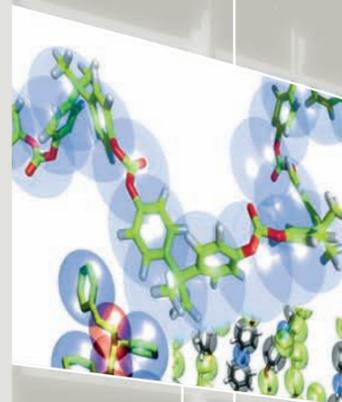




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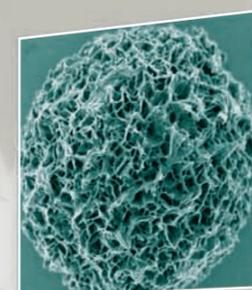
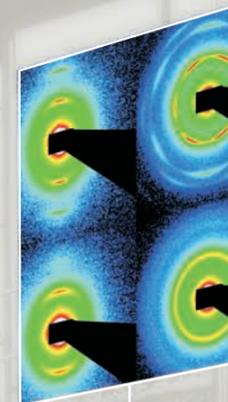
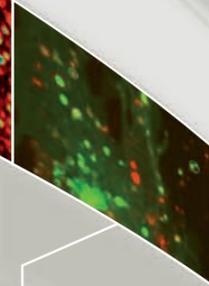
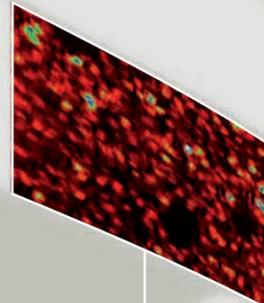
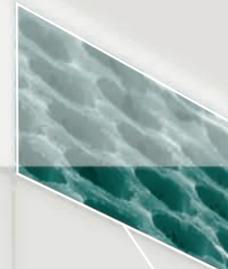
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# Polymer Research 2009

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MAX-PLANCK-GESELLSCHAFT

Polymer Research 2009

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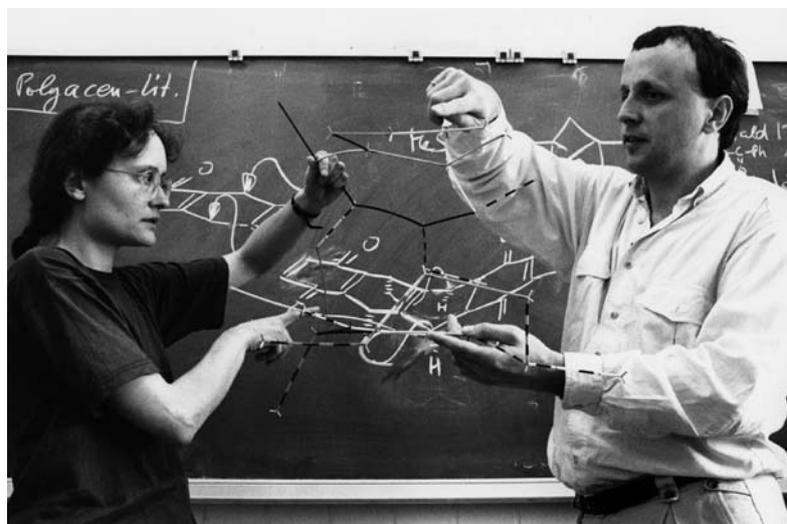


## From the Past to the Future

G. Wegner

Synthetic polymers were portrayed a mere curiosity by the leading organic chemists. They were considered an interesting but rather exotic playground by physical chemists and physics was barely interested in materials which showed such a complex and parameter dependent behavior as were polymers available in the years 1950-1970. And yet, polymers had become a major field of growth for the chemical industry worldwide and increasing amounts of polymers – frequently called “plastics” in a simplifying and generalizing context – were thrown into a seemingly unsaturable market. The reason was that synthetic polymers had developed into the growth engine for mass production of advanced technology products in rapidly growing markets of the automotive, aerospace, electronics and packaging industries, just to mention a few of the important areas. In consequence, industry was in need to find scientifically trained experts and contacts to research groups who could assist in understanding the materials properties in response to the ever growing complex requests of the markets. This was particularly true in Germany where the chemical industry had become a major supplier of polymer materials for the world market in the late 1970s.

The landscape of academic research in the field of polymers was rich but extremely scattered into small and highly specialized individual groups at the time. It was felt by the scientific community that the critical mass was lacking to bring the field of polymer science to a similar level of competence, international competitiveness and excellence as was seen for other fields in Germany. This was the background for deliberations started by the Max Planck Society (MPS) around 1978 which eventually led to the foundation of the Max Planck Institute for Polymer Research on June 1st, 1983 by the Senate of the MPS. The mission of the new institute was to carry out research with the aim to explore and establish fundamental insights into the properties of polymer materials and their performance in the context of the relevance of polymers for the development of advanced technologies. Moreover, polymers were understood to become a platform to study complex behavior of matter in very general terms. The latter requested a strong contribution of theoretical physics and gave the stimulus to develop the new institute soon into an internationally leading center for “soft-matter” research. This included certain aspects conventionally covered by biophysics and molecular biology, where typical research questionnaires centered around the nature and consequences of “molecular recognition” among alike and dislike macromolecules, biocompatibility of materials in medicine and similar issues. Professor Erhard W. Fischer and Professor Gerhard Wegner were appointed as the founding directors representing physics and chemistry of polymer materials. The campus of the Johannes Gutenberg University of Mainz was selected as the site of the new institute in the light of an expected close cooperation with both the departments of chemistry and physics.



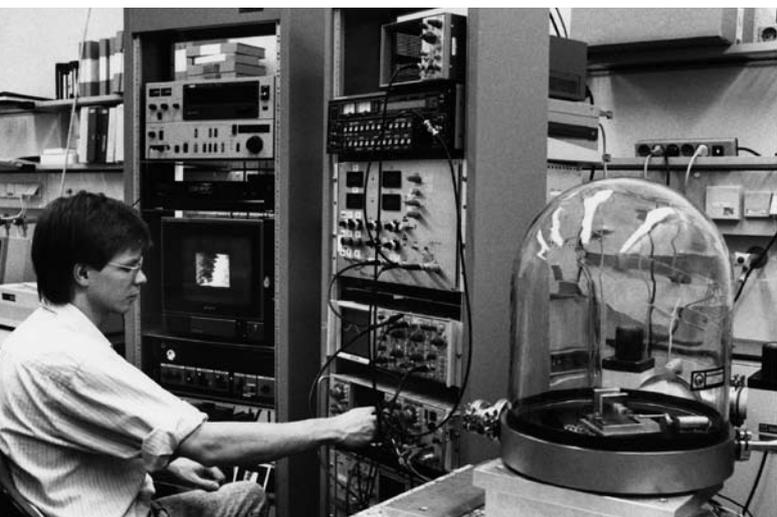
*Adelheid Godt (PhD student) and Dieter Schlüter (project leader) (1989).*

In fact, Mainz had won a competition of several cities for the instalment of the new institute, among them Hamburg, Braunschweig, Bayreuth and Darmstadt. The option was taken for Mainz in the light of the excellent offer of the Johannes Gutenberg University for a building lot in close neighborhood to the Mainz University's campus and for the reason that there existed a strong research activity in both polymer chemistry and physics. A fertile ground for cooperations was prospected. Moreover, Mainz was in geographical neighborhood to the major industrial research and development centers with which cooperations were foreseen.

Scientific work at the institute started in autumn of 1984 in temporary laboratories. At the same time, Professor Hans W. Spiess was appointed as a further director at the institute to develop the field of polymer spectroscopy. The fourth department covering the area of synthetic macromolecular chemistry was established by Professor Klaus Müllen at the end of 1989. In 1993, Professor Wolfgang Knoll joined the institute as a director for surface science of polymer materials. In 1995 the originally intended number of six departments was completed with the appointment of Professor Kurt Kremer as the director of the institute's theory department.

Professor Erhard W. Fischer retired from his official duties in 1997 and holds an emeritus status at the institute. In 2002 Professor Hans-Jürgen Butt succeeded him as director of the institute's polymer physics department.

Additionally, two external members of the Max Planck Society, Professor Kurt Binder, theoretical physicist at the University of Mainz, and Professor George Fytas, chemist and director at F.O.R.T.H. and the University of Heraklion, Crete, Greece were appointed by the President of the Society.



*Stefan Buchholz (PhD student in the team of Jürgen Rabe) at self-built STM (1989).*

When Professor Gerhard Wegner retired in February 2008, his position was endowed to Professor Katharina Landfester. She was firmly installed in September 2008. Her department was renamed as “Physical Chemistry of Polymers”. Professor Knoll left the institute in April 2008.

The institute is located at the edge of the campus of the University of Mainz on its own premises since 1988, when the first part of the present set of buildings was completed. Extensions to adapt to the growing number of staff, instrumentation, and scientist activities became available at the end of 1990 and in early 1998. A further building to accommodate the strong theory group and give more space to NMR-facilities and academic support forces was finished late 2006. The available laboratory space including mechanical, electrical, and electronic workshops amounts to roughly 6,000 m<sup>2</sup>. There is also a conference center with a lecture hall that seats an audience of more than 400 people, lecture and seminar rooms, a library, and a small cafeteria. Science at the institute was to be organized in research projects in which scientists of different groups and of different expertise interact with each other, with students, and with visiting scholars. From the very beginning the mission statements included that the institute should develop and perform as a platform to give young scientists the chance to become independent in fields relevant to the overall scientific goals of the institute. Besides training of doctoral students in cooperation with the local university but also other international universities postdoctoral research associates were attracted to the institute and installed as project leaders for a limited number of years. They were given the chance to build their own research groups with the understanding that they would contribute to the well-defined portfolio of the institute for the time of their membership to the institute. This policy has been academically most successful in raising highly qualified academics who have spread polymer science research and teaching at the professorial level not only across German universities but also internationally.

The scientific objectives of the institute as a whole are directed to synthesis of macromolecular systems and their exact structural characterization as well as to the deve-

lopment and application of new methods to reveal and understand the relationships between microscopic and macroscopic properties and functions of polymer materials. Besides the analysis of already technically relevant polymers, new materials with unconventional properties are made and investigated for their functional properties. A number of new experimental and theoretical methods have been developed since the institute came to life which serve towards a better understanding of structure property relationships and have helped to gain a quantitative theoretical description of polymer systems. Work at the institute thus contributes significantly to the advancement of polymer-based technologies.

Major research topics include

- Synthetic macromolecular chemistry (new synthetic methods, polymers with unconventional structures, systems of selective functionality, e.g. electronic or ionic conductivity, polyelectrolytes, hybrid polymers containing organic, inorganic or biological components)
- Structure and dynamics of macromolecular systems with special emphasis on polymer theory
- Thermodynamics, phase transitions, and critical phenomena (including the physics of polymer blends, block copolymers, and glass transition phenomena)
- Surface and interface science of polymers
- Supramolecular architectures of macromolecules (shape-persistent macromolecules, liquid crystalline polymers, model membranes, ultrathin films, polymers at surfaces)
- Nanoscopic structures, their self-assembly and function
- Special physical properties (electrical and electro-optic phenomena, nonlinear optics, deformation behavior of glassy polymers, surface properties)
- Methodological developments (solid-state NMR-, EPR- and mass spectrometry, dielectrics, nonlinear optics, surface plasmon optics, scanning probe microscopy, i.e. STM, AFM, and SNOM, scattering methods including neutron and X-ray reflectometry, light-scattering and chromatography methods for the characterization of polymer solutions, computer-based simulations).



*Anna Cristadoro (PhD student in the team of Hans Joachim Räder) working the mass spectrometry lab (2007).*

The institute has maintained a large activity in research projects supported by sources other than the Max Planck Society including direct interactions with interested national and global industry.

The institute is considered a national and international center of scientific and academic training ever since it was founded. It rapidly grew to be a leading place in Europe for the training of graduate students in all polymer related fields except polymer engineering and processing.

Along these lines, the institute is home to the “International Max Planck Research School for Polymer Material Science” (IMPRS-PMS) and it hosts the European fellowship program Early Stage Research Training (EST) “Analytical Methods in the Development of Science and Technology of Polymers”. In 2008 it won a national competition for excellence in graduate research training and was awarded with special support together with the departments of chemistry and physics of the local university (Graduate School of Excellence MAterials science IN MainZ - “MAINZ”). All these means allow the institute to attract and select the very best students for its graduate research and training activities across Europe. In consequence the institute hosted constantly ca. 150 graduate research students per year in its premises.

More than 660 doctoral theses have been completed since 1984 based on research work carried out in the institute, frequently in close cooperation with the departments of chemistry and physics of the University of Mainz and (external) members of university institutes. Former graduates from the institute are found throughout German and European industry in leading positions. Similarly, the very active program in postdoctoral training of international scientists has led to a situation that many of the former research associates hold now chaired academic positions internationally, including the United States and Canada, Japan, China and Europe. Over the last two decades the institute has typically hosted fifty to sixty post-doctoral research associates per year. Among the former research staff scientists (“project leaders”), approximately forty gained the habilitation or similar qualifications while working with the institute and hold now professorships in other academic institutions.

The strong connection with the University of Mainz is not only reflected in the considerable number of graduated students who are working with the institute but are registered with the university’s biology, chemistry and physics Departments, but is also manifested by cooperative research projects. Noteworthy is the joined activity in the DFG (German Research Foundation) supported Collaborative Research Centers (Sonderforschungsbereich) “From Single Molecules to Nanoscopic Structured Materials” (SFB 625). An additional center of excellence is concerned with “Physics of Colloidal Dispersions in External Fields” (Transregio SFB TR6) including further academic institutions in Germany in addition to the University of Mainz.

The important role of nanosciences and nanotechnology is marked by an integrated EU project entitled “NAIMO”.

The short history of the institute is rich of scientific developments which nucleated from here or were at least significantly influenced by contributions from this place.



*Markus Retsch (PhD student in the team of Ulrich Jonas) and Julia Braunagel (PhD student in the team of Ingo Köper) discussing molecular recognition (2007).*

Most noteworthy is the foundation of modern interest in surface science of polymeric materials which started here in the mid-eighties when the institute organized a national research project on “Ultrathin Layers of Polymers - ‘UDS’ as novel materials in optics, electronics, and biomedicine.”

Similarly, modern interest in the phenomena related to the glassy state of polymers and organic materials started here with the foundation of a now terminated ‘Center of Excellence (SFB)’. The contributions to the methodology of NMR spectroscopy which are key to today’s knowledge on the dynamical properties of polymers need to be mentioned as well. Contributions to the synthetic methodology, notably in the area of polyconjugated and all-aromatic macromolecules were basic to further significant work concerning unconventional electrical and optical including nonlinear optical properties of polymers. More recently strong computer simulation efforts in conjunction with analytic theory complement the experimental activities leading to new joint developments.

Cooperation with industry has always played an important role and was significantly supported over the years by the materials research programs of the German Federal Ministry of Education and Research. In addition, numerous direct interactions with larger and smaller industries has always been common and characteristic for the institute’s research strategy. The latter was based from the very beginning of the institute on the fact that the production, processing, application, and technology of polymeric materials are rich sources of most intriguing phenomena worth to excite scientific as well as academic interest.

For the future we expect a strong extension towards even more complex macromolecular structures and assemblies of both synthetic and biological origin. The original mission statement of the institute namely to be an internationally highly visible and nationally leading center of modern research on polymeric materials and thereby be also a training center for experts in this important field of industry and advanced technology may for good reasons continue to serve as a guiding principle to the future.

