Physics D: Applied Physics 43 (2010) 455406.
- [16] M. Solar, H. Meyer, C. Gauthier, O. Benzerara, R. Schirrer, J. Baschnagel, In Press, Wear 2011
- [17] non exclusive licence of know-how between the CNRS and CSM Instruments society (CH) L08119 (2008), on the world exploitation of the in situ vision device (for friction/scratch apparatus)

## Self-Evaluation

In 2008, the AERES report has clearly identified the two research axes of the team, having each of them an interdisciplinary approach: mechanics-physics of the bulk damage and mechanics-physics of the surface. For the second topic, the committee concluded that the risk incurred to start this subject was not negligible because the team needed to design its experimental devices. The team was identified as well linked to other research activities of the ICS. However the group should improve an unique point: improve its international impact by publishing in journals having better impact factors. It is important to note that the worldwide research production on our topic is still fairly low, even if the publication and citation rates have increased since 2000. Only 2460 publications are found for the topics (scratch\* AND polymer\*) OR (indentation AND polymer\*) on the ISI Web of Science. In the same time, the sum of all citations is only of 33337 (April 2011). The analysis of the first 100 authors by record count shows that members of the team are at the top: C. Gauthier (rank 2, with 27 papers on this topic), R. Schirrer (rank 5 with 25 papers on this topic) and H. Pelletier (rank 23 with 13 papers on this topic). Since 2008 the team has principally focused his research activity on the mechanics-physics of polymer surfaces. In 2009 Prof. C. Fond left the team to develop a research activity centered on the bulk polymer behavior for civil engineering applications in a mechanical engineering laboratory.

### Statement on human resources

The team has evolved a bit in size, while refocusing his activity on the tribology of polymer.

**Recruitment:** A. Rubin, Assistant Professor at UdS (sept 2009), T. Roland, Assistant Professor at INSA Strasbourg (sept 2011), one engineer to develop the experimental activity (2011)

**Retirement:** R. Schirrer Senior Researcher at the CNRS (dec 2010)

**Mobility:** H. Pelletier (researcher full time position 2006-2008) now Assistant Professor (INSA Strasbourg), then HDR in 2011

In the period from 2007 to 2011 the group has supervised 6 PhD theses and collaborated with 2 post-docs. The team has enlarged the number of the and internationalized origin of the students, and our PhD students obtained easily their Post Doc positions:

E. Charrault, defended dec 2008, funding: MESR, origin: Strasbourg University, Current position: post-doc (Montreal since 2009)

M. Solar, defended june 2010, funding: Alsace Region, origin: INSA Strasbourg, Current position: post-doc (Groningen since 2010)

T. Chatel, defended nov 2010, funding: MESR origin: Strasbourg university, Current position: post-doc (INSA Strasbourg since 2011)

M. Mansha, defended sept 2011, funding: Pakistan Postgraduate Scholarship Program (SFERE), origin: Engineer in Pakistan



J. Lejeune, starting 2010, funding: Alsace Region (IRTG Freiburg-Strasbourg), origin: ECPM Strasbourg

E. Grespan, starting 2011, funding: German Funding (IRTG Freiburg-Strasbourg), origin: Italian with Erasmus Mundus Master degree

A.-L. Durier, origin: PhD degree ENSAM Paris, funding: ARCELOR MITTAL Belgium post-doc (2008-2009) Current position: looking for permanent employment

L. Jacomine, origin: PhD degree INSA Strasbourg, funding: ANR MatetPro (2010-2012), origin: PhD degree INSA Strasbourg

### Statement on financial supports

Financial support is well balanced between public and private origins. For example, the nanoindenter - nanoscratch device (380 k€) was funded by the CPER Nanomat (200 k€) with some help of the scientific council of UdS, the risk-taking programme of the CNRS and completed by the team (60 k€). The team obtained a few contracts (160 k€) during the last 4 years, that allows us to update our experimental device park, and to present our work. Details are:

- ☞ ANR MatetPro "Myrheca" (2008) (150k€)
- ☞ Starting grants Scientific Council UdS (2010) (60k€)
- ☞ CPER Nanomat (2008) (200k€)
- ☞ Grant for risk-taking program "Physics, Chemistry & Biology" (2009) (50k€)
- ☞ Funding project PMNA Young Researcher (promised 2011) (100 k€)
- ☞ PostDoc funded by Arcelor Mittal (Belgium) (2008) (100k€)
- ☞ PhD sponsored by Arkema, GRL Pau (2008-2010) (30k€)
- ☞ PPF (research fund) on the scratching of polymer (2005-2008) (60k€)

### Statement on scientific collaborations

#### Interactions with internal ICS activities

Through the thesis of E. Charrault, we started a collaboration with P. Marie from the former group "Adhesion and Colloids" on the relationship between friction and dynamic adhesion on polymer surfaces. The dynamic JKR apparatus was developed during this thesis. This collaboration was continued by the PhD of G. Klein, for which Y. Holl was the supervisor. This PhD was a part of an European Project for which tribological and friction behavior of latex films were analysed in our team.

Through the thesis of M. Solar (2007-2010) we started collaboration with the Theory Group (J. Baschnagel) on molecular modeling of nanoindentation tests in glassy polymer films. This collaboration will be continued in the future as most of our results at local scale cannot be analysed without the help of this point of view.

P. Kélicheff has collaborated with us to analyse the tribological behavior of some technical coatings. First interesting results on the tribological behavior of PEEK thin films at high temperature allow us to expect some interesting industrial applications.

#### Collaborations with national groups

Several of our publications during the last four years were written with groups located outside the ICS, as a result of fruitful collaborations.

With M-C Baietto (LaMCos-INSA Lyon), we have analysed the damage mechanism of the cracking during the scratching. Following this, we have measured for them the true contact area for elastic coating of various thicknesses, and various ratio of Young modulus. They needed these results to validate their numerical model of the elastic contact for mono and multiple points.

We largely collaborate with the group of C. Croutxe-Barghorn (LPIM UHA), working on photopolymerized coatings, currently through an ANR project. Previously we have trained one of their PhD students in the use of our devices and in the scratch analysis. For the future, we will collaborate through the "polymer glazing" project

#### International research interactions

Recently, we have extended these research interactions, through the thesis of J. Lejeune and E. Griespan, in particular through the IRTG Freiburg-Strasbourg (Projects C4 and C5 as principal investigators, and as collaborator Project B3). For the first two collaborations the subject is the analysis of the self healing of surfaces and the effect of physical and chemical functionalization on the adhesion.

Many dynamic JKR measurements are currently made for the CRP Gabriel Lippmann located in Luxembourg (M. Moreno), to analyse the effect of nanopatterned surfaces on the adhesion. This starting collaboration allows us to plan on this topic academic collaborations, as pre-industrial applications, with researchers from Switzerland Germany and Luxembourg (and Mulhouse).

To realize specific nano-roughness geometries on borosilicate lenses for friction studies we worked with H. Fouckhardt from the group "Integrierte Optoelektronik und Mikrooptik" (TU Kaiserslautern, Germany) which has the know-how for optical micro- and nano-texturation. This new collaboration will ensure original samples for our nano-rheology studies on polymers.

### Statement on scientific productions

In the period of 2007 to 2010, we published 25 articles in peer-reviewed international journals. The impact of these publications is significantly increased. A publishing evaluation is presented compared to the evolution of the number of permanent researchers in the team. 2007-2010: 4 permanent researchers (C. Gauthier, R. Schirrer (< 2010) V. Le Houérou (>2006), H. Pelletier (>2006) A. Rubin (>2009))

- ☞ Number of articles – 25
- ☞ Journals – from the classification given by ISI web, publications classified into two topics: "Materials Sciences", "Polymer Science" and "Physics, Applied"

Langmuir (1) / Journal of Physics D - Applied Physics (1) / Journal of Polymer Sciences part A (1) / Journal

of Polymer Sciences part B (1) / Polymer International (1) / New Journal of Chemistry (1) / Applied Physics A: Materials Science & Processing (1) / Materials Science and Engineering B-Advanced Functional Solid-State (1) / Journal of Materials Research (1) / Journal of Materials Science (2) / Materials letters (1) / Dental Materials (1) / Journal of Coatings Technology and research (1) / Progress in Organic coatings (1) / Surface and Coatings Technology (1)

“Engineering, Mechanical” principally in better impact factor journals of this group.

Wear (3) / Tribology International (3) / Tribology Letters (2) / Proceedings of the Institution of Mechanical Engineers Part J: Journal of Engineering Tribology (1)

As a reminder, during the period 2003-2006 the group was composed with 2 permanent researchers (C. Gauthier R. Schirrer) and has published: Journal of Materials Science (1) / Tribology Letters (1) / Wear (1) / Tribology International (3) / Thin Solid Films (1)

For this last period, publication impact is:

☞ Average impact factor of the journals: 1.93

☞ Average number of citations per article: 2.2

☞ h-index of the permanent staff: 16

☞ m-index of the permanent staff: 0.8

☞ Nber of patents: 1 licence of knowhow

☞ Nber of Invited International Conferences: 7

☞ Nber of Award Conferences: 3

Finally, the group has also presented 47 talks and posters at international conferences, 31 national conferences with proceedings and 13 seminars in national and international labs. Half of these talks have been made by our students.

### Further professional activities

#### Teaching activities

In addition to this training by research the group has been involved in the following training related activities:

- Every fall semester permanent researchers taught some courses on mechanics of polymers (V. Le Houérou), Physics and Adhesion of the Surfaces (A. Rubin) Contact Mechanic and Tribology of Polymeric Surfaces (C. Gauthier) and Tribology of Inorganic Materials (H. Pelletier) in the Master2 programme on Polymer Engineering, in the Master II programme on Surface Engineering and in the last year of the INSA Engineering School.
- In 2010, C. Gauthier taught courses in a Thematic School organized by GFP (French Polymer Group) as for Doctoral School (JEPO School for polymer PhD students).
- C. Gauthier was Dean of the Faculty of Engineering and Technology Sciences (2007-2008) then, after association with the Physics Faculty, Vice Dean of the Faculty of Physic and Engineering, responsible of the Engineering Department (2009-2010).
- After being the head of the Engineering Sciences Master, C. Gauthier is now the head of the Engineering Surface Master.
- Since 2010, H. Pelletier is the head of the last year of Mechanical Department of the INSA Strasbourg.

#### Organized workshops, seminars, ...

In the period 2007 to 2011 members of the group have been involved in the organization of seminars, workshops, etc. A non-exhaustive list includes:

- Organizers of the International Francophone Tribology Days 2011 – 100 participants
- Member of organizer committee "Scientific Day of the Materials and Nanoscience Pole of Alsace", 2011 and 2008 Strasbourg
- Member of scientific committee of the 44th French Rheology Congress, 2009
- Principal organizer of the session "Mechanics and Physics of surfaces and contacts" during the Condensed Matter Congress JMC 11 2008.

#### Biomedical engineering resources platform

The team will participate in the platform as a scientific support. H. Pelletier will be the head of the platform of the biomedical Engineering Resources (Implant for Healthcare Strasbourg) that will be created in the heart of the University Hospital of Strasbourg. This engineering platform will regroup the competences dedicated to the development of new implantable medical devices, such as prosthetic implants ; from design to prototype and we will participate in the characterization of bioactive functionalized surfaces.

#### Valorisation of instrumental developments and licence transfer

As recognized by the 2008 AERES committee, one of our specificities is to develop devices which allow us to record mechanical information without being model dependent. Our microvisioscratch has previously been patented, and in 2008 a non exclusive license of know-how has been signed between the CNRS and the society CSM Instruments (Switzerland), leader of the tribology device builders. Currently we test the commercial version of this in-situ vision, included in our new nanoindentor nanoscratch tester.

#### Overall statement

Following the recommendations of the 2008 AERES report, the group has focused its principal activity on the Mechanics-Physics of Polymeric Surfaces, confirmed its national leadership and largely improved its international impact. The team has developed its scientific collaborations inside and outside the laboratory, well balanced between national and international collaborations, academic and industrials. 30% of our publications from 2007 to 2011 were signed with colleagues from the theory group or in collaboration with researchers in chemistry or numerical simulation. These collaborations will be continued and facilitated by the IRTG Freiburg-Strasbourg. We have also started some new international collaborations (Luxembourg, Germany, Italy...), each time focused on a specific point (structured surfaces, coatings,...). The group encourages its assistant professors to build the international research network. A. Rubin obtained a visiting grant to go to the Riken laboratory at Tokyo, even if the seism has interrupted her visit. H. Pelletier will go to the Roma University in the summer 2011.

# Platform on Nanomechanics and Micromechanics

**Permanent staff:** Christian Gauthier (Full Professor UdS), Damien Favier (Instrumental Engineer CNRS), XX (Materials Engineer CNRS), Hervé Pelletier (Assistant Professor INSA Strasbourg), Mounir Maaloum (Full Professor UdS), Christophe Contal (Technician UDS), Patrick Kekicheff (Research Director), Jean Iss (Research Engineer CNRS)

## General description of the novel platform

The tribology and the contact mechanics are a research topic for which the characteristic scale may vary from the nanometer to the millimeter scale. Depending of the scale, the contact behaviour is linked to physics or mechanics.

As a unique and original position, the scientific research tools located at the Institute allow us to work at all of these scales. These powerful tools, such as AFM, nanoindenter, SFA, dynamic JKR or microscratch, are accessible for characterization and are also deployed for original research. This report presents some advances in the development of these tools, coupling sometimes two kinds of physical measurements.

Conscious of the opportunity, and taking advantage of the recently arrived the nanoindenter, we have decided to create a platform on nanomechanics and micromechanics. The purpose of this platform is to make these techniques available to other researchers from the Cronenbourg campus or private companies (as a part of the platform for the Institut Carnot "MICA") and thus to facilitate transfer of knowledge towards the materials science community.

## Tools and staff

The research platform is the way chosen

- to improve the access of these devices for the research community,
- to train permanent and young researchers to use these devices,
- to propose this scientific expertise to industrials,
- to anticipate the necessity of the rejuvenation of this instrumental park.

Liquid AFM, SFA, micro and nanoscratch testers, micro and nanoindenter testers, surface topography profilers (contact and interferometric) are the main devices.

For the starting phase, all of the teams having these devices accept the principle to give 20% of the working

time into the common pool. The platform will interact with all the research activity of the ICS even if the formal attachment concerns the axis "Polymer and Interface". One engineer will be recruited. This engineer will have the mission to split his working time between experiments further PMTP group, training the young researchers, and the management of the access schedule to the experimental devices.

The convention of the research platform between ICS and INSA of Strasbourg must be signed in the second semester 2011. This agreement will deal the main guidance to the management of the Platform. Before officially start this platform, we have signed a convention between ICS and INSA to welcome assistant professors as permanent researchers at the Institute (spring 2011).

## Quality management

At the starting phase of the platform, to be in accordance with the applied rules of CNRS platforms, and considering the fact that ICS is a member of the recently created Institut Carnot "MICA", the question of the "quality in research" will be addressed. Like for the other platforms of the ICS, we will certainly benefit from the experience acquired by other Laboratories already involved in this quality approach (IS2M and ISL as partners of the Institut Carnot "MICA").

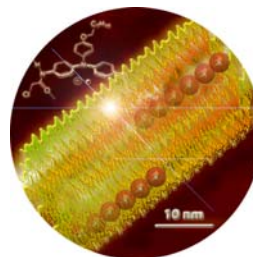


# Axis 3: Self-Assembled Systems

## SAMS Research Group

Head of the Group **Nicolas Giuseppone**

**Towards Information-Gaining  
Supramolecular Systems and  
Materials**

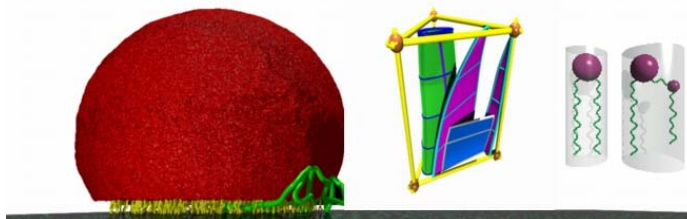
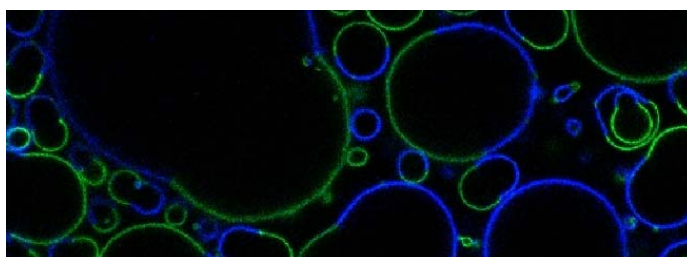


The understanding and the control of self-assembly processes in chemical systems, possibly in dynamic interaction with external stimuli or fields, are among exciting problems for materials science and beyond. Our team focuses on the synthesis and the study of programmed molecules which can spontaneously self-assemble in nano-objects with new functional properties. We also develop information-gaining systems which combine several hierarchical organization levels in space and time.

## M<sup>3</sup> Research Group

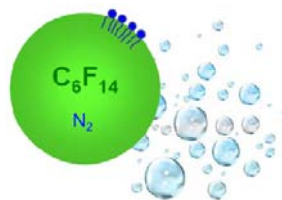
Head of the Group **Carlos Marques**

**Bringing the Science of Self-Assembled  
Bilayers to the Next Level**



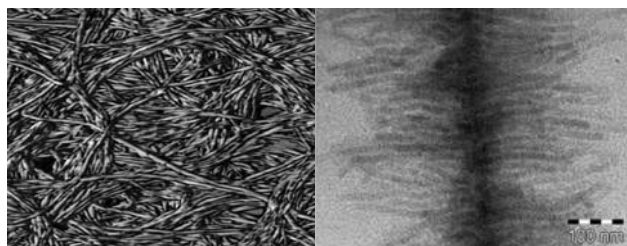
Research in the Mcube group is geared towards the understanding of the physical properties of phospholipid bilayers. The study of these self assembled two-dimensional structures is at the cross roads of exciting and promising present fields of scientific research, posing fundamental theoretical and experimental challenges for the physicist, and opening into a wide ground of potential applications in materials science, biophysics, pharmacy and cosmetics. We take up the challenge of designing fully functional membrane systems by articulating *membrane architecture* with *membrane function* under the most relevant *non-equilibrium conditions*.

SOFFT Research Group

Head of the Group **Marie-Pierre Krafft****Fluorinated Self-Assembled Systems for Biomedical Applications and Materials Science**

We take advantage of the fluororous effect to organize soft matter at the nanometer scale. In particular, we focus on *compartmented* self-assembled systems. Our projects aim at conferring function to these systems via decoration with nanoparticles. We also want to develop the potential of these systems as contrast agents in diagnostic, therapy, and as biomedical tools.

Sycommor

Head of the Group **Jean-Michel Guenet****Elaboration and Properties of Complex Architectures from Multicomponent Systems**

Novel and original molecular architectures involving covalent polymers and/or self-assembled systems are elaborated through a controlled growth of nano, meso, and microstructures by physical processes. These new architectures are expected to shed light on functional properties in unusual environments. Further developments may lead to the making of functional materials, such as opto-electronic devices, reactive porous materials or hydrophobic materials.

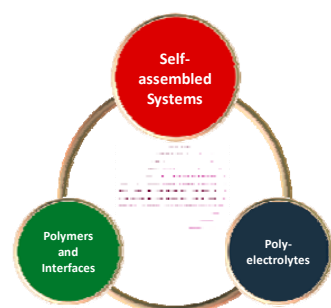
# Self-assembled Systems

## An overview of the axis

**Involved research groups : 4 Teams of Research:** SAMS, M3, SOFFT, Sycommor

**Permanent staff:** 2 Professeurs UdS, 4 Directeur de Recherche CNRS, 3 Maîtres de Conférences UdS, 8 Chargés de Recherche CNRS, 1 Ingénieur de Recherche CNRS, 4 Technicians

**Keywords:** biological and bioinspired systems · self-organized synthetic systems · bottom-up nanofabrication



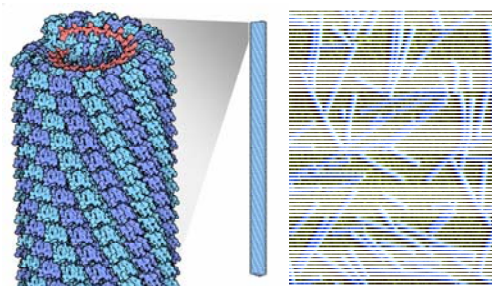
The axis “Self-assembled Systems” rests on a multidisciplinary vision, articulated around a broad and unique set of competences at ICS, and with the aim of building new objects for materials science. The targeted objectives are in relation

with a series of current scientific challenges which often require crossed expertise to be addressed, going from synthetic chemistry to theoretical physics. These fundamental investigations are also intended to evolve towards applications in biology, medicine, materials, and nanosciences.

## Self-assemblies: where it is and where it is going

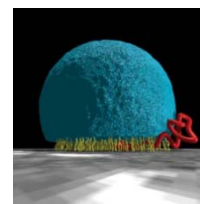
Self-assembled systems<sup>[1,2]</sup> result from the spontaneous organization which occurs between some well-defined molecules, thanks to their complementary weak supramolecular interactions such as hydrogen bondings, van der Waals forces, ion pair recognition,  $\pi$ - $\pi$  interactions, *etc.* Self-assemblies are programmed by the information contained in their initial molecular or macromolecular individual components, and which reversibly aggregate in structures of higher dimension and complexity.<sup>[3]</sup> Depending on the specificity of the supramolecular interactions, the resulting self-assemblies can present a high degree of order, as it occurs for instance during the recognition process of proteins for the formation of viral capsides (Figure 1), or can be less organized and softer as in the case of micelle formation.

The main biological functions of living systems mostly rely on these basic interaction principles and, despite their high complexity, those are important sources of inspiration for developing new synthetic self-assemblies.<sup>[4]</sup> For instance, chemists have shown that it is possible to use self-assemblies based on phospholipid bilayers, *i.e.* liposomes, to transport and deliver bioactive compounds; some of these drug carriers are nowadays commercially available and used in particular to cure cancer.<sup>[5]</sup>



**Figure 1.** Tobacco mosaic virus has a rod-like appearance (300 nm x 18 nm). Its capsid is made from 2130 molecules of coat and one molecule of genomic single strand RNA 6400 bases long. The coat protein self-assembles into the rod like helical structure (16.3 proteins per helix turn) around the RNA which forms a hairpin loop structure.

Another very fundamental interest in this liposome area is related to the dynamics of the phospholipid bilayer itself, which constitute by essence a probe to understand what soft matter is. At ICS, the M<sup>3</sup> research group is one important leader in this field. Recently, they published an article in collaboration with the theory group (*frontcover Physical Review Letters*),<sup>[6]</sup> where stained end-grafted DNA molecules about 20 micrometers long are scraped away and stretched out by the spreading front of a bioadhesive vesicle. Tethered biotin ligands bind the vesicle bilayer to a streptavidin substrate, stapling the DNAs into frozen confinement paths. Image analysis of the stapled DNA gives access, within optical resolution, to the local stretching values of individual DNA molecules swept by the spreading front, and provides evidence of self-entanglements.

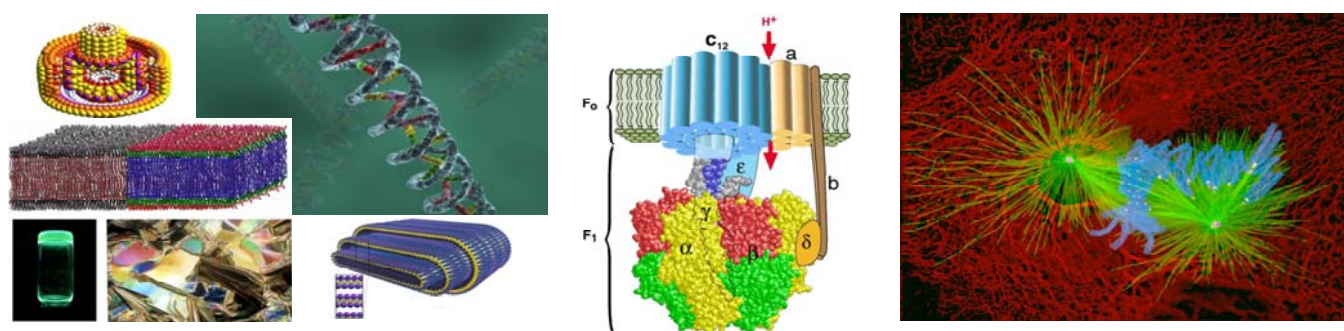


In self-assembled systems, one may also refer to the replacement of hydrogen bondings by superhydrophobic interactions developed by fluorinated chains for the base pairing in functional nucleic acids, opening new possibilities for bio-inspired systems.<sup>[7]</sup> One of the internationally recognized group in the chemistry of perfluorinated self-assemblies is the SOFFT research group at ICS. Recently, they published a comprehensive review<sup>[8]</sup> where they show that (perfluoroalkyl)alkyl diblocks (*F<sub>n</sub>H<sub>m</sub>*) which are so simple, yet produce exceptionally large organized circular self-assembled domains at the



surface of water and on solid substrates. They also form composite films, including, in the case of gemini (perfluoroalkyl)alkyl tetrablocks, organized stacks of nano-objects. *FnHm* diblocks can act as surfactants, strengthen bilayer membranes, stabilize vesicles and strongly modify their behavior in biological media, and control the phase behavior of phospholipid monolayers.

However, even for the most advanced ones, current artificial systems are still, and by far, less complex than those encountered in biological systems. To go further, and to bridge the gap between self-assemblies and self-organized systems,<sup>[9]</sup> between inanimate matter and living systems,<sup>[10]</sup> it is necessary to study far from equilibrium the dynamic of these objects which are able of adaptation as a function of their environment, and as a function of time (Figure 2).



**Figure 2.** From self-assembled to self-organized systems: some examples of well-known artificial and biological structures, and which differ in their level of complexity, going from simple liquid crystal mesophases up to the cytoskeleton protein machinery in action during the cellular division.

Self-assembly is also a unique and powerful technique for constructing a large range of nanostructures which are required to improve the properties of numerous functional devices going from solar cells, light emitting diodes, and field effect transistors,<sup>[14]</sup> to molecular motors<sup>[15]</sup> having high potentials for nanotechnologies (Figure 3).



**Figure 3.** Self-assemblies processes provide the opportunity to design materials with attractive chemical and mechanical properties based on their ability to assemble into periodic structures with nanoscale domain spacings (left). These properties lead for instance to numerous straightforward applications in the emergent domain of soft organic electronics (middle and right).

Recently, the SAMS research group, with the collaboration of colleagues in theory and AFM at ICS, discovered a highly interesting system which could have a deep impact on the design and casting of organic materials for electronics. They demonstrated that triarylamine based building blocks can respond to visible light exposure by the formation of cationic radicals that hierarchically self-assemble into molecular wires, which in turn combine within larger fibers (*frontispiece cover Angewandte Chemie*).<sup>[16]</sup> The stimuli-responsive supramolecular scaffold, which is created by charge transfer and reversibly broken up

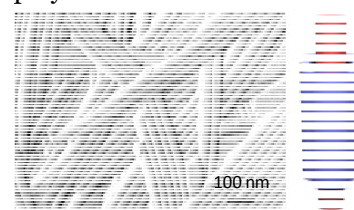
Moreover, in nanosciences, the so-called “bottom-up approach”<sup>[11]</sup> is fully related to the control and to the programming<sup>[12]</sup> of supramolecular interactions to yield larger objects, through hierarchical self-assemblies in space, with new or improved functionalities. Many economical aspects of first importance are here related to these developments. For instance, the impetus to scale down electronic components for increasing the power of computer calculations will soon face the physical limits associated with “top-down” manipulations, and self-assemblies are intended to offer new opportunities for this growing market. One can for instance illustrate this idea with the construction of rotaxanes<sup>[13]</sup> which are able to play the role of molecular switches oscillating between two stable states, and which have high potentials for the construction of molecular computers.

by heating, prevents the quenching of holes within the wires and can be trapped and oriented between electrodes. This totally original material presents conductivity properties close to sorted metallic carbon nanotubes.



In general, the intermolecular forces involved in self-assemblies being very weak, the presence of defects in these systems represent also an important feature of investigation. Indeed, because mistakes are possible during the fabrication of these objects – as it happens during the replication of double strand DNA for similar reasons (mutations) – scientists will have to find new ways to correct them, or even conversely, to take advantage of them (in a sort of directed evolution)!! These properties of reversibility are also favorable to design systems where a self-assembled one adapts its structuring to a static template, possibly polymeric, to yield hybrid materials. The Sycommor research group is interested in this approach and they have recently formed fibrils of polymers with diameters of  $14 \pm 6$  nm sheathed by

self-assembled nanotubes with inner diameters of 21 nm. These complex architectures have been studied by AFM and contrast variation in SANS.<sup>[17]</sup> They have





been produced very pure at the scale of 10 g by simple physicochemical processes such as gelation and heterogeneous nucleation and by tuning physical parameters (concentration and temperature).

Today, all the previously highlighted topics are identified among the major scientific challenges for the coming century: up to where will it be possible to develop supramolecular self-assemblies?<sup>[18]</sup> The importance of this question is clearly evidenced by the growing number of research groups working in this field, not only in Europe, but also in the United States and in Asia. As we will show in the following sections, we believe that our Institute is able to bring a major scientific contribution and to play a key role in this huge international competition.

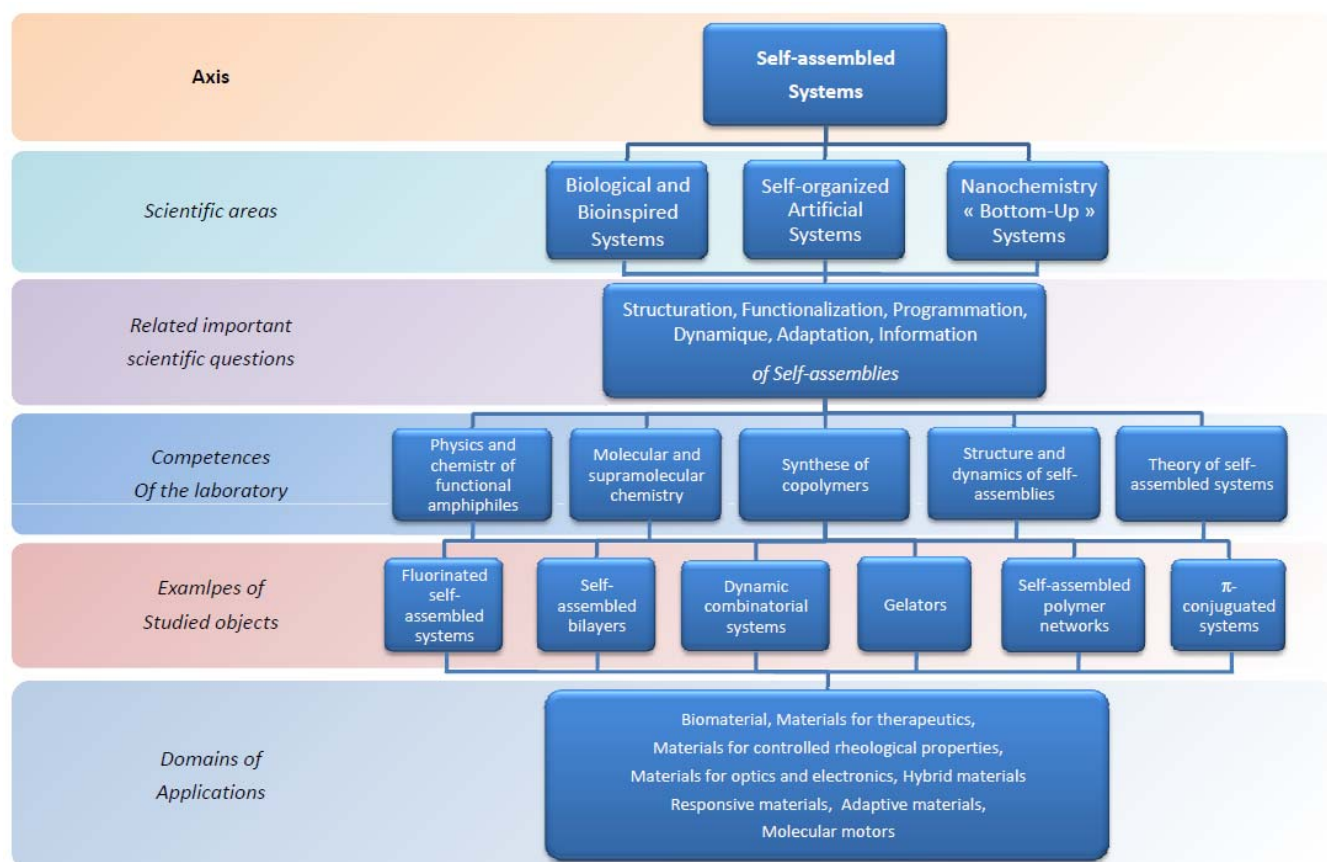
## Structuring of the axis

A number of ambitious projects along this research axis are today performed at the Institut Charles Sadron, thanks to an exceptional combination of high level competences: *i*) in physics and chemistry of functional amphiphiles, *ii*) in organic synthesis and supramolecular chemistry, *iii*) in the synthesis of block copolymers, *iv*) in the physics related to the structuration and the dynamic of self-assemblies, and *v*) in the theory and simulation of these systems (Figure 4). These competences are distributed within four research teams (SAMS, M<sup>3</sup>, SOFFT, and

Sycommor), each one being also specialized in more specific objects such as *i*) fluorinated self-assembled systems and interfaces, *ii*) phospholipid bilayers, *iii*) dynamic combinatorial systems, *iv*) gelators, *v*) self-assembled polymer networks, and *vi*)  $\pi$ -conjugated systems. These objects, often built for addressing the previously raised fundamental questions, are also the vectors of potential applications in domains such as *i*) biomaterials including those for therapeutics and diagnostics, *ii*) materials for sustainable development, *iii*) responsive and adaptive “smart” materials, *iv*) materials for optics and electronics, *v*) hybrid materials, and *vi*) molecular motors.

In addition, we are currently witnessing the strengthening of collaborations operating with the theory group on a number of experimental projects; a theory group which itself starts developing biophysics approaches that are linked by essence to self-assembly processes.

Thus, by bringing these broad and deep theoretical and experimental skills, together with the historical know-how of the laboratory, that are polymer synthesis, electronic microscopies; atomic force microscopy; light, neutron, and X-ray scatterings; advantageously completed by the characterization platform (SEC-GPC, DSC, NMR, etc.), the ICS holds a unique potential in France to succeed in providing a major scientific contribution towards self-assembled systems, with the objective of taking a leadership at the international level within the next five years.



**Figure 4.** Organization chart of the axis highlighting the major scientific questions related to self-assembled system. To address them, a number of necessary competences are brought by the involved research groups (SAMS, M<sup>3</sup>, SOFFT, and Sycommor). Examples of studied objects and targeted applications illustrate both the diversity and the coherence of the axis.

- [1] Supramolecular Chemistry And Self-assembly Special Feature, *Proc. Natl. Acad. Sci. USA*. **2002**, 99.
- [2] This field of research has been clearly targetted by the CNRS as a strategic domain in its project "horizon 2020". *Contrat d'objectifs 2009-2013 du CNRS avec l'Etat*, 25 juin 2009.
- [3] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, **1995**, New York.
- [4] C. Sanchez, H. Arribart, M. M. Giraud, *Nature Materials* **2005**, 4, 277.
- [5] R. Langer *et al.*, *Nature Nanotech.* **2007**, 2, 751.
- [6] G. Nam, M. L. Hisette, Y. L. Sun, T. Gisler, A. Johner, F. Thalmann, A. P. Schröder, C. M. Marques, and N.-K. Lee, *Phys. Rev. Lett.*, **2010**, 105, 08810
- [7] H.Y. Tae, A.J. Link, D.A. Tirrell, *Proc. Natl. Acad. Sci. USA*. **2007**, 104, 13887.
- [8] M.P. Krafft, J. Riess, *Chem. Rev.* **2009**, 109, 1714-1792.
- [9] Systems far from equilibrium, crossed by energetic fluxes and capable of increasing their complexity in an autonomous manner.
- [10] S. Mann, *Angew. Chem. Int. Ed.* **2008**, 47, 5306.
- [11] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, 254, 1312.
- [12] The programming of chemical systems rests on the structural information stored at the molecular level and on its reading at the supramolecular one, using non-covalent interactions.
- [13] J. F. Stoddart *et al.*, *Topics in Curr. Chem.* **2005**, 249, 203.
- [14] J. C. Scott, G. G. Malliaras, *The chemistry, physics and engineering of organic light-emitting diodes*, in *Semiconducting polymers*, Wiley-VCH, **2000**.
- [15] V. Balzani, A. Credi, M. Venturi, *Molecular devices and Machines*, Wiley-VCH, **2004**.
- [16] Moulin, E., Niess, F., Maaloum, M., Buhler, E., Nyrkova, I., Giuseppone, N., *Angew. Chem. Int. Ed.* **2010**, 49, 6974.
- [17] D. Dasgupta, Z. Kamar, C. Rochas, M. Dahmani, Ph. Mesini, J.M. Guenet *Soft Matter* **2010** 6 3576
- [18] What we don't know? *Science*, special issue - 125<sup>th</sup> anniversary - on hard questions that point to critical gaps in our scientific knowledge, **2005**, 309, 95.

# SAMS Research Group

Head of the group *Nicolas Giuseppone*

**Permanent staff:** Dr. Nicolas Giuseppone (Professor UdS) 2008 –, Dr. Emilie Moulin (Chargé de Recherche CNRS) 2009 –, Dr. Gad Fuks (Maître de Conférences UdS) 2010 –, Céline Desvignes (Technician CNRS) 2008 –

**Non-permanent researchers (2008-2011): 9 post-doctoral associates** (Dr. Gabriela Cormos 2008-2009; Dr. Prasad Polavarapu 2008-2009; Dr. Juan-Cid Martin 2009-2011; Dr. Faris El Badri 2010-2011 ; Dr. Jan Weiss 2011- ; Dr. Eric Busseron 2011- ; Dr. Yves Ruff 2011- ; Dr. Cristina Misuraca 2011- ; Dr. Jose Miguel Navarro 2011-) / **12 PhD students** (Shengguang Xu – defended 2009 (cotutelle) ; Lara Tauk – defended 2009 ; Paolo Neviani – defended 2010 (cotutelle) ; Rémi Nguyen – defended 2010 ; Frédéric Niess – defended 2011 ; Guangyan Du – defense planed 2012 ; Adrian Wolf – defense planed 2013 ; Stefano Zanirati – defense planed 2013 ; Yunjie Xiang – defense planed 2014 ; Joe Armao – defense planned 2014 ; Thesis Firmenich – defense planed 2014 ; Quan Li – defense planed 2015) / **8 Master students.**

**Keywords:** supramolecular chemistry · systems chemistry · hierarchical self-organization · smart materials

The SAMS research group has been created in February 2008 with the hiring of Prof. Giuseppone at ICS, in order to start a new line of research dedicated to supramolecular chemistry at the frontier with materials science. Hereafter, we will describe the progresses that have been accomplished during these last three years, together with some upcoming projects.

## Towards Information-gaining supramolecular systems and materials

Today, one of the greatest challenges facing physics, chemistry, and (bio)materials science is to fabricate functional nano-objects. Using bottom-up strategies, efforts to understand and control supramolecular recognition, dynamic recombinations, and selection processes in complex systems, possibly in interaction with external *stimuli* or fields, offer promising challenges for the fabrication of new (bio-inspired) materials.<sup>[1]</sup> In particular, elaborated performances characterizing biological systems result from multiple levels of hierarchical organization both in space and time. However, and despite the numerous achievements based on the use of supramolecular architectures, a major gap remains to be bridged between inert and living systems.<sup>[2-4]</sup> In particular, we do not yet understand how complexity emerges from simple chemical building blocks within open systems. We also know very little about the possible relationships between the environmental “information” and the resulting self-organization of such systems. In this direction, we are currently witnessing the birth of the field of “Systems Chemistry”, focusing on multi-components systems which exhibit properties that their single components could not produce individually.

The objectives of our research projects are part of this bundle of explorations and thus aim at reaching a better understanding of complex systems, self-organization, and emergence of order from chaos. In particular, we want to address fundamental questions related to the thermodynamics and kinetics of self-organizing matter, possibly far from equilibrium. For instance, we study the emergence of cooperative behaviors and of information transfer between components that function within coupled networks of reactions, in order to design minimal autonomous systems. The fundamental knowledge produced

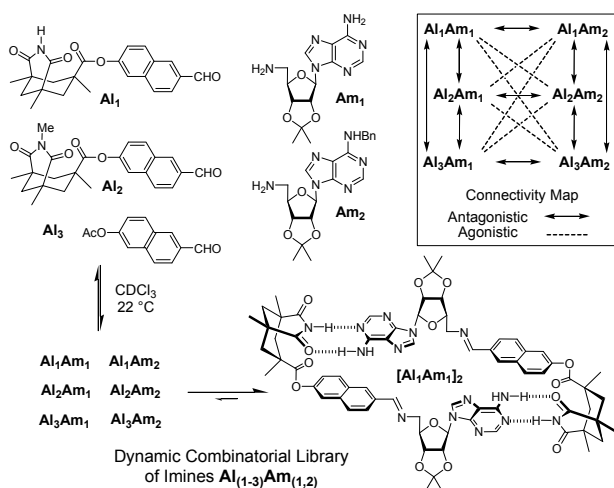
is also intended to implement the design of new classes of “smart” materials, which will not be only responsive but which will be also able to self-fabricate (with exponential growth) upon an initial stimulus provided in their environment.<sup>[5]</sup>

## Implementing self-replication processes in chemical networks and materials science

The Darwinian Theory describes the evolution of biological species and links it to their “information gaining” properties. As it is commonly accepted, an evolving system should be able of three fundamental features: *i*) to metabolize, *ii*) to self-replicate, and *iii*) to undergo mutations. Thus, self-replication represents one of the keystones which allow distinguishing between non-living and living systems. We believe that artificial self-replicating systems will have to be integrated in the chemistry of materials science for developing future generations of smart autonomous systems and devices.<sup>[6]</sup>

## Merging dynamic combinatorial systems and self-replication processes

Dynamic Combinatorial Chemistry (DCC) rests on the design and the study of libraries of species connected by reversible (supra)molecular bonds.<sup>[7]</sup> It is a very attractive domain of modern chemistry because it associates combinatorial features together with the spontaneous self-organization of molecules. Dynamic Combinatorial Libraries (DCLs) are governed by thermodynamics and are consequently subjected to the influence of internal or external parameters that can reversibly modify the expression of their constituents through selection/adaptation. Recently, we have demonstrated the possibility to couple DCC with self-replicating systems.<sup>[5]</sup> We described the first example of a dynamic combinatorial library which strongly amplifies one component from a pool of reshuffling constituents by self-selecting a product that constitutes its own target, i.e. the one capable of self-replication (Figure 1).

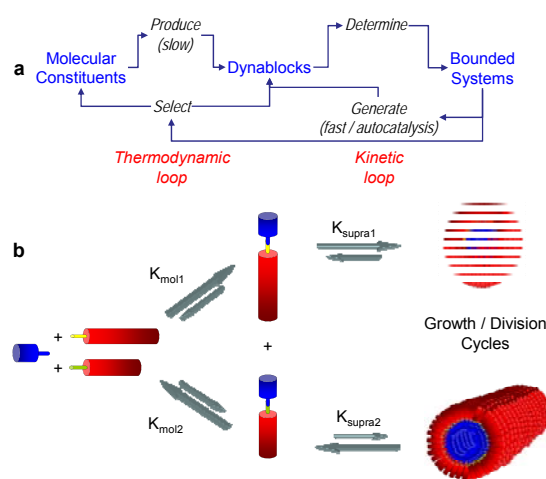


**Figure 1.** Representation of a library obtained by mixing aldehydes ( $\text{Al}_1$ - $\text{Al}_3$ ) and amines ( $\text{Am}_1$ ,  $\text{Am}_2$ ). In this combinatorial set, only one imine, namely replicator  $\text{Al}_1\text{Am}_1$ , can self-assemble through hydrogen bonds and produce homodimer  $[\text{Al}_1\text{Am}_1]_2$ .

In this seminal proof of concept, we have demonstrated that the expression of the components in the library evolves along both kinetic and thermodynamic biases that both lead to the amplification of the best replicator. From a “Darwinian” point of view, such a system illustrates the selection of the most efficient self-replicator by the destruction of the entities which are not (or less) able to replicate themselves.

### Extending dynamic combinatorial self-replication towards large self-assemblies

Although our initially reported DCLs amplify the best duplicator and decrease its competitors, it does not present a strong autocatalytic behavior, i.e. an exponential growth at the early time of the reaction. With this objective, we have subsequently described another DCL which avoids the drawback of product inhibition by taking advantage of the growth/division cycles of soft micellar self-assemblies, and which displays a particular case of autocatalysis, namely *autopoiesis*, where the system has a semipermeable boundary which regenerates its own components.<sup>[8]</sup> To set up our study, we first designed a new type of amphiphilic molecular objects that, because of their reversible connections and through molecular recombination, allow the production of various types of micellar self-assemblies in water. These objects were constructed by using the reversible connection between hydrophilic and hydrophobic blocks, thus leading to dynamic amphiphilic block (dynablocks) (Figure 2). Here, the molecular constituents compete at the subnanometer scale for the reversible production of dynablocks having different amphiphilic ratios, mainly determining the formation of the bounded structures at the tens of nanometer scale. Then, in a first *autocatalytic loop*, these self-assemblies are able to generate their own formation by increasing exponentially the rate of the dynablock condensation and they entirely fulfill the required characteristics of a minimal autopoietic process. Moreover, in a second *thermodynamic loop*, the self-assemblies almost perfectly discriminate between the incorporated dynablocks and thus favor the preferential synthesis of their own blocks, thus maintaining the integrity of their bounded structure.



**Figure 2. a)** Synergistic constitutional relationships observed at two length scales within a model minimal self-replicating DCL described in **b)**. **b)** Competing dynablocks and associated structures - Red rods: hydrophilic blocks; Blue rods: hydrophobic blocks.

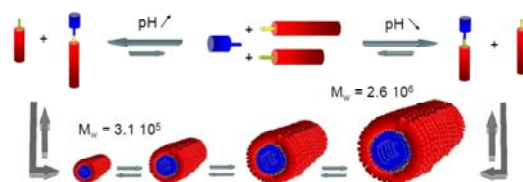
Such a system, combining cooperative processes at different length scales in networks of equilibria and displaying autocatalysis within DCLs, is of interest for the understanding of the emergence of self-organizing collective properties but also for the design of responsive systems as described hereafter.

## Implementing responsive dynamic combinatorial processes in materials science

To date, DCC has been mainly limited to relatively small (supra)molecules; its implementation toward the design of large self-assemblies, capable of producing nano-structures at mesoscale, would lead to the development of a new class of responsive nano-systems.<sup>[9,10]</sup>

### Responsive dynamic combinatorial mesophases

In a first project, we have<sup>[8]</sup> extended the chemistry of dynablocks by showing the possibility to reversibly trigger the shapes and sizes of micellar nano-objects by an external effector, i.e. pH modulations (Figure 3).



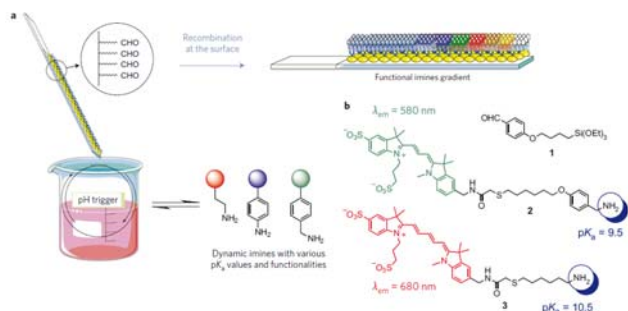
**Figure 3.** Dynablocks are shown to concomitantly reorganize their molecular combinations and supramolecular mesoscale structuring upon pH modulations – example of the analogic size-variation of cylinders.

In this example, we have demonstrated for the first time that it is possible to use the fundamental rules of DCC in order to enrich the toolbox for the design and the control of large responsive nano-structures based on microphase separation.<sup>[11]</sup> The variation of the concentration ratio

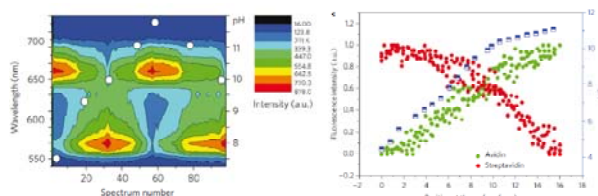
between only two dynablocks is sufficient – while not necessarily limited – for the production of a huge number of virtual nano-structures within the bounded group of their possible composition. In other words, the pH modulation results in a signal transduction involving a binary treatment at the molecular level and a subsequent analogic response at the supramolecular level. The possibility to digitally regulate the analogic structuring of nano-objects as well as their associated physical properties, over the control of their various molecular combinations in libraries, is of interest for the development of a new class of responsive systems and “smart” materials. In another example, we have also demonstrated the possibility to switch between aggregates of different topologies, for instance micelles and vesicles.<sup>[12]</sup>

### Responsive dynamic combinatorial surfaces

Self-assembled monolayers (SAMs) are nano-objects with a number of useful properties that link molecular-level properties to interfacial phenomena. Recently, we achieved the first example demonstrating the possibility to tailor the functionalization of surfaces with the selection processes of DCC by controlling the (bio)molecular composition of SAMs – in space and time – from a set of dynamic constituents that can selectively be anchored through pH modulation.<sup>[13,14]</sup> Our general approach exploits the property of imine-based dynamic covalent mixtures to differentially recombine amines with aldehydes upon pH modulation (Figures 4 and 5).



**Figure 4.** a, An aldehyde-terminated surface is progressively removed from a solution of various functional amines as the pH is varied. Each amine combines a single functionality associated with a unique physical property (colored dots) for a given pKa, which thus leads to a gradient of functional imines. b, Chemical structures used to design a first model system: triethoxysilane aldehyde **1**, Cy3 benzylamine **2** and Cy5 alkylamine **3**.



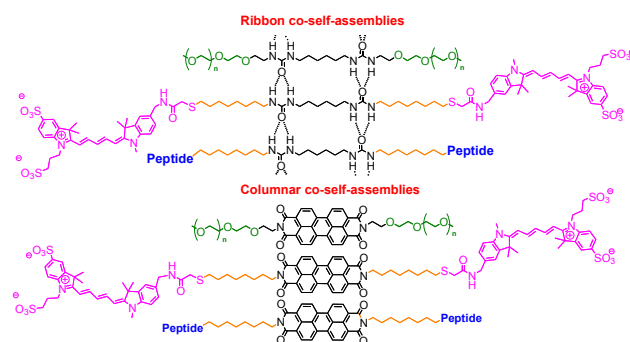
**Figure 5.** Left, Contour plot of the 96 fluorescence spectra recorded from the mixture presented in Figure 4, and that displays the complex 2D-gradient of the dynamic self-assembled monolayer as a function of pH (white dots). Right, a protein gradient obtained from an avidin–fluorescein (green dots), streptavidin–Texas red (red dots) mixture as a function of the pH (blue squares).