# Research Programs

# Structure and Dynamics



## Structure and Dynamics

K. Kremer, H.W. Spiess

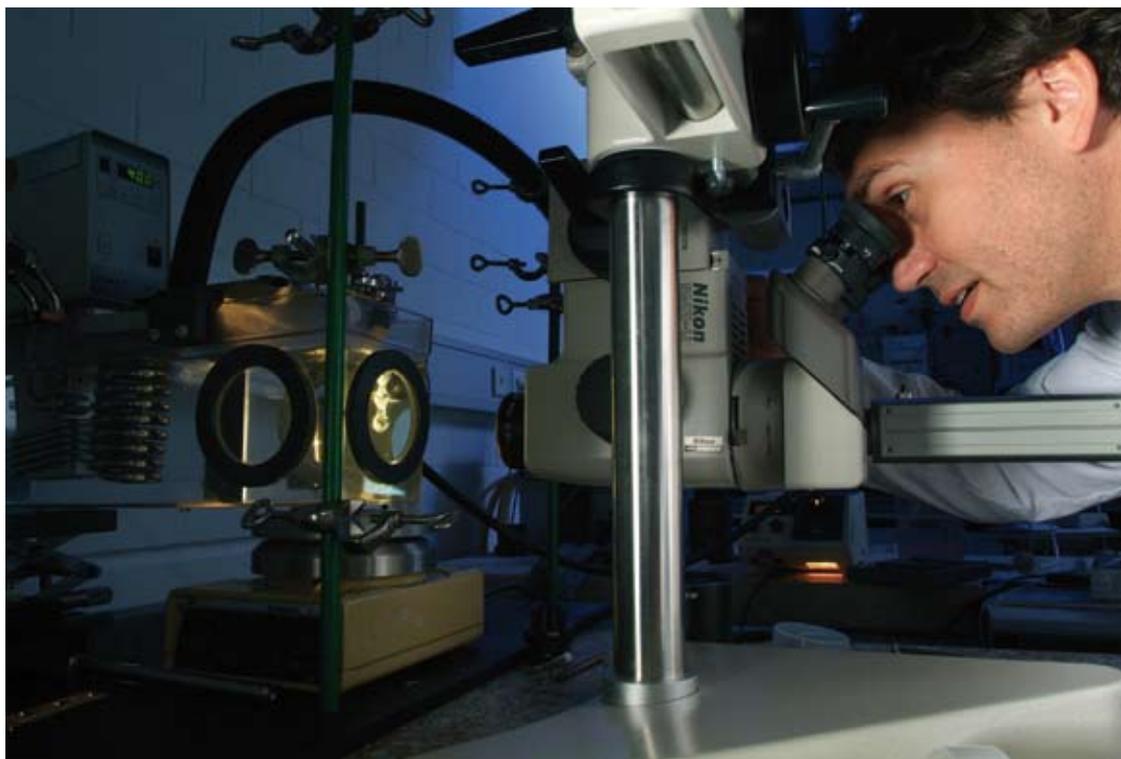
The experimental and theoretical understanding of the structural and dynamical properties of macromolecular systems is a central objective of the institute's work. On the way to achieving complex self-assemblies and functional materials the understanding of basic structural and dynamical, or relaxational aspects and mechanisms is an indispensable part of rational materials design. Many projects in this field of research are currently being pursued, of which a small subset is described below. These activities range from the analytic theory of single macromolecules to multiscale simulations of complex aggregates, and from the structure of hydrogels or ionic aggregates to instabilities in colloidal flow. The latter project illustrates that non-equilibrium phenomena are attracting increasing attention. Though the theory of single chains might seem rather well-known, there are still many unsolved problems which are of direct relevance to either numerical modeling or experimentation. A typical problem of this class is a single chain under strong tension. The dynamics can no longer be described within the Rouse scheme and the nonlinearity, originating from bond length constraints, dominates the behavior leading to shock waves propagating through the molecule. While such complicated situations on the single polymer molecule level allow for analytical treatment, complicated amorphous and structurally organized macromolecular systems are investigated by systematic multiscale modeling strategies.

These methods have been developed in the institute for more than ten years and are being applied to a number of problems, among them amorphous polymer melts with and without low molecular weight additives and polymers under constraints. In a recent extension liquid crystalline macromolecules and peptides close to a (metal) surface have been studied. Along another line, by systematically linking all atom force field simulations, it was shown how we could determine the time-scaling within a multiscale approach. This was then used to predict diffusion constants of i.e. a polystyrene melt of up to 50 kDa molecular weight in excellent agreement to the experiment without any adjustable parameter.

Structure formation and controlled assembly are the focus of joint simulations and various experiments and

cover both ionic systems and hydrogen bond dominated hydrogels. The formation of DNA, or charged dendrimer assemblies, can be linked to co- and counterions, but also to pH effects, and are studied by UV spectroscopy. Details of interaction between the macroions and counterions can directly be studied by ESR spectroscopy. This method allows us to determine whether the counterions are metastably bound or whether the localization is transient with only a short time effect that has direct influence on the overall polyelectrolyte conformations. These conformations and the assembly of polyelectrolytes due to counter- and salt ion condensation are also studied extensively by computer simulations. For a model, which is adjusted in its parameters to correspond to polyparaphenylenes (PPP), the typical size of such aggregates as a function of salt ion valence was determined by computer simulations. Though related, the situation in hydrogels can be somewhat different. Photo crosslinkable systems of PNiPAAm can be used as actuators and are sometimes termed as smart materials. To characterize their structure and function a whole set of experimental techniques is employed including various spectroscopic methods and surface plasmon resonance (SPR).

Theoretically structure formation in block copolymer systems quite often is studied by self consistent field methods. Extensive simulations now have been employed to carefully study their possibilities and limitations. In an extension another option to steer structure formation is through spatial confinement. Block copolymers, where the attraction of the wall to one component is varied, are perfect candidates for such an investigation.



Of course, not only structural aspects are being investigated, but to an equal extent those of dynamical properties. A special situation occurs in semi-crystalline polymers as the amorphous and crystalline regimes are governed by significantly different mobilities of the chain segments. This is of immediate relevance to processing properties. Here, NMR spectroscopy offers unique opportunities for linking structural information to diffusion constant measurements. It has been established that the interface between the crystalline and non-crystalline regions plays a vital role in determining not only chain diffusion between the two regions, but also processability. While the previous example dealt with polymer diffusion in a varying polymeric surrounding, the dynamics of confined macromolecules is another topic of high interest. Especially when confinement occurs on a nanoscale, mobility is significantly influenced by conformational constraints. To study the mobility, the diffusion of poly(isoprene) (PI) in nanoporous aluminium oxide was investigated by fluorescence correlation spectroscopy. Due to the special structure of the nanoporous matrix material this can be extended to observe even single molecules.

Transport properties are not only considered for polymeric systems. Polymer-based biodegradable nanoparticles as drug carriers can be designed to reach target tissue very effectively and may even pass the blood brain barrier. Such particles produced by miniemulsion polymerization can be fluorescently labeled and followed in *in vivo* or *in vitro* experiments to demonstrate the high potential of such a strategy. These objects are typically rather fluffy and deformable. Hollow silica microcapsules, however, are much more rigid and can also be employed as carrier materials. These capsules, with a diameter of about  $1\mu\text{m}$ , have been synthesized and their elasticity measured via an AFM and/or Brillouin scattering.

So far equilibrium properties have mostly been discussed. A better understanding of these properties is what we are basing our research on with an extension of our activities to non-equilibrium situations, which certainly occur more frequently in nature. In many cases externally driven systems are of high interest. Almost all biological systems are permanently driven by a continuous supply of energy. In a typical experimental situation the driving force can originate from fields (electric, shear etc.) or temperature (energy). Given this, it is useful and appropriate to begin with rather idealized theoretical models or experimental systems.

Theoretically non-equilibrium phenomena are tackled in two ways. On the one hand, we employ macroscopic hydrodynamic theory to study driven complex fluids and the instabilities therein, leading to phenomena such as convective flow. This in turn influences the structure. Typical examples studied by this approach are liquid crystals or ferrofluids. While in the first case shear and temperature gradients drive the systems, magnetic fields are used for ferrofluids. On the other hand, when it comes to conformational distortions of a macromolecule in a flow field, or the deformation of the charge distribution around a polyelectrolyte, or a charged colloid, mesoscopic computer simulations are the method of choice. Due to the coupling of different methodologies such complex problems can currently be approached. Recently, the combination of lattice Boltzmann and molecular dynamics simulations allowed us to work on the first steps towards the study of turbulent drag reduction by solvated polymers.

From the experimental point of view, colloidal suspensions offer many ways to directly observe non-equilibrium problems. Soft colloid-like systems and stiff cylindrical bottle brush polymers are especially susceptible to shear fields. By varying shear and density they show lyotropic behavior. The variation of density in addition allows manipulation of the shape of the interaction potential. Another important property of colloidal suspensions is the strong dielectric contrast between the colloid and the surrounding water. In non-uniform electric fields this leads to a motion of the colloids due to dielectrophoretic forces. This effect can also be used to control the motion of individual colloids or to study transient effects due to the switching on and off of the electric field. While colloidal systems are important, model systems allowing a deeper insight into non-equilibrium phenomena, polymers, such as polystyrene in cyclohexane, or low molecular weight mixtures, display fascinating phenomena as a result of the competition of the time derivative of the temperature (i. e. cooling rate) and phase transition kinetics. This competition creates very interesting intermediate structures of oscillatory behavior and a variety of characteristic droplet sizes upon phase separation.

# Single Chains: Non-linear Polymer Dynamics

T.A. Vilgis

*Keywords: Single polymer chains, dynamics, stretching and dynamics, non linear dynamics*

Why do we care about single polymer chains? Are there still unanswered questions? After more than 50 years of polymer theory the list of unsolved problems concerning single chains has become even longer rather than shorter. Indeed, only some basic questions are being studied and mainly by using simplified methods, e.g. Gaussian chains, Rouse-Zimm dynamics, etc.

## Dynamics of stretched chains under tension

Usually the dynamics of polymers are well described by the so-called Rouse model which is based on several assumptions, e.g., that the chains have no interaction and can be represented by a simple bead-spring model. Therefore, the probability distribution is a Gaussian function of exponential form. Obviously, Gaussian chains can be stretched to an extension beyond their own contour length. Such severe drawbacks have also dramatic consequences for the dynamics, as visible in the corresponding stochastic equation for single chain dynamics: The dynamics are not very sensitive to elongations of the chain. In several experimental situations, such as fatigue of materials or crack propagation, the deformation state of the chains close to the tip of the crack experience extremely large deformations and (line) tensions. Therefore, a more detailed and general theory for chains under high stress and large extension is the basis for many applications beyond classical polymer theory.

Chain dynamics under strict and hard constraints are not very practical, since the corresponding theories require Lagrange multipliers and are not easy to handle. On the other hand, a deep knowledge of polymer chains using the FENE-potential provides a sound basis for detailed studies of polymer chains with certain bond-bond interactions beyond the Gaussian (entropic) spring. The FENE-potential describes a polymer chain where each nearest neighbor bond-bond interaction is described by a strongly anharmonic spring, so that the entire chain can only be stretched up to a certain limit, which corresponds to the maximum chain extension.

The advantage of this model is obvious. For small deformations it yields to all well-established results well-known in textbooks. For large deformations, however, it yields new insights into the physics of single chains, especially the dynamics.

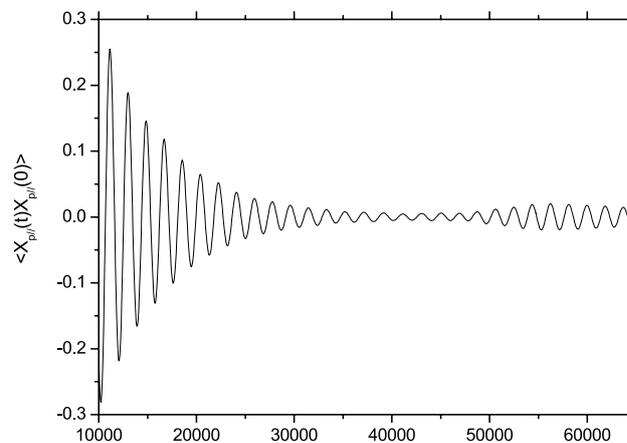
## Relaxation versus propagation

Polymer chains with small deformations relax their correlations according to the Rouse model. This is only possible because the chain has access to a large number of configurations which can be explored. In the case of strong deformation the number of accessible chains becomes significantly reduced, so that the nature of the anharmonic spring dominates. In high stretching regimes the chain cannot relax anymore, since the number of available states (entropy) becomes too small to enable diffusive motions. It behaves like a one-dimensional solid with “non-linear” acoustic waves.

## Solitons at high deformations?

Naturally the chain dynamics can no longer be described by simple relaxations since the mass of the beads becomes relevant. Due to the nonlinear nature of the bond potential new effects show up. For stretching ratios larger than a critical value the modes are no longer independent, but they exchange energy, the polymer modes become coupled by the non-linear intra chain interaction and produce “solitons”, see Fig 1.

It is evident that such a class of non-linear models offers a new and deeper insight into polymer dynamics, e.g., chain rupture and crack propagation in elastic materials.



**Fig. 1:** The profile of the relaxation of a polymer chain with high deformation. The oscillations are damped, but the energy exchange between the modes takes place and the correlation increases again.

**Crosslinks to other projects:** Non-Equilibrium Soft Matter Dynamics, Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels, Mechanics, Rheology and Dielectric Spectroscopy Laboratory

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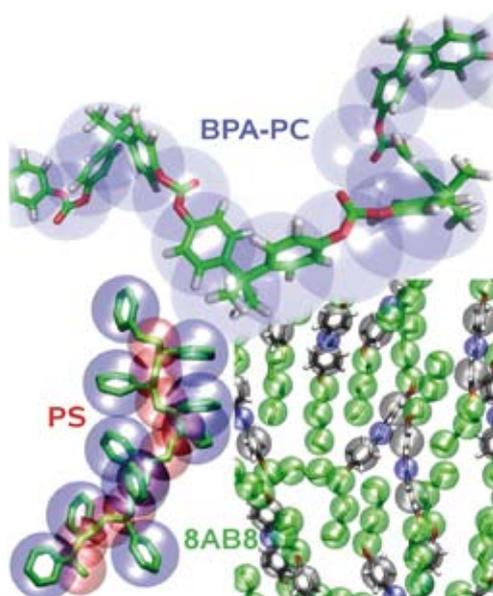
M. Febbo, A. Milchev, V. Rostiashvili, D. Dimitrov, T.A. Vilgis: Dynamics of a stretched nonlinear polymer chain *J. Chem. Phys.* **129**, 154908 (2008).

# Multiscale Modelling of Structurally Organized Systems

C. Peter, N.F.A. van der Vegt

*Keywords: molecular simulation, coarse graining, multiscale modelling, liquid crystals, biomolecules, peptides*

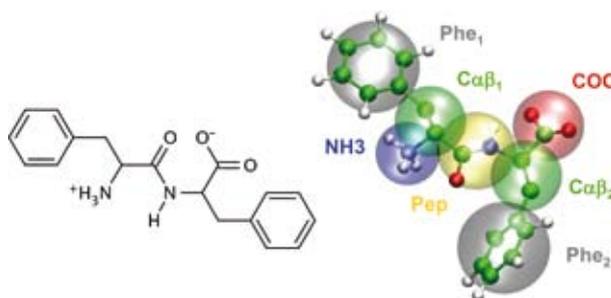
Many physical phenomena in biology, chemistry, and materials science involve processes occurring on long time and large length scales (mesoscopic scales), typical examples being structural and dynamical phenomena in polymer melts, phase transitions, nanostructure formation, but also protein folding or aggregation of amphiphiles into micelles or membranes. Computer simulations with models that use atomistic or even higher levels of resolution most often can (and should) not be employed to capture these time and length scales. For this reason, mesoscale (coarse-grained) models are being developed. Ideally, these models stay reasonably close to the atomistic (chemical) structure of the material so that after the CG simulation so-called inverse-mapping procedures can be employed where atomistic coordinates are reintroduced that correspond to the simulated CG structure.



**Fig. 1:** Snapshots of selected molecules from CG simulations of Bisphenol A-Polycarbonate (BPA-PC), polystyrene (PS), and an azobenzene-containing liquid crystalline compound (8AB8) indicating both coarse grained particles and atomistic coordinates obtained through inverse mapping.

We develop methods to “design” such types of CG models that are close to an underlying atomistic description and that can thus be used to carry over chemical information from the higher-resolution (atomistic) level to the mesoscale (CG) model. These aspects are important for the investigation of *chemically realistic* systems on *long time* and *large length scales*, in particular for structure formation processes which heavily rely on chemically specific (attractive) interactions between molecules, examples being some types of liquid crystalline systems or biomolecular aggregation phenomena.

Our approach where several resolution levels are intimately linked *hierarchically* by construction is particularly useful if one aims at a *multiscale* simulation model, i.e. a model where in a single simulation two or more levels of resolution are used at the same time (*hybrid* model) or the level of resolution can be changed at will during the course of the simulation (*adaptive* model).



**Fig. 2:** Coarse grained and atomistic representation of a model dipeptide.

**Crosslinks to other projects:** Modeling Interactions of (Bio)molecules with Surfaces, Multiresolution Simulation Methods, Permeation of Polymers – Computational Approaches

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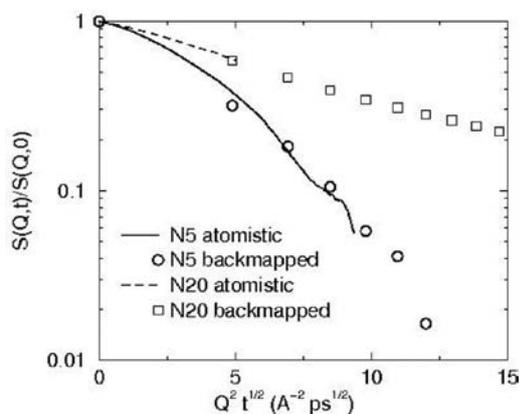
# Predicting Polymer Dynamics without Adjustable Parameters

K. Kremer

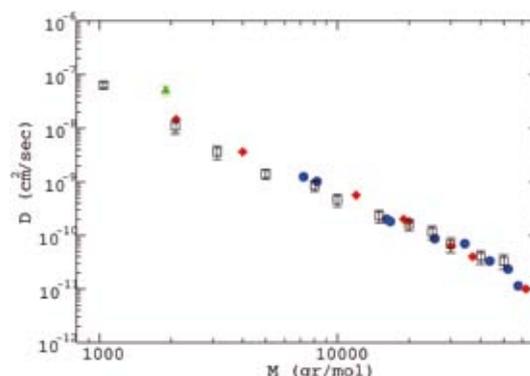
*Keywords: molecular simulations, multiscale modelling, polymer dynamics*

The dynamics of polymer melts are quite well understood in terms of the classical Rouse model and the reptation model. The Rouse model, which describes the motion of a simple random walk in a heat bath, applies reasonably well to polymer melts, where the chains are short, but long enough to exhibit well-defined random walk conformations. For very long chains the reptation model applies, which takes into account that the polymer chains cannot pass through each other. As a consequence the chains have to diffuse along their own, coarse-grained contour. The characteristic length scale of the confinement of the motion due to the non-crossability is the tube diameter and the related chain length, the entanglement length  $N_e$  or molecular weight  $M_e$ . Recently a so-called primitive path analysis allowed us to determine  $M_e$  from chain conformations in melts, which were in very good agreement with rheological experiments. While the asymptotic models are established, the crossover between the two regimes is not well understood. One reason is that  $N_e$  is quite different for different polymers leading to pronounced chemistry specific effects in the crossover regime. It varies in melts from only about 6 repeat units for BisphenolA-polycarbonate (BPA-PC) to about 150 for polystyrene. For BPA-PC even a well defined Rouse regime is missing because of the small value of  $N_e$ . For a better understanding of this regime computer simulations are an appropriate tool. Still it is not possible to

perform all atom simulations of a multiple chain melt, which covers the relevant chain length and time regime. However, systematic coarse-graining allows us not only to study the diffusion, but by means of inverse mapping also the dynamics on small and intermediate time scales with atomistic resolution. Fig. 1 shows the example of BPA-PC for very short ( $N=5$ ) and intermediate ( $N=20 > N_e$ ) chains. The dynamic scattering function  $S(Q,t)$  of single chains in a melt is obtained in two ways. First, for the shorter times, by direct all atom simulations, secondly by performing a coarse-grained simulation, reintroducing the atomistic details and then calculating  $S(Q,t)$  from those conformations.