The DynaSAMS approach opens an interesting research framework related to the design of a new kind of responsive interfacial systems that can adapt their constitutions to external parameters. The results obtained with the formation

of various mixed (bio)functional gradients demonstrate the broad potentialities of the method and the possibility to use proteins from the avidin family makes the protein gradient transferable to most biotinylated molecules / nanoparticles by a simple recognition reaction. Beyond, it is assumed that this approach is not limited to the formation of gradients, but that it would be readily extended to the design of responsive interfacial nano-(bio)objects.

### Multifunctional co-self-assemblies

This subproject deals with the understanding of the dynamic combinatorial reorganization of two families of supramolecular polymers: the first one based on bis-urea ribbons, and the second one based on columnar stacking of perylenes. Within each family, we want to co-self-assemble the same core unit, but mixing different lateral groups having different functionalities; for instance structuring functionalities (such as hydrophilic PEG units), with biorecognition units (such as peptides), and fluorescent probes (such as cyanine molecules). This project has already required a lot of synthetic efforts before going to physico-chemical analyses, and we have now successfully achieved the fabrication of promising monomeric units such as the one described in Figure 6.



**Figure 6.** Two kinds of multifunctional co-self-assemblies under development in our group. Top, the supramolecular core unit is based on bis-urea derivatives; and bottom, the supramolecular core unit is based on perylene bis-imide derivatives.

We are currently starting the dynamic study of these self-assemblies with a series of questions to address such as: can the supramolecular polymerization proceed spontaneously by blocks or in perfectly alternating sequences? Can the supramolecular polymers reorganize their sequence depending on solvents, temperature, or on presence of external nanoparticles or biological targets? Are they of potential interest as multifunctional (bio)materials?

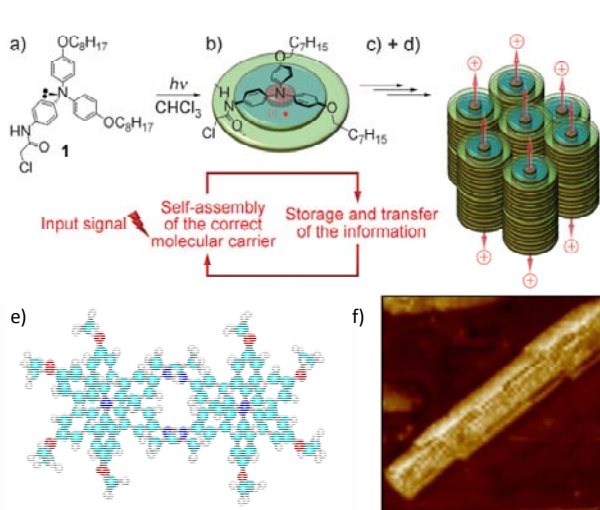
## Implementing new responsive self-assembly units and processes in materials science

Another important target for chemistry at its interfaces with materials science is to find new responsive supramolecular units. For instance, organic photonic and optoelectronic materials are shown to benefit from their supramolecular self-assembly within highly organized aggregates such as vesicles, nanotubes, layers. New

implementations towards responsive versions of these systems will be of first importance in the future.

## Light-responsive supramolecular wires as metallic interconnects

Triarylamine-type molecules are inserted in numerous electro-optical devices such as organic light emitting diodes (OLEDs), organic solar cells, organic field effect transistors (OFETs), non-linear materials, and even as photoconductors for the Xerox<sup>®</sup> process in laser printers and photocopiers. However, this molecular core was never described as a structuring precursor that would be able to self-assemble in ordered supramolecular architectures, possibly with enhanced physical properties. Recently, we discovered the unique behavior of precursor **1** (Figure 7).<sup>[15]</sup>

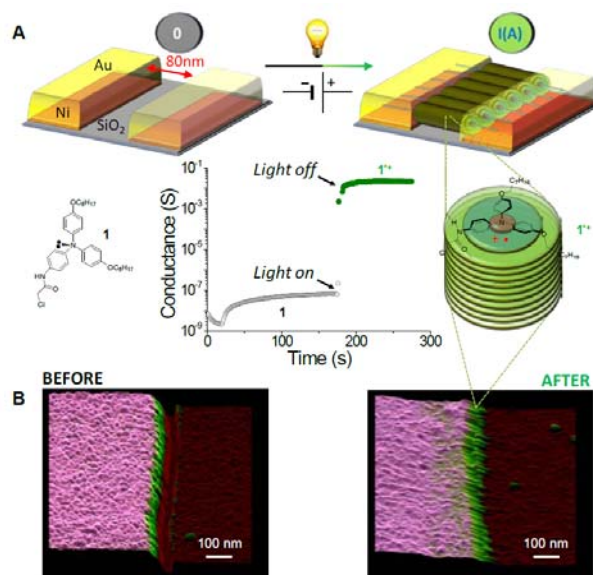


**Figure 7.** (a-d) Hierarchical self-assembly processes that occur upon light irradiation of the neutral triarylamine **1**. (e) Molecular modeling of the stacked structures based on high resolution AFM imaging (f).

In this work, we have described a firmly new kind of responsive self-assembly process that rests on simple light exposure. The organizing process starts by the formation of a triarylammonium cationic radical upon light stimulation. This radical can in turn be transferred to other neutral triarylamines, thus allowing the supramolecular polymerization of units containing a delocalized cationic radical. Moreover, we have demonstrated that these molecular wires, which protect holes from quenching, can combine into very strongly packed bundles of larger fibers. This phenomenon represents a sort of “supramolecular living radical polymerisation” process which can be simply triggered by charge transfer and be reversibly broken up by heating. It provides new insights in charge transfer self-assemblies and opens a number of interesting possibilities by using these triarylamine synthons as new stimuli-responsive supramolecular scaffold because they can be associated, as we have demonstrated latter on, to other molecular fragments. From a conceptual point of view, the stimulation of this system with light (or an oxidant) creates an electronic signal which induces the building of the correct self-assembled carriers – *i.e.* the supramolecular wires – which in turn are able to stabilize and transfer this first electronic

signal over space and time. Thus, we have here a minimal example to design *de novo* stimuli-responsive chemical systems displaying a very fundamental synergistic and dynamic structure/fonction relationship, *i.e.* that are able to receive, store, conduct, and exchange physical information by self-organization and emergence. In addition, in collaboration with Alexander Semenov and Irina Nyrkova, we have performed a very important and deep experimental and theoretical investigation of the supramolecular triarylamine nanowires (STANWs) self-assembly process, which revealed its self-replicating nature. These results constitute the first example of a responsive and self-replicating *functional* system, which will pave the way for thinking in terms of combined smart and autonomous materials.<sup>[5]</sup>

We then took advantage of this triggering capability to determine quantitatively the conductivity properties of the supramolecular assembly when spontaneously trapped between metallic electrodes (Figure 8).



**Figure 8.** Triggered self-assembly process of STANWs using a nanotrench setup, together with typical associated conductance measurement and corresponding AFM imaging of the gap.

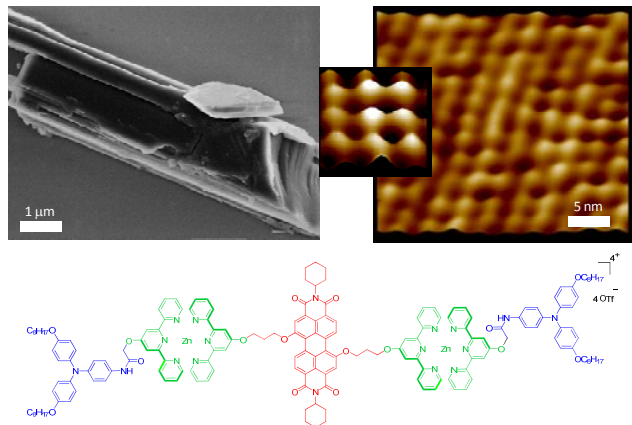
Along these investigations, we have discovered that STANWs display extraordinary metal-like conductivity properties similar to sorted single-wall carbon nanotubes (*i.e.* a very low resistivity and its monotonic decrease with temperature down to 1.5 K).<sup>[16,17]</sup> The share of the electronic wave function of the STANWs with the metallic substrate is likely the fundamental reason explaining the six orders of magnitude gain in interface resistance compared to classical conjugated polymers. It illustrates how straightforward bottom-up self-assembly strategy can directly coincide with the top-down methodology of patterning metallic circuitry. The first generation of STANWs already presents tremendous potential for making novel processable optoelectronic nano-devices.

### Other functional light-responsive materials for organic electronics

Going further with STANWs, we have probed their capacity to self-assemble with modified substituents. For instance, we have shown that by linking two correctly designed triarylamine moieties by Zn<sup>2+</sup> coordination units, it

is possible to self-assemble, upon simple visible light stimulation, these metal complexes within spherical nanoparticles with very low polydispersity.<sup>[18]</sup>

Another important result obtained recently in the extension of our work on STANWs, is their coupling with electron acceptors (i.e. perylene moieties) by linking them using coordination chemistry (Figure 9).



**Figure 9.** SEM and AFM imaging of a light-triggered self-assembly of a triarylamine-perylene Zn<sup>II</sup> complex.

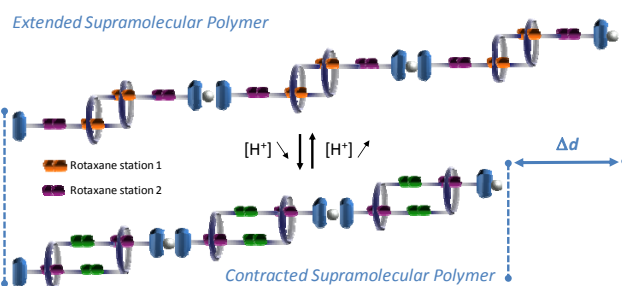
In this system, the light-triggered self-assembled structure consists in a square-like association of molecular complexes, which then grow in two-dimensional layers using the STANWs as branching points, these latter being piled in highly organized 3D millefeuilles at higher concentrations. This kind of geometry is particularly promising for the creation of nanosized supramolecular heterojunctions, which can favor both optimized charge separation and migration for the design of ideal solar cells (IRTG collaboration). All our approaches of STANWs will be intensively developed further within the next five years.

## Coupling nanoscopic to macroscopic motions in materials science

The dynamic nature of mechanical bonds within mechanically interlocked molecules (MIMs) allows for the components to undergo relative internal movements, i.e. translation and circumrotation. However, although numerous efforts have been devoted to the design and synthesis of MIMs, no coupling of nanoscopic motion to macroscopic scale has been achieved yet.

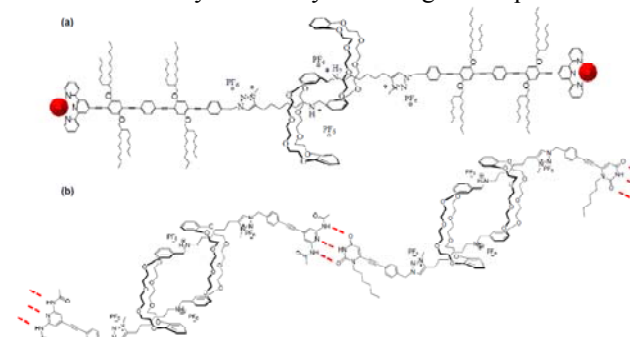
### Coupling of nano-mechanical motions in non-covalent supramolecular polymers

In the present project, we have focused our work on a novel kind of responsive supramolecular polymers which display a reversible and tunable contraction/extension of their momomers between two well-defined positions (Figure 10).



**Figure 10.** Representation of a bistable, pH-responsive, rotaxane-based molecular shuttle, that polymerises by metallo-supramolecular or H-bonding recognition patterns.

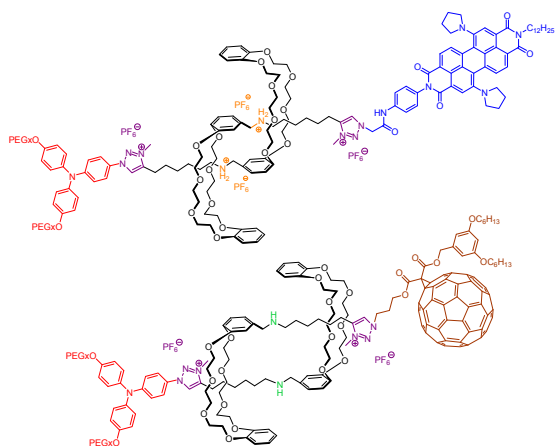
We have performed intensive synthetic investigations toward this direction in the last three years and the first promising polymers have been now synthesized and have been engaged for structural investigations. In Figure 11, we present two examples of complementary monomeric chemical structures that have been already obtained and which are currently studied by scattering techniques.



**Figure 11.** Examples of two synthesized and polymerized structures of bistable rotaxanes that are able to produce supramolecular contraction/extension upon pH-modulations.

### Supramolecular coupling of molecular motions in functional mesophases

Another advanced project in our group rests on combining *i*) supramolecular nanoswitches using bistable rotaxane chemistry with *ii*) large microphase separations, and together with *iii*) transitions in optic and electronic properties. In that direction, we have designed and synthesized dissymmetric double-threatened bi-functional rotaxanes having a hydrophilic electron donor group on one side, and a hydrophobic electron acceptor on the other side (Figure 12). We have planned that, by tuning accurately the volume ratio between these two groups, and depending on the contraction/extension of the mechanical interlock, we will be able to transfer the molecular motion to a transition between two kinds of mesophases. In addition, because of the optoelectronic nature of the donor (triarylamine) and acceptor parts (perylene or fullerene), we are expecting, concomitantly to the phase transition, a switch in the functional behavior of the system, for instance producing (or not producing) electron or energy transfer. We have already proved the possibility to contract and extend these entities, and supplementary investigations are intensively pursued in collaborations to fully understand the intriguing optoelectronic properties measured for these materials.



**Figure 12.** Examples of two original functional amphiphilic bistable rotaxanes which were synthesized by our group.

**Collaborations within the axis:** C. Marques, D. Sarazin, M. Schmutz.

**Collaborations with other teams in the ICS:** G. Decher, I. Kulic, J.-F. Lutz, M. Maaloum, I. Nyrkova, M. Rawiso, A. Semenov.

**Collaborations outside the ICS:** L. Allouche (UdS), E. Buhler (Paris VII), M. Cecchini (ISIS, Strasbourg), B. Doudin (IPCMS, Strasbourg), S. Hacke (IPCMS, Strasbourg), A. Herrmann (Firmenich, Geneva), S. Ludwigs (Stuttgart University), P. Samori (ISIS, Strasbourg).

**Local networks and affiliations:** Labex CSC (Chimie des Systèmes Complexes) – International Center for Frontier Research in Chemistry (icFRC - RTRA).

**Active European Network:** ESF-COST on Systems Chemistry – IRTG on soft matter science – 2 ITN Marie Curie (DYNANO and READ)

**Financial supports and grants as Principal Investigator:** ERC StG (SysChem) – ANR blanche (Dynablocks) – 2 RTRA-icFRC (Multiself and Supralight (coupled to IRTG)) – Firmenich SA (Partners to win) – 2 CNRS (Starting grant and IR Valo) – 2 UdS (Starting grants Scientific Council) – CPER Nanomat – European Science Foundation COST (Systems Chemistry) – 1 Marie Curie People (integration grant, NaDyPe)

**Grants as Network Member:** 2 ITN Marie Curie (DYNANO and READ) – ANR blanche (Multiself)

[1] Moulin, E., Giuseppone, N. – *Reactions in Dynamic Assemblies* Encyclopedia of Supramolecular Chemistry – From molecules to nanomaterials Wiley-VCH, **2011**.

[2] Giuseppone, N., Lutz, J.-F., *Catalytic Accordions* *Nature*, **2011**, 475, 40-41.

[3] Giuseppone, N., Schmitt, J.-L., Allouche, L., Lehn, J.-M., *Driven Evolution of Dynamic Combinatorial Libraries of Helical Strands* *Angew. Chem. Int. Ed.* **2008**, 47, 2235-2239.

[4] Herrmann, A., Giuseppone, N., Lehn, J.-M., *Imine Based Liquid Crystals for the Controlled Release of Bioactive Materials* *Chem. Eur. J.* **2009**, 15, 117-124.

[5] Giuseppone, N., *Towards Self-fabricating Materials* Invited article for the special issue on the Origin of Chemical Evolution *Acc. Chem. Res.*, **2011**, in progress.

[6] Moulin, E., Giuseppone, N., *Dynamic Combinatorial Self-replicating Systems*

*Topics in Current Chemistry*, **2011**, published on line DOI:10.1007/128\_2011\_198.

[7] Xu, S., Giuseppone, N., *Self-Duplicating Amplification in a Dynamic Combinatorial Library*

*J. Am. Chem. Soc.* **2008**, 130, 1826-1828.

[8] Nguyen, R., Allouche, L., Buhler, E., Giuseppone, N., *Dynamic Combinatorial Evolution within Self-Replicating Supramolecular Assemblies*

*Angew. Chem. Int. Ed.* **2009**, 48, 1093-1096. • Hot paper *Angewandte*

[9] Moulin, E., Giuseppone, N. *Dynamic Constitutional Devices* *Supramolecular Chemistry*

Pan Stanford Publishing, **2011**, in press.

[10] Moulin, E., Cormos, G., Giuseppone, N., *Dynamic Combinatorial Chemistry as a Tool for Material Science*

Invited tutorial review

*Chem. Soc. Rev.*, **2011**, published on line DOI: 10.1039/c1cs15185a.

[11] Nguyen, R., Buhler, E., Giuseppone, N., *Dynamic Block Copolymers (Dynablocks) : Structural Modulation of Responsive Combinatorial Large Self-assemblies*

*Macromolecules*, **2009**, 42, 5913-5915.

[12] Jouault, N., Nguyen, R., Rawiso, M., Giuseppone, N., Buhler, E., SANS, SAXS, and Light Scattering Investigations of pH-responsive Dynamic Combinatorial Mesophases

*Soft Matter*, **2011**, 7, 4787-4800.

[13] Tauk, L., Schröder, A., Decher, G., Giuseppone, N., *Hierarchical Functional Gradients of pH-Responsive Self-Assembled Monolayers using Dynamic Covalent Chemistry on Surfaces*

*Nature Chemistry*, **2009**, 1, 649-656.

[14] Giuseppone, N., Tauk, L., Decher, G., Schröder, A., *Method for preparing chemical gradients on surfaces by grafting aldehyde and amine groups*

PCT Int. Appl. (**2010**), WO 2010149925 A1 20101229.

[15] Moulin, E., Niess, F., Maaloum, M., Buhler, E., Nyrkova, I., Giuseppone, N., *The Hierarchical Self-Assembly of Charge Nanocarriers: A Highly Cooperative Process Promoted by Visible Light*

*Angew. Chem. Int. Ed.* **2010**, 49, 6974-6978. • Frontispiece cover *Angewandte*

[16] Faramarzi, V., Niess, F., Moulin, E., Maaloum, M., Dayen, J.-F., Beaufrand, J.-B., Doudin, B., Giuseppone, N., *Triggered Self-fabrication of Supramolecular Organic Nanowires as Metallic Interconnects*

**2011**, Submitted for publication.

[17] Giuseppone, N., Doudin, B., Faramarzi, V., Dayen, J.-F., Niess, F., Moulin, E., *Conduction électrique par des assemblages supramoléculaires de triarylamines (CNRS, UDS)*

French patent application FR1058954 filed on October 29, **2010**.

US patent application US61/418645 filed on December 1, **2010**.

[18] Moulin, E., Fuks, G., Niess, F., Giuseppone, N., *Cooperative Light-triggered Self-assembly of Triarylamine Nanospheres*

Invited paper for the Special Emerging Investigator Issue *Chemical Commun.*, **2011**, in press.



## Self-Evaluation

### Creation of the group and human resources

The SAMS research group was officially created in February 2008, immediately after the evaluation of the past AERES session, so as the team was not evaluated at that time. However, the committee mentioned its very positive opinion regarding the starting of a new line of research in supramolecular chemistry at the ICS (*cf.* report 2008). The creation of the team was associated to the opening of a professorship at the Faculty of Chemistry and for which Dr. Nicolas Giuseppone, previously chargé de recherche CNRS in the Lehn laboratory, was elected. The team was immediately strengthened by the hiring of a technician (Céline Desvignes) who has been instrumental in the starting, reinforcing, and stabilizing processes. Later on, Dr. Emilie Moulin succeeded in her application as a chargé de recherche (section 12) and brought to the team her exceptional knowledge in organic synthesis. Finally, in 2010, Dr. Gad Fuks was recruited as a Maître de Conférence in the team, a position opened by the Faculty of Chemistry to finalize the operation of the SAMS research group creation. He brought additional knowledge in the synthesis of (bio)macromolecules and nanoparticles, and in electronic microscopy as well.

Recruiting students was our main concern when starting the team, especially because of our intrinsic activity which rests on chemical synthesis, a domain requiring important manpower if a positive outcome is expected!! Thanks to a number of financial supports (see below), and because of a series of additional efforts to be attractive in our scientific approach and its diffusion, we have managed very well in increasing the size of the group. By taking a snapshot of the team in October 2011, we will reach a very good size with 4 permanents and 13 post-docs and PhD students. It should be here mentioned that we have also importantly improved our scientific level of recruiting since we started the group. At the first time, we had to recruit some people with relatively weak backgrounds, requiring a lot of everyday management, but now we can attract very bright and talented collaborators with impressive records. For instance, we have been recently able to hire a new PhD student who graduated from the University of California at San Diego, and post-docs having experiences in the best laboratories worldwide (Prof. Stupp – Northwestern; Prof. Rebeck – Scripps San Diego; Prof. Hunter – Sheffield; Prof. Laschewsky – Berlin). We believe that this point means a lot in terms of the perceived quality of our work, and this important (recent) raising will certainly be fruitful in terms of scientific results and outcomes in the near future.

Our duty is also to confer people coming in our lab the necessary skills and knowledge to succeed in their future carrier. Although we don't have yet long-time records to assess precisely this feature, we can argue that after 3 PhD defenses, one of our former students is Assistant Professor in China (Shandong University), the second one joined the Research and Development laboratories of Samsung SNRC (Netherlands), and the last one is offered a post-doctoral position at The Scripps Research Institute. We hope to keep improving all these aspects in the future, and we are confident that our new students and collaborators have all the qualities and willing to do so.

### Statement on financial supports

One of the most important requirements to start our research activity/laboratory has been to succeed in raising funds, especially with the costs associated to our synthetic activity in terms of manpower and chemicals/furniture. A series of applications and projects were designed and submitted for evaluation locally, nationally, and internationally with a very high rate of success. First of all, University of Strasbourg and CNRS helped us at the very beginning with starting grants to equip part of our laboratories, which were totally empty of small equipment to work. We were also supported by the CPER Nanomat which provided the group with a UPLC/Mass spectrometer Waters instrument, a unique tool of characterization for us. Still at the local level, we also were granted several times by the icFRC foundation, based on project refereed by international panels, and we were able to finance people and a peptide synthesizer for instance. At the national level, we succeeded in an application at the ANR (programme blanc) and an ANR (Emergence) as a Principal Investigator of a 4 year project. As a partner, we also succeeded in another ANR (programme blanc) for the extension of our conducting supramolecular materials in spintronics. Within a network of 16 research teams in Strasbourg, and led by Prof. J.-M. Lehn, we also recently obtained the Labex *Chemistry of Complex Systems* granted by the government. At the international level, we have attracted funds from industry (Firmenich SA, Geneva) which has recently signed a contract with us for a 3-year PhD student. We also succeeded in several Marie Curie Programs (an Integration grant for a Post-doctoral fellow, and 2 International training networks with one PhD each associated to numerous exchange facilities all over Europe). Finally, the biggest achievement in terms of financial support was to succeed in the most competitive European competition for young researches, the ERC Starting Grant, which awarded us for a 5-year project with an amount of 1.5 M€. Hereafter, we present a list of the financial supports with the associated amounts obtained (as partner or principal investigator (PI)).

- ☞ ANR Emergence (2011) (250 k€) (PI)
- ☞ Labex CSC (2011) (15 M€ total over 10 years) (Partner)
- ☞ Marie Curie ITN(1) (2011) (250 k€ to SAMS Partner)
- ☞ Marie Curie ITN(2) (2011) (250 k€ to SAMS Partner)
- ☞ ANR blanche (2011) (150 k€ to SAMS Partner)
- ☞ Marie Curie People (2011) (50 k€) (PI)
- ☞ Firmenich SA (2011) (180 k€) (PI)
- ☞ CNRS/Région (2011) (100 k€) (PI)
- ☞ ERC (2010) (1.5 M€) (PI)
- ☞ icFRC RTRA (2010) (120 k€) (PI)
- ☞ ANR blanche (2009) (520 k€) (PI)
- ☞ icFRC RTRA (2008) (150 k€) (PI)
- ☞ CPER Nanomat (2008) (120 k€) (PI)
- ☞ CNRS (2008) (50 k€) (PI)
- ☞ Scientific council of UdS (1) (2008) (25 k€) (PI)
- ☞ Scientific council of UdS (2) (2008) (45 k€) (PI)

**Total** (granted in 2008-2011 and for 2008-2015) ≈ **3.8 M€**

### Statement on scientific collaborations

During these first three years, we have tried to develop a network of active collaborations both within and outside the ICS. Our decision to join the ICS was originally strongly motivated by the opportunities to collaborate with physicists. Indeed, working on large self-assemblies with complex

systems requires state-of-the-art characterization measurements and also, to go further in the understanding of the systems, theoretical knowledge. In particular, we have developed a strong interaction with Dr. Michel Rawiso for scattering techniques, including neutrons, but more particularly X-rays (SAXS and WAXS). Static light scattering investigations were successfully achieved on two projects with Dr. Dominique Sarazin. We have also engaged what we believe long term collaborations, and which is now entering a very productive phase, with the group of theory (Dr. Irina Nyrkova and Dr. Alexander Semenov). Another very fruitful interaction came with AFM characterization of several of our self-assembled systems (Prof. Mounir Maaloum); this is becoming now a more and more regular collaboration with possible interesting projects to develop, not only for us but also from the physics point of view (e.g. conducting AFM). Other knowledge and techniques were also very important for several projects developed in our team, we could cite for instance the interaction with Prof. Gero Decher (collaboration on surface chemistry, especially by bringing expertise in ellipsometry and quartz microbalance techniques), or with Dr. Andre Schröder (confocal microscopy). A starting collaboration on supramolecular assembly of covalent polymers is now engaged with Dr. Jean-François Lutz. We believe that the development of this unique range of interactions within the ICS constitutes an important asset in succeeding in our own projects, and that it might create also opportunities for the other groups to make interesting physics on original objects.

We also built an important external network, both in France and abroad, to go further in the understanding and valorization of our ideas and systems. Among the strongest, we will cite the very tight connection we pursue from the beginning with the group of Prof. Eric Buhler in Paris for dynamic light scattering and SANS experiments. Other important scientific opportunities came with the group of Prof. Bernard Doudin at the IPCMS of Strasbourg which is specialized in organic nano-electronics and spintronics. We are currently engaged in a very important program of scientific investigations and valorization, up to the industrial developments with the support of FIST. We will also mention the long-lasting collaboration we pursue with Dr. Lionel Allouche on DOSY NMR (Strasbourg Esplanade Campus), and with whom we have developed the first examples of deconvolution of DCLs using this technique. Other very recent collaborations have been engaged for photophysics (Prof. Stefan Hacke, IPCMS), and supramolecular chemistry at surface (Prof. Paolo Samori and Dr. Marco Checcini, ISIS). Internationally, thanks to the IRTG network created by Jörg Baschnagel between Strasbourg and Freiburg, we have also started collaboration with the group of Prof. Sabine Ludwigs (who has now moved to Stuttgart) on spectroelectrochemistry with possible development towards solar cell devices. Industrial collaboration was also engaged with Firmenich SA (Switzerland) for the implementation of some of our systems in the domain of flavors and fragrances. Other international interactions were developed within several European networks which, if not having the same objective than the previous collaborations regarding the impact on a specific work, have nonetheless resulted in sharing ideas towards the exchange of students and international meetings. These

networks (1 COST and 2 ITN) represent a total of about 20 research groups at the forefront of supramolecular chemistry and systems chemistry all over Europe, thus including our own group at this level of excellence.

#### Statement on scientific productions

On average, scientific production is probably the best indicator to characterize the real quality of a scientific work. Because the group started from scratch very recently and because it has taken time before arriving at that level of manpower and for starting all the current projects, we are obviously facing a shift between the present structure of the team and the measured outcome (metrics). However, we can already state on very good records, our policy being to favor quality of publications prior to quantity.

For the period **2008-2011**

☞ Number of articles – **20**

☞ Journals – *Nature / Nature Chemistry / Angewandte Chemie / Journal of the American Chemical Society / Chemical Society Review / Accounts of Chemical Research /*

☞ Average impact factor of the journals – **15**

☞ Average number of citations per article (published in the group on the period 2008-2010) – **14,2**

☞ h-index of the permanent staff – **23**

☞ m-index of the permanent staff – **1.8** (h-index/n-years)

☞ Number of patents – **3**

☞ Number of Invited International Conferences – **12** (including Gordon and ESF high-level Conferences)

☞ Number of other invited talks and seminars – **10**

#### Statement on scientific diffusion

Due to our position at the University (one Professor and one Maître de Conférences), an important task is also to transmit scientific knowledge. This has been performed for instance by taking in charge new courses on supramolecular chemistry of biopolymers and biomaterials, as well as entering in already existing programs of supramolecular chemistry and organic synthesis. We have also taken the responsibility of a set of courses dealing with polymer synthesis and formulation which will start in 2012. Other investments at the University (Prof. Giuseppone elected as representative of Professors at the Faculty, and Dr. Gad Fuks being responsible of ACMOs for the teaching laboratories) gave us strong interactions and recognition from colleagues. Our teaching activities also attracted numerous Master students in the SAMS group.

Another aspect of scientific diffusion is the organization of conferences. In December 2011, we will chair a 4-day International COST Conference on the implementation of Supramolecular Chemistry in Systems Chemistry, with an invited panel of 18 top-level scientists in the field.

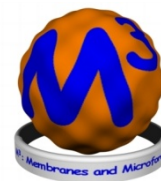
#### Overall statement

By looking at the scientific quality of the research performed (*cf.* research report), together with the various self-evaluations criteria going from grants to scientific collaboration, production, and diffusion, we can honestly claim a strong success in the creation of the SAMS research group. We are clearly in the process to become part of the very best world leaders in systems chemistry. We will next explain in the “projects part” how we plan to achieve this objective as soon as possible.

# M<sup>3</sup> Membranes and Microforces (Mcube)

Head of the group *Carlos Marques*

**Permanent staff:** Marc Basler, CNRS technician, Prof. Thierry Charitat, UoS Professor; Jean Iss, CNRS Engineer; Dr. Patrick Kékicheff, CNRS Senior Scientist; Dr. Carlos Marques, CNRS Senior Scientist; Prof. Tatiana Schmatko, UoS Assistant Professor, Dr. André Schröder, CNRS Scientist and Prof. Fabrice Thalmann, UoS Assistant Professor.



**Non-permanent staff for the period 2007-2011. 7 Post-doctoral associates:** S. Balko (Fulbright, 08/09-10/12), N. Bushmarina (ANR, 10/01-10-09), W. Caetano (FAPESP, 07/09-08/06), W. Dantas (CAPES, 08/12-09/12), E. Duarte (FAPESP, 08/12-09/12), M. Greenall (Marie-Curie, 10/06-12/06), C. Haluska (LEA, 07/01-07/12). **16 PhD students:** B. Amoussou (Nancy/Strasbourg, defended 11/12), M. Bauer (Strasbourg/Saclay/Regensburg, expected 11/11), C. Campillo (IRTG Grenoble/Strasbourg, defended 08/06), A. Hemmerlé (Strasbourg, expected 13/09), L. Hermann (Strasbourg, expected 13/09), M-L Hissette (IRTG Strasbourg/Constance, defended 07/09), M. Khaksar (IRTG Strasbourg/Constance, expected 11/11), L. Lagarde (Strasbourg/P&G, expected 12/09), L. Malaquin (Strasbourg/Saclay, defended 09/11), C. Marcopoulos (Strasbourg, expected 11/09), O. Mertins (Porto Alegre/Strasbourg, defended 08/05), P. Santos (São Paulo/Strasbourg, expected 12/06), N. Schulmann (Strasbourg, TSP/MCube, expected 11/12), Y. Sun (IRTG, Strasbourg/Constance, defended 10/12), G. Weber (Strasbourg, expected 12/09), J. Wolff (Strasbourg, expected 12/09). **3 visiting professors:** R. Itri, 3 months, USP; M. Kilfoil, 3 months, MacGill; C. Mendonza, 3 months, UNAM; T. Kuhl, 6 months, UC Davis. **10 Master students**

**Keywords:** self-assembled phospholipid bilayers · vesicles · liposomes and supported membranes · structure · characterization and control of soft matter by microforce techniques

The Charles Sadron Institute is a major player in the development of Soft Matter, where the making of basic science in the Chemistry and the Physics of Polymers, Colloids and Surfactants naturally extends into applications for the materials of tomorrow. The M<sup>3</sup> group “Membranes and Microforces” was founded in January 2005 under the responsibility of Carlos Marques, and contributed to the mission of the Institute by developing and structuring with other groups research at the ICS on self-assembled systems.

group’s scientific production and current projects can be found on the website <http://mcube-ics.u-strasbg.fr>.

For convenience we organize the presentation of our research results in the three chapters below, the reader will certainly perceive the multiple interconnections resulting from a shared interest by the group members for membranes and for the physics of self-assembled Soft Matter.

## Bringing the science of self-assembled bilayers to the next level

Research in the Mcube group is geared towards the understanding of the physical properties of self-assembled phospholipid bilayers. Our conviction is that self-assembled two-dimensional structures are at the cross roads of exciting and promising present fields of scientific research, posing fundamental theoretical and experimental challenges for the physicist, and opening into a wide ground of potential applications in materials science, biophysics, pharmacy and cosmetics, only to mention a few. The group Mcube brought together scientists with complementary competences in experimental and theoretical physics, that share a common interest in the field. The group is collectively engaged in several collaborative structures and projects, with teams in France and abroad: ANR SlidTetherLig, COFECUB “Photoresponsive Liposomes”, two successive IRTGs on Soft Condensed Matter, GdR 3070 CellTiss, GdR 3334 SupraMol Assemblies, ... and it actively participates in calls for new collaboration programs ITN, COST, ESF P2M, ... More information about the

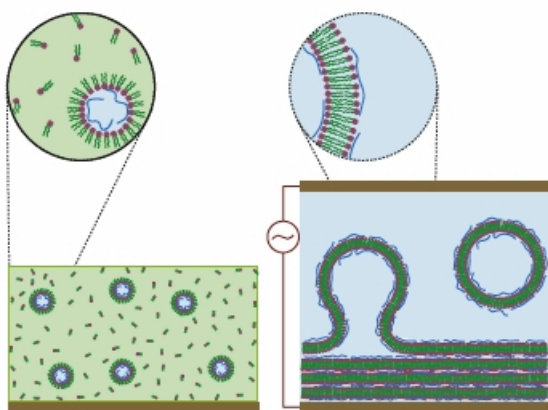
## Lipid bilayers

Phospholipids self-assemble in solution as fluid bilayers of typically 5 nm thickness, leading to lamellae structures of planar, cylindrical, spherical or even more complex geometries. When the bilayers enclose an inner spherical or cylindrical space one refers to these assemblies as vesicles or liposomes. In the living realm, where phospholipid bilayers build the walls of cells and cellular organelles, vesicles and liposomes provide simple models to understand cell wall properties: transport, fusion, mechanical resistance,... Depending on the actual self-assembly conditions, single or multiple layer vesicles can be prepared in a large size range, from liposomes as small as a few tens of nanometers to giant unilamellar vesicles (GUVs) as large as one tenth of a millimetre. Following seminal work by Helfrich, who first recognized the importance of the membrane bending elasticity, extensive theoretical and experimental studies contributed to the writing of one of the finest chapters in modern statistical physics of soft condensed matter. Interestingly, fluid bilayers also inspired many fundamental studies in Mathematics, particularly in topology and differential geometry, some of these studies bearing a direct impact on the physical description of the membranes. Research in the field of two-dimensional lipid assembly is now

opening exciting new perspectives towards many new directions, an effort that we are proud to join and keen to contribute to.

**New giant unilamellar vesicles**

Giant Unilamellar Vesicles are a choice system for studying and micro-manipulating lipid bilayers under an optical microscope, providing information on structure or mechanical properties. We studied various composite vesicles made from *in situ* polymerization of poly(NIPAM) polymerization and explore the rich behavior of these membrane coated gelly-balls under temperature and osmotic changes.<sup>[13,14]</sup>



**Figure 1.** Electroformation of giant unilamellar vesicles from an inverse phase precursor, allowing the direct incorporation of water-soluble species inside and outside the vesicle.

We have discovered that a simple modification of the well-known method of giant vesicle electroformation allows for a direct addition of water-soluble species to the phospholipid bilayers, solving thus a recurrent problem in vesicle formation by electroformation.<sup>[19]</sup>

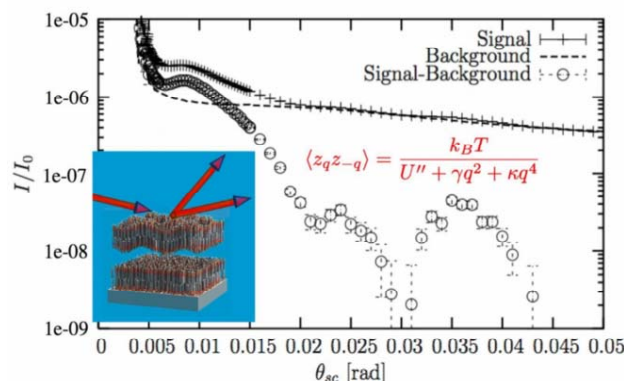
**Fluctuation and destabilization of supported membranes**

The dynamics of lipid membranes has an intrinsic multiscale character. Equilibrium and non-equilibrium fluctuations as well as destabilization or topological changes involve complex mechanisms in a range of length scales from a nanometer to many micrometers. Thanks to optical microscopy experiments on giant vesicles, large length scales are now better understood but accessing smaller length scales is still challenging and presently only achieved by numerical simulations. A major challenge resides thus in accessing experimentally sub-optical properties and understanding the relations connecting the different scales involved in fluid membrane dynamics.

We have investigated membrane fluctuations, protrusion modes and destabilization mechanisms leading to vesicle formation.<sup>[8]</sup> A refined analysis of the bilayer fluctuations requires a full characterization of the fluctuations spectrum, that is the fluctuations amplitude at a given spatial length

scale. We have developed a new x-ray off-specular scattering experiment at ESRF, in collaboration with J. Daillant (CEA-Saclay). The main difficulty of this experiment is due to the weakness of the scattering volume. Surface sensitivity was considerably enhanced by taking advantage of total external reflection at the Si-water interface, but the intensity scattered by the fluctuating bilayer remains two or three orders of magnitude lower than bulk scattering (see Figure 1). We developed a rigorous calculation of specular and off-specular X-ray reflectivity of supported membranes. More precisely, we computed the correlation functions of the membranes only by approximating the interaction potentials as quadratic functions.

Thanks to specular reflectivity, we determine the perpendicular structure of the samples, whereas off-specular reflectivity gives access to lateral inhomogeneities of the membranes. By performing a simultaneous analysis, we characterize both structure and parameters of the fluctuation spectrum: tension, rigidity and interaction potentials. By studying single supported bilayers, we measure for the first time the effective microscopic tension related to protrusions inside the membrane (about 80 mN/m). Long-range fluctuations are determined by moving the membrane away from the substrate by the addition of an adsorbed membrane. Therefore we precisely measure the interaction potential between neutral membranes in a state of equilibrium.



**Figure 2.** Off-specular scattering experiments: (+) off-specular data; (-) scattering by bulk; (o) signal after background subtraction, i.e. scattering by floating bilayer.

In order to better understand the influence of the substrate on lipid bilayer dynamics, the diffusion law of DMPC and DPPC in Supported Lipid Bilayers (SLB), on different substrates, has been carefully investigated by using FRAPP (Fluorescence Recovery After Patterned Photobleaching).<sup>[17]</sup>

Over micrometer length scales, we demonstrate the validity of a Brownian diffusive law both in the gel and the fluid phases of the lipids. Measuring the diffusion coefficient as a function of temperature, we characterize the gel-to-liquid phase transition of DMPC and DPPC. It is shown that different results can be obtained, depending on the substrate and on the method used for bilayer preparation. In particular, we have shown that preparation of the bilayers from vesicle fusion leads to larger scattering

of the diffusion data and of the transition temperature shifts.

**Phase coexistence and domain formation in lipid bilayers**

As soon as one considers membranes comprising two lipid species or more, and biological membranes have a very complex composition indeed, one expects the possibility of lipid segregation. On the other hand, it is natural to assemble lipids of complementary physical and chemical properties together in order to design membranes with optimal responsive properties with respect to their environment (light, charge, stress of flow). It is therefore important to properly characterize the different segregated domains and to understand the principles underlying phase coexistence in lipid membranes.

Contributing to the development of new tools to inspect the level of molecular organization in phase separated domains, we have studied coexisting ordered and disordered liquid phases in a ternary giant vesicle, by combining measurements of fluorescence lifetime and polarization in a two-photon geometry. We measure the order parameter of fluorescent probes that segregate selectively into the different domains and correlate probe wobbling degrees of freedom with the degree of cholesterol enrichment.<sup>[15]</sup>

Theoretically, we have recently achieved an important step towards developing a friendly tool for predicting the phase behaviour of binary and ternary mixtures containing cholesterol.<sup>[27]</sup> Starting from the concept of order parameter that underlies the so-called gel to lipid main transition, we proposed a simple mean-field Gibbs free-energy displaying the most essential features of the ternary saturated/unsaturated/cholesterol systems. Our model provides the most accurate prediction to date of such a Gibbs ternary phase diagram (see Figure 3). Unlike previous attempts, it requires as input only basic knowledge on the single lipids main transition, basic features of the lipid-cholesterol binary coexistence gap and a single additional free parameter. We illustrate the potential of our approach by sketching a scenario for the morphological evolution of ternary phase diagrams with temperature. Work is currently under way to extend the approach to other lipids as well as to more complex situations - quaternary mixtures, non-vanishing surface tension - that can easily be incorporated into the picture. This work will hopefully give birth to a user-friendly web-based interface for predicting the phase behaviour of systems containing arbitrarily chosen lipid species, which is the middle term goal that we aim at.

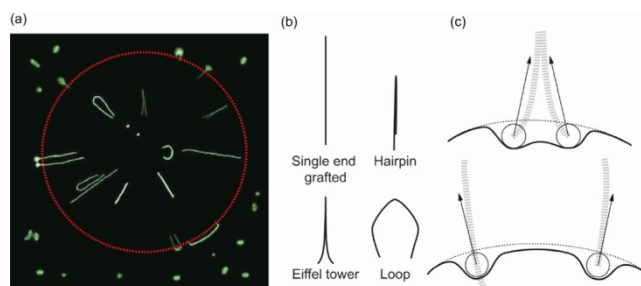


**Figure 3.** Prism representation of the temperature variation of the ternary phase diagram for a mixture of saturated and unsaturated lipids and cholesterol.<sup>[27]</sup>

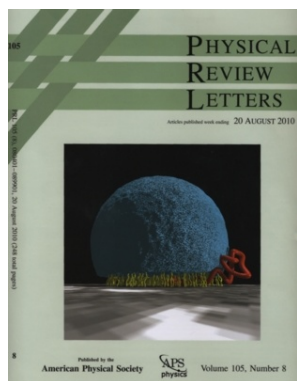
**DNA - membrane interactions**

We have developed a technique to study interactions between a fluid membrane and a single polymer, two soft objects subject to thermal fluctuations.<sup>[3, 11]</sup> We graft long lambda-phage DNAs by one or both ends on a flat substrate coated with streptavidin receptors, and induce adhesion of giant vesicles bearing biotin ligands in the membrane on this carpet. We showed that during the adhesion of the vesicle, the membrane has a steamroller effect on the end-grafted DNAs, which are stretched and confined in a frozen conformation. A quantitative analysis of fluorescence microscopy reveals the different interactions determining the confinement process – see Figure 4.

We show that the macromolecules are trapped in a membrane 'tunnel', defined by the multiple biotin-streptavidin links that have connected the bilayer to the substrate during the adhesion. Stretching of the DNA can be controlled by the amount of biotinylated phospholipids that regulates the kinetics of adhesion of the membrane. The analysis also reveals that there is a strong correlation between the density of fluorescence inhomogeneity along a string of DNA and the tortuosity of the tunnel.



**Figure 4.** (a) Fluorescence image of single and double end-grafted DNAs, confined under the membrane of a giant unilamellar vesicle adhered to a bio-functional substrate. The DNA orientation results from the radial forces exerted by the membrane during the formation of the adhesive contact. Local fluorescence heterogeneity provides information about the DNA confinement tunnel, and a careful analysis of the loop shapes reveals the strength and direction of the forces acting on the DNA during the stretching and confinement process; (b, c) different observed configurations and model for explaining the formation of 'Eiffel Tower' conformations.



We interpret these inhomogeneities as evidence of the existence for self-entanglements, labile states that were trapped and frozen by the advancing membrane front.<sup>[24]</sup>

In collaboration with Damien Baigl, ENS Paris, we were able to reversibly photo-induce collapsed

and adhered states of the grafted DNAs using the photosensitive molecule AzoTAB.<sup>[29]</sup>

## Specific adhesion and molecular recognition

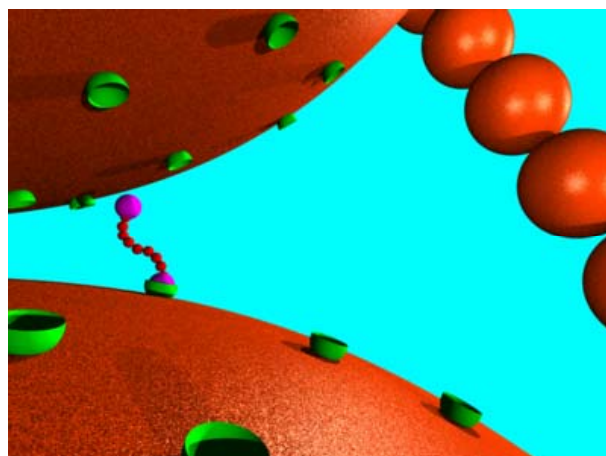
The quantitative determination of reaction or association rate coefficients is a major issue in the field of chemical physics. In a certain number of cases, these rates depend on the time it takes for the reactive species to occupy a specific mutual spatial and orientational configuration that enables subsequent association or reaction step. Such rates are known to be limited by diffusion. Biochemistry offers numerous examples of multi-molecular association (formation of large long-lived complexes) where the mutual diffusion movement of the intervening species is expected to be a key factor controlling the association dynamics. Moreover, the assumption of viscous hydrodynamics is reasonable for large molecules. The relative simplicity of the association kinetics in homogeneous solutions is lost when one of the reactive species is immobilized near a surface, and deriving the correct association rate in this situation is a challenging issue, even though the volume kinetic coefficient  $k_{on}$  is known.

### Influence of colloidal rotational dynamics on the rate of specific adhesion

A team from ESPCI Paris, managed to turn a super-paramagnetic colloidal beads system into a powerful analytical tool for studying the specific adhesion kinetics promoted by ligand-receptors pairs bounded to surfaces. The contribution of the Mcube to this breakthrough was to provide an accurate theoretical and computational framework in order to interpret the experimental set of data in terms of microscopic dynamics. In <sup>[6]</sup> was derived the average association time between colloidal beads in a number of relevant limits, spanning from the single ligand-receptor case to many distributed ligands over the surface. We also provide justification for the scaling between the association coefficient  $k_{on}$  and the number of active ligands.



This approach was used to extract the effective capture radius of tethered biotin-streptavidin ligand-receptor pairs in the experiments reported in <sup>[11]</sup>.



**Figure 5.** Schematic representation of a bridging connection developing between two rotating colloids. A spacer that provides for some exploration region carries the ligand. Adhesion occurs when a ligand finds and sticks to a receptor on the opposing surface.

Molecular recognition makes life possible. Molecular recognition emerges at the nanometer scale, when the size of the interacting partners becomes sufficient to establish multiple competing mutual interactions between them (such as directional hydrogen bonding), resulting in an efficient discrimination between matching and mismatching ligand-receptor pairs. Open questions arise when it comes to understand these specific interactions beyond the chemical and shape complementarity framework (the lock and key paradigm of Emil Fischer). For instance, one may wish to understand the influence of the local mechanical properties and the contribution of the configurational entropy to the equilibrium affinity constant  $K_a$  of the interacting pair.

### Influence of softness on molecular recognition

In reference<sup>[22]</sup>, we introduced a simple model of soft interacting patterned objects. It is shown that if properly designed, soft interacting partners can display a non-monotonic affinity constant  $K_a$  when the stiffness parameter is increased. Alternatively, we discuss the possibility of coding information within the mechanical stiffness pattern, irrespective of any shape consideration. The approach introduced in [22] seems particularly well suited to study, in the future, both specific and non-specific interactions between a macromolecular object in solution and a membrane of given lipid composition, especially in the presence of lipid mixing entropy. A well documented example of such a situation is provided by the interaction between a charged Cytochrome C protein and a mitochondrial membrane containing negatively charged lipids.

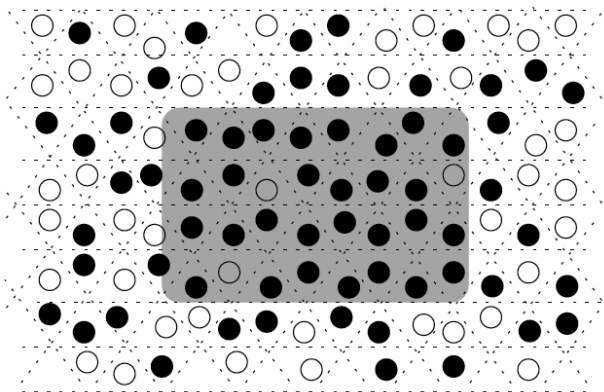


Figure 6. Conjecture: the tendency of the lipids in a membrane to phase separate should favour non-selective adhesion.

### Sliding tethered ligands

SlidTetherLig is an ANR funded collaboration project between Mcube and Lions in Saclay that proposes a new paradigm for the design of tethered ligands by introducing sliding grafts that will allow for unprecedented adaptability of the spacer length. The design is based on the sliding character of the topological complex formed by a polymer and a ring; it gives rise to a new category of tethered ligand-receptor interactions. These new objects are expected to allow finely tuning the binding kinetics and the interaction force range in the many different systems where ligand-receptor interactions play a determinant role.

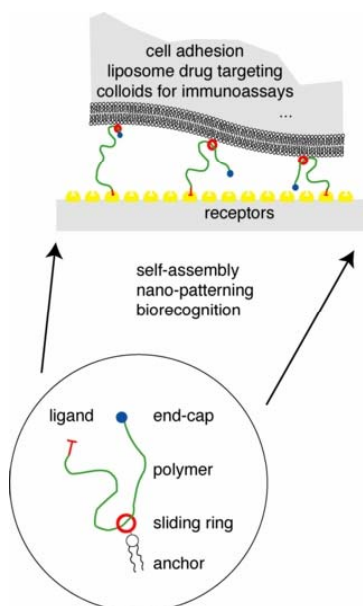


Figure 7. The SlidTetherLig project has a double ambition: i) to deliver a new family of biotechnological tools for building soft nanointerfaces and ii) to open new perspectives in stealth liposome technology by self-assembling a new type of stealth liposomal vector for drug delivery.