**Fig. 1:** Dynamic single chain scattering function from the original atomistic simulations and from the backmapped conformations for  $Q=0.2\text{\AA}^{-1}$  as indicated. For  $N=5$  the atomistic simulations were carried out to about 120ns.



**Fig. 2:** Self-diffusion coefficient of PS melts as a function of the molecular weight from CG MD simulations (open squares) and experimental data (full symbols) ( $T=463\text{K}$ ).

The time scaling is obtained independently from mean square displacements. There is no further adjustable parameter involved and the agreement is excellent. By connecting these two data sets we can cover the full dynamic range in the scattering functions.

Coarse-grained simulations can be used to directly calculate diffusion constants of polymers in a melt. We performed such studies for PS. The calibration of the coarse-grained simulation time, as a function of chain length, was obtained by a combination of all atoms, united atoms and coarse-grained simulations for shorter chains and intermediate lengths. Based on this we were able to obtain diffusion coefficients for the whole crossover from unentangled Rouse chains to entangled chains ( $M_w=50000\text{ g}\cdot\text{mol}^{-1}$ ), again without any fit parameter.

**Crosslinks to other projects:** Multiscale Modelling of Structurally Organized Systems, Multiresolution Simulation Methods

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# Structure Formation by Ionic Interaction

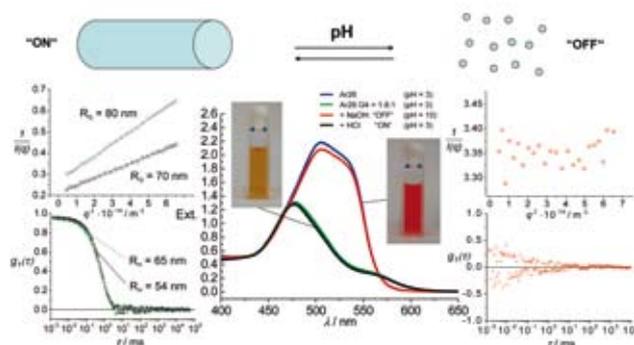
F. Gröhn, C. Holm, D. Hinderberger

Keywords: Polyelectrolytes, self-assembly, dynamics, ESR/EPR

Most natural polymers such as DNA and proteins are polyelectrolytes and many applications from paint to pharmaceuticals are based on charged macromolecules. Yet many fundamental questions regarding structure and dynamics of these complex systems that consist of polyelectrolytes and many small counterions are still unanswered. In addition, polyelectrolytes can be chains, spheres rods or other architectures, and many-body interactions of ions can give rise to self-organized and responsive nanostructures.

## Switchable nanoassemblies

A variety of structures and functions in natural systems is realized by ionic supramolecular structures, for example DNA-histone complexes. The main advantage of association by non-covalent interaction over a molecular synthetic design is the ability of rearrangement, leading to “self-healing” or “switchable” systems that can respond to external triggers. Therefore, it is desirable to develop concepts for a synthetic design of such structures. We have shown that “electrostatic self-assembly” of macroions and multivalent organic counterions can yield well-defined assemblies that are stable in solution and can have a variety of shapes. For example, dendrimeric macroions can associate with multivalent aromatic sulfonate dye counterions: depending on counterion structure, cylindrical assemblies, spheres, core-shell particles and vesicles can be formed. Key is the combination of electrostatics with mutual secondary interaction of the counterions.



**Fig. 1:** Switching of electrostatically self-assembled structures via pH: “on” and “off” means aggregates and single dendrimers, respectively; center: UV-VIS spectra; left and right, light scattering results (reprinted with permission from I. Willerich, F. Gröhn, *Chem. Eur. J.* **14**, 9112-9116 (2008).)

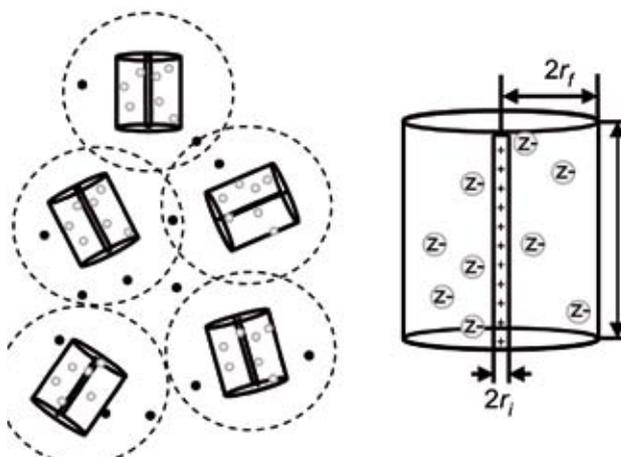
Aggregation can be switched “on” and “off” through pH. As association is based on ionic interaction, increasing the pH and deprotonating the dendrimer amine groups, the driving force for assembly ceases and aggregates disassemble into their building blocks (Fig. 1). Switching between the 100nm-size supramolecular structure and 5nm building blocks can be reversibly repeated.

Examples for other structures resulting from “electrostatic self-assembly” are finite-sized networks from stiff building units, porphyrin-decorated cylindrical brushes and DNA-flowers and toroids. The potential of this method may be that a variety of functions can be directly introduced in the assembly formation either through counterions or through macroions.

## Macroion-counterion interaction

The interaction of the many counterions surrounding the highly charged macroions is a fundamental question in polyelectrolyte solutions. Due to the complexity of the systems with several, sometimes counteracting effects (attractive and repulsive electrostatic interactions, preferential solvation, hydrophobic interactions, entropic effects) very little understanding is gained from experimental results. EPR spectroscopy on spin-carrying counterions, such as the dianion of Frey’s salt, offers the chance to selectively and sensitively study the distribution of counterions and the dynamics of the interaction involved in polyelectrolyte solutions. In fluid solutions the spectral line-shapes indicate rotational dynamics of all counterions on a subnanosecond timescale, which in turn implies that the electrostatic attachment of the counterions is transient.

This *dynamic electrostatic attachment* combined with the enhanced concentration of counterions close to the macroion chains leads to frequent collisions of the spin-carrying counterions. The resulting line broadening due to spin exchange can be analyzed in terms of models for the radial distribution of counterions.



**Fig. 2:** Sketch of the cylindrical cell volume description of polyelectrolytes by the CCCM (charged cylindrical cell model).  $L$ =chain length,  $r_i$ =initial and  $r_f$ =final radial coordinate of the cylindrical volume. Counterions of charge  $z^-$  within the cylindrical volume are shown in gray, those outside of it in black.

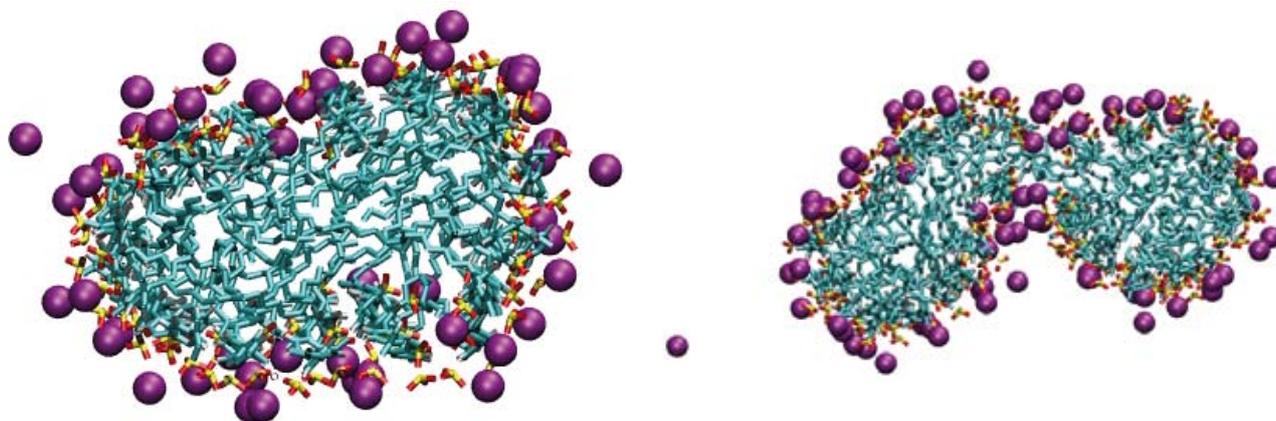
For PDADMAC in mixtures with organic solvents of both higher and lower permittivity, the experimental data are consistent with the  $r^2$ -scaling suggested by a charged cylindrical cell model (CCCM, see Fig. 2), based on locally stretched chain conformations. In pure water, however, the polyelectrolyte chains seem to adopt a different conformation on the length scale of a few nanometers that is probed by these experiments.

### Aggregation of semi-flexible polyelectrolytes

Bundling phenomena of charged semi-flexible polyelectrolytes are known to occur for biopolymers such as actin and DNA in the presence of multivalent counterions, but also in certain cases of hydrophobically modified sulfonated poly-paraphenylenes even for monovalent counterions. To what extent this condensation transition is kinetically dominated, or if the resulting structures are the results of thermodynamic equilibrium processes, has been studied by a coarse-grained semiflexible bead-spring model in the presence of trivalent counterions, modeling DNA on a coarse-grained level.

Our results show for a small range of Bjerrum lengths, that finite size polyelectrolyte bundles exist at thermodynamic equilibrium. Furthermore we demonstrated the absence of large energy barriers even for large bundles (contrary to some theories), and the existence of a narrow range of coupling parameters in which counterion entropy can balance the attractive forces between rods.

Another instance of bundle formation was investigated for a solution of hydrophobically modified sulfonated poly(p-phenylene) oligomers (PPP) via atomistic simulations. Light scattering experiments in the group of Prof. Wegner suggested that the number of PPP oligomers in the cross section is around 10-19 for monovalent  $\text{Na}^+$  and around 60 for divalent  $\text{Ca}^{2+}$  counterions. Our simulations showed that the basic packing of the PPP oligomers does not change upon increase of the counterion valency, but instead the interaction among bundles goes from repulsive to attractive, suggesting that the observed aggregate size of 60 oligomers is due to aggregation of several bundles (i.e. bundle of bundles).



**Fig. 3:** Top view of bundles of size  $N=14$  (left) and  $N=20$  (right) oligomers with  $\text{Ca}^{2+}$  counterions.

**Crosslinks to other projects:** Polymer Characterization, EPR Spectroscopy

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# Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels

U. Jonas, G. Fytas, D. Hinderberger

*Keywords: Responsive hydrogel, poly(N-isopropylacrylamide), PCS, EPR*

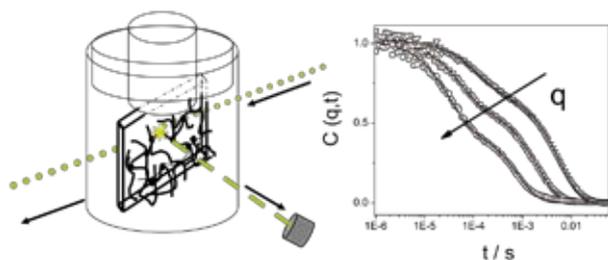
## Responsive hydrogels

Water swollen networks of polymers with a lower critical solution temperature (LCST) represent responsive hydrogels, which undergo a volume transition from a swollen state at low temperatures to a collapsed state with low water content at higher temperatures. These hydrogels are often termed “smart” materials that can find application in sensor and actuator systems. In particular thin films of photo-crosslinkable poly(N-isopropylacrylamide) (PNIPAM) with a thickness around one micrometer are currently under investigation as temperature-responsive sensing matrix.

An intrinsic characteristic of these gels is the presence of structural and dynamical inhomogeneities on several length- and time scales, starting at a few nanometers and milliseconds. Appropriate characterization methods targeted at these inhomogeneities are photon correlation spectroscopy (PCS), fluorescence correlation spectroscopy (FCS), surface plasmon resonance (SPR), optical waveguide spectroscopy (OWS), and electron paramagnetic resonance spectroscopy (EPR).

## Micro-PCS investigation

The currently developed micro light scattering technique ( $\mu$ PCS), schematically shown in Fig. 1 left, can probe thermal concentration fluctuations in surface-attached PNIPAM gel layers swollen in ethanol. At the equilibrium swelling state, the relaxation function exhibits two decays in the time range between 1  $\mu$ s and 1s with pure diffusive behavior (Fig. 1, right). The fast cooperative diffusion increases with crosslinking density as a result of the decrease in the dynamic network mesh size. In contrast to the frozen

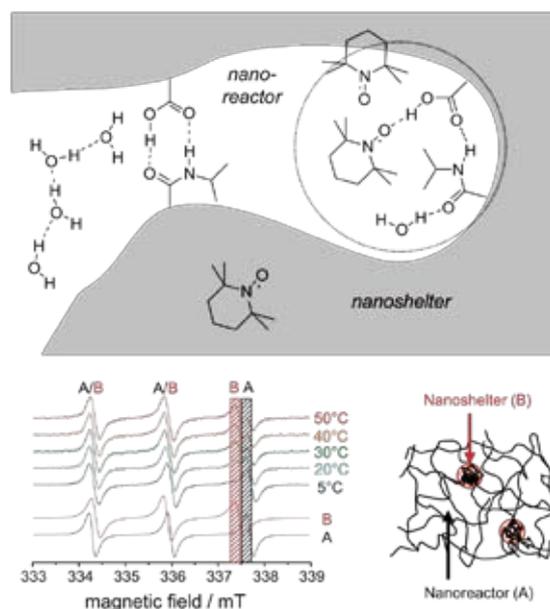


**Fig. 1:** Experimental  $\mu$ PCS setup and typical gel correlation curve with slow and fast modes in ethanol.

inhomogeneities in conventional gels, the slow diffusion in the present anchored layers was found to be ergodic and might relate to structural inhomogeneities. Complementary information can be obtained from the tracer diffusion in the same hydrogels investigated by FCS

## EPR investigation

The dynamic and chemical behavior of a paramagnetic tracer molecule (the spin probe) inside the gel matrix can be measured by temperature-dependent EPR spectroscopy (Fig. 2). The thermally induced collapse, as “seen” by the spin probe on the molecular scale, proceeds over a substantially broader temperature range than indicated by the sharp macroscopic volume transition. The spin probe also samples the hydrophilic and hydrophobic environments, suggesting a discontinuous collapse mechanism with a coexistence of collapsed and expanded network regions and a concurrent inhomogeneity in chemical reactivity. The hydrophilic regions form nanoreactors, which strongly accelerate the spin probe decay while the hydrophobic regions act as nanoshelters, protecting enclosed spin probes from the decay.



**Fig. 2:** Structure-property model of the hydrogel network deduced by EPR measurements of spin probe diffusion/decay.

**Crosslinks to other projects:** EPR Spectroscopy, Functionalized Surfaces for Optical Biosensors, Diffusion in Nanoporous Media and Dense Polymer Systems by FCS

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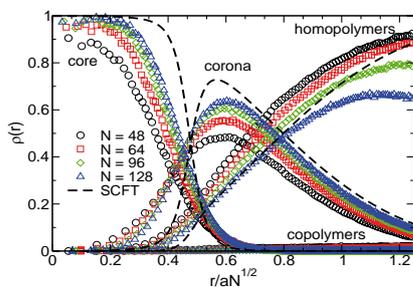
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# Critical Phenomena in Soft Matter

K. Binder

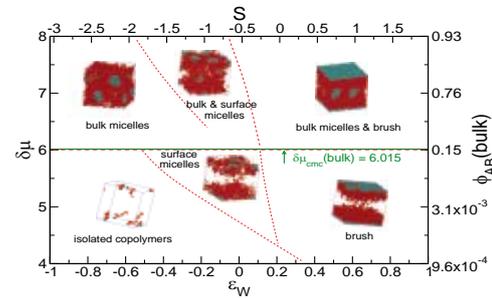
**Keywords:** Micelles, block copolymer mesophases, polymer brushes, Monte Carlo simulations, molecular dynamics

Mixtures of asymmetric  $A_f B_{1-f}$  block copolymers with homopolymers (B) of the same length are a convenient model system where Monte Carlo simulations can be very efficiently implemented, by generalization of a semi-grandcanonical algorithm (for example, interchanges of homopolymers with blockcopolymers of precisely the same conformation are attempted). This approach can be applied to test the self-consistent field theory (SCFT) of micelle formation (Fig. 1). In this case, the number of chains per micelle start at about  $(4-8) N^{1/2}$ , so the micelles are rather large, but the SCFT method is nevertheless not yet an accurate approach.



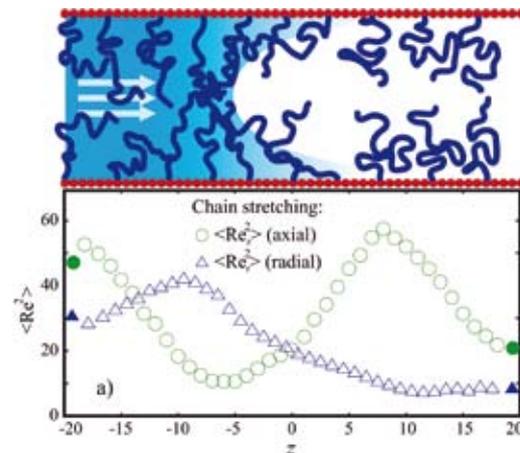
**Fig 1:** Radial density profile of core, corona, homopolymers of type B, and isolated copolymers, plotted as a function of the scaled distance  $r/aN^{1/2}$  ( $a$  being the size of an effective monomeric unit), according to Monte Carlo simulations of the bond fluctuation model. Four different chain lengths are shown. According to SCFT, all curves should collapse on the broken curves (calculated for a chemical potential difference  $\delta\mu=5.78$  and  $\chi N=90$ , as appropriate for the simulation).

This investigation can be extended to consider the interaction with walls having a preferential attraction of one component (A). Depending on the concentration  $\phi_{AB}$  of the copolymers in the bulk (that we control via the chemical potential difference  $\delta\mu$ ) and the spreading parameter  $S$  of the wall (that we control via the strength of the preferential attraction  $\epsilon_w$ ) a rich phase diagram is predicted (Fig. 2).



**Fig. 2:** Diagram of states as a function of  $\delta\mu$  and  $\epsilon_w$ . Phases containing micelles in the bulk compete with formation of surface micelles and/or polymer brushes, respectively.

Also polymer brushes interacting with a molecular solvent of variable quality have been studied (applying molecular dynamics methods). The advantage of such studies is that nonequilibrium phenomena can also be studied, such as the filling of a brush-coated capillary by a simple fluid (Fig. 3).



**Fig. 3:** Variation of the chain mean square end-to-end distance in radial direction and along the axis of a tube within an interval of 10 Lennard-Jones diameters on both sides of the actual meniscus position of a simple LJ fluid filling a capillary.

**Crosslinks to other projects:** Polymers and Colloids in Non-Equilibrium Conditions, Single Polymer Adsorption on a Solid Substrate, Computational Physics: Advances in Mesoscopic Simulation Methods

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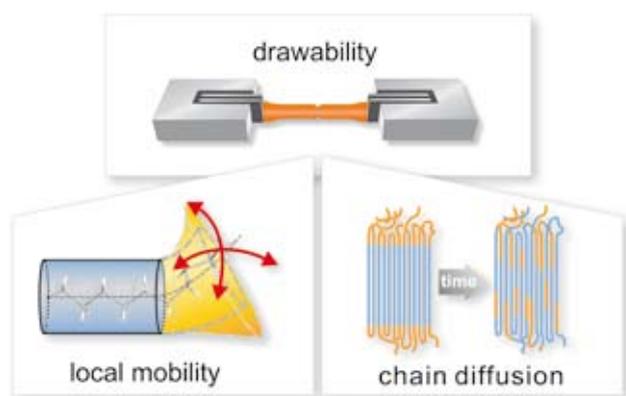
# Chain Diffusion in Semi-Crystalline Polymers

R. Graf, H.W. Spiess

*Keywords: Polymer dynamics, polymer crystallization, solid-state NMR*

The material properties of polymers strongly depend on molecular motions within a broad range of time and length scales from local molecular reorientations to collective translational chain diffusion. In amorphous polymers, such as polycarbonate, large angle phenyl rotations described by  $180^\circ$  flips in combination with additional oscillations, could be studied using  $^2\text{H}$  and  $^{13}\text{C}$  solid-state NMR methods. The broad, heterogeneous Gaussian distribution of flip angles is found to reflect the heterogeneity of the molecular packing arrangements in the amorphous material.

In semi-crystalline polymers such as poly(ethylene) (PE) local chain motions in the crystallites, at the interface to non-crystalline regions as well as the chain translation from crystalline to non-crystalline regions are dynamic processes crucial for numerous macroscopic properties of the material. The broad variety of material properties of PE depend on different local morphologies, which are determined by the crystallization conditions. Samples crystallized from an entangled melt are much more heterogeneous compared to samples crystallized from a dilute, almost disentangled solution, where the obtained crystallites consist predominantly of chain folds.



**Fig. 1:** Macroscopic properties such as drawability are determined by local molecular mobility and collective chain translation.

The differences in the conformation of the polymer chains in the non-crystalline areas have been investigated by local molecular dynamics as well as by a study of chain diffusion on the nm length scale. The temperature dependence of the chain diffusion allowed us to relate our findings to thermodynamic quantities and to known local dynamic processes in the crystalline areas. Indeed, the local dynamic order parameter was substantially higher and temperature independent in the case of the solution-crystallized sample, indicating a higher local mobility in the case of the melt-crystallized sample. However, the opposite was observed for the chain diffusion coefficient. Remarkably, the temperature dependence of the diffusion coefficients provided the same activation enthalpy ( $\sim 50 \pm 5$  kJ/mol) for the two samples. The activation enthalpy, however, reflects only the energetic aspect of a transition state in the dynamic process. The differences in the observed chain diffusion coefficients are then attributed to conformational entropy differences between the chains in the non-crystalline regions of solution crystallized and melt-crystallized samples. This difference is estimated as  $\Delta S = 27$  J/K where the entropy barrier for the solution crystallized sample is lower, consistent with the order parameters for the conformational degrees of freedom determined from the residual dipole-dipole couplings noted above.

Chain diffusion of course also requires mobility in the crystalline regions themselves. We also considered the relationship between local chain motions in the crystallites and chain diffusion. Local jump rates determined from direct observation of  $\text{CH}_2$  dynamics in the crystallites, however, are always higher than the effective jump rates determined from the chain diffusion, and exhibit different temperature dependences. This indicates that local motions of  $\text{CH}_2$  groups in PE crystallites do not always lead to translation of the whole polymer chain, in particular at an elevated temperature. Previously, observations for linear alkenes showed a similar behavior and could be explained by taking a minor thermal expansion on the crystal lattice into account.

**Crosslinks to other projects:** Solid-State NMR Spectroscopy

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# Matter Diffusion in Nanoporous Media and Dense Polymer Systems by Fluorescence Correlation Spectroscopy

G. Fytas, K. Koynov

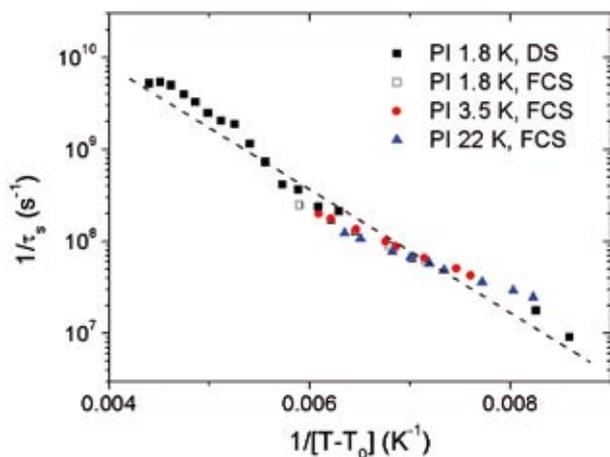
**Keywords:** Fluorescence correlation spectroscopy, tracer diffusion, spatial confinement and interaction, nanoporous alumina scaffolds, hydrogels, multicomponent polymers

A fundamental topic in polymer physics is the motion of highly confined matter in nanopores, nanovessels, nanoslits and nanofluidic channels. In recent years, fluorescence correlation spectroscopy (FCS) has emerged as a powerful tool for investigating the diffusion of fluorescent entities in various environments. In this project, an integrated approach embraces (i) measurement of the local friction in undiluted bulk polymers and relating tracer diffusion to the  $\alpha$ -relaxation ( $\tau_s$ ), (ii) study of tracer diffusion in the presence of interaction in hydrogel systems and (iii) investigation of molecular and macromolecular diffusion under spatial confinement in anodic aluminium oxide (AAO) containing a hexagonal array of cylindrical nanopores.

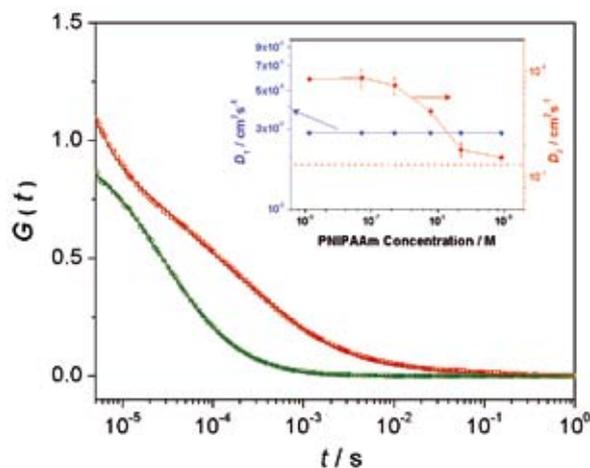
In polyisoprene (PI) melts with different glass transition temperatures,  $\tau_s$  can be successfully predicted (Fig. 1) from the diffusion coefficient  $D$  of molecular dyes using a length comparable to the Kuhn segment.

The exact value, however, depends on the molecular diffusant. FCS can extend the range experimentally accessible for measuring  $\tau_s(T)$  beyond nanoseconds.

In biosensors, the diffusion of analytes in hydrogels depends on size, network swelling and interaction. Interaction can strongly slow down material transport as shown by the complex diffusion of a charged dye in PNIPAAm aqueous solutions (Fig. 2). In addition to its fast free diffusion, the dye undergoes a slow diffusion that approaches the translation diffusion of PNIPAAm chains in the dilute regime. The slow  $D_2$  depends on the strength of the interaction and the dye residence time in the FCS volume. AAO has considerable potential as a platform for the design of 1D diffusion experiments under confinement and controlled interaction with the nanopore walls. Such experiments can be performed on a single molecule level in the presence of external forces.



**Fig. 1:** Segmental relaxation dynamics of PI 1.8K vs. the distance from the ideal glass transition  $T_g$ . MD calculations and dielectric relaxation ( $\blacksquare$ ) and computed ( $\tau_s = b^2/6D$ ) from FCS of ( $\square$ ) PI 1.8K, ( $\bullet$ ) PI 3.5K, ( $\blacktriangle$ ) PI 22K.



**Fig. 2:** Fluorescence intensity autocorrelation  $G(t)$  for free rhodamine diffusion in water (green) and in PNIPAAm aqueous solutions (red) at 293 K represented by a single  $D_1$  and two  $D_1$  and  $D_2$  diffusion coefficients, respectively. Inset: The variation of  $D_1$  and  $D_2$  with PNIPAAm concentration. The dotted red line indicates diffusion of a single PNIPAAm chain.

**Crosslinks to other projects:** TIR-FCS Studies of Diffusion and Flow Near a Liquid-Solid Boundary, Field Enhanced Dynamic Light Scattering at Interfaces, Light Scattering, Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels, Polymers at Surfaces and Interfaces.

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# Nanoparticles for Central Nervous System Targeting

C.K. Weiss

*Keywords: Nanoparticles, biomedical application, in vivo experiments, miniemulsion polymerization*

Biodegradable poly(*n*-butylcyanoacrylate) (PBCA) nanoparticles are examined for use in drug delivery to the central nervous system (CNS). Although the mechanism and the requirements are not completely elucidated, these particles are known to permeate the blood brain barrier (BBB) enclosing and protecting the CNS. For this reason they are ideal candidates for delivering drugs to the brain or other organs of the CNS. Polysorbate or poloxamer functionalization of PBCA particles seems to enhance the permeating abilities.

Miniemulsion polymerization is a convenient way to prepare poly(*n*-butylcyanoacrylate) nanoparticles and simultaneously control their size and surface properties. First, the monomer butylcyanoacrylate (BCA) is dispersed in an acidic, aqueous surfactant solution to yield a stable miniemulsion. For the stabilization of the miniemulsion anionic surfactants, like sodium dodecylsulfate (SDS), can be used as well as nonionic surfactants such as polysorbates or poloxamer.

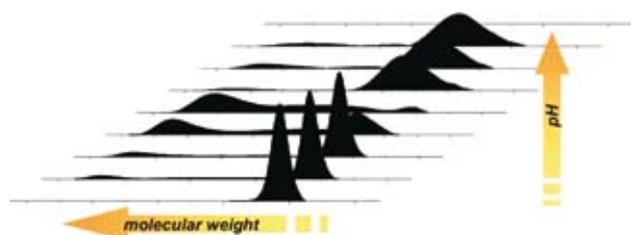
In order to initiate the polymerization of BCA, hydrophilic nucleophiles are added to the system. The choice of nucleophile determines the functionalization of the particle surface. With this technique unfunctionalized, amino acid functionalized and methoxy poly(ethylene oxide) (MePEG)-functionalized particles, ranging between 60–200 nm, can be prepared. Particle size can easily be adjusted by the amount of surfactant used during the preparation process.

Furthermore, the miniemulsion approach offers the possibility of controlling the PBCA molecular weight. When BCA droplets are polymerized in acidic medium, a narrowly distributed short chain polymer can be obtained. At an intermediate pH a broad distribution occurs while at

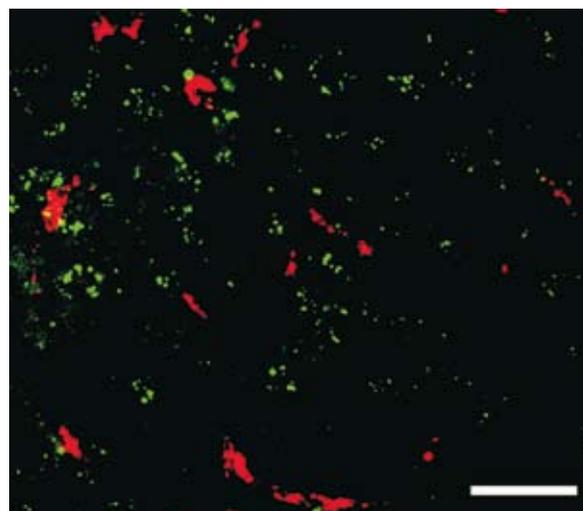
a high pH a shorter chain polymer is generated (Fig. 1).

The particles can be labeled with a fluorescent dye or loaded with bioactive substances such as vitamins and drugs.

*In vivo* experiments with fluorescence labeled polysorbate decorated PBCA-particles clearly demonstrated the particles' ability to permeate the BBB into CNS organs. Brain and retina sections of rats, treated with various doses of fluorescence labeled particle dispersions showed a concentration dependence of the BBB permeation of polysorbate functionalized PBCA-nanoparticles. Applied in low concentrations, the particles were located in or at the organs' microvessel cells, visualized by colocalization of the fluorescence signals derived from stained endothelial cells and the labeled particles. After higher dosage the particles were no longer associated with the microvessels but could be clearly localized in the CNS organs (Fig. 2).



**Fig. 1:** Evolution of molecular weight of PBCA with increasing polymerization pH.



**Fig. 2:** Microsection of a rat brain after administration of polysorbate-functionalized PBCA nanoparticles. Red signal: stained microvessels, green signal: nanoparticles.

These results clearly indicate that the polysorbate decorated particles are indeed suitable candidates for CNS-targeted drug delivery systems.

Synthesis by the miniemulsion technique offers various opportunities for surface modification as the introduction of specific ligands for receptor targeting. These possibilities will eventually help to shed further light on the mechanism of BBB permeation.

**Crosslinks to other projects:** Polymeric Nanoparticles and Interaction with (Stem) Cells: Uptake, Intracellular Trafficking and Cellular Responses, Multifunctional Polymer Capsules, Bio-responsive Hybrid Nanoparticles

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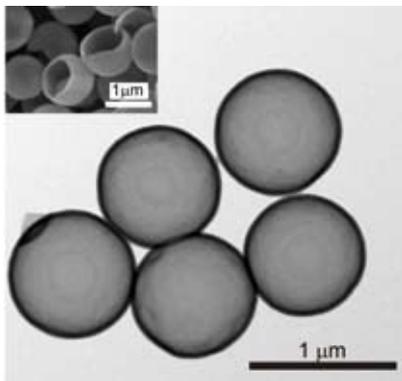
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# Elasticity of Hollow Microcapsules

G.K. Auernhammer, D. Vollmer, M. Kappl, G. Fytas

*Keywords: Elasticity, capsules*

The mechanical properties of hollow particles are crucial for their response to mechanical forces such as shear, flow, compression. They therefore determine the range of possible applications. We have developed a procedure to prepare monodisperse hollow silica capsules of well-defined and tuneable thickness, using polystyrene (PS) particles as templates. The PS particles were coated with a silica shell, following the Stöber method. Subsequently, the PS cores were burnt away, yielding intact silica capsules even at a layer thickness of 15 nm (see Fig. 1). The shell thickness could easily and sensitively be tuned by the composition of the reaction mixture. These extremely lightweight particles not only extend the range of density matching, but also enable the capsules to be loaded with chemicals.