The SlidTetherLig project has so far delivered cyclodextrin rings with one or two attached cholesterol molecules that anchor very effectively the construct to bilayers or to monolayers at the air water interface. Inclusion complexation with POE polymers and end-capping has also been achieved. Work in progress deals with the attachment of a bio-specific moiety to one polymer end.

## Out-of-equilibrium: morphology, mechanics and dynamics

Development of theoretical tools for the understating of membrane or adhesion behavior requires most often to go beyond equilibrium thermodynamics or statistical mechanics: the control of adhesive patches with strong binders such as biotin-streptavidin pairs or the rupture of peroxidized bilayers provide interesting challenges for future work in non-equilibrium physics. In the recent past, we dealt with a number of systems requiring a tailor-made description to understand shape, growth and motion.

### Microtubule organization

We study<sup>[1]</sup> a microtubule growth model where the increase in size of the plus-end is perturbed by collisions with other microtubules and show that such a simple mechanism of constrained growth can induce ordered structures and patterns from an initially isotropic and homogeneous suspension.

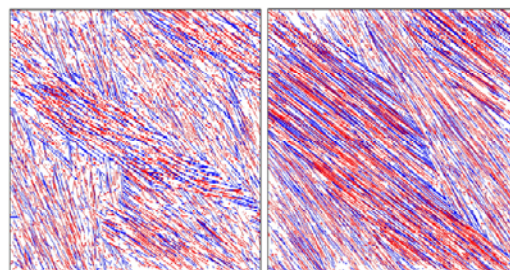


Figure 8. An initially homogeneous and isotropic solution of microtubules might grow into an oriented state if growth of a given filament requires not finding other filaments on its path as it grows.

### Colloidal propellers

We studied the design principles of the simplest colloidal propeller, an architecture built from four identical spheres that can couple translation with rotation to produce controlled drift motion.<sup>[25]</sup>

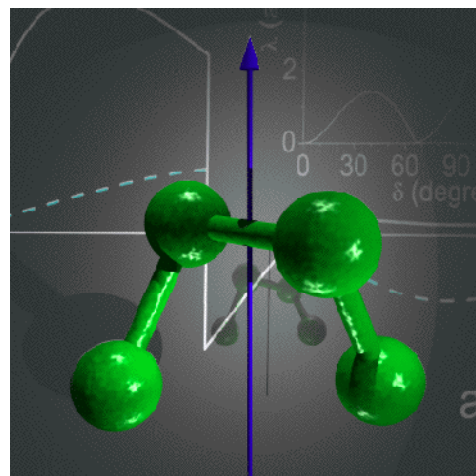


Figure 9. The simplest propeller made from an assembly of colloidal spheres. We have shown how the propelling efficiency, i.e the efficiency of transformation of rotation into translation depends on the geometrical characteristics of the aggregate.

## Pebble shapes

Expertise in dealing with the characterization of shapes by means of curvature, as required for the thermal analysis of membrane shape fluctuation, has lead us to collaborate with Philippe Düringer from the Geology Department of Strasbourg and with Douglas Durian from U-Penn in Philadelphia on the explanation and characterization of erosion shapes. Our work<sup>[5,26]</sup> was met with a strong interest from the scientific and non-scientific press around the world, from the Daily Telegraph to the Toronto Star, or from Nature News to Le Figaro. Our curvature distribution method has since been studied and used by scientists in Archeology or Geology, and models have been taken on by theoretical physicists and mathematicians.

**Collaborations in the axis:** N. Giuseppone, J.M. Guenet, M. Schmutz.

**Collaborations with other teams in the ICS:** A. Johner, J. Farrago, J. Wittmer, G. Decher, I. Kulic, M. Rawiso, Y. Holl.

**Collaborations outside the ICS:** Strasbourg: Yves Mély at the Pharmacy Department, Philippe Düringer from the Geology Department of the Uds, Andrew Griffiths from ISIS. France Brigitte-Pépin Donat from the CEA in Grenoble (IRTG Soft Matter), Jérôme Bibette at ESPCI in Paris, Jean Daillant at the CEA in Saclay (ANR SlidTheterLig), Bernard Tinland in Marseille, Damien Baigl at the ENS in Paris, INRA in Nancy. Abroad: Rosângela Itri and Maurício Baptista at the University of São Paulo (COFECUB), Georg Maret at the university of Konstanz (IRTG Soft Matter), Douglas Durian at the University of Pennsylvania in Philadelphia, Tonya Kuhl from UC Davis, Nam Lee from Seoul University (KOSEF), Carlos Mendoza from the UNAM, Stefan Schiller from Freiburg and Wolfgang Meier from Basel, Ashutosh Chilkoti from Duke University and Shigeyuki Komura from Tokyo Metropolitan University.

**Networks:** International Research Training Group Soft Matter, COFECUB, KOSEF.

[1] Baulin, V.A.; Marques, C.M.; Thalmann, F. Collision induced spatial organization of microtubules. *Biophys. Chem.*, **2007**, *128*, 231.

[2] Thalmann F.; Farrago, J. *J.Chem.Phys.* **2007**, *127*, 124109.

[3] Schmatko, T.; Bozorgui, B.; Geerts, N.; Frenkel, D.; Eiser E.; Poon, W. C. K. A cluster phase in lambda DNA coated colloids. *Soft Matter* **2007**, *3*, 703.

[4] Caetano, W.; Haddad, P.S.; Itri, R.; Severino, D.; Vieira, V.C.; Baptista, M.S.; Schröder, A.; Marques, C.M. Photo-induced destruction of giant vesicles in methylene blue solutions. *Langmuir*, **2007**, *23*, 1307.

[5] Durian, D.J.; Bideaud, H.; Düringer, P.; Schröder, A.; Marques, C.M. Shape and erosion of pebbles. *Phys. Rev. E.*, **2007**, *75*, 021301.

[6] Lee, Nam-Kyung; Johner, A.; Thalmann, F.; Cohen-Tannoudji, L.; Bertrand, E.; Baudry, J.; Bibette, J.; Marques, C. M. Ligand-Receptor Interactions in Chains of Colloids: When Reactions Are Limited by Rotational Diffusion. *Langmuir*, **2008**, *24*, 1296.

[7] Geerts, N.; Schmatko, T.; Eiser, E. Clustering versus percolation in the assembly of colloids coated with long DNA. *Langmuir* **2008**, *24*, 5118.

[8] Charitat, T.; Lecuyer, S.; Fragneto, G. Fluctuations and destabilization of single phospholipid bilayers, *Biointerphases*, **2008**, *3*, FB3.

[9] Clauzel, M.; Kékicheff, P.; Adams, J.; Johannsmann, D. Internal dynamics in drying latex films: a study based on fluorescence anisotropy and acoustic dissipation. *Soft Materials*, **2008**, *6*, 1.

[10] Jourdainne, F. L.; Lecuyer, S.; Armtz, Y.; Picart, C.; Schaaf, P.; Senger, B.; Voegel, J.-C.; Lavallo, P.; Charitat, T. Dynamics of Poly(L-Lysine) in Hyaluronic Acid/Poly(L-Lysine) Multilayer films studied by fluorescence recovery after pattern photobleaching. *Langmuir*, **2008**, *24*, 7842.

[11] Cohen-Tannoudji, L.; Bertrand, E.; Baudry, J.; Robic, C.; Goubault, C.; Pellissier, M.; Johner, A.; Thalmann, F.; Lee, Nam-Kyung; Marques, C. M.; Bibette, J. Measuring the Kinetics of Biomolecular Recognition with Magnetic Colloids. *Phys. Rev. Lett.*, **2008**, *100*, 108301.

[12] Hissette, M.-L.; Haddad, P.; Gisler, T.; Marques, C. M.; Schröder, A.P. Spreading of bio-adhesive vesicles on DNA carpets. *Soft Matter*, **2008**, *4*, 828.

[13] Campillo, C.C.; Schröder A.P.; Marques, C.M.; Pépin-Donat, B. Volume transition in composite poly(NIPAM) Giant Unilamellar Vesicles. *Soft Matter*, **2008**, *4*, 2486.

[14] Campillo, C.C.; Schröder A.P.; Marques, C.M.; Pépin-Donat, B. Composite gel-filled giant vesicles: Membrane homogeneity and mechanical properties. *Mat. Sci. Eng. C*, **2008**, *29*, 393.

[15] Haluska C. K.; Schröder A. P.; Didier, P.; Heissler, D.; Duportail, G.; Mély, Y.; Marques, C. M. Combining fluorescence lifetime and polarization microscopy to discriminate phase separated domains in giant unilamellar vesicles. *Biophys. J.*, **2008**, *95*, 5737.

[16] F.Thalmann and N.-K.Lee, *J.Chem.Phys.* **2009**, *130*, p074102.

[17] Scomparin, C.; Lecuyer, S.; Ferreira, M.; Charitat, T.; Tinland, B. Diffusion in supported lipid bilayers: influence of substrate and preparation technique on the internal dynamics. *EPJ E*, **2009**, *28*, 211.

[18] Tauk L.; Schröder A. P.; Decher G.; Giuseppone N. Hierarchical functional gradients of pH-responsive self-assembled monolayers using dynamic covalent chemistry on surfaces *Nature Chemistry*, **2009**, *1*, 649.

[19] Mertins O.; Silveira, N. P.; Pohlmann, A. R.; Schröder A. P.; Marques, C. M. Electroformation of giant vesicles from an inverse phase precursor. *Biophys. J.*, **2009**, *96*, 2719.

[20] Riske, K.A.; Sudbrak, T.P.; Archilha, N.L.; Uchoa, A.F.; Schröder, A.P.; Marques, C.M.; Baptista, M.S.; Itri, R. Giant vesicles under oxidative stress induced by a membrane-anchored photosensitizer. *Biophys. J.*, **2009**, *97*, 1362.

[21] Arnold, C.; Thalmann, F.; Marques, C.M.; Marie, P.; Holl, Y. Surfactant Distribution in Waterborne Acrylic Films. 1. Bulk Investigation. *J. Phys. Chem. B*, **2010**, *114*, 9135.

[22] F.Thalmann, *EPJE* **2010**, *31*, 441.

[23] Malaquin, L.; Charitat T.; Daillant, J. Supported bilayers: combined specular and diffuse x-ray scattering. *EPJ E*, **2010**, *31*, 285.

[24] Nam, G.; Hissette, M.L.; Sun, Y. L.; Gisler, T.; Johner, A.; Thalmann, F.; Schröder, A.P.; Marques, C.M.; Lee, N.K. Scraping and Stapling of End-Grafted DNA Chains by a Bioadhesive Spreading Vesicle to Reveal Chain Internal Friction and Topological Complexity. *Phys. Rev. Lett.*, **2010**, *105*, 088101. (PRL cover)

[25] Mendoza, C. I.; Marques, C. M.; Thalmann, F. Enhanced shear separation for chiral magnetic colloidal aggregates. *Phys. Rev. E*, **2010**, *82*, 060401.

[26] Roth, A. E.; Marques, C. M.; Durian, D. Abrasion of flat rotating shapes. *J. Phys. Rev. E*, **2011**, *83*, 031303.

[27] Wolff, J.; Marques, C. M.; Thalmann, F. Thermodynamic Approach to Phase Coexistence in Ternary Phospholipid-Cholesterol Mixtures. *Phys. Rev. Lett.*, **2011**, *106*, 128104.

[28] Dasgupta D.; Srinivasan S., Rochas C., Thierry A., Schröder A. P., Ajayaghosh A., and Guenet J. M. Insight into the gelation habit of oligo(para-phenylene vinylene) derivatives: effect of end-groups. *Soft Matter*, **2011**, *7*, 2797.

[29] Sun, Y. L.; Mani, N. K.; Baigl, D.; Gisler, T.; Schröder, A. P.; Marques, C. M. Photocontrol of end-grafted lambda-phage DNA. *Soft Matter*, **2011**, DOI: 10.1039/C1SM05046J. (Soft Matter inside cover)

[30] Thalmann, F.; Billot, V.; Marques, C.M. Lipid bilayer adhesion on sparse DNA carpets: theoretical analysis of membrane deformations induced by single end-grafted polymers. *Phys. Rev. E* **2011**, in press.



## Self-Evaluation

The previous AERES visiting committee underlined *i*) the “good organization and coherence of a young team ... with a very good international visibility ... confirmed also by the geographic origin of the visiting scientists, invited speakers for seminars and PhD students”; *ii*) “the originality of the emergent problems tackled in the group, with well conceived projects and a fruitful theory/experiments combination, albeit not always directly connected to the ICS main subjects”; *iii*) the very important impact of the group publications, in spite of its limited volume and *iv*) the lack of chemical synthesis support for some of the group projects. The following data will show that the group has not only worked towards the consolidation of the group strengths praised by the visiting committee, but that it has also addressed its criticisms. In particular, MCube research is now fully integrated with the Institute main subjects, self-assembly being presently a key science domain at the ICS.

### Statement on human resources

The group permanent staff for the period 2007-2011 had three CNRS scientists, and two, then three Uds professors since Tatiana Schmatko, a young assistant professor of the University of Strasbourg joined the group in the Summer 2009. Thierry Charitat was promoted to full professor in 2010, and Fabrice Thalmann defended his Habilitation à Diriger des Recherches (HDR) the same year, bringing to four the total number of HDRs in the group.

We hosted during this period 7 post-doctoral fellows and we supervised 16 PhD students from Austria, Benin, Brazil, China, France, Germany, Iran, the UK, Russia and the US. PhD students that have already defended joined companies, started a post-doc or found a permanent position in academia. Post-doctoral fellows have found a permanent position or started a second post-doc. The group has also hosted visiting professors from the Universities of UC Davis, MacGill, São Paulo and UNAM.

Beyond the human resources aspects described above that were directly related to the development of the MCube scientific projects, the group has also welcome a sizable number (~ 5 per year) of internships from high-schools and from the bachelor and the master programs. Contracts with industry also lead to temporary hiring of graduate of post-graduate collaborators.

### Statement on financial supports

Grant support for PhD students, Post-Doctoral fellows and visitors included: the French Ministry for Research, the CNRS, the Alsace Region, the CEA, the Chateaubriand foundation, the Proctor and Gamble company, the Benin Ministry of Higher Education, the Brazilian agencies CAPES, CNPQ and FAPESP, the French ANR, the European Marie-Curie program for Human Mobility, the Fulbright Foundation, the

BASF company, the LEA laboratory ICS/MPIP-Mainz, the IRTGs Soft Matter Physics Strasbourg-Grenoble-Konstanz and Soft Matter Materials Strasbourg-Basel-Freiburg.

Other grants over 50 K€ included an ANR grant (PI Marques), and P&G and BASF contracts.

### Statement on scientific collaborations

The group has an extensive record of collaborations with other teams from the Charles Sadron Institut and from elsewhere in France and abroad. Below follow all collaboration connections: those that translated into joint publications and those that are still developing, those localized in time and those that extended over many years.

Internally, at the ICS, we have collaborated over the years with the theory group. Albert Johner has been a theory partner on many of the papers we have published, Jean Farago has collaborated with the group on theoretical and experimental problems, and we co-supervise a PhD student with Joachim Wittmer. Experimental and theoretical work performed in the group has benefited and lead to publications with Nicolas Giuseppone, with Yves Holl and with Jean-Michel Guenet. Current and developing collaborations concern also Marie-Pierre Krafft, Michel Rawiso, Marc Schmutz and Christian Gauthier.

In Strasbourg, we have collaborated with the group of Yves Mély at the Pharmacy Department and with Philippe Durringer from the Geology Department of the Uds, and we have an ongoing collaboration with Andrew Griffiths from ISIS.

In France, we have collaborated and are publishing/have published with Brigitte-Pépin Donat from the CEA in Grenoble (IRTG Soft Matter), with the groups of Jérôme Bibette at ESPCI in Paris and Jean Daillant at the CEA in Saclay (ANR SlidTheterLig), with Bernard Tinland in Marseille, with Damien Baigl at the ENS in Paris and with several partners from the INRA in Nancy.

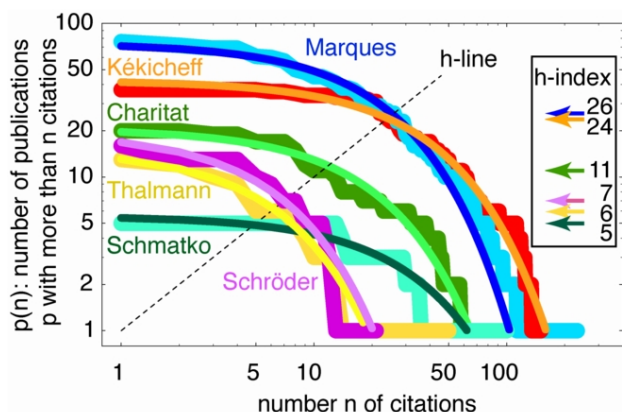
Abroad, several collaborations developed and led to publications with the groups of Rosângela Itri and Maurício Baptista at the University of São Paulo (COFECUB), of Georg Maret at the university of Konstanz (IRTG Soft Matter), of Douglas Durian at the University of Pennsylvania in Philadelphia, with Tonya Kuhl from UC Davis, with Nam Lee from Seoul University (KOSEF) and with Carlos Mendoza from the UNAM. Current developing collaborations involve the IRTG Soft Matter partners Stefan Schiller from Freiburg and Wolfgang Meier from Basel, Ashutosh Chilkoti from Duke University and Shigeyuki Komura from Tokyo Metropolitan University.

### Statement on scientific productions

We have published 30 articles over the reference period January 2007 to June 2011, covering a wide spectrum of journals: Phys. Rev. Let., Soft Matter, Biophys. J., Langmuir, J. Phys. Chem. B, J. Chem. Phys., Biointerphases, Phys. Rev. E, Biophys. Chem., EPJE, Mat. Sc. & Eng. C, Soft Materials, Nat. Chem. with impact factors in the range [1.8-7.3]. The total impact of our publication record is 103.2 and the

average impact is 3.44. These articles have so far been cited 144 times.

The total number of papers published by all group members over their scientific careers amount to 148, with a total number of citations of 4385. Figure 10 displays the distribution  $p(n)$  of number of articles  $p$  with at least  $n$  citations, against citation number  $n$ , for all the group members.



**Figure 10.** The distribution  $p(n)$  of number of articles  $p$  with at least  $n$  citations, against citation number  $n$ , for all the group members. The continuous line is an exponential fit to the data. The  $h$  index corresponds to the intersection between the  $p(n)=n$  line and the data.

The Figure clearly shows that the group has a full range of seniorities. Indeed career lengths extend from 10 years to 27 years long, with a range of  $h$  and  $m$  indices. ( $h, m$ ) indices are the as follows: C.M (26,1.1); P.K. (24,0.9); T.C. (11,0.8); A.S. (7,0.4); F.T. (6,0.9); T.S. (5,0.5).

Group members have presented 16 invited talks in international conferences during the reference period, and a comparable number of seminars at the invitation of other laboratories/research groups.

#### Further professional activities

The full teaching load of the group is detailed in the individual summaries (fiches individuelles). The group members teach Physics courses at the different Bachelor's and Master's levels: Electromagnetism, Wave Optics, Statistical Physics and Statistical Thermodynamics, Quantum Mechanics, Mechanics, Soft Condensed Matter, Self-Assembly, Complex Fluids, Physics for Biology. They are responsible for a range of other teaching duties at the Strasbourg University from the organization of the physics lectures for chemistry and biology, to the counseling of the Director of the Physics Department on the teaching of physics to the CAPES, CAPLP and Agrégation de Physique. Other national teaching responsibilities include the composition of the Physics 1 examen for the "Concours Communs Polytechniques".

The group members have been/are also engaged in various professional instances, such as the ICS Council, the ICS board of directors, the Consortium of Theoretical Physics of Strasbourg, the Physics Department Council or the Physics Department hiring committee and the National Committee of the CNRS.

The group members were in charge of the ICS seminars for the reference period. They have also organized several meetings/conferences including the 467th Wilhelm and Else Heraeus Seminar, Biophysics of membrane transformations, and a GDR CellTiss meeting on membrane Physics.

#### Overall statement

The establishment of the MCube group at the ICS has led to a strong development of research on the Physics of Self-Assembled Membranes. The group was successful in establishing itself as an important international contributor to this field, and has developed a firm network of collaborations with other groups in France, in Europe and elsewhere. AERES recommendations were followed; the volume of the group publications has increased, while keeping their high impact; collaborations with groups in Chemistry at the ICS or elsewhere reinforced the group potential to use new molecules tailored for the group membrane systems. It is fair to state that the past reference period has seen the rising international role of our group. Our success constitutes the foundations for the ambitious group project presented in the part of the ICS Project for 2013-2017.

# Functional Fluorinated Self-Assembled Systems for Biomedical and Materials Sciences (SOFFT)

Head of the Group : *Marie Pierre Krafft*

**Permanent staff** : Dr. Marie Pierre Krafft (CNRS Research Director) ; -Dr. Gilles Waton (CNRS Research Associate) ; -Nicole Benoît (CNRS Technician).

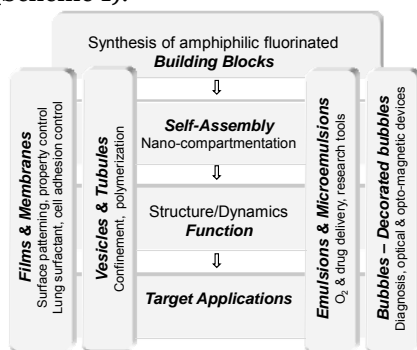
**Non-permanent researchers 2007-2011 : 5 post-doctoral associates** - Dr. Simona Rossi (ANR JeuxBulles, 18 mois, 2007/2008) ; - Dr. Csongor Szijarto (ANR JeuxBulles, 18 mois, 2008/2010) ; - Dr. Gergana Nikolova (CE NanoMagDye, 12 mois, 2008/2009) ; - Dr. Jun Ma (CE NanoMagDye, 12 mois, 2009/2010) ; - Dr. Prasad Polavarapu (CE NanoMagDye, 12 mois, 2010/2011) **5 PhD students**: Elisa Maillard (Co-Dir. M. Pinget (CEED), CE BARP+, Thesis defense nov. 07), Caroline de Gracia Lux (BDI, Thesis defense sept. 2010) ; Phuc Nghia Nguyen (CE + Industry, Thesis defense scheduled oct. 2012) ; Artem Kovalenko (ANR AirDeco Thesis defense scheduled oct. 2013), Melanie Eichhorn (IRTG Co-Dir. K. Anselme (Mulhouse), defense scheduled march 2014). **3**

## Master students

**Keywords:** Fluorinated amphiphiles · Fluorocarbons · Fluorous phases · Monolayers · Vesicles · Emulsions · Microbubbles · Oxygen transport · Lung surfactant · Contrast agents · Diagnosis · Surface nanopatterning.

International attention is presently being focused on the use of fluorinated phases and components for a wide range of areas extending from organic synthesis, separation methods, synthesis of nanomaterials and biomolecules recognition. A recent challenge consists in tailoring 2D and 3D systems that allow confinement of the reactants, orientation of the reactions, facilitation of catalyst recovery, surface patterning, etc.

The general objective of the team is to design, elaborate and study self-assembled systems made of fluorinated amphiphiles, and to understand the interactions between fluorinated and non-fluorinated chains. The fluorinated chains, which are extremely hydrophobic and lipophobic at the same time, are prone to induce segregations at the nano- and micrometric scales. Using these segregations, we create compartments in self-organized interfaces or objects, such as monolayers, bilayers, emulsions, microbubbles, surface hemimicelles, vesicles, and tubules (Scheme 1).<sup>[1, 2]</sup>



**Scheme 1.** Research activities of the SOFFT team.

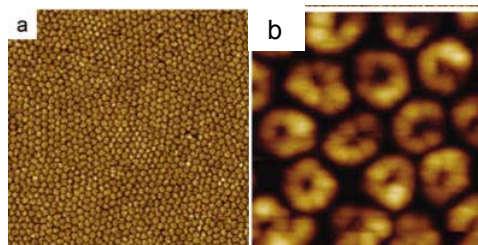
We aim at endowing fluorinated self-assembled systems with functionalities in order to develop their potential in materials sciences (templates for the elaboration of nanostructured surfaces) and in

medicine (lung surfactant, oxygen transport, ultrasound diagnostic, cell adhesion).