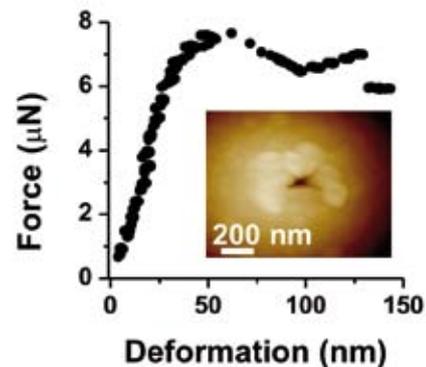
**Fig. 1:** Transmission electron microscopy image of hollow silica spheres with a diameter of 790 nm and a shell thickness of 37 nm. Inset: SEM image of several broken shells.

## Force-distance curves on hollow silica particles

The elastic modulus of the bulk and hollow silica particles was determined by AFM force spectroscopy. Prior to force measurements we imaged the particles to determine their shape and surface roughness. Force-versus-distance curves on hollow silica particles were obtained by applying a point load to their tops with an AFM tip (see Fig. 2). When tip and particle came into contact, the sphere started to deform. Further approach leads to a linear increase of the force. For deformations much smaller than the shell diameter, the approaching and retracting curves were almost congruent and linear, indicating fully reversible/elastic behavior. However, when further increasing the loading force, the linear dependence of the deformation on the applied force breaks down. A negative slope of the force-deformation curve indicated buckling of the shell.

Increasing the deflection even further leads to irreversible damage of the shell. The inset of Fig. 2 shows a shell punctured by an AFM tip.

The Young modulus of the shell material was about 18 GPa. Surprisingly, it neither depended on shell thickness nor on particle size for the shell sizes investigated. The elastic modulus of silica particles synthesized by the Stöber method was slightly lower than that of fused silica due to incomplete condensation.



**Fig. 2:** Deformation of a single hollow silica sphere under increasing cantilever deflection. 1.9 μm sized silica capsule with a shell thickness of 70 nm. Inset: AFM image taken after the approach curve showed a jump in. The dark spot in the middle of the particle depicts piercing of the shell.

## Mechanical moduli by Brillouin light scattering, BLS

BLS is a powerful method for measuring the longitudinal and transversal sound velocities and mass densities in hybrid materials. The acquired data allowed us to determine the Young modulus of the constituting parts of the hybrid material. This nondestructive technique could be applied even in turbid samples, e.g. colloidal crystals. In crystals of silica/PMMA hybrid particles with silicon cores, the density of Stöber synthesized silica cores was found to be lower than that in fused silica. Here it was also possible to detect hardening of the silica cores, probably due to methyl methacrylate impregnation of the cores, which were subsequently polymerized to PMMA. The elastic modulus of PMMA shells exceeded those of bulk PMMA. Removal of the silica cores by hydrofluoric acid did not change the Young modulus of the polymer in the shell.

**Crosslinks to other projects:** Colloid Probe Technique, Multifunctional Polymer Capsules

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# Non-Equilibrium Soft Matter Dynamics

H. Pleiner

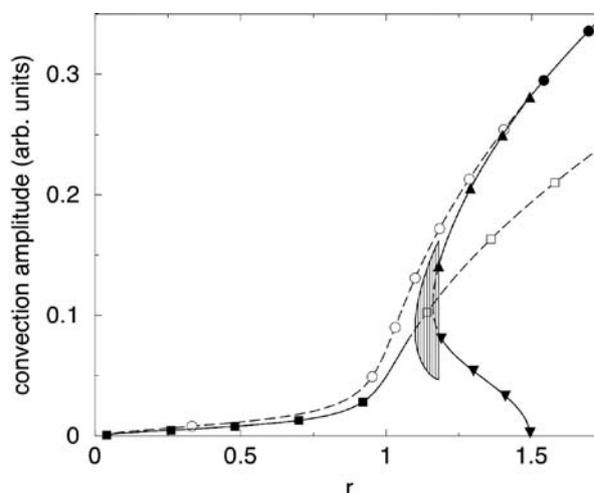
**Keywords:** Convective instabilities, pattern formation, ferrofluids and ferrogels, Rosensweig instability, complex membranes

Soft matter is characterized by the existence of internal structures and properties that can easily be addressed and modified by all kinds of external fields or forces. The appropriate additional degrees of freedom relax on macroscopic time scales influencing the static and dynamic properties of the materials profoundly. New phenomena are possible, e.g. the stress plateau in nematic liquid crystal elastomers under strong perpendicular stretch. Here, relative rotations of the director and the polymeric network modify the nonlinear elastic behavior preserving, however, the standard linear anisotropic elasticity.

Due to their sensitivity to external fields these materials are easily driven far out of equilibrium. We study theoretically liquid crystal, viscoelastic and magnetic fluids and gels, as well as multi-phase, composite and heterogeneous materials. An example of the latter are frustrated banana liquid crystals in a splay-bend texture. Far from a state of equilibrium new phenomena occur such as convective flow in regular patterns, when a colloidal solution is subject to a large temperature gradient (Fig. 1). This can be used during processing those materials to obtain new structures with novel properties. Here the enormous density contrast between the immersed particles and the fluid solvent molecules and the large Soret coefficient are instrumental for the detailed bifurcation mechanisms. The former aspect allows gravity-induced sedimentation to influence the bifurcation scheme in the form of the existence of non-unique stationary solutions as well as the coexistence between a stationary convective and a convection-free solution. It is shown that in experiments this situation can lead to a hysteretic behavior of the system.

For ferrofluids, where the particles are ferromagnetic monodomains, a homogeneous magnetic field can replace the temperature gradient as the driving instability force. The resulting stationary convection velocity, however, is rather small and determined by the balance of concentration advection and sedimentation.

In chiral smectic liquid crystal systems, concentration and temperature gradients can trigger the rotation of the helical structure (Lehmann effect). This is at least partly a dissipative non-equilibrium process.



**Fig. 1:** Bifurcation diagram for different patterns: Rolls (circles), squares (squares), stationary crossrolls (triangles), and oscillatory crossrolls (striped area). Dashed lines represent unstable patterns.

The inverse procedure, rotating the helical structure (by means of an external rotating magnetic field), can result in a particle and heat current. The former can be used as a particle pump when applied across a membrane or film. In ferrofluids and ferrogels the magnetic polarizability is instrumental in developing a free-surface spike instability in an external normal field (Rosensweig instability). The driving force results from the field focusing effect at deflected interfaces between media of different magnetic susceptibilities. It is, therefore, also possible to get this type of instability in thin magnetic films or membranes. The crucial point for a successful nonlinear description of this instability lies in its dynamical nature: It can be viewed as thermally activated surface waves, whose velocity goes to zero at the threshold thus allowing the growth of stationary spikes. This perspective allows the solution of the adjoint linear eigenvalue problem, a prerequisite for deriving the standard coarse-grained description employing amplitude equations.

**Crosslinks to other projects:** Phase Separation Under Continuous Cooling: Droplets and Satellite Droplets, Non-equilibrium Phenomena in External Shear Field, Polymers and Colloids in Non-equilibrium Conditions

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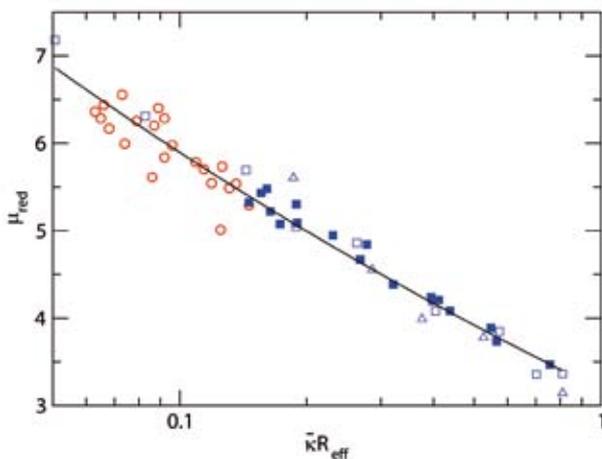
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# Polymers and Colloids in Non-Equilibrium Conditions

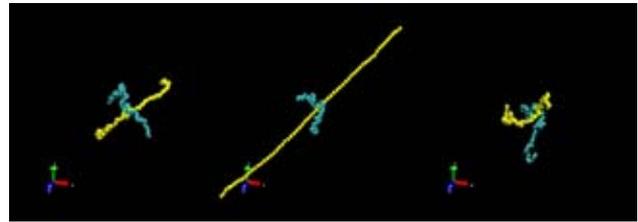
B. Dünweg

*Keywords: Colloidal electrophoresis, polymers in turbulent flows*

Many soft-matter systems may be considered as reasonably well understood in terms of their structure in thermal equilibrium. The situation is quite different when the systems are subjected to external driving. Computer simulations under well-controlled conditions offer a theoretical insight which is otherwise difficult to achieve. We have recently focused on the velocity response of charged colloidal spheres to an external electric field (electrophoresis). The simulations take into account the electrostatics of the colloids and the ions, the hydrodynamics of the solvent, and the non-trivial structure of the charge clouds. One approach is to run a coupled simulation of colloid and surrounding lattice Boltzmann fluid (“raspberry model”) with explicit point charges for the ions and another one to solve numerically the electrokinetic equations. Progress has been made in understanding the low-salt case. The theory is difficult, since the usual Debye-Hückel screening mechanism is not in effect. The ion clouds overlap, leading to non-trivial colloid-colloid interaction.



**Fig. 1:** Dimensionless electrophoretic mobility  $\mu_{red}$  for a salt-free system, as a function of the effective screening parameter in units of the colloid radius, comparing simulations (open squares, triangles) and experiments (closed squares, circles).



**Fig. 2:** Typical conformation of a polymer chain in solvent. The blue chain is in thermal equilibrium, while the yellow chain is subject to a turbulent flow.

Moreover, the hydrodynamic flow is not confined to the vicinity of the particles (both in contrast to the high-salt case). The system is studied by simulating a single colloid, where interaction with other colloids is replaced by interaction with the periodic images. Salt-free systems can be mapped approximately onto corresponding “salty” systems by an effective screening length that takes the ionic strength of the counterions into account. The problem has four relevant dimensionless parameters. Good agreement with experiments is obtained within such a parameterization.

We also study the dynamics of polymers in a turbulent flow. A standard simulation of turbulence (without polymer) generates output that is fed, as a fluctuating boundary condition, into a hybrid simulation (lattice Boltzmann plus polymer) that “zooms in” to resolve the smaller length and time scales. This multiscale approach is necessary to cope with the very different scales in the problem (monomer size, polymer coil size, size of smallest eddies, flow as a whole). This is relevant for drag reduction, which is still poorly understood.

**Crosslinks to other projects:** Non-Equilibrium Soft Matter Dynamics, Theory of Single Chains, Computational Physics: Advances in Mesoscopic Simulations

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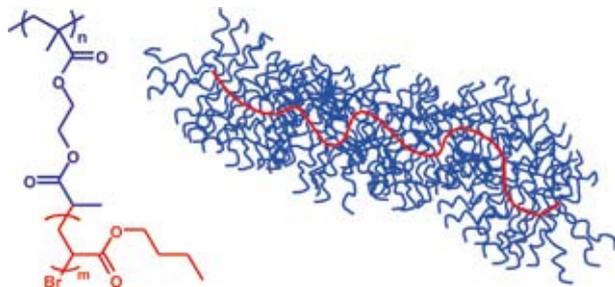
# Non-Equilibrium Phenomena in External Shear-Field

S. Rathgeber

*Keywords: Non-equilibrium phenomena, rheology*

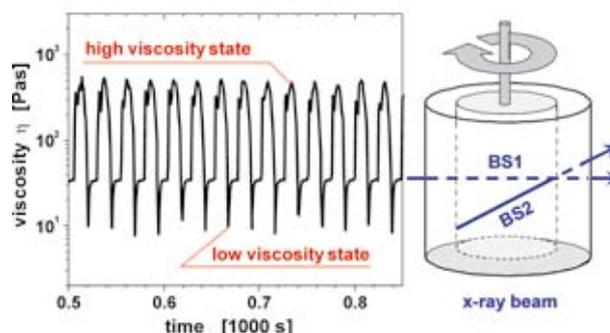
Due to the low compliances and long relaxation times in soft matter systems the coupling between an applied shear field and structure can be very strong with the consequence that shear can induce phase transitions. Dynamic phase transitions do not only take place between steady states, but also can result in non-equilibrium phenomena leading to chaotic-like or oscillating rheological response. We studied these non-equilibrium phenomena in concentrated bottlebrush polymer (BB) solutions.

In BB linear side chains are densely grafted to a linear polymeric backbone (see Fig. 1). Due to steric overcrowding of the side chains, BB in solutions form stiff, cylindrical, and shape-persistent structures exclusively on the basis of intramolecular excluded volume interactions. BB exhibit lyotropic behavior. With increasing polymer content  $\Phi_p$  a phase transition from an isotropic phase to a biphasic region, coexistence of isotropic and a hexagonal phase, is observed. A pure hexagonal phase is never reached. Instead, increasing  $\Phi_p$  further leads to a melting of the structure due to interpenetration of the BB. This re-entrant melting transition indicates an ultra-soft interaction potential, i.e. their potentials remain finite or diverge very slowly for zero separation of the BB.



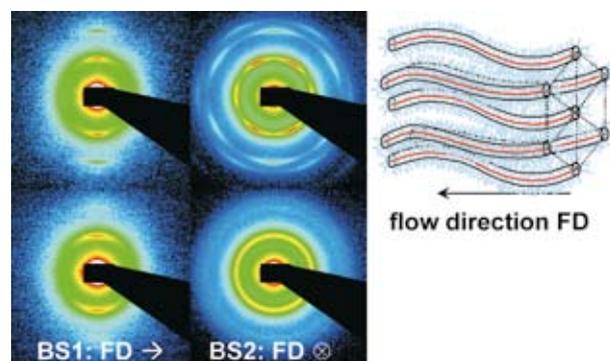
**Fig. 1:** Structure of the BB with poly(*n*-butyl) acrylate side chains grafted to a poly(alkyl methacrylate) backbone.

We performed *in situ* rheological, time-resolved small-angle x-ray scattering (SAXS) experiments on a concentrated BB solution in the biphasic region. These experiments allow a direct correlation between the rheological response and the structural changes occurring in the sample. In the strain-controlled mode, i.e. the motor applies a certain velocity of rotation and adjusts whatever angular momentum is necessary to keep the rotor velocity to the set point, we observed an oscillating rheological response of the sample with periodic changes in the viscosity of two orders of magnitude (see Fig. 2).



**Fig. 2:** Rheological response of the BB solution (21 vol. % in toluene) and a sketch of the shear geometry with the two x-ray beam setups, BS1 and BS2, respectively.

During the rheo-oscillations the BB are highly aligned in flow direction (see Fig. 3: Bragg peaks in the BS1 SAXS pattern). For the low viscosity state the isotropic ring pattern obtained in BS2 reveals a melt-like structure in the plane perpendicular to the flow direction. In the high viscosity state a six-fold pattern appears which can be attributed to a hexagonal arrangement of the center-of-masses (CM) of the aligned BB. The hexagonal structure orientates in such a way that closed packed planes slide over each other.



**Fig. 3:** SAXS pattern: high (top) and low (bottom) viscosity state marked by the red lines in the rheological response (Fig. 2) and a sketch of the hexagonal structure.

In conclusion, the rheo-oscillations are due to a shear induced phase transition between a low viscosity shear molten state and a high viscosity hexatic phase. The rheometer successively adjusts the force applied to the sample to keep the velocity of rotation constant (high/low viscosity=high/low force). This leads to a periodic cycling between melting and recrystallization.

**Crosslinks to other projects:** Mechanics, Rheology and Dielectric Spectroscopy Laboratory

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# Phase Separation Under Continuous Cooling: Droplets and Satellite Droplets

D. Vollmer, G.K. Auernhammer, H. Pleiner

*Keywords: Nucleation, binary solutions, non-equilibrium dynamics*

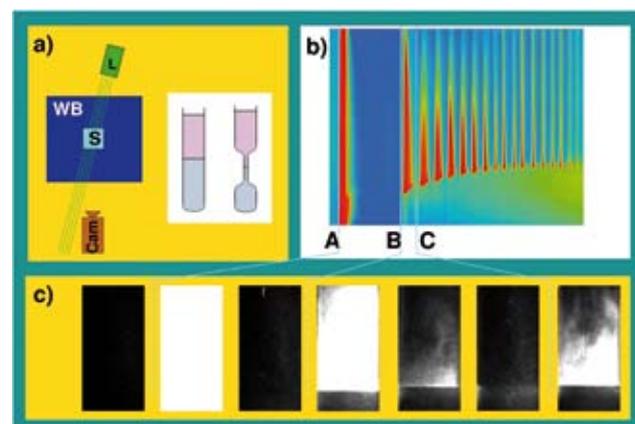
Phase separation of multi-component mixtures involves a complex interplay of thermodynamic and transport processes. The time scales of these processes can be separated by rapid jumps of temperature or pressure (quenches) in order to study them under well-controlled conditions. Compared to quenches, however, most processes in nature and technology take place under slow and gradual changes (ramps). In this case the different mechanisms involved in phase separation are all concurrently present, and their interaction is poorly understood. Qualitatively new features can arise, like oscillations in turbidity and apparent heat capacity.

To test the influence of physical parameters (molecular weight, diffusion constants, viscosity) in oscillatory behavior, we investigated vastly different systems - polymer (e.g. polystyrene in cyclohexane) as well as low molecular mixtures (e.g. methanol in hexane). Despite these differences all mixtures studied showed oscillations in a vast range of experimentally accessible parameters. This behavior does not even depend on purity, but is also observed in mixtures of ethanol with native kitchen-grade vegetable oil.

Four characteristic processes contribute to the oscillations: (i) driving the system by continuous cooling slowly increases super-saturation; (ii) rapid formation of droplets occurs once super-saturation approaches a critical value; (iii) droplet coarsening is initially fast, but eventually becomes much slower than the driving due to increasing inter-droplet distance; (iv) sedimentation of large droplets cleans up the system eventually leading to an almost droplet-free system. Since sample height and width do not influence duration and frequency of oscillations, hydrodynamic instabilities and convection are virtually ruled out as the origin of the oscillations. In contrast, the size of the meniscus between the coexisting phases has an impact on the oscillation period, i.e. the time between two turbidity maxima or peaks in specific heat. If the coexisting phases are separated by a wide meniscus (e.g. in a rectangular cell) the period is shorter compared to a narrow meniscus (modified hourglass cell).

Merging of droplets with the meniscus may lead to local re-dispersion of smaller droplets, satellite droplets, which act as seeds for the formation of new droplets.

We often observed oscillations in either the upper or the lower phase, but seldom in both. To investigate the underlying mechanism, we modeled the phase separation using the Cahn-Hilliard equation including the effect of gravity. Our approach was motivated by the experimental observation that sedimentation is fast compared to nucleation and coarsening. To account for this, we automatically moved the droplets to the corresponding phase once they had reached a defined size. Depending on the initial composition either both (symmetric oscillations) or only one of the phases oscillate (asymmetric oscillations). In the asymmetric case, a larger number of droplets sediment from the majority into the minority phase. Thus, in the minority phase super-saturation is reduced and droplet formation is inhibited.



**Fig. 1:** a) Top view of the experimental set-up. The sample *S* is placed in a water bath (WB) and illuminated with a light source (*L*) from behind. A camera (Cam) takes the images of the scattered light. Transparent regions appear black and turbid ones white. Two different sample geometries are used, a rectangular cuvette and a modified hour glass; b-c) space-time plot for a sample oscillating 17 times between a transparent and a turbid state over a temperature range of almost 20 K (abscissa: time; ordinate: sample height). Strong scattering is represented in red and no scattered intensity in blue.

**Crosslinks to other projects:** Non-equilibrium Soft Matter

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# Colloids in Electric Fields: Localized Hydrodynamic Instabilities

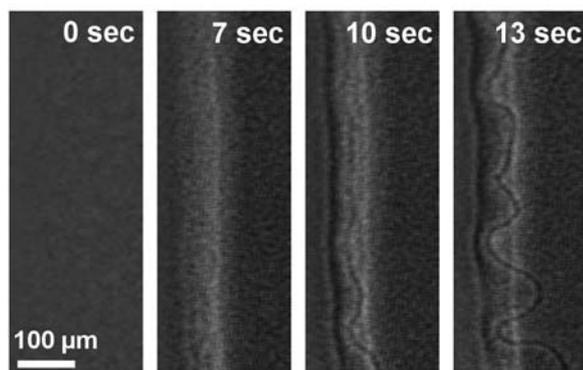
D. Vollmer, G.K. Auernhammer, H.-J. Butt

*Keywords: Dielectrophoresis, hydrodynamic instability*

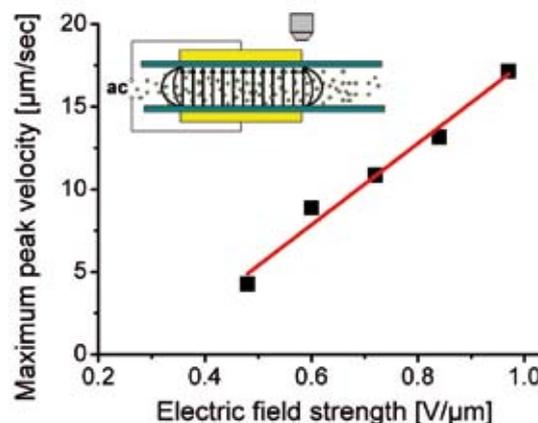
The response of colloidal suspensions to external electric fields depends strongly on colloid concentration and the interaction potential between the colloids. Gradients of AC electric fields exert forces on colloids along the field gradient due to the dielectric contrast between the colloids and the surrounding carrier fluid (dielectrophoretic force, DEP force). This effect can either be used to control the motion of single colloids in optical traps or to confine colloids in suspension in a so-called electric bottle. In the latter the colloidal suspension is sandwiched between two glass slides which are locally covered with transparent electrodes (insert to Fig. 2). When an electric field is applied, the field strength sharply decreases at the edge of the electrodes. The dielectrophoretic force is present only in these field gradients and, as a strong segregating force, acts against diffusion.

In our experiments, we focused on the transient events shortly after switching on the electric field. We assumed that colloid motion arises both from the DEP force and from hydrodynamics.

In the non-linear field gradient at the edges of the electrodes, the force exerted on the colloids is inhomogeneous. Colloids near the maximum of the DEP force move faster than colloids in lower gradients. This leads to a zone depleted of colloids around the local maximum of the DEP force (see Fig. 1, bright zone, 2nd image). The time required for formation and growth of the depletion zone decreases with increasing field strength.



**Fig. 1:** An initially homogeneous colloid suspension (1st frame) develops a zone depleted of colloids (light area, 2nd frame) at the maximum of the DEP force when subjected to an inhomogeneous AC electric field. At high fields ( $> 0.2 \text{ V}/\mu\text{m}$ ) hydrodynamic instability develops in the depletion zone. In these images the DEP force is pointing from left to right.



**Fig. 2:** The peak velocity of the instability depends on field strength. Extrapolation yields a threshold field strength value of  $0.3 \text{ V}/\mu\text{m}$  below which no instability occurs. Insert: Central cut through the set-up perpendicular to the observation plane.

At high enough applied fields (Fig. 1:  $1 \text{ V}/\mu\text{m}$ ), the high field (left) side of the depletion zone becomes unstable and a wave-like instability travels through the depletion zone. This implies that the colloids do not move homogeneously but their velocity depends on position. Whereas the timescale and velocity (Fig. 2) of this instability strongly depends on the applied field strength, its length scale is given by the sample geometry.

While depletion can be explained within the single colloid picture, the inhomogeneities in the electric field eventually lead to hydrodynamic flow at higher field strength due to viscous drag. The observed wave-like instability is an instability of this hydrodynamic flow. In this regime, the force acting on the colloids can be considered equivalent to a volume force acting on the suspension on a coarse-grained level. This effective force depends on the colloidal concentration and on the DEP force per colloid. In the depletion zone, colloid migration leads to a decrease of colloid concentration. Thus, the decreasing colloid concentration can eventually lead to a situation where the volume force density in the region of maximum DEP force is lower than in regions outside the maximum of the DEP force, however high the DEP force per colloid. This inversion of the volume force density can give rise to a hydrodynamic instability, similar to the situation of a denser fluid layered above a less dense fluid (Rayleigh-Taylor instability).

**Crosslinks to other projects:** Mechanics, Rheology and Dielectric Spectroscopy Laboratory, Polymers and Colloids in Non-Equilibrium Conditions

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# Surfaces and Interfaces



# Surfaces and Interfaces

H.-J. Butt

Characterizing interfaces, studying processes which are dominated by interfaces, and making surfaces with a specific structure and function are key activities of the Max Planck Institute for Polymer Research. Surfaces and interfaces of soft materials are not only interesting per se. They are essential when it comes to small objects. Objects, which at least in one dimension extend only over microns or nanometers, have a high surface-to-volume ratio. Their properties are dominated by interfaces rather than gravitation or inertia.

A whole range of techniques for the characterization of surfaces is available at the institute. For structural analysis scanning probe microscopes such as atomic force microscopes, a scanning tunneling microscope, and a near field optical microscope are used. They are complemented by scanning electron and several light microscopes. X-ray reflectometry gives detailed information on film thickness, roughness and mean composition of thin polymer films. Adsorption processes are monitored by surface plasmon resonance, ellipsometry, or by the quartz crystal microbalance. With the colloid probe technique, surface forces between particles and planar surfaces are measured.

We not only use existing techniques, but constantly improve devices, develop new methods or modify techniques to apply them to special problems encountered during a project. One example is the new technique developed to measure adhesion on a fast time scale. Usually adhesion between particles is measured on the 0.1 s time scale and longer. To understand the adhesion process better we developed a new force microscope, which is able to measure adhesion for contact times down to 10  $\mu$ s. This instrument allowed us to distinguish between different binding processes.

Measuring surface forces is not only interesting in itself, but also helps us to understand the aggregation process of particles. The aggregation of nanoparticles is used in several projects, e.g. to obtain phononic crystals.

Processes, rather than a system in equilibrium, become increasingly the focus of our research. A typical example is the project “evaporation of microdrops”. So far only the evaporation of macroscopic drops could be measured, mainly by optical techniques. To measure the evaporation process of small drops a special technique was developed, which is based on atomic force microscopy. The question is, how do liquid droplets of diameters significantly below 0.1 mm evaporate from a solid surface and

how do the surface properties influence the evaporation process?

At a fundamental level one of the unanswered questions concerns the structure of polymers at a solid surface. Polymer-solid contacts are important for adhesion, coating, and (nano)composites.

Several projects are devoted to the polymer-solid interface, e.g. “polymers at surfaces and interfaces”, “modelling and interactions of macromolecules and biomolecules with surfaces” and “ordering of polydisperse systems in the presence of interfaces”.

An understanding of interfaces is also a prerequisite for making micro- or nanostructures because their behavior is dominated by surface effects. Structuring polymer surfaces by selective deposition, by etching and by methods with no net mass change, is one of the main topics of the institute. A focused ion beam allows us to structure surfaces on the 10 nm scale. In some projects the focus is to coat surfaces with a homogeneous, thin layer rather than lateral structuring. This is for example achieved by plasma polymerization. Using plasma polymerization, solid surfaces can be coated with a wide variety of polymers. Making surfaces with properties for a specific function was the aim of several projects. For example, complex architectures have been designed for biomolecule detection by optical techniques. Surfaces made of hybrid materials are applied in photoactive layers.

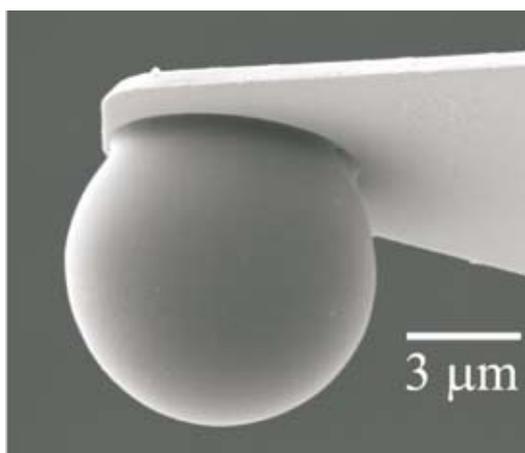


## Colloid Probe Technique

M. Kappl, H.-J. Butt

*Keywords: Atomic force microscopy, surface forces, colloids, adhesion*

Since its invention more than 20 years ago, the atomic force microscope (AFM) has become an essential tool in nanotechnology routinely used to image surfaces at nanometer resolution. It can also be applied to measure surface forces down to some 10 pN. In this force spectroscopy mode, the AFM tip that sits at the end of a micro-machined cantilever is moved up and down while the deflection of the cantilever is recorded, which acts as a force sensor. A common problem when comparing AFM force measurements to theoretical models is the poorly defined geometry of the AFM tip. A possible solution is to replace the AFM tip by a colloidal particle of well-defined spherical shape. This so-called colloidal probe technique has the additional advantage of free choice of the probe material. Attachment of colloidal particles (size 1-50  $\mu\text{m}$ ) is usually done with a micromanipulator using an optical microscope. The particles are fixed either by a tiny amount of glue or by sintering them onto the cantilever (Fig. 1).

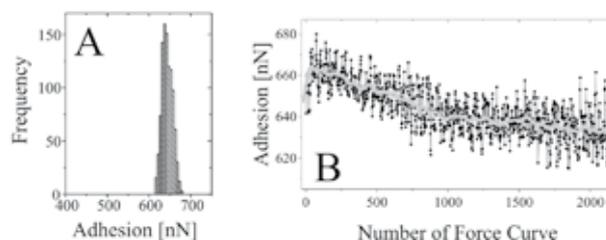


**Fig. 1:** Polystyrene sphere sintered to the end of an AFM cantilever to act as a colloid probe.

At the MPI-P, the colloid probe technique is used in a broad range of studies, ranging from fundamental aspects of adhesion and friction to more application-relevant systems, like adhesion of dust particles to fibers

of oil filters, or the adhesion of drug particles for asthma treatment to carrier substances. One recent study addressed the well-known fact that all adhesion experiments show wide distributions of adhesion forces rather than a single value. Naively one would expect that adhesion forces between similarly prepared particles of equal size should always be the same. This is, however, not the case. Wide distributions are typically observed and adhesion forces vary typically by a factor of two to ten. Surface roughness and surface heterogeneity have been suggested as a cause of this variation. In our study we used model systems with minimum roughness and heterogeneity such as freshly cleaved mica or silicon wafers which were probed with AFM tips and colloid probes.

The adhesion between a glass colloid probe and a silicon wafer was measured on an evenly spaced grid on an area of 500 nm x 500 nm and shows that under almost ideal conditions, relative variations (i.e. standard deviation divided by mean value) of the adhesion force can become less than 2% (Fig. 2A). When plotting the adhesion forces as a time series (Fig. 2B) two types of variations are apparent: a fast, random noise and slower fluctuations. Random noise is due to thermal vibrations and noise in the detection system. The slower fluctuations are probably caused by plastic deformation and structural changes in the material at the nanocontact, which was confirmed by SEM images of the AFM tip's wear.



**Fig. 2:** (A) Histogram of adhesion forces measured between a glass particle of 4.0  $\mu\text{m}$  diameter and a silicon wafer. (B) Adhesion force measured versus time. The grey curve resembles the slow overall trend due to structural changes of the contact.

**Crosslinks to other projects:** Scanning Probe Microscopy, Elasticity of Hollow Silica Microcapsules, Piezorheology: Rheo-optics on the Microscale.

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# Nanolithography with Nanoparticles

K. Landfester

*Keywords: Monodisperse nanoparticles, structured surfaces, nanopillars*

Among the many phenomena revealed and provided by nanoscience, the functionalization of a surface by nanopatterning certainly holds promise for a large number of attractive applications. A prominent example is the deposition of self-assembled monolayers e.g. by microcontact printing in order to control wettability, adhesion, friction, and wear. For the manipulation of the wettability of a surface, highly ordered arrays of nanopillars are apparently not necessary. However, in the case of field emitters a high degree of translational order of the nanopattern is extremely helpful in identifying individual emitters when applying scanning tunneling microscopy or spectroscopy for their characterization.

The micellar approach for creating highly structured surfaces exhibits some inherent drawbacks; the maximum interparticle distance determined by the diameter of the micelles is limited to approximately 150 nm as in larger block-lengths of the involved polymer chains a spherical shape of the resulting micelles is no longer guaranteed. Larger distances between individual nanostructures such as pillars are, however, desirable for many applications. Another characteristic difficulty with the micellar approach is related to the preparation of alloy particles, only possible for a few systems due to the problem of selectively ligating different alloy components within the micellar core.

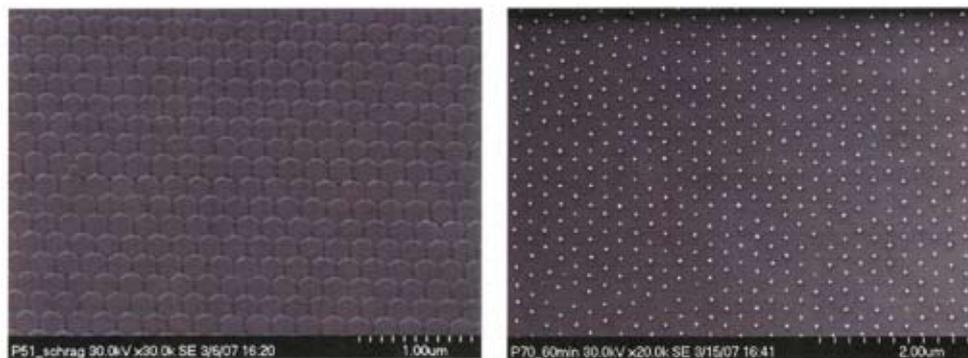
To overcome these drawbacks, an alternative approach and novel technique was introduced based on miniemulsions loaded with a metal precursor complex and stabilized within water by surfactants. After direct polymerization in this way solutions of colloidal particles are obtained, which, like in the micellar approach, will self-assemble into hexagonally ordered arrays after a corresponding drop is deposited onto a substrate.