## Using F-alkylated chains to promote self-assembly

### Size-controlled surface micelles of (F-alkyl)alkyl diblocks and tetrablocks

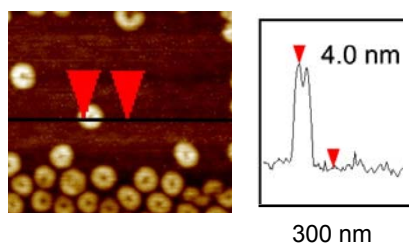
We have obtained monolayer films of a series of semi-fluorinated alkanes  $C_nF_{2n+1}C_mH_{2m+1}$  ( $F_nH_m$ ,  $n = 4, 6, 8, 10$  et  $m = 14, 16, 18, 20$ ) which, when transferred onto silicon wafers or deposited by spin-coating, consist of dense carpets of surface hemimicelles (30-40 nm in diameter, 3-4 nm in height; Figure 1).<sup>[1, 3, 4]</sup> The molecular orientation of the diblocks within the micelles ( $F_n$  chains up) was determined by X ray reflectivity (Collab. M. Maaloum, P. Muller, ICS). The hemimicelles were also evidenced at the air/water interface by grazing incidence small angle X ray spectroscopy (ESRF Grenoble; Collab. M. Goldmann, INSP, Paris).<sup>[5]</sup>



**Figure 1.** AFM images (tapping mode) of Langmuir monolayers of F8H16 transferred on silicon wafers at  $7 \text{ mN m}^{-1}$  (a :  $1 \times 1 \mu\text{m}$ , b :  $150 \times 150 \text{ nm}$ , topography).<sup>[1]</sup>

This behavior was shown to be characteristic of non polar hydrocarbon (HC)/fluorocarbon (FC) amphiphiles. Newly synthesized gemini FC/HC tetrablocks  $(C_nF_{2n+1}CH_2)(C_{m-2}H_{2m-3})CH-CH$

$(C_nF_{2n+1}CH_2)(C_{m-2}H_{2m-3})$  ( $di(FnHm)$ ), when spread on solid surfaces by Langmuir-Blodgett or spin-coating, self-organize in arrays of hemimicelles with a diameter of  $\sim 40$  nm and a height of  $\sim 4$  nm, comparable to those obtained with diblocks (Figure 2).<sup>[6]</sup>

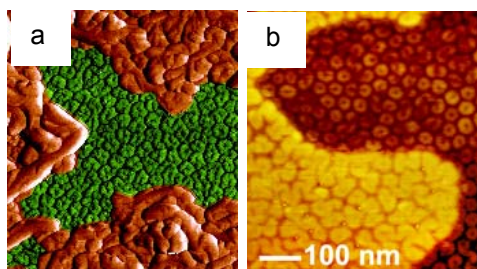


**Figure 2.** Film of  $di(F8H20)$  deposited by spin-coating on mica. The surface micelles have been individualized by « scratching » using the AFM probe. The profile gives the height of the micelle.<sup>[6]</sup>

The mechanism of formation of these objects was determined to depend solely on a critical surface concentration, and their morphology is controlled by the molecular structure of the diblocks, independently of the compression conditions.<sup>[3]</sup> A theoretical treatment of the surface micelles of  $FnHm$  diblocks has shown that the micelles are stabilized by the electrostatic interactions of the dipole moments of the  $CF_2-CH_2$  bonds that are located at the junction of the two blocks. (Collab. A. Semenov, J.-F. Legrand, ICS).

### Collapse and rearrangements in films of hemimicelles

We have established that the numerous compression isotherms of  $FnHm$  monolayers that were published since 1991 are only partial, and that if compression is resumed beyond the published collapse pressure, there appears a coexistence plateau, followed by a second pressure rise.<sup>[4]</sup> AFM and Brewster angle microscopy determine that the « high » phase of the interfacial film is a *bilayer* in the case of diblocks<sup>[4]</sup> and a second layer of micelles in the case of tetrablocks (Figure 3).<sup>[6]</sup> In both cases a monolayer of hemimicelles remains present, even at the highest pressures, demonstrating considerable sturdiness. Deposition of diblocks, or tetrablocks, by spin coating results in the formation of the same stratified film.



**Figure 3.** AFM images after transfer onto solid substrates of stratified films formed by a)  $FnHm$  diblocks and b)  $di(FnHm)$  tetrablocks when spread on water. b) shows two levels of self-assembled surface micelles, which appears to be the first reported example of film made of stacked self-assembled objects.<sup>[4, 6]</sup>

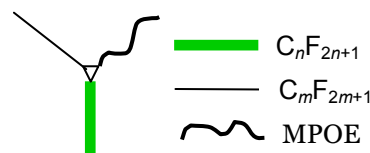
The surface hemimicelles, with their diameter of a few tens of nanometers, which can be controlled by adjusting the length of the hydrocarbon spacer, constitute promising self-assembled organic templates

for organization of nanoparticles and for studying the adhesion cell response. Surface micelles of diblocks and tetrablocks are being reviewed.<sup>[7]</sup>

The behavior of  $F$ -films at various other important interfaces is being investigated. The capacity of these surfactants to form either flexible or rigid interfaces has implications on the ability of these surfactants to form water-in- $CO_2$  emulsions or microemulsions. Dynamical and rheological studies of fluorinated phosphocholine-based films adsorbed at the pressurized  $CO_2$ /water interface could be controlled with the fluorocarbon/hydrocarbon ratio (Collab. F. Boury, Angers).<sup>[8]</sup>

### Synthesis of star-shaped triaffine amphiphiles for film and micelle compartmentation

The synthesis of novel fluorinated molecules is key for the elaboration of nano-compartmented systems. We have synthesized star-shaped triphilic amphiphiles having a lipophilic hydrocarbon chain, a hydrophilic monomethyl ether poly(oxyethylene) chain (MPOE), and a hydrophobic and lipophobic  $F$ -chain.<sup>[9]</sup>

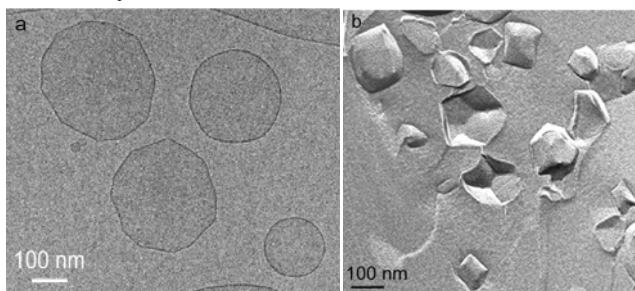


**Scheme 2.** Molecular structure of the triphilic amphiphiles.

A library of six MPOE 3- $F$ -alkyl-3-alkoxypropanoate, pure and monodisperse,  $(C_nF_{2n+1})(C_mH_{2m+1}O)C=CHC(O)(OCH_2CH_2)_yCH_3$  ( $n = 5, 7$ ;  $m = 8, 10, 14$  et  $y = 2-7$ ), has been obtained from a single multi-step synthesis involving MPOE 350, a commercial mixture of 6 oligomers. Strong repulsions between these three types of chains are anticipated that should promote segregated domain formation in water or in organic solvents. Preliminary observations have indeed shown that these polyphiles form compartmented micelles.

### Faceted, yet fluid vesicles

The first example of polyhedral unilamellar vesicles with a fluid bilayer has been obtained from octyltrimethylammonium  $F$ -octanoate,  $C_7F_{15}COO-C_8H_{17}N^+(CH_3)_3$  (OTAPFO).<sup>[10]</sup> This catanionic amphiphile readily forms spherical vesicles, which acquire facets over time (Figure 4), while maintaining their bilayer membrane in the fluid state.



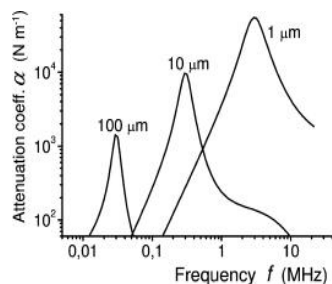
**Figure 4.** a) Cryogenic transmission electron microscopy (TEM) and b) freeze fracture TEM of vesicles formed by OTAPFO ( $11 \text{ mmol L}^{-1}$ ) in water. The faceted vesicles are the main population after one month at  $25^\circ\text{C}$ .

Segregation between fluorinated anions and hydrogenated cations is likely at the origin of this rearrangement. Such segregation would induce a non-zero local curvature of the bilayer, and consequently formation of an angle. The ability of fluorinated amphiphiles to control the structure and properties of phospholipid vesicle bilayers has been recently reviewed.<sup>[11]</sup>

## Microbubbles for multimodal imaging modalities and multi-scale devices

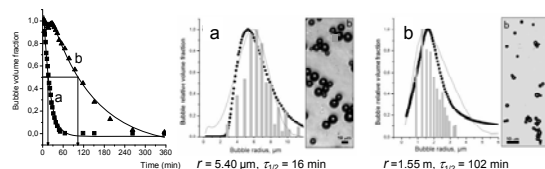
### Engineering of FC-stabilized soft-shell microbubbles (ANR JeuxBulles)

Gaseous microbubbles (MBs), osmotically stabilized by fluorocarbon gas, have recently been identified as potential intravascular oxygen carriers. MBs are also highly efficient contrast agents ultrasound (US) diagnosis. For these two application fields, it is necessary to obtain MBs that are small, narrowly dispersed and stable. With the ICS workshop we have designed and built devices that allow the acoustical determination of the bubbles' size and stability characteristics. They measure the attenuation coefficient,  $\alpha$ , of an ultrasound wave in the presence of a suspension of the MBs.<sup>[12-14]</sup>  $\alpha$  is maximal when the excitation frequency is equal to the resonance frequency of the bubbles, the latter being proportional to their size (Figure 5). We have also developed protocols that allow preparation of narrow monomodal populations of MBs.<sup>[15]</sup>



**Figure 5.** Variation of the attenuation coefficient of an ultrasound wave that propagates through an aqueous dispersion of MBs as a function of sound frequency.

This methodology enabled us to obtain an unexpected result on MBs stabilized by an FC gas, *F*-hexane, and with a shell of dimyristoylphosphatidylcholine (DMPC). Contrary to the commonly accepted dogma, we have determined that small bubbles ( $\sim 1.5 \mu\text{m}$  of radius) could be significantly more stable than larger bubbles ( $r \sim 5.5 \mu\text{m}$ ) of same composition, in spite of the much larger Laplace pressure to which they are subjected (Figure 6).<sup>[16]</sup>

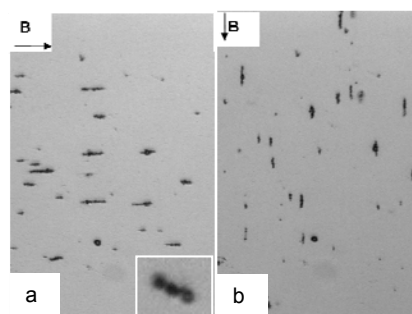


**Figure 6.** MBs with a shell of DMPC stabilized with *F*-hexane. Acoustical measurements show that, unexpectedly, the half-life of the small bubbles (b,  $r 1.5 \mu\text{m}$ ) is substantially longer (102 min) than that of the larger bubbles (a,  $r 5.4 \mu\text{m}$ , 16 min); particle size histograms and optical micrographs are shown for the two bubble populations.<sup>[13]</sup>

We have assigned this phenomenon to the existence of a co-surfactant effect of *F*-hexane toward DMPC at the air/water interface, despite the fact that PFH is deprived of polar head or dipole moment. Because the partial pressure of *F*-hexane is higher in the smaller bubbles than in the larger ones, the co-surfactant effect is also stronger. The higher surface tension lowering in small MBs leads to a decrease in Laplace pressure, and, consequently, to increased stability. We have found a similar co-surfactant effect of *F*-hexane with other phospholipids, establishing the generality of the phenomenon. The effect is maximal with DPPC at  $37^\circ\text{C}$ , which may have implications in the use of FC gases in the design of new lung surfactant substitutes and *i.v.* O<sub>2</sub> carriers. Evaluation of new shell components for MBs identified *F*-alkyl amphiphilic phosphates as leading to exceptionally long half-lives.

### Decorated MBs for multi-modal imaging modalities and multi-scale devices (ANR AirDeco; Europ. Contract Nanomagdye)

MBs incorporating iron oxide nanoparticles (NP) were recently proposed as bimodal contrast agents for US and magnetic resonance (MR) imaging and for enhancement of gene delivery by simultaneous exposure to magnetic and US fields. We succeeded in producing MBs decorated with iron oxide NPs ( $\text{Fe}_3\text{O}_4\text{NP-decoMBs}$ ) using direct self-assembly of appropriate *F*-surfactants with bare NPs, or of NPs grafted with *F*-alkyl chains. Preliminary optical and confocal microscopy studies allowed imaging of collections of MBs and confirmed the presence of NPs on their surface. They also demonstrated that the NPs are mobile in the interfacial film (Collab. G. Pourroy, J.-Y. Bigot, IPCMS Strasbourg). When submitted to a magnetic field the  $\text{Fe}_3\text{O}_4\text{NP-decoMBs}$  align themselves along the direction of the field (Figure 7).<sup>[17]</sup>



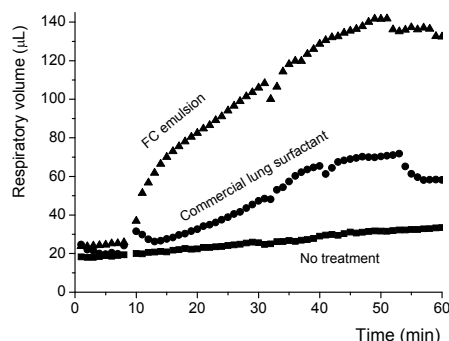
**Figure 7.** MBs decorated with  $\text{Fe}_3\text{O}_4\text{NPs}$ . When submitted to the magnetic field B, they align horizontally (a) or vertically (b), depending on the direction of B.

## Assessing the potential of fluorinated self-assemblies in biomedical sciences

Another objective for the SOFFT team is to explore the potential of *F*-systems in medicine and biology.<sup>[18, 19]</sup>

### FC and lung surfactant

We have studied the interactions between a *FC* gas and a monolayer of dipalmitoylphosphatidylcholine (DPPC), the latter being the major component of the native lung surfactant (*Collab. T. Vandamme, Fac. Pharmacie, Illkirch*).<sup>[20]</sup> The *FC* gas was found to effectively inhibit the formation of the liquid condensed (LC) phase of DPPC during monolayer compression. It also facilitates re-spreading of the DPPC molecules during expansion, which is indispensable for normal breathing. Moreover, the *FC* gas permits to hinder the insertion of serum proteins in the lung surfactant film, which may be useful to treat inflammatory processes.<sup>[21]</sup> A patent has been filed on use of *FC*s in the design of new synthetic lung surfactant substitutes destined to neonates and adults. Investigations have shown that the respiratory volume of premature rabbits, deficient in native lung surfactant, was significantly increased by administration of a *FC* preparation (*Collab. Boeringer-Ingelheim, Biberach*).



**Figure 8.** The respiratory volume of premature rabbits increases more effectively and faster when a *FC* emulsion is administered, as compared to a commercial lung surfactant substitute.

Basic background information about the impact of *F*-surfactants on phospholipid film has been gathered for the development of pulmonary drug delivery systems and lung surfactant substitutes (*Collab. O. Shibata, Nagasaki*). Miscibility within mixed Langmuir monolayers of DPPC and (*F*-octyl)pentanol or (*F*-octyl)phosphocholine, and the absence of LC domains of DPPC, were demonstrated on the micrometer scale.<sup>[22]</sup> (*F*-octyl)undecanol was found to enhance the effectiveness of a model pulmonary surfactant preparation containing the Hel peptide in terms of integrated hysteresis area preservation and maximum reachable surface pressure.<sup>[23-25]</sup>

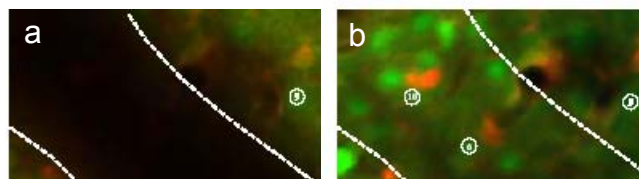
### FC emulsions and *in vivo* O<sub>2</sub> transport

#### Pancreatic cell preservation and adhesion control

We have demonstrated that oxygenated *FC* emulsions are beneficial to the pancreatic cells, the Langerhans islets, which are highly sensible to necrosis (European bioartificial pancreas project).<sup>[26]</sup> *FC* emulsions strongly inhibited adhesion of MIN6  $\beta$  cells to their culture dishes. In addition, we have found that *FC* emulsions induce detachment of the already adherent cells and promote their aggregation in pseudo-islets. Contrary to isolated cells, these pseudo-islets are able to secrete insulin.

#### Structural and functional brain imaging

Although highly promising, brain imaging using the two-photon microscopy technique has so far been hindered by the fact hemoglobin and red cells strongly adsorb and diffract light. We have prepared highly concentrated fine and stable *FC* emulsions that allow oxygenation and survival of rats deprived of their blood by perfusion using this emulsion. The emulsions do not interfere with two-photon microscopy and allows a much improved visualization of the neuronal cells and monitoring of neurological processes (Figure 9) (*Collab. B. Weber, ETH Zurich*).<sup>[27]</sup>



**Figure 9.** Two-photon micrographs of the somato-sensorial cortex of a rat (depth 180 nm). In a) the presence of red blood cells and hemoglobin, the vessel absorbs and scatters the light, preventing visualization of the cells. b) After exanguino-perfusion with the *FC* emulsion, the vessel becomes transparent, enabling observation of astrocytes (red) and neurons (green).<sup>[27]</sup>

**Collaborations in the axis:** M. Schmutz.

**Collaborations with the other teams of the ICS:** A. Semenov.

**Collaborations in Strasbourg:** G. Pourroy (IPCMS), J.-L. Gallani (IPCMS), B. Donnio (IPCMS), T. Vandamme (Fac. Pharmacie), S. Sigrist (CEED Strasbourg).

**Collaborations in France and abroad:** M. Goldmann (INSP Paris), F. Boury (INSERM Angers), M. Vazquez (CSIC Madrid), J. Schrader (Dusseldorf), B. Weber (Zurich), O. Shibata (Nagasaki), I. Bernhard (Saarbrücken).

**Collaboration with industry:** Guerbet (Aulnay-sous-Bois).

**Local network:** International Center for Frontier Research in Chemistry (icFRC - RTRA).

**European Networks:** Nanomagdye (7<sup>th</sup> PCRD, NMP), IRTG Soft Matter, 1 ITN pending.

**Financial Support:** CNRS/Région (BDI), Europe (BARP+; Nanomagdye), ANR (Jeux Bulles ; AirDeco), Guerbet.

- [1] M. P. Krafft, J. G. Riess, *Chem. Rev.* **2009**, *109*, 1714-1792.
- [2] M. P. Krafft, *J. Fluorine Chem. Special Issue on Fluorine Chemistry in France (Invited)* **2011**, in press.
- [3] A. González-Pérez, C. Contal, M. P. Krafft, *Soft Matter* **2007**, *3*, 191-193.
- [4] C. de Gracia Lux, J.-L. Gallani, G. Waton, M. P. Krafft, *Chem. Eur. J.* **2010**, *16*, 7188.

- [5] L. Bardin, M.-C. Fauré, D. Limagne, C. Chevillard, O. Konovalov, E. Filipe, G. Waton, M. P. Krafft, M. Goldmann, P. Fontaine, *Langmuir* **2011**, *in press*.
- [6] C. de Gracia Lux, M. P. Krafft, *Chem. Eur. J.* **2010**, *16*, 11539-11542.
- [7] M. P. Krafft, *Acc. Chem. Res. (Invited)* **2011**, *in preparation*.
- [8] F. Tewes, M. P. Krafft, F. Boury, *Langmuir* **2011**, *in press*.
- [9] M. Sanchez-Dominguez, N. Benoit, M. P. Krafft, *Tetrahedron* **2008**, *64*, 522-528.
- [10] A. González-Pérez, M. Schmutz, G. Waton, M. J. Romero, M. P. Krafft, *J. Am. Chem. Soc.* **2007**, *129*, 756-757.
- [11] M. P. Krafft, *Biochimie (Invited)* **2011**, *in press*.
- [12] F. Gerber, G. Waton, M. P. Krafft, T. F. Vandamme, *Artif. Cells Blood Subst. Immob. Biotechnol.* **2007**, *35*, 119-124.
- [13] S. Rossi, G. Waton, M. P. Krafft, *ChemPhysChem* **2008**, *9*, 1982-1985.
- [14] S. Rossi, G. Waton, M. P. Krafft, *Langmuir* **2010**, *26* 1649-1655.
- [15] S. Rossi, C. Szijjártó, F. Gerber, G. Waton, M. P. Krafft, *J. Fluorine Chem. Alain Tressaud ACS Award Issue (Invited)* **2011**, *in press*.
- [16] P. N. Nguyen, T. T. T. Dang, G. Waton, T. Vandamme, M. P. Krafft, *submitted* **2011**.
- [17] G. Nikolova, P. N. Nguyen, J. Ma, G. Waton, N. Benoit, M. P. Krafft, L. T. Phuoc, G. Pourroy. Conference Paper, *Hybrid Materials*, Strasbourg, **2011**.
- [18] M. P. Krafft, J. G. Riess, *J. Polym. Sci. Part A: Polymer Chem.* **2007**, *45*, 1185-1198.
- [19] M. P. Krafft, J. G. Riess in *Advances in Fluorine Science-Fluorine and Health. Molecular Imaging, Biomedical Materials and Pharmaceuticals*, A. Tressaud, G. Haufe, Eds. Elsevier: Amsterdam, **2008**, Chap. 11, pp. 447-486.
- [20] F. Gerber, T. F. Vandamme, M. P. Krafft, *C. R. Acad. Sci. (Chimie)* **2009**, *12*, 180-187.
- [21] F. Gerber, M. P. Krafft, T. F. Vandamme, *Biochim. Biophys. Acta-Biomembranes* **2007**, *1768*, 490-494.
- [22] S. Nakamura, H. Nakahara, M. P. Krafft, O. Shibata, *Langmuir* **2007**, *23*, 12634-12644.
- [23] H. Nakahara, M. Tsuji, Y. Sato, M. P. Krafft, O. Shibata, *J. Colloid Interf. Sci.* **2009**, *337*, 201-210.
- [24] H. Nakahara, S. Lee, M. P. Krafft, O. Shibata, *Langmuir* **2010**, *26*, 18256-18265.
- [25] H. Nakahara, M. P. Krafft, A. Shibata, O. Shibata, *Soft Matter* **2011**, *in press*.
- [26] E. Maillard, M. Juszczak, C. Kleiss, M. C. Sencier, A. Langlois, C. Vohouhe, W. Beigier, M. Sanchez-Dominguez, M. P. Krafft, M. Pinget, P. Johnson, S. Sigrist, *Cell Transplant.* **2011**, *in press*.
- [27] F. Haiss, R. Jolivet, M. T. Wyss, J. Reichold, N. B. Braham, F. Scheffold, M. P. Krafft, B. Weber, *J. Physiol.* **2009**, *587*, 3153-3158.

## Self-Evaluation

The previous evaluation of the AERES has recognized that the SOFFT team had an “*excellent 2004-2007 scientific production both in quality and quantity and a very good international visibility*”. The results and the perspectives has been judged “*original and promising, with a very satisfying equilibrium between fundamental approaches and applications*”. It was concluded that, “*despite its small size, the group present excellent results and warrant to be sustained*” and that “*its interaction with the thematic on polymers is to be encouraged*”.

### Statement on human resources

During the 2007-2011 period, the SOFFT team has recruited 5 post-doctoral research associates, 5 Ph.D students and 3 Master students. Among the four post-docs who have left the SOFFT team, S. Rossi and G. Nikolova have now permanent positions in Industry in Italy and Bulgaria, respectively; C. Szijarto is in post-doc in Sweden; and J. Ma is in post-doc in China. Our two Ph.D students who have performed their defense have found post doc positions, E. Maillard in Oxford (UK) and C. de Gracia-Lux in San-Diego (CA, USA).

### Statement on financial supports

Since our last European Contract (BARP+, Development of a Bioartificial Pancreas; 1.5 M€ over 3 years; Partner) that ended in 2007, we have found financial support from the European Commission and from the ANR.

☞ European Contract Nanomagdye (1 M€ over 3 years; 2008-2011) (Partner)

☞ ANR Blanc JeuxBulles (200 k€ over 3 years; 2007-2010) (Principal, and sole, Investigator)

☞ ANR Blanc AirDeco (600 k€ over 3 years) (PI)

We have also obtained 12 k€ (Master Student expenses) from Guerbet to synthesize new *FnHm* diblocks as components of <sup>19</sup>F IRM contrast agents.

### Statement on scientific collaborations

**Internal Collaborations in the ICS:** A large part of our work on surface micelles has been done with M. Maaloum (AFM) and P. Muller. We are tightly collaborating with M. Schmutz (electron microscopy).

**Collaboration in Strasbourg:** We have a collaborative work with Dr. G. Pourroy (IPCMS, European Contract *Nanomagdye*) on microbubbles decorated with nanoparticles with the aim of developing multi-modal imaging contrast agents. We shall also study their optical and opto-magnetic properties (*Collab. Dr. J.-Y. Bigot, IPCMS, AirDeco ANR*).

**National and International Collaborations:** Concerning the biomedical applications of our systems, we have long-lasting collaborations with the Faculties of Pharmacy of Illkirch (Prof. T. Vandamme, Laboratoire CAMB) and Nagasaki (Prof. O. Shibata) (lung surfactant substitutes). Recently, we have established links with the Laboratoire de Biophysique Moléculaire at Orléans (Dr. C. Pichon and Dr. P. Midoux) (microbubble-mediated transfection), the University of Düsseldorf (Prof. J. Schrader) (contrast agents for <sup>19</sup>F MRI) and the ETH Zürich (Prof. B. Weber) (oxygen delivery).

### Statement on scientific productions

Here are some indicators from ISI Web of knowledge on the scientific production of the SOFFT Team on the 2007-2011 period.

☞ Number of articles – **28**

☞ Journals – *Chem. Rev / JACS / Chem. Eur. J. / Langmuir / Soft Matter / BBA / J. Polym. Sci. A / JCIS / Biochimie / ChemPhysChem / Tetrahedron / Cell Transplant. J. Physiol.*

☞ Average impact factor of the journals – **6.00**

☞ Average number of citations per article (published by SOFFT in the 2007-2010 period) – **5,5**

☞ h-index of the permanent staff:

M.P. Krafft: h-index: **26**; Results found: **118**; Sum of the times cited **2094**; Average citations per item: 18.05

G. Waton: h-index: **14**

☞ m-index of the permanent staff (m-index = h-index/n years):

M.P. Krafft: m-index: **1.3**

☞ Total number of patents – **9**

☞ Total number of Invited International Conferences:

M.P. Krafft: **26**.