It was demonstrated that the miniemulsion polymerization technique allows the preparation of highly uniform and practically monodisperse latex particles containing hydro-

phobic metal complexes like platinum(II)acetylacetonate, indium(III)acetylacetonate, zinc(II)tetramethylheptadionate, zincphthalocyanine, and chromium(III)benzoylacetonate, respectively, with different loading capacities.

For some platinum and iron complexes the homogeneity of the latexes can be improved even further by adapted emulsion techniques. By choosing different amounts of surfactant, the particle size can be adjusted between 100 and 260 nm. To obtain larger particles up to 370 nm for a given metal complex, an additional feeding of monomer was performed. In this way, the particles can be easily modified by changing the polymer or the copolymer composition. By using a pure polymer core and adding semicontinuously a complex/monomer mixture, it leads to particles increased in size which can contain additional metal complexes. The methodology was also applied for the preparation of alloyed Fe/Pt particles. The concentration relations were analyzed by inductively coupled plasma spectroscopy (ICP) and, by energy dispersive X-ray spectroscopy (EDX). Deposited onto a substrate, the high homogeneity of the particle size results in hexagonally well-ordered monolayers of the metal containing polymer particles.

Once these nanoparticles are obtained, they can be used as nanomasks for subsequent etching steps according to the recently developed recipes for preparing hexagonally ordered arrays of nanopillars or cylindrical nanoholes in Si<sup>15</sup>. The present work aims at demonstrating the potential of the miniemulsions by preparing highly ordered arrays of nanopillars and nanoholes in Si with distances between these structures well above those accessible to the micellar technique. On the other hand, the previously developed recipe to fabricate masks made of amorphous Si with hexagonally arranged nanoholes can immediately be applied to the miniemulsion technique thereby opening the possibility of transferring the hole pattern into any underlying substrate.



**Fig. 1:** Metal-containing polymeric nanoparticles before (left) and after (right) plasma etching.

**Crosslinks to other projects:** Reactions in Confined Geometries

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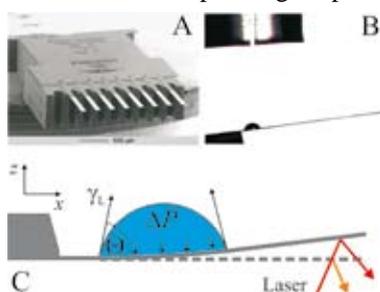
# Evaporation of Microdrops

E. Bonaccurso, K. Graf, H.-J. Butt

*Keywords: Evaporation modes, evaporation law, microdrops, microcantilevers, atomic force microscope*

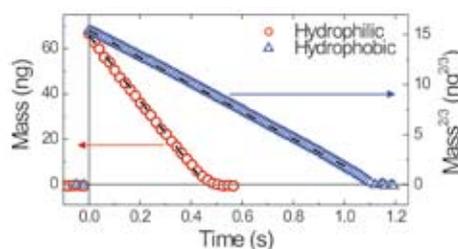
The evaporation of sessile drops on solid surfaces has attracted renewed interest in the last decade. In particular, drops with diameters much smaller than 1 mm are in the focus of fundamental and applied research, due to the development of microfluidics and inkjet technology. Phenomena, which are negligible at the macroscopic scale, start to be relevant or even dominate at the small scale. Unfortunately classical techniques for studying drop evaporation fail in the micron scale.

Here we introduce a new technique to measure simultaneously the mass and shape of an evaporating sessile microdrop: Atomic force microscope (AFM) microcantilevers. A microdrop evaporating from an AFM cantilever leads to a bending of the cantilever. This bending is detected. The resolution is 100 pg in mass and 5 ms in time. Water microdrops are deposited on native (hydrophilic) and hydrophobized silicon cantilevers via ink jetting (Fig. 1). The drop causes the cantilever to bend upwards due to its surface tension pulling upwards at the drop rim and its Laplace pressure pushing downwards over the contact area. The drop mass also changes the resonance frequency of the cantilever. We track this frequency over time and measure the change of mass of the evaporating drop.



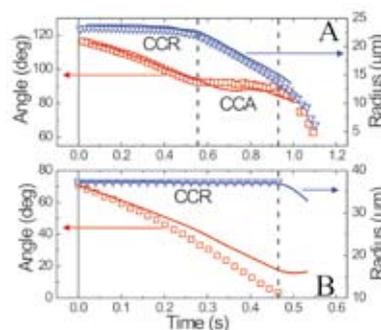
**Fig. 1:** (A) SEM image of a silicon chip with eight attached cantilevers. (B) side view of a cantilever with drop deposited at its base and inkjet capillary used for drop generation. (C) Scheme of the equilibrium configuration of a drop on a cantilever:  $\Theta$  is the equilibrium contact angle,  $\gamma_L$  is the liquid surface tension,  $\Delta P$  is the Laplace pressure.

Using this technique it was possible to measure the evaporation law of sessile water microdrops which are different on hydrophobic and hydrophilic surfaces. The first is of the type “ $m^{2/3} \propto \text{time}$ ” and the second “ $m \propto \text{time}$ ” (Fig. 2).



**Fig. 2:** Evaporation law (drop mass vs. time) of water microdrops on hydrophobic and hydrophilic surfaces (open symbols) and linear fits (black lines).

Also the evaporation time is different for drops of similar initial mass. This is mainly due to the different evaporation modes of the microdrops. On a hydrophobic surface drops evaporate at a higher, and for longer time constant, contact angle (CCA-mode). On a hydrophilic surface drops evaporate with the rim pinned, i.e. with the contact radius constant (CCR-mode), while the contact angle decreases with time (Fig. 3).



**Fig. 3:** Contact angles and radii of water microdrops vs. time, on hydrophobic (A) and hydrophilic (B) surfaces. Data points are from resonance frequency measurements of the cantilevers (open symbols) and from video microscopy imaging (continuous lines).

We experimentally verified the evaporation laws and modes of such small water drops for the first time with our setup. On hydrophobic surfaces we found that they agree with those of macroscopic drops. On hydrophilic surfaces a discrepancy was found. During the last stage of evaporation the Young equation, which relates the contact angle with the interfacial tension, fails to describe the drop shape.

**Crosslinks to other projects:** Microlenses by Evaporation of Drops, Polymer Brushes on Nanomechanical Cantilever Sensors

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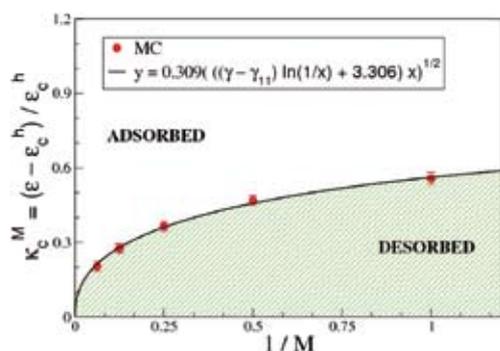
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# Single Polymer Adsorption on a Solid Substrate

T.A. Vilgis

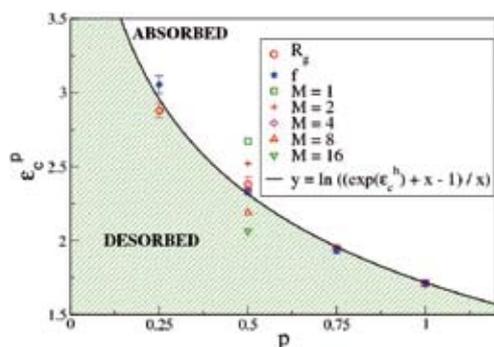
*Keywords: Multiblock and random copolymer adsorption, adsorption kinetics*

Adsorption of single homo- and hetero-polymers on a solid substrate is common in nature and important in many applications: biosensors, adsorption of biopolymers on membranes, pattern recognition, etc. We have studied this phenomenon analytically and by means of an off-lattice bead-spring dynamic Monte Carlo simulation model. In the case of a multiblock AB-copolymer (where monomers A are sticky but monomers B are neutral) it has been theoretically shown that the problem at hand can be reduced to an effective homo-polymer. Based on this idea and some simple scaling arguments we have obtained the corresponding phase diagram.



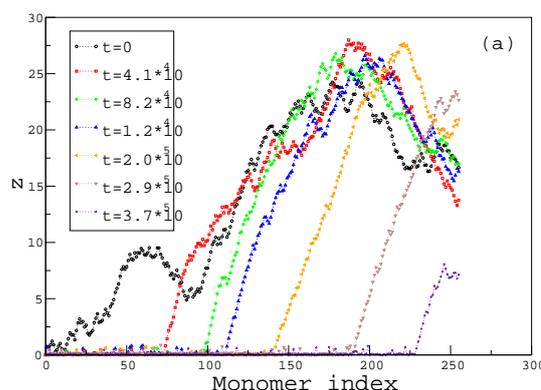
**Fig. 1:** Phase diagram for a AB-multiblock copolymer. The critical adsorption energy is plotted vs. inverse block length.

The random copolymers with a quenched disorder are characterized by the fraction  $p$  of the A monomers. It has been shown that despite the quenched AB – sequence the adsorption can be described within the scope of the annealed approximation. The corresponding phase diagram is shown in Fig. 2.



**Fig. 2:** Critical adsorption point vs. the composition  $p$  for random copolymers.

The adsorption kinetics of a single polymer chain on a solid substrate in the regime of strong physisorption has also been studied. The underlying notion of a “stem-flower” polymer conformation (see Fig. 3), and the related mechanism of “zipping” during the adsorption process are shown to lead to a Fokker-Planck equation with reflecting boundary conditions for the time-dependent probability distribution function  $P(n, t)$  of the number of adsorbed monomers.



**Fig. 3:** Snapshots of an  $N=256$  chain conformation taken at successive times during the adsorption process. The  $z$  coordinate of the  $i$ -th monomer is plotted against monomer index  $i$ . The “stem-flower” polymer conformation can be clearly seen.

The theoretical treatment predicts that the mean fraction of adsorbed segments grows with time as a power law  $t^{0.66}$ . The instantaneous distribution of train lengths is predicted to follow an exponential relationship. The corresponding probability distribution functions for loops and tails are also derived. The complete solution for the  $P(n, t)$  is obtained numerically from the set of discrete coupled differential equations and shown to be in perfect agreement with Monte Carlo simulation results. In addition to homo-polymer adsorption we also studied the regular multiblock copolymers and random copolymers and demonstrated that their adsorption kinetics may be considered within the same theoretical model.

**Crosslinks to other projects:** Functionalized Surfaces, Materials with Controlled Interface Structure

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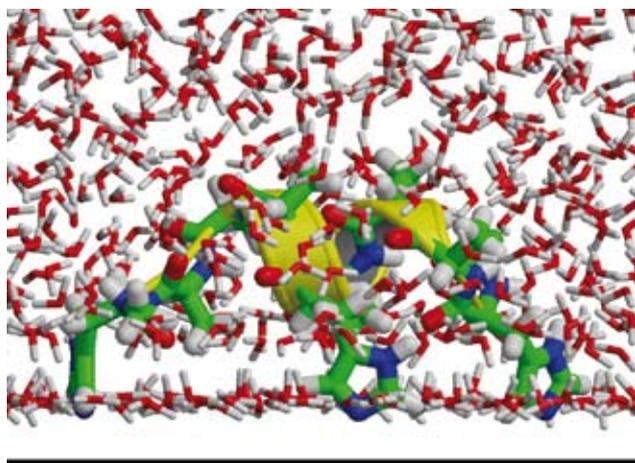
# Modeling Interaction of (Bio)Molecules with Surfaces

N.F.A. van der Vegt, L. Delle Site

*Keywords: Surface interaction, molecular building blocks, DFT calculations, molecular simulations*

Chemically realistic modeling procedures for describing the interaction of organic molecules, macromolecules and biological peptides with inorganic surfaces are of considerable interest in various fields. Progress in the development of adhesives, polymer nanocomposites, bioanalytical devices, etc. crucially depends on our understanding of surface interaction and its influence on macromolecular conformations.

We work on developing force field models that describe the interaction of polymer repeat units and biomolecular building blocks with inorganic and metal surfaces. Classical molecular dynamics simulations are used to study surface binding of oligopeptides in water (see Fig. 1) and the interface between metaloxides and polymers.



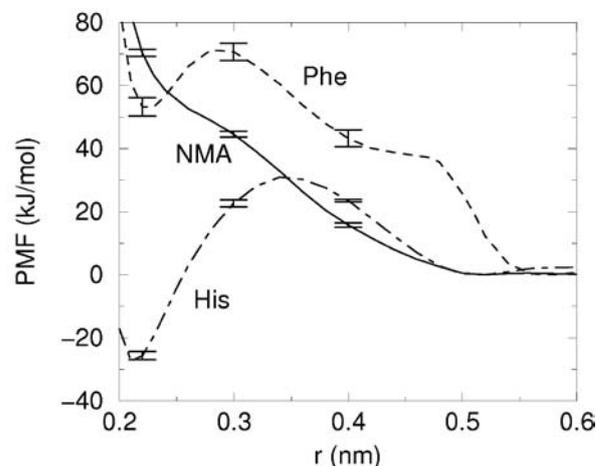
**Fig. 1:** Binding of a histidine tag (*His-Ala<sub>3</sub>-His-Ala<sub>3</sub>-His*) to a *Pt(111)* surface in liquid water.

Classical surface interaction potentials are developed using an iterative dual-scale modeling procedure. Quantum-mechanical density functional calculations are performed to obtain surface interaction energies and near-surface molecular geometries for selected conformations of small organic molecules. In parallel, classical atomistic simulations are used to further sample the molecular conformation space near the surface and to overcome energy barriers such that all global conformational minima are considered at the quantum mechanical level. Quantum-mechanically calculated energies are used to define the

classical model and the classically sampled conformations are fed back into the quantum mechanical calculation procedure. In a very computationally economic way, this iterative procedure renders a classical surface interaction model in which the surface interaction energies and the corresponding near-surface molecular conformations are consistent at the classical and quantum-mechanical levels. Following this approach, it is now possible to take into account electron delocalization effects in the interaction of amino acids with metal surfaces and to fully consider the water-solute and water-surface interaction present in hydrated systems.

Fig. 1 shows a snapshot of the binding of a short, alpha-helical histidine tag to a platinum surface in water. Free-energy calculations, based on molecular simulations of the solid/aqueous-organic interface at ambient conditions, quantify the affinity of surface binding of different amino acid side chains (Fig. 2).

Combination of building block approaches to modeling surface interaction with coarse-grained peptide models and multi-resolution simulation methods significantly extend the scope and applicability of modeling surface interaction in biomolecular and synthetic macromolecular systems.



**Fig. 2** Free energy (potential of mean force) as a function of the distance between amino acid residues (*Phe* and *His*) and peptide backbone (*NMA*) and a *Pt(111)* surface in liquid water (300 K). *Phe* is repelled by the hydrophilic platinum surface, *His* is strongly attracted.

**Crosslinks to other projects:** Multiscale Modelling of Structurally Organized Systems, Multiresolution Simulation Methods

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# Ordering of Polydisperse Systems in the Presence of Interfaces

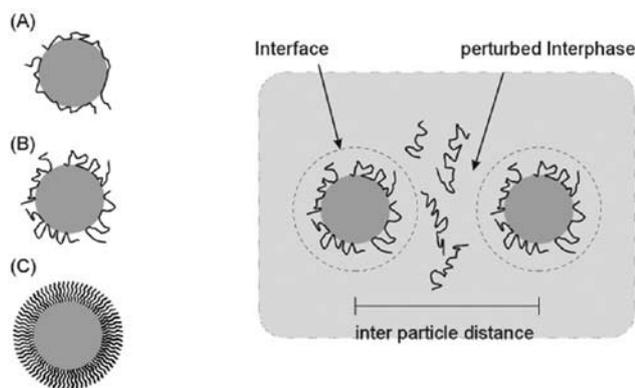
J.S. Gutmann, R. Berger

**Keywords:** Nanomechanical cantilever, ATRP, nanocomposites, mechanical properties

We investigate the impact of the structure of a metal oxide/polymer interface on the bulk properties of a surrounding polymer. The system studied acts as a model system for particle-reinforced nanocomposite materials. Special emphasis is put on the question: in which way does the structure of a polymer close to the metal oxide/polymer interface perturb the structure in the bulk of the system?

An oxidic interface is generated as surface of small colloidal  $\text{SiO}_2$  or  $\text{TiO}_2$  particles. Monodisperse particles in a size range between 10 nm-100 nm are studied. The use of monodisperse colloidal particles allows us to easily vary the average spacing between the polymer/solid interfaces via a control of inorganic volume fraction and precisely describe the geometry of the interface at the same time.

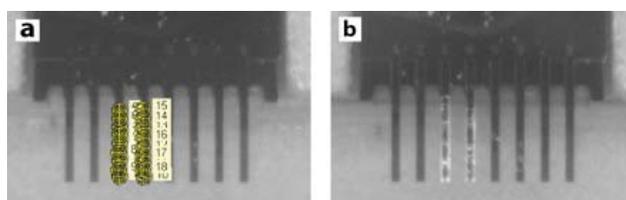
The direct contact of the polymer at the interface is also specifically tailored. We use particles decorated with adsorbed polymer chains (A in Fig. 1), polymers grafted to the interface (B) and polymers grafted from the interface (C).