☞ Number of Invited International Conferences in the 2007-2010 period.

M.P. Krafft: **7**

#### Further professional activities

☞ M.P. Krafft is co-editor (with Prof. P. Fletcher, Univ. Hull and Prof. R. Strey, Köln Univ.) of the Surfactant Section for Current Opinion in Colloid and Interface Science.

☞ M.P. Krafft is a member of the Scientific Committee of the *XI<sup>th</sup> and XII<sup>th</sup> Intl. Symposia on Blood Substitutes* (Beijing, 19-22 oct. 2007; Parma 25-28 août 2009) and of the Scientific Committee of the *Intl. Soft Matter Conference* (Soft Matter Composites SoftComp) (Grenade 5-8 juillet 2010).

☞ The SOFFT Team has co-organized (with Dr. F. Leroux, ECPM) the *XI French Colloquium of the Fluorine Chemistry*, Obernai, mars 2011.

☞ M.P. Krafft is a member of ANR Committees on Nanosciences and Materials since 1999.

☞ G. Waton is responsible for the Permanent Formation in the ICS.

☞ M.P. Krafft is a member of the Executive Committee of the "Groupe d'Intérêt Scientifique" (GIS) Fluor.

#### Overall statement

Our analysis is that the SOFFT Team has the expertise, knowledge and international visibility to develop successfully original systems self-assembled powered by the superhydrophobic forces generated by perfluoroalkyl chains. The Team is well integrated in the "Self-Assembled Systems" Axis, and benefits from the environment of the ICS, which provides a unique hub of scientific and technical competences in the field of Soft Matter. Let us mention light and X ray scattering, AFM, electron microscopy and theory. We have developed interlinks with the IPCMS, with which we are already collaborating for all topics on hybrid organic/inorganic systems. We also have collaborations with the Faculty of Pharmacy of Illkirch and with other groups in France and abroad for the biological evaluation of our systems. We are also interconnected with the Laboratories that work on Fluorine in France, Germany and England, with opportunities to participate to ITNs. We are convinced that this network will allow us to have significant contribution in the field in the next five years. We are aware, however, that we need to reinforce our team in manpower. Our immediate priority is to recruit a young CR2 Chemist who will be in charge of the synthesis of original fluorinated building blocks (macrocycles, bolaamphiphiles, triaffines, ...). His/her first project will be to synthesize line-active surfactant designed to stabilize rafts in bilayer membranes in collaboration with the MCube Team. In conclusion, we think that, owing to the expertise of the SOFFT Team, the ICS can make breakthrough in the field of self-assembled systems directed by superhydrophobic forces, with significant contribution in the fundamental (structure, dynamics,...) and applied sides.



# Organized Complex Molecular and Macromolecular Systems (SYCOMMOR)

Jean-Michel Guenet

**Permanent staff :** J.M. Guenet (DR1) M. Brinkmann (CR1) D. Collin (CR1) P. Mésini (CR1) D. Rogez (CR1) D. Sarazin (CR1), B. Lotz (DREm), P. Martinoty (DREm), M. Schmutz (IR1), C. Blanck (Assistant Ingénieur), A. Collard (1/2), L. Herrmann, C. Saettel (1/2) (Technicians)

**Non-permanent staff (2007-2001): 4 post-doctoral fellows** D. Dasgupta, S. Uttiya, R. Covis, N. Sangeetha **10 PhD students**, Z. Kamar (int. cosupervision, 28/09/2010), C. Vergnat (ICS co-supervision, 4/03/2010), L. Hartmann (France co-supervision, 2011), N. Kayunkid (2012), A. Sarbu (ICS co-supervision), A. Reisch (2009), T.T.T. Nguyen (2010), J. Davila (2011), A. Khan (2012), T. Djuric (visiting, 2011), **7 Master students**

**Keywords:** covalent polymers · organogels · thermoreversible gels · self-assembled systems ·  $\pi$ -conjugated systems · nucleation and growth · heterogeneous nucleation · epitaxy

## Introduction

Following a major recommendation of the AERES steering committee in 2008, namely “*promoting collaborative research within ICS*”, we have set up early 2010 a new research team composed of physicists, physical chemists and chemists of highly complementary expertise. Our team is a merger of the former SYCOMMOR team (*Systèmes Complexes Moléculaires et Macromoléculaires Organisés*), of which it has kept the name, and the former MPMM team (*Morphogénèse de Polymères et Matériaux Moléculaires*). Meanwhile, P. Mésini, from the SAMS team, decided to join in. This new team aims at developing a multidisciplinary approach for preparing novel and original molecular architectures involving covalent polymers and/or self-assembled systems through a controlled growth of nano, meso, and microstructures by physical processes (crystallization, thermoreversible gelation, phase separation, heterogeneous nucleation,...). The elaboration and study of these new architectures are primarily intended for understanding the functional properties in unusual environments. Further developments may lead to the making of functional materials, such as opto-electronic devices, reactive porous materials, hydrophobic materials,...

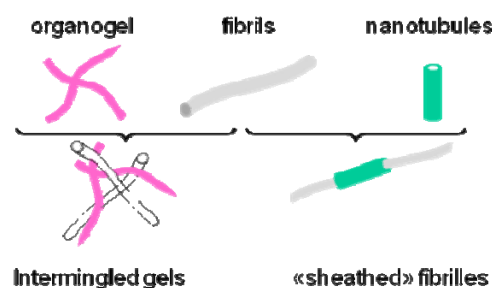
The strengthening of the team is taking shape through an ANR application involving all team members focused on the *design of hybrid architectures*. Joint publications have already appeared on this topic, and one co-supervised PhD student has recently been hired.

The present report presents a selection of investigations carried out essentially in the former teams, yet they highlight the relevancy of our teams regrouping.

## Hybrid architectures self-assembled systems/covalent polymers

We have developed the making and characterization of new molecular architectures consisting of covalent polymers and functional fibrillar organogels. As a rule,

these organogels cannot be processed into materials on account of their poor mechanical properties as their fibrillar structure is chiefly obtained at rather low concentrations. The use of a covalent polymer matrix can be an appropriate choice for retaining the original organogel fibrillar structure while allowing a better tractability of the system. The originality of our approach consists in using thermoreversible gels of covalent polymers together with physical processes for achieving the fine, mesoscopic dispersion of the organogels into the polymer network. This is made possible because these covalent polymer gels also possess a similar fibrillar morphology, particularly an average mesh size in the micrometer range. While these novel molecular architectures may be relevant for applications in functional materials the primary goal of these investigations is to establish a proof of concept.



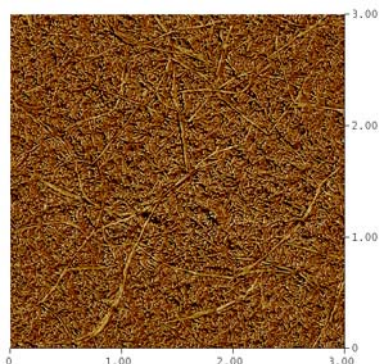
**Figure 1.** Sketch of the two types of hybrid systems.

Two systems have been considered: *intermingled gels* where the organogel grows within the polymer gel with little perturbation; and “*sheathed*” *fibrils* where nanotubes encapsulate polymer gel fibrils.

The feasibility of intermingled gels has been investigated as a function of polymer, organogel concentration and temperature, by differential scanning calorimetry (DSC), optical microscopy, and AFM. The organogel was made up from  $\pi$ -conjugated oligo (phenylene vinylene) (OPV) while the polymer gel was prepared from isotactic polystyrene (iPS) or syndiotactic polystyrene (sPS). OPV organogels change colour at the SOL-GEL transition (yellow to green).

We have observed that a mesoscopic dispersion of one gel into another could be achieved<sup>[1]</sup> provided the mesh size of either gel is in the micrometer range (see Figure

2). For smaller mesh size, microscopic phase separation occurs. These results were confirmed by SAXS and SANS. Basically, we can keep the organogel concentration rather low ( $0.004 \text{ g/cm}^3$ ), and so retaining the optical property while increasing dramatically the elastic modulus of the ternary gel. This process is totally reversible as the organogel can be melted and then reformed by cooling without altering the polymer gel.



**Figure 2.** AFM image of an intermingled gel <sup>[1]</sup>. Organogel= large cross-section fibrils, polymer gel= small cross-section fibrils.

*Sheathing polymer fibrils*, namely encapsulation of polymer gel fibrils by nanotubes (synthesis by P. Mésini see below) has been investigated by DSC, AFM and scattering techniques, SANS and SAXS.

We have observed by DSC that the formation exotherm and the melting endotherm of the nanotubes vanished when incorporated in a ternary system with iPS. Although the nanotube structure was still present in the ternary gel as ascertained by SANS, their formation was clearly concurrent with the polymer gel formation. We have concluded that nanotube formation is nucleated by iPS gel fibrils. AFM experiments have shown that the iPS fibril cross-section increased under these conditions, which is consistent with a sheathing process. SANS experiments have shown that only those fibrils with a diameter in register with the inner diameter of the nanotubes are sheathed;<sup>[2]</sup>

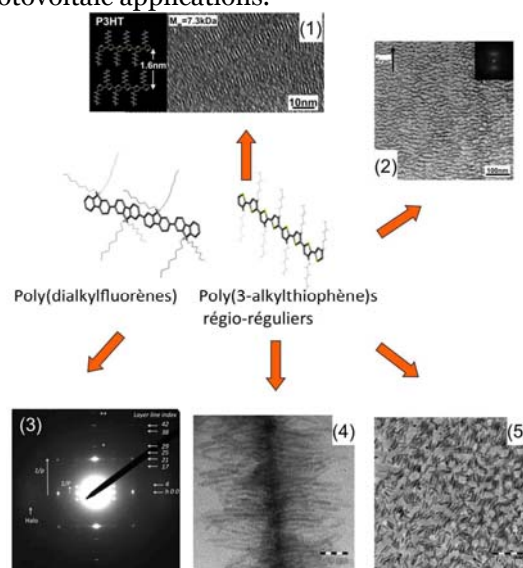
This sheathing process is a low-energy path for physically modifying fibrils surface. This may have applications whenever finely dispersed media are required (e.g. catalysis, filtering membranes for capture of pollutants at the molecular level,...).

In these two systems, the solvent used for gel formation is extracted by supercritical  $\text{CO}_2$ , a process which preserves the original morphology and opens the way for preparing solid functional materials.

## Morphogenesis of $\pi$ -conjugated polymers and small molecules

This research topic is motivated by the understanding of the correlations existing between charge transport properties in organic thin films of  $\pi$ -conjugated materials and the structure/morphology at multiple length scales of these materials. The team has a strong experience in: *morphogenesis* of conjugated polymers and small molecules using epitaxial growth <sup>[3]</sup>, and

*multi-scale structural analysis* of  $\pi$ -conjugated materials (pentacene, regioregular polythiophenes and polyfluorenes) using transmission electron microscopy (TEM) (electron diffraction, High-resolution TEM, dark field imaging).<sup>[3]</sup> The original combination of TEM and epitaxial growth of  $\pi$ -conjugated polymers was used to address following important issues in the field of plastic electronics : i) the correlation between macromolecular parameters (Mw, PDI) and crystallization mode (extended vs folded) of P3HT (2), ii) the determination of structural models for poly(9,9-di(n-octyl)fluorene-2,7-diyl) (PFO) and P3HT [4], iii) the investigation of the semi-crystalline structure/nanomorphology of P3HT films using HR-TEM<sup>[4]</sup> and iv) the growth of highly oriented and nanostructured P3HT fibers with a shish-kebab structure.<sup>[5]</sup> The recent research activity is also focused on the elaboration of oriented/nanostructured hybrid films comprising semi-conducting polymers and inorganic nanoparticles (CdSe, metals) to obtain highly oriented and nanostructured thin films suitable for photovoltaic applications.

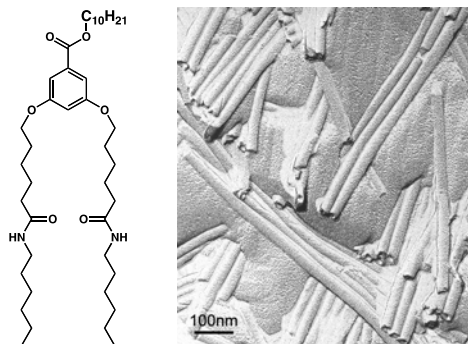


**Figure 3.** 1) HR-TEM image of an oriented film of regioregular poly(3-hexylthiophene) grown by directional epitaxial crystallization. The inset illustrates the arrangement of P3HT chains in the crystal. 2) Bright Field TEM image of an oriented P3HT film showing the periodic alternation of crystalline lamellae (dark stripes) and amorphous interlamellar zones (brighter areas). 3) Diffraction pattern of an oriented PF2/6 film grown onto an oriented PTFE substrate. 4) Bright Field TEM image of a P3HT fiber showing a shish-kebab structure. 5) Bright Field TEM image of a highly oriented and nanostructured hybrid film made of a semi-crystalline matrix of P3HT harboring CdSe nanorods in the amorphous interlamellar zones.

## Nanotubular architectures

In the group we had been conducting the synthesis of a series of aromatic diamide organogelators (Figure 1). We have studied the structure of those gels at the microscopic level by using the techniques mastered in our group. The goal of these studies was to identify the molecular parameters that govern their self-assembly, and organic synthesis has been used to modify these parameters in order to control shapes and dimensions.

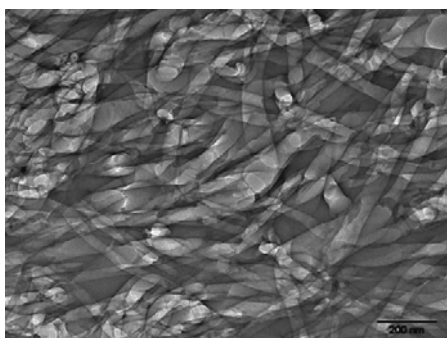
The approach has successfully given different shapes (lamellae, ribbons)



**Figure 4.** Left Structure of the series BHPBn. The length of the ester chain allows the control of the shape of the self-assembly. For instance  $n = 10$  gives nanotubes (see Figure below). Right : self assembled nanotube of diamide BHPB10. Freeze fracture-TEM

We had previously shown that we were able in apolar organic solvents to form nanotubes of 30 nm diameters and several  $\mu\text{m}$  lengths in apolar solvents (Figure 2). We are now using those nanoobjects to synthesize new materials. These nanotubes can be used as templates to form large mesopores in organic resins by a “molding” process<sup>[6]</sup>: the tubes are formed in a mixture of monomer/crosslinkers, which yields a thermoreversible gel. Photopolymerization of this gel yields a resin containing the nanotubes. When the nanotubes are leached out with a dissociating solvent, they leave cylindrical pores. The morphology and size corresponds closely to those of the templating tubes, as shown by TEM and porosimetry (Figure 3). Basic treatment of the mesoporous resin can be used to functionalize the pores and synthesize mesoporous catalysts;<sup>[7]</sup> The resulting materials were tested as catalysts for a model reaction and showed an activity similar to the one of alkaline-substituted mesoporous silica.

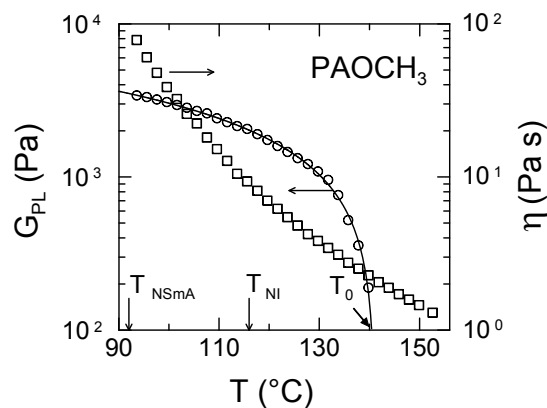
We have been also able to derivatize those tubes to make them reactive on their surface without altering the tubular structure, especially by click reactions.<sup>[8,9]</sup> The tubes remained self-assembled even though the final molecules would not spontaneously re-assemble into nanotubes. This will allow, by supercritical drying, to fabricate reactive aerogel that are also good candidates for catalyst supports. The same reactive nanotubes will be used to sheathe fibrils as described above.



**Figure 5.** Mesoporous resin synthesized with BHPB10 as a template. TEM of a microsection

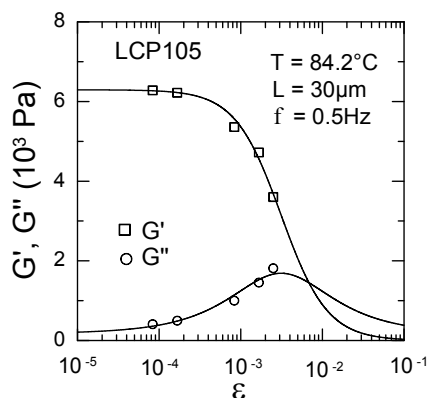
## Structures in the supercooled state of glass-forming polymers

This work was performed as part of studies dealing with the glass transition. Understanding the glass transition is of interest to several fields from soft matter to material sciences and biophysics. However, despite more than half a century of intense research, the glass transition remains mysterious and is still one of the great enigmas of contemporary physics.

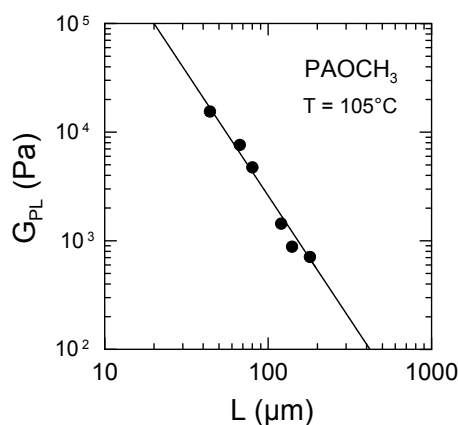


**Figure 6.** Temperature-dependence of the elastic plateau  $G_{PL}$  showing the existence of the gelation temperature  $T_0$ , and of the viscosity  $\eta$  deduced from the  $G''$  behavior. Unlike  $G_{PL}$ ,  $\eta$  shows no anomaly at  $T_0$ . The solid line corresponds to a fit of the  $G_{PL}$  data with equation  $G_{PL} = G_0(T - T_0)^{-1}$ . The thickness of the sample is  $\sim 50 \mu\text{m}$ .  $T_G = 22^\circ\text{C}$ .

In recent years, we have shown by studying the rheological behavior of some polymer melts, either flexible or liquid crystalline, the existence of a temperature  $T_0$  above which the low frequency response is liquid-like ( $G' \sim f^2$ ,  $G'' \sim f$ , where  $f$  is the frequency), and below which it is gel-like ( $G' \sim \text{constant}$ ,  $G'' \sim f$ ). We explained this unexpected change in behavior by a percolation-type mechanism of pre-glassy elastic clusters (known in the literature as Fischer's clusters), which correspond to long-range and long-lived density fluctuations that are kinetically frozen at the time scale of the experiment, hence their elastic character. The mechanical response of the sample is, therefore, the sum of two different contributions: one corresponds to the flow response of the polymer melt and the other to the elastic response of the network formed by the pre-glassy elastic clusters.



**Figure 7.** Typical strain dependence of the real  $G'$  and imaginary  $G''$  parts of the shear modulus of LCP 105, observed at a temperature  $T$  below  $T_0$ . The solid lines are the results of a simultaneous fit of the  $G'$  and  $G''$  data with the equations associated with the Payne effect.  $T_G = 38^\circ\text{C}$ .



**Figure 8.** Variation of the elastic plateau  $G_{PL}$  as a function of the decrease in sample thickness, provoked by a static compression of the sample.

Our study focused on different types of polymer-liquid crystal and was based on the capability of our piezorheometer to perform measurements as a function of the sample thickness at very weak strain ( $\sim 10^{-4}$ ) and under non-sliding conditions.<sup>[10]</sup> It is shown, as with previously studied polymers, the existence of an elastic network formed by the pre-glassy elastic clusters (Figure 6). The existence of this network was supported by new experiments dealing with a) the response of the sample as a function of the strain amplitude, which can be explained by the Payne effect associated with the breakdown of a filler network (Figure 7), b) the response of the sample subjected to static compressions (Figure 8) and c) the response of a polymer melt (far from the glass transition) filled with silica particles, the silica particles playing the role of the pre-glassy elastic clusters. The presence of the pre-glassy clusters invalidates the widely accepted assumption of ergodicity in the supercooled state.

An extension of this study would be to investigate glass formers composed of small molecules.

**Collaborations within the axis:** SAMS (M. Schmutz, D. Sarazin), SOFFT (M. Schmutz), M3 (M. Schmutz, J.M. Guenet)

**Collaborations with other teams at ICS:** IMI (P. Mésini, M. Schmutz), MP (M. Schmutz), CMP (M. Brinkmann, J.M. Guenet, M. Schmutz)

**External collaborations:** A. Ajayaghosh (NIIST, Trivandrum, India), A.K. Nandi (IACS, India), D. Lopez (ICTP, CSIC, Madrid), N. Kutsevol (Kiev Univ., Ukraine), H. Itagaki (Shizuoka Univ., Japan), C. Rochas (CERMAV, Grenoble), A. Wagner (UdS, Strasbourg), J. Parmentier (UHA, Mulhouse), C. Daniel (Salerno Univ., Italy), Dr. A. Sanchez-Ferrer (ETH- Zürich, Suisse), Prof. H. Finkelmann (Albert-Ludwigs Univ., Freiburg, RFA), Pr. H. Pleiner (MPI, Mainz, RFA), Pr. H. Brand (Universität, Bayreuth, RFA), Dr. B. Donnio (IPCMS, Strasbourg), J.M. Lehn (UdS, Strasbourg), I. Kraus (IPCMS, Strasbourg), C. Serra (LIPHT, Strasbourg), Ziessel R. (ECPM, Strasbourg), G. Mosser (UPMC-Collège de France, Paris), Artzner F. (Univ. Rennes), Prof. J.F. Nicoud, (Pharmacie, Strasbourg), Dr I. Schalk (ESBS, Strasbourg), Prof. A. Banerjee (IACS, Kolkata, India), M. Mauzac and A. F. Mingotaud (IMRCP Toulouse), N. Leclerc (LIPHT, ECPM), S. Ludwigs (U. Freiburg), S. Grigorian (U. Siegen, ), U. Asawapirom (Nanotec, Thai), C. Chandezon (CEA, Grenoble), O. Ersen (IPCMS), R. Pansu (ENS Cachan) R. Resel (TU Graz, Autriche)

**Contracts:** ANR PNANO MYOSOTIS (M. Brinkmann, partenaire ICS), Projet PHC franco-thaïlandais (M. Brinkmann), Conectus (P. Martinoty), ANR Blanc MALOWA (P. Martinoty, partenaire ICS), PROCOPE (P. Martinoty), IFCPAR (Centre franco-indien, J.M. Guenet, coordinateur ICS), Fédération de Recherche CNRS 2863 Rhéologie et interface en milieux dispersés (P. Martinoty, partenaire ICS), IcFRC (Mésini, coordinateur), CNRS Prise de Risque PCB antibiogels (Mésini, partenaire ICS), Association Vaincre la Mucoviscidose (P. Mésini, partenaire ICS).

**Techniques available in the team:** DSC, TEM, cryomicroscopy, cryofracture, light scattering, optical microscopy, piezo-rheometer.

**Other techniques used:** AFM, FESEM, SANS, SAXS and WAXS (time-resolved at synchrotron radiation facilities), confocal microscopy.

- [1] D. Dasgupta, S. Srinivasan, C. Rochas, A. Ajayaghosh, J.M. Guenet *Langmuir* **2009**, *25*, 8593
- [2] D. Dasgupta, Z. Kamar, C. Rochas, M. Dahmani, P. Mésini, J.M. Guenet *Soft Matter* **2010**, *6*, 3576
- [3] M. Brinkmann and P. Rannou, *Adv. Funct. Mat.*, **2007**, *17*, 101.
- [4] M. Brinkmann and P. Rannou, *Macromolecules*, **2009**, *42*, 1125.
- [5] M. Brinkmann, F. Chandezon, C. Julien-Raban and R. P. Pansu, *Adv. Funct. Mat.* **2009**, *19*, 2759.
- [6] F. X. Simon, N. S. Khelfallah, M. Schmutz, N. Diaz, P. J. Mesini, J. Am. Chem. Soc. **2007**, *129*, 3788.
- [7] T.-T.-T. Nguyen, F.-X. Simon, N. S. Khelfallah, M. Schmutz, P. J. Mesini, *J. Mater. Chem.* **2010**, *20*, 3831.
- [8] T.-T.-T. Nguyen, F.-X. Simon, M. Schmutz, P. J. Mésini, *Chem. Commun.* **2009**, 3457.
- [9] T.-T.-T. Nguyen, F.-X. Simon, J. Combet, M. Schmutz, P. J. Mésini, *Soft Matter* **2011**, *7*, 1121.
- [10] O. Pozo, D. Collin, H. Finkelmann, D. Rogez, P. Martinoty, *Phys. Rev. E*, **2009**, *80*, 3, 1801.

## Self-Evaluation

**Background.** The SYCOMMOR Team is the merger of two groups (former Système Macromoléculaires et Supramoléculaires Organisés (SMSO) and Morphogénèse de Polymères et Matériaux Moléculaires (MPMM)). The new team has also integrated one synthetic chemist (PMe). The structure of the team is bound to evolve further in the next years due to the retirement of several members (D. Rogez, B. Lotz, P. Martinoty). The team has therefore initiated a reorientation of its research activity so as to organize highly complementary expertise of the former groups (e.g. chemical synthesis of self-assembling molecules, advanced structural analysis by Transmission Electron Microscopy (TEM), controlled thin film growth, thermo-dynamic behavior by DSC, Rheology, scattering techniques with neutrons or X-Rays) around a **joint project** on complex “hybrid” materials. The term hybrid refers here to the association of two classes of systems : *i*) self-assembling entities (organogelators, nanoparticles, organometallic complexes) and *ii*) polymers (pi-conjugated semi-conducting polymers, polyolefins). The association of these two classes of materials is taken as an opportunity to generate new functional materials with potential interest in catalysis, plastic electronics, light materials with functional properties,... The “double” expertise of the team in polymer science and in self-assembling systems is therefore a key advantage to address this new and original project with reasonable success.

### Statement on human resources

The former AERES evaluation pointed at a lack of PhD students in the two former groups now merged in the new SYCOMMOR team. Not less than 9 PhD students and 4 postdoctoral researchers have been hired in the period 2007-2011. Two researchers have left the group (A. Thierry and D. Rogez) and several emeritus researchers are also planned to leave in the next years (P. Martinoty and B. Lotz). This brings forth a stringent need for hiring at least *i*) one Maître de Conférence to strengthen the group’s activity in structure-based research of hybrid materials and *ii*) one technician in chemical synthesis. Beside, the successful application to EU and ANR funding will allow to hire several postdoctoral researchers in the coming five years.

### Statement on financial supports

The following grants have been awarded in the period 2007-2011:

- European project small HYMEC (MB)
- ANR project PNANO MYOSOTIS (MB)
- Thai-French PHC project (2007-2008) (MB)
- IFPCAR (Indo-French centre) project with Pr. Ajayaghosh (JMG)
- ANR project MULOWA with Pr. B. Jamart (PMA, DC)
- Conectus (2007-2010) (PMA)
- ANR MYOSOTIS (MB)

- icFRC support (Chemistry RTRA, Strasbourg) (PMe)
- Prise de risque Physique-Chimie-Biologie ‘ANTIBIOGEL’ with I. Schalk ESBS (PMe)

It is worth mentioning that the group has been awarded two ANR projects (MATISSE and PICASSO) and one EU project (HYMEC).

### Statement on scientific collaborations

While the structure of the team is such that a large palette of complementary expertises are already found within the team, numerous collaborations have been started on various levels.

Collaborations have been established with other groups within the ICS. The polyelectrolytes necessary to build up the anti-fouling multilayers have been synthesized in the Sycommor team. Structural studies of gelators and nanotubes have been done with the PSM group (M. Rawiso, J. Combet) and theoretical models for the nanotubes have been established by the theory group (I. Nyrkova, A. Semenov).

On the Cronenbourg campus, the morphogenesis of pi-conjugated materials relies on tight collaborations with the INESS (T. Heiser) and the LIPHT (N. Leclerc, low-bandgap polymers) within the new consortium on organic photovoltaics (MATEOH-PV). Moreover, strong collaborations within the TEM platform are in progress with the IPCMS on TEM tomography (O. Ersen). At the national level, a longstanding collaboration set with the LEMOH (F. Chandezon, SPRAM), in Grenoble, strengthened by a joint thesis (L. Hartmann) and the ANR project MYOSOTIS. Other partners e.g. the ENS Cachan (R. Pansu) are also involved. On the European level, the TEM expertise has motivated two PhDs from TU Graz (Austria) and Uni. Siegen (Germany) to spend several stays in the group. An important collaboration with the group of S. Ludwig (Uni. Freiburg) has been initiated within the IRTG. On the international level, a franco-thai PHC project has attracted PhD students and one visiting professor (R. Traiphol) to the group.

The expertise of the team in physical chemistry of gelation processes, synthesis of organogelators is internationally recognized, as evidenced by the participation in different national and international projects. JMG has set up a longstanding collaboration with several groups in India on organogelators (Ajayaghosh). JMG has been visiting professor at the Shizuoka University in 2009, whereas BL was a temporary Graduate Faculty Member of the University of Akron (2008-2009).

International collaborations have been initiated with: India, Japan, Ukraine, Italy, Austria, Germany, Thailand, USA, Taiwan, South Korea, Switzerland.

### Statement on scientific productions

The team has contributed 50 publications to the axis “Self-Assembled Systems”

- ☞ Number of articles – **50** (+ 26 with other teams)
- ☞ Journals – *Macromolecules* / *JACS* / *Soft Mater* / *Adv. Mat.* and *Adv. Funct. Mat.*

☞ Average impact factor of the journals – **4.2**  
 ☞ Average number of citations per article (published in the group on the period 2007-2010) – **8** (941 citations/year)

☞ h-index of the permanent staff – **59**  
 48 (B. Lotz), 28 (J. M. Guenet), 20 (M. Brinkmann), 22 (M. Schmutz), 19 (P. Martinoty), 13 (P. Mésini), 9 (D. Sarazin) and 8 (D. Collin).

☞ m-index of the permanent staff – **X,X** (h-index/n-years)

☞ Number of patents – **3**

☞ Number of Invited International Conferences – **43**

**Book:** *Polymer-solvent Molecular Compounds*, Elsevier 2008 (author JMG)

permanent staff of a given group.

### Further professional activities

#### Teaching activities

During the last 4 years, PMe had between 60 and 80 h (equiv. TD) of teaching, mainly polymer chemistry in the Master of Materials Science. MB gave also 12 h of teaching within the same master. This teaching increased the number of master trainees in the group and in the whole ICS. The number of students that choose polymer as their specialty has increase from 1 in 2007 to 10 in 2010.

#### Organization of congresses

- Organizer POLYSOLVAT-8 an IUPAC conference (Strasbourg 2010, JMG)
- Organizer 12th Colloquium French society of Microscopy (Strasbourg, 2011, MS)
- Co-organizer “*Polymer-solvent Complexes and Intercalates*, POLYSOLVAT-7” (Marrakech, 2008, JMG)
- Co-organiser symposium of JMC11 (Strasbourg, 2008, MS)
- Co-organiser Indo-french seminar “*Self-assembled hybrid systems: materials of the future?*” (India, 2011, JMG)
- Co-organiser ELECMOL’08 (MB),
- Co-Organizer symposium N E-MRS-2011 (MB),
- Co-organizer conference MNPC’11 (MB)
- Organizer Colloque National GFP (Strasbourg 2007) (PMe)
- Co-Organizer 10th European Conf. on Liquid Crystals (ECLC-2009), COLMAR (France) 19-24/042009 (PMA)

#### Various commitments

- Chairman French society of Microscopy (2008-2009), vice-chairman (2010-2011) (MS)
- Chairman Consortium of Microscopy users of Uds (MS)
- Member of MEST network (Microscopie électronique à transmission et sonde atomique) (MS)
- Deputy director of the ICS (PMe)
- Elected member of the UFR de Physique et d’Ingénierie of Uds (MS)
- Members of the Laboratory Council (MS, JMG)

- General Secretary of the GFP (Groupe Français des Polymères), ongoing (2009-, JMG)
- Member of the EPSRC (Engineering and Physical Sciences Research Council, GB, JMG)
- Member of the MATEOH-PV consortium Strasbourg (MB)
- Member of the specialist commission 28 (material sciences) at Uds (MB)
- President of the East - GFP (PMe)
- Members of the “Fédération de recherche J. Villermaux pour la Mécanique, l’Energie et les Procédés” (PMA, DC, DR)
- Member of the international scientific committee of POLYCHAR conferences (JMG)

#### Miscellaneous.

Referee activity for:

- **Scientific journals:** Adv. Mat., Adv. Funct. Mat., Angewandte Chemie Int. Ed., Biomacromolecules, Chemistry of Materials, J. Am. Chem. Soc., Soft Mater, Macromolecules, Phys. Rev. B, Phys. Rev. E, Langmuir, J. Physical Chemistry B, Macromolecules, Polymer, European Polymer Journal, J. Polymer Sci. Physics Ed.,...

- **Funding agencies:** NSF, ANR, NSERCC (Canada), CZ, Suisse, EPSRC (UK)

Proceedings editor

POLYSOLVAT-7 “*Polymer-solvent Complexes and Intercalates*”, *Macromol. Symp.* 273, **2008** (Editor JMG)

Awards.

2007 CNRS Bronze medal (MB)

2010 Prize GFP/SFP (MB)

### Overall statement

This team is a new one and as such the research dynamics is at its very beginning although collaborative research has already led us to joint publications. While one part of the activity of the team is well represented by the “*Self-Assembled Systems*” axis of the ICS, we believe that the materials science aspect of the team’s research is not sufficiently emphasized. It is therefore suggested to create a new research axis at the ICS centered on “*functional polymeric and molecular materials*” wherein the research activity of our team would fit better. The hiring of a “Maître de Conférence” with expertise in structural characterization of self-assembled/polymeric thin films is still an important request along with the hiring of a technician in organic chemistry.

# Microscopy Platform

Permanent staff (all CNRS member): Schmutz Marc IR1 and Christian Blanck AI

## Background and context:

The platform was created in 2010 after the in-house mobility of Christian Blanck.

The equipment of the platform consists of two TEMs, one state-of-the-art 200kV cryo TEM installed in 2008 and a 120kV routine TEM. The latter is very old (26 years) but still in excellent working conditions. The platform is also equipped with all ancillary equipment for TEM. Finally the platform is equipped with a rather unique technology namely cryo fracturing. There are only a few labs in France equipped with the latter and we developed a unique way of investigating self-assembled systems in organic solvent.

The platform interacts with the different teams of the institute and is also contacted by several laboratories from Strasbourg and France for specific collaborations. There is not yet a lot of industrial collaborations and that point should be improved.

The platform is part of the French excellence network METSA for studying soft matter structure by cryo EM and cryo fracture preparation.

The different results obtained with the help of the platform are described in the different parts of this report.

## Most significant publication obtained in collaboration with teams outside of ICS.

- [1] Carn, F., Durupthy, O., Fayolle, B., Coradin, T., Mosser, G., Schmutz, M., Maquet, J., Livage, J., Steunou, N. Assembling vanadium(V) oxide and gelatin into novel bionanocomposites with unexpected rubber-like properties 2010) *Chemistry of Materials*, 22 (2), pp. 398-408.
- [2] Dif, A., Henry, E., Artzner, F., Baudy-Floc'h, M., Schmutz, M., Dahan, M., Marchi-Artzner, V. Interaction between water-soluble peptidic CdSe/ZnS nanocrystals and membranes: Formation of hybrid vesicles and condensed lamellar phases (2008) *Journal of the American Chemical Society*, 130 (26), pp. 8289-8296.
- [3] \* Petitjean, A., Cuccia, L.A., Schmutz, M., Lehn, J.-M. Naphthyridine-based helical foldamers and macrocycles: Synthesis, cation binding, and supramolecular assemblies (2008) *Journal of Organic Chemistry*, 73 (7), pp. 2481-2495. IF 4,2
- [4] Bardelang, D., Camerel, F., Margeson, J.C., Leek, D.M., Schmutz, M., Zaman, Md.B., Yu, K., Soldatov, D.V., Ziessel, R., Ratcliffe, C.I., Ripmeester, J.A. Unusual sculpting of dipeptide particles by ultrasound induces gelation (2008) *Journal of the American Chemical Society*, 130 (11), pp. 3313-3315.
- [5] Chivrac, F., Pollet, E., Schmutz, M., Avérous, L. New approach to elaborate exfoliated starch-based nanobiocomposites (2008) *Biomacromolecules*, 9 (3), pp. 896-900.
- [6] Thiot, C., Schmutz, M., Wagner, A., Mioskowski, C. A one-pot synthesis of (E)-disubstituted alkenes by a bimetallic [Rh-Pd]-catalyzed hydrosilylation/hiyama cross-coupling sequence (2007) *Chemistry - A European Journal*, 13 (32), pp. 8971-8978.
- [7] \* Camerel, F., Ziessel, R., Donnio, B., Bourgoigne, C., Guillon, D., Schmutz, M., Iacovita, C., Bucher, J.-P. Formation of gels and liquid crystals induced by Pt□Pt and π-π\* interactions in luminescent σ-alkynyl platinum(II) terpyridine complexes (2007) *Angewandte Chemie - International Edition*, 46 (15), pp. 2659-2662.

\* Frontpiece of the journal.





# International Research Training Group “Soft Matter Science” (IRTG)

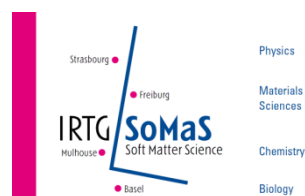
Coordinators: Günter Reiter (Freiburg), Jörg Baschnagel (Strasbourg)

**Permanent staff :** **Freiburg** Prof. Eckhard Bartsch (UF), Prof. Alexander Blumen (UF), Prof. Christian Friedrich (FMF), Dr. Sabine Ludwigs (UF until spring 2011, since then professor at the University of Stuttgart, Germany), Prof. Rolf Mülhaupt (UF/FRIAS), Prof. Günter Reiter (UF), Prof. Jürgen Rühle (IMTEK), Dr. Stefan Schiller (FRIAS) / **Strasbourg** Prof. Jörg Baschnagel (UdS), Dr. Martin Brinkmann (Chargé de Recherche CNRS), Prof. Gero Decher (UdS), Prof. Nicolas Giuseppone (UdS), Dr. Marie-Pierre Krafft (Directeur de Recherche CNRS), Dr. Vincent Le Houérou (Maître de Conférences UdS), Dr. Pierre Lutz (Directeur de Recherche CNRS), Dr. Carlos Marques (Directeur de Recherche CNRS), Dr. Philippe Mésini (Chargé de Recherche CNRS), Dr. Hendrik Meyer (Chargé de Recherche CNRS), Dr. Hervé Pelletier (Maître de Conférences UdS), Prof. Pierre Schaaf (UdS), Dr. Alexander Semenov (Directeur de Recherche CNRS), Dr. Joachim Wittmer (Directeur de Recherche CNRS), Prof. Yves Holl (UdS), Prof. Mounir Maaloum (UdS), Dr. Tatiana Schmatko (Maître de Conférences UdS), Dr. André Schröder (Chargé de Recherche CNRS) / **Mulhouse** Dr. Karine Anselme (IS2M, Directeur de Recherche CNRS) / **Basel** Prof. Wolfgang Meier (University of Basel)

**Non-permanent researchers :** **1 post-doctoral associate (DFG funded)** (Dr. F. Ziebert) / **7 PhD students (funded by French sources)** (C. Higy – project B2, J. Lejeune – project C5, J. Longo – project C2, P. Polińska – project A1, A. Shvets – project B4, A. Weinberger – project A2, A. Wolf – project A4) / **11 PhD students (DFG funded)** (M. Eichhorn – project C1, C. Gillig – project A1, E. Grespan – project C4, J. Helfferich – project C3, A. Kiesling – project B3, N. Matahiyan – project A2, A. Peukert – project A3, M. Rothfelder – project B2, K. Tremel – project A5, M. Vielhauer – project B1, C. Yao – project C2)

**Keywords:** French-German graduate school · soft matter science · chemistry · physics · biology · engineering

## IRTG Soft Matter Science: What is it ?



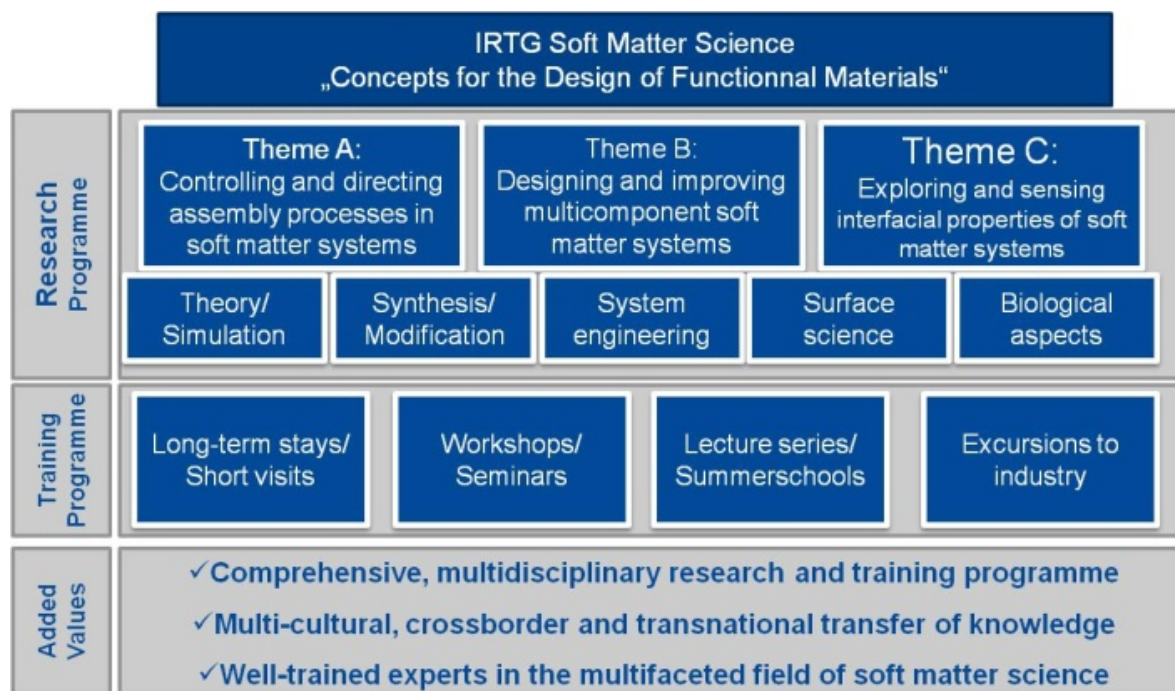
The International Research Training Group (IRTG) “Soft Matter Science: Concepts for the Design of Functional Materials” is a French-German graduate school between the

universities of Freiburg and Strasbourg (and with colleagues from Mulhouse and Basel). The IRTG officially started on October 1<sup>st</sup> 2010 and will last until end of March 2015.

In Germany, a structured doctoral training at the university, similar to that of the *École Doctorales* (EDs) in France, does not exist in general. In order to offer the possibility for such a training the Deutsche Forschungsgemeinschaft (DFG) provides as an instrument the so-called “Graduate College”, the international version of which is the IRTG. An IRTG is

created for 4.5 years after a positive 2-step review process, a “Pre-proposal” and an “Establishment proposal”, the latter document being evaluated on site in one day by an international committee (in our case, on April 1<sup>st</sup> 2010, Freiburg).

Each IRTG has a specific research field. (This feature is a main difference to a French ED whose research field is in general very broad.) The field of our IRTG is soft matter science. The IRTG aims at advancing our understanding in this field and at developing concepts for the design of advanced materials. This requires an interdisciplinary approach with input from physics, chemistry, biology and materials science. The IRTG provides knowledge from these disciplines through the participating scientists (8 from Freiburg, 14 from Strasbourg, and 1 from Mulhouse and Basel; see Figure 1). It integrates this knowledge into a research and qualification programme (*cf.* the sections below and Scheme 1). The aim of this programme is to provide the 21 PhD students (see Figure 1) with an interdisciplinary and multicultural qualification enabling them to compete in the international job market.



**Scheme 1.** Conceptual outline of the IRTG. The Research Programme on soft matter science is divided into three themes which are interconnected and supported by various scientific competences (Theory/Simulation, etc.). A complementary Training Programme aims at broadening the horizon (scientifically and culturally) of the PhD students. Both programmes intend to confer the listed Added Values to the PhD training within the IRTG.

On the German side, the IRTG is funded by the DFG; on the French side, by the UdS, the Région Alsace, the icFRC, and the CNRS. Additional financial support comes from the French-German University (DFH/UFA) which has recently acknowledged our IRTG as a *French-German Graduate College* (after a positive review of our DFH/UFA proposal in July 2011).

## IRTG Soft Matter Science: Activities

### Research programme

Soft matter science explores systems characterized by two main features: *i*) The systems contain *mesoscopic structures* with length scales of tens of nanometers to about one micrometer, resulting from the large size and ability of aggregation of their constituents, e.g., polymers, colloids or aggregates of surfactants. *ii*) The interactions in these systems are in general *weak*, i.e., comparable in strength to thermal fluctuations, and often *complex*, since the constituents can be composed of moieties with competing affinities.

Both features impact the behavior of soft matter. Soft matter systems have the unique capacity of being highly susceptible to weak stimuli. Small external forces can induce significant responses allowing for highly flexible

behavior, often in the form of macroscopic changes due to the mesoscopic (re-) structuring of the system. On the other hand, competing interactions are at the origin for one of soft matter's most striking properties: the ability to self-assemble, i.e., to spontaneously order over regions much larger than the size of the constituent molecules. Self-assembly and responsiveness offer great opportunities for the design of materials with specific functionalities.

In the framework of this broad scientific context the IRTG proposes a research programme consisting of three interconnected themes (see Figure 1): (A) *Controlling and directing assembly processes in soft matter systems*; (B) *Designing and improving multicomponent soft matter systems*; (C) *Exploring and sensing interfacial properties of soft matter systems*. Each theme comprises several PhD projects (21 in total, cf. Figure 1; currently all except 3 PhD positions are filled) which were elaborated for the “Establishment proposal” by supervisors from the partner countries. The supervisors will host the PhD student(s) during short-term visits and long-term stays and provide their complementary expertise to help the student(s) advance the research project efficiently. This international research environment is a true added value, both scientifically and culturally, for the PhD students whose work in turn also provides an added value for the supervisors by establishing or strengthening the collaboration between them.

Theme A: Controlling and directing assembly processes in soft matter systems				
A1	Transient self-assembled networks	Friedrich / Wittmer	1	1
A2	Dynamic nanostructures in self-assembled lipid bilayers	Schiller / Marques / Meier (Basel)	1	1+1
A3	Self-assembled nanoribbons and nanotubes of aromatic diamideesters	Reiter / Mésini	1	
A4	Self-assembled donor-acceptor amphiphilic polymers	Ludwigs / Giuseppone		1
A5	Controlled nucleation and growth of conjugated polymers	Ludwigs / Brinkmann	1	
Theme B: Designing and improving multi-component soft matter systems				
B1	Macromolecular nanohybrid molecules	Mülhaupt / Lutz	1	
B2	Polymer multilayers at solid substrates	Rühe / Decher	1	+1
B3	Influence of nanofillers on the properties of polymer latex films	Bartsch / Meyer	1	1
B4	Colloidal stabilization by unattached homo- and copolymers	Bartsch / Semenov	1	1
Theme C: Exploring and sensing interfacial properties of soft matter systems				
C1	Interactions between biological systems and patterned surfaces	Rühe / Kraft / Anselme (Mulhouse)	1	
C2	Development of mechanically responsive sensors	Schiller / Schaaf	1	1
C3	Modeling late stages of spin coating	Blumen / Baschnagel	1	
C4	Frictional and adhesive properties of polymer surfaces and films of controlled structure and function	Reiter / Le Houérou	1	
C5	Mechanics of surface recovery + reconstruction after deformation	Mülhaupt / Pelletier		1
Total number of PhD stipends :			12	7+2

**Figure 1.** The three thematic areas (Theme A to C) with their associated PhD projects (A1 to C5). The names of the German and French supervisors are indicated in blue and red, respectively. The last-but-one column shows the number of PhD stipends granted by the DFG. The last column gives the number of PhD stipends funded by French sources (and Swiss sources for project A2).

### Qualification programme

Around the research programme, the IRTG proposes a complementary qualification programme consisting of introductory and advanced courses, seminars, workshops and “training camps”. In part, this training programme has been inspired by that of the EDs in Strasbourg, to which the IRTG is affiliated. Our programme is open to all interested students from the partner universities and, upon agreement, its events will be acknowledged by the local EDs.

**Courses.** Specific courses are held annually in the framework of the “SoMaS Summer School” (one week in July in Mittelwihr, Alsace). The school addresses scientific topics pertinent to the studied soft matter systems, offers the students the possibility to present their work by posters (and for some selected also in “Master Classes”), and invites career-oriented talks to expose job opportunities inside and outside academia after the PhD. The first SoMaS school took place from July 10-15, 2011.

**Seminars and visiting researchers.** The IRTG invites national and international experts in soft matter and materials science to contribute to the research and qualification programmes. These contributions involve long-term visits of researchers who will also participate in specific research projects, multi-day visits for a block seminar and extensive discussions, or one-day visits for a lecture.

**Workshops.** Workshops, where all participants of the IRTG (students and supervisors) meet to discuss progress and new ideas, are organized alternately in the Freiburg and Strasbourg areas. They are open to other participants from outside the IRTG. At these workshops, the students present their results (in English). Two of these workshops already took place

(December 17, 2010 in Strasbourg; April 15, 2011 in Freiburg). Moreover, as a complement to the workshops, one-day “students-only” meetings shall be organized by the students themselves, where practical and scientific problems will be discussed among the students (without the supervisors).

In addition, the IRTG, jointly with the FRIAS, has organized an international discussion meeting on the challenges in and potential of polymer physics (May 4-6, 2011 in Schluchsee, Germany).

**Training camps.** PhD students (and supervisors) from the participating universities, who employ the same instrumentation or theoretical approaches, meet to exchange their experience on how to use the equipment or on how to apply theoretical/numerical tools. This can also include collaborative practical work on the experimental or theoretical/numerical tools. These training camps are organized by the students. One such training camp on the relationship between controlled changes of topography, mechanical properties of surface and cell adhesion already took place (June 16-17, 2011 at Schauinsland, Germany; organiser: E. Grespan); another one on the viscoelastic response of soft matter will be planned (organisers: C. Gillig/P. Polińska).

### Annotations

**Abbreviations used in the text:** UF = University of Freiburg, FMF = Freiburger Materialforschungszentrum, FRIAS = Freiburg Institute for Advanced Studies, IMTEK = Institut für Mikrosystemtechnik.

UdS = Université de Strasbourg, IS2M = Institut de Science des Matériaux de Mulhouse.

icFRC = international center for Frontier Research in Chemistry.

DFH/UFA = Deutsch-Französische Hochschule/Université Franco-Allemande.

**IRTG website:** <http://www.softmattergraduate.uni-freiburg.de>