**Fig. 1:** Surface functionalization and incorporation of athermally decorated particles into a polymeric matrix.

Depending on the nature of the polymer binding at the interface the interaction between polymer and chemical identical polymer matrix is determined by entropy. Such entropic factors have shown to lead to autophobic dewetting at an interface, if the contacting molecular weights are not carefully matched.

To elucidate the influence of entropically driven demixing in interface dominated systems, we investigate athermal bulk matrices with different molecular weight distributions. Differences in molecular weight distributions are generated either by use of different polymerization routes (e.g. anionic or radical polymerization) or by mixing of several well-defined polymers.



**Fig. 2:** Microcantilevers coated with a polymer layer using a drop on demand technique; a) before b) after spotting.

The influence of the interface on the polymeric interphase is further investigated with respect to mechanical and electrical properties. Since the parameter space under investigation (colloidal particle size, polymer type, surface immobilization,  $M_w$  and molecular weight distribution) is large the mechanical properties have to be initially screened in order to assess their perturbation from unfilled bulk behaviour. This rapid mechanical characterization is carried via a mode analysis of resonating microcantilevers, onto which the nanocomposite material is applied using drop on demand techniques (Fig. 2). The atomistic nature of the change in bulk behavior is addressed using scattering techniques such as microfocus x-ray scattering and neutron scattering on samples with appropriately labelled polymers. Electrical properties are investigated via mapping of surface potential with scanning probe techniques.

**Crosslinks to other projects:** Microfocus GIXAXS Measurements on Micromechanic Structures, Polymer Brushes on Nanomechanical Cantilever Sensors, Scanning Probe Microscopy, Advanced Materials for Solar Cell Applications

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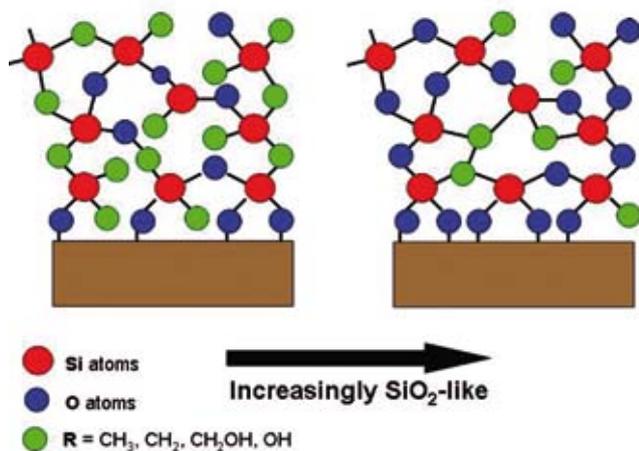
# Mechanical Properties of Plasma Polymerized Thin Films

R. Förch, R. Berger

*Keywords: Plasma polymer, multilayers, hardness, adhesion*

Plasma-assisted polymerization is a highly versatile method for the deposition of thin polymer-like materials on almost any substrate. Our efforts are focused on the development of thin films exhibiting novel properties in the area of biomaterials and scanning probe based data storage media. Precursors such as hexamethyl disiloxane (HMDSO) and norbornene have recently shown exciting properties. HMDSO has been known as a precursor in industrial PECVD processes for barrier and optical coating and its application today ranges from different automobile parts to packaging, corrosion protection and various optical components.

The plasma-assisted deposition of HMDSO is generally carried out under excess oxygen. The chemical composition of the deposited layers is largely determined by the gas flow ratio of HMDSO to oxygen and the process power input. By varying either one of these, while keeping all other conditions constant, the  $\text{SiO}_x$ -like films deposited will vary considerably in their chemical structure – from largely inorganic  $\text{SiO}_2$ -like material to one characterized by a significant hydrocarbon component resembling an inorganic-organic composite.



**Fig. 1:** Schematic of possible network structures.

Thus, hard  $\text{SiO}_2$ -like films can be formed using a high HMDSO: $\text{O}_2$  gas ratio, while softer, reactive films can be formed using a low HMDSO: $\text{O}_2$  ratio. We explored the properties of multilayers consisting of nanometer thick alternating hard and soft coatings. Such multilayer structures show promising results for applications in the area of scanning probe based storage, where the medium should be soft enough to be deformed as a result of a load or a change in temperature, while at the same time it should minimize wear of the probe tip during read-out.



**Fig. 2:** The phase contrast image obtained by scanning force microscopy showed a contrast between each of the HMDSO layers assigned to alternating mechanical properties. Dark contrast corresponds to soft and bright contrast to hard material.

The ability to influence the physical and chemical properties of plasma deposited HMDSO layers enables the tailoring of the macromolecular structure and chemical properties of the layers. As such, those films containing a significant hydrocarbon component can easily be surface-activated in a subsequent 1-3 second plasma modification process to produce highly reactive surfaces. Such surfaces have recently been shown to exhibit promising results as adhesives for silicon-to-silicon bonding and show an adhesive strength approaching typical values observed for epoxy glues. The highest value observed so far is a shear strength of 8 MPa. The advantages of adhesives based on plasma deposited layers are (i) they can be applied as nm-thick films, which is imperative for  $\mu$ - and nanometer devices, (ii) they were shown to retain their adhesive properties at temperatures exceeding 400 °C, thus opening up possibilities for high temperature applications and (iii) they are resistant to aggressive media.

Crosslinks to other projects: Colloidal Lithography for the Preparation of Metallic Nanostructures with Optical Resonances, Scanning Probe Microscopy

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# Functionalized Surfaces for Optical Biosensors

J. Dostálek

**Keywords:** Biosensor, surface plasmon resonance, surface plasmon-enhanced fluorescence spectroscopy

## Introduction

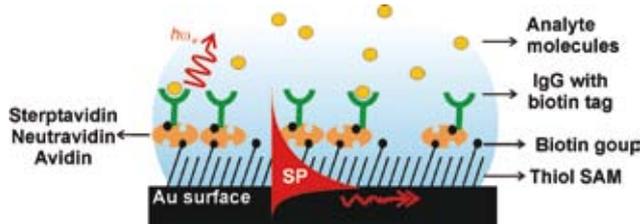
During the last two decades increasing attention has been paid to biosensors for the rapid and sensitive detection of chemical and biological species. In optical biosensors, biomolecular recognition elements (BRE) are typically attached to a surface, and the capture target analyte contained in a sample is optically detected through induced refractive index changes or fluorescence light emission. In these applications, surface architecture for the immobilization of BREs is of key importance as it has to provide a large binding capacity, non-fouling properties and to retain biological activity of BREs.

## Methods

Spectroscopy of surface plasmons and optical waveguide modes were employed for *in situ* characterization of functionalized gold surfaces supporting surface plasmon resonance (SPR) and surface plasmon-enhanced fluorescence spectroscopy (SPFS) biosensors. The immobilization of immunoglobulin G (IgG) recognition elements was performed by using mixed thiol self-assembled monolayers (SAM) and UV cross-linked dextran and N-isopropylacrylamid-based hydrogel films.

## Results and discussion

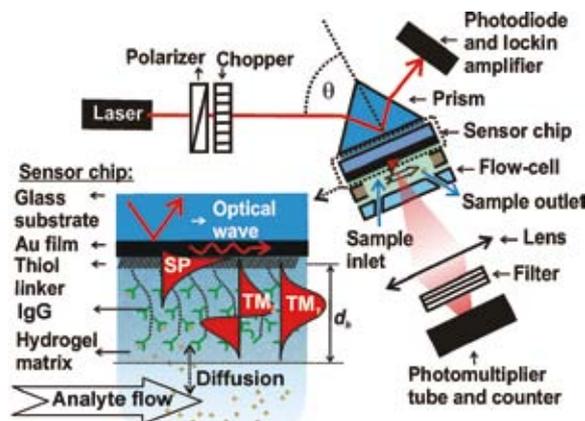
Metallic surfaces modified by thiol SAM with biotin or carboxylic acid groups can be used for the immobilization of BREs, see Fig. 1. This two dimensional architecture typically allows for the immobilization IgG antibody recognition elements with surface concentrations up to  $2 \text{ ng} \times \text{mm}^{-2}$ .



**Fig. 1:** Surface architecture based on thiol SAM and streptavidin-biotin interaction for immobilization of IgG antibody receptors probed with surface plasmons (SPs).

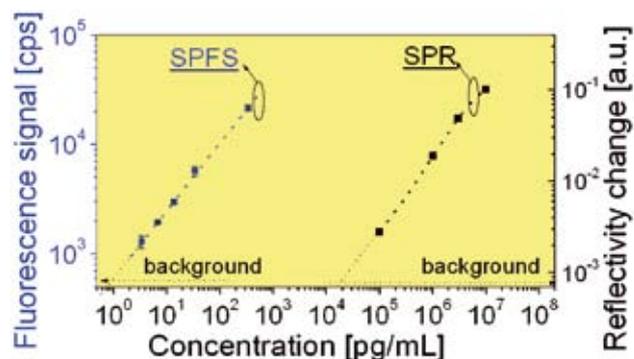
Developed hydrogel binding matrices allowed for the immobilization of IgG molecules with orders of magnitude larger than surface coverage (up to  $160 \text{ ng} \times \text{mm}^{-2}$ ). The hydrogel matrices were prepared in a highly swollen state

(water content  $> 90 \%$ ) which allowed for an efficient diffusion of target molecules, see Fig. 2. Carboxylic groups were introduced into a hydrogel matrix enabling the immobilization of IgG receptors through lysine groups and active ester chemistry.



**Fig. 2:** Surface architecture employing a hydrogel binding matrix on the top of SPR and SPFS sensors.

Hydrogel binding matrices were applied in optical biosensors. Fig. 3 shows the comparison of direct (SPR) and fluorescence spectroscopy (SPFS) detection of prostate specific antigen (PSA) employing a dextran film functionalized with a-PSA antibodies. The SPFS biosensor relying on a sandwich immunoassay enabled the highly sensitive detection of PSA with the limit of detection as small as  $40 \text{ fM}$  ( $1.4 \text{ pg mL}^{-1}$ ).



**Fig. 3** Calibration of direct and fluorescence spectroscopy-based detection of PSA for dextran hydrogel matrix (thickness  $d_h=800 \text{ nm}$ ) functionalized with IgG antibodies against PSA.

**Crosslinks to other projects:** Evanescent Wave Optics, Size and Interaction Dependent Mobility in Hydrogels

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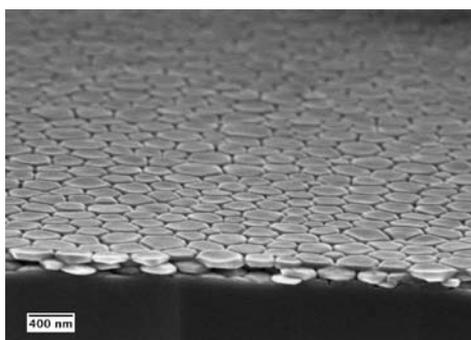
## Materials with Controlled Interface Structure

J.S. Gutmann

**Keywords:** Block copolymers, hybrid materials, mesostructures, templates, self-assembly, nano-objects, photonic materials

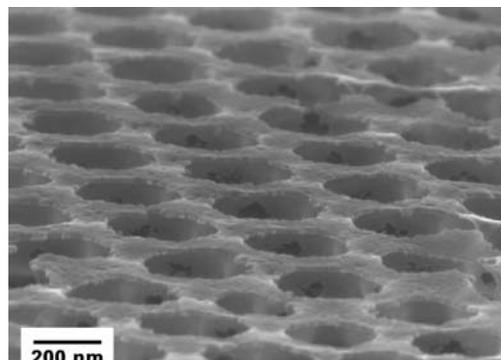
Rational design of functional materials aims at the preparation of devices with a specific functionality. Not only the chemical composition has to be controlled, but in addition the interfacial structure has to be carefully tuned. Many functional materials such as photocatalysts, or photoactive layers, depend on a specific shape and spacing of their interfaces because their functionality is commonly limited by transport phenomena.

To control the interfacial structure of large samples, top-down lithographic approaches, such as focussed ion beam etching, are not practical. Self-assembly of a structure-directing template provides a bottom-up route to materials with large sample volumes and controlled morphology. After a certain morphology is achieved the template may either be extracted or may remain inside the composite material, depending on the application. Lyotropic block copolymer phases acting as liquid crystalline templates are useful when structuring inorganic materials in the nanometer range (Fig. 1).



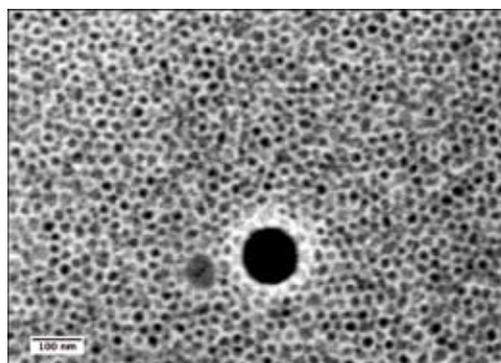
**Fig. 1:** Multilamellar titania film in which the thickness and diameter of the resulting platelets is controlled by the molecular weight of the used polymer.

The type of block copolymer used is not limited to the linear A-B type block copolymer. Linear A-B-A triblock copolymers with a large middle block, for example, allow for the formation of crew-cut micelles with a large micellar core. These large micelles can then be decorated with a precursor for metal oxides leading to highly ordered macroporous networks when deposited on a supporting substrate.



**Fig. 2:** Templating of macroporous structures via film casting of crew-cut micelles from A-B-A triblock copolymers.

Other block copolymer architectures such as amphiphilic bottle brush copolymers may also be used to structure inorganic materials. In these materials the structuring polymer not only acts as a template. The bulky macromonomer itself can be used to add a second, potentially orthogonal, functionality. In the templated titania shown in Fig. 3 the titania particles are surrounded by a ceramic shell consisting of a nonstoichiometric silicon-oxycarbide with orthogonal electronic properties.



**Fig. 3:** Mesostructured titania film in which the pores are filled with a silicon-oxycarbide ceramic derived from the templating polymer.

**Crosslinks to other projects:** Advanced Materials for Solar Cell Applications, Microfocus GIXAXS Measurements on Micromechanic Structures

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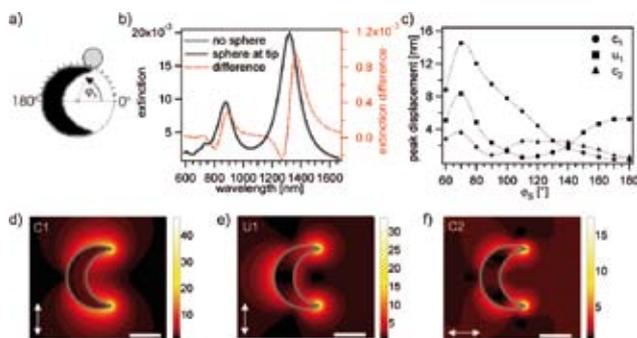
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# Detuning of Individual Plasmonic Antennae by Attachment of Dielectric Colloids

M. Kreiter, R. Berger

*Keywords: Plasmon, sensing, dielectric, single-object*

Optical sensors based on the localized surface plasmon resonances of metal nanoparticles are promising candidates for pushing the limits of label free detection down to the ultimate limit of real time single molecule sensitivity. This sensing technique employs the resonant oscillations of the free electrons in metal particles which can be observed as characteristic peaks in their extinction and scattering spectra. The spectral position of these peaks is highly dependent on the dielectric properties of the resonators' surrounding, which may change upon binding of any analyte with a refractive index contrast relative to the surrounding under study. A currently debated goal in terms of sensing with plasmonic resonators is the label-free detection of the binding and unbinding of an individual biomolecule to an individual resonator. In order to further push the detection limit towards such single molecule sensitivity, systematic optimization of the material, size and shape of the plasmonic resonator must be achieved. For this purpose, it is advantageous to use well-defined model analytes which mimic a biomolecule binding event. Then, different resonators can be benchmarked by comparing their response to this standard.

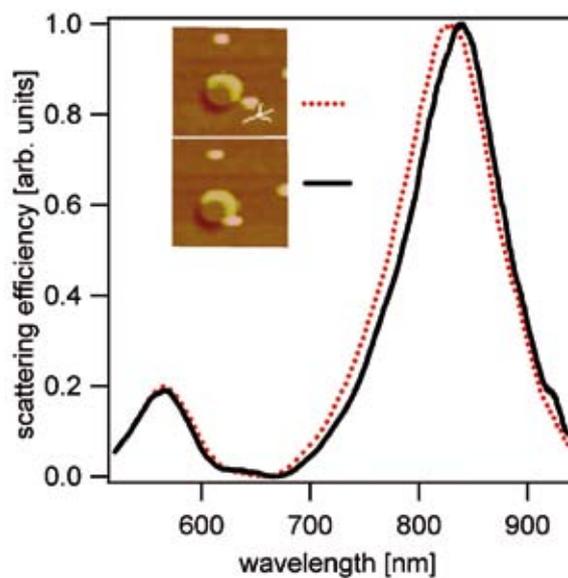


**Fig. 1:** a) Sketch of the crescent-shaped resonator and an attached sphere; b) resonance shift upon particle attachment c) influence of the sphere position for three different resonances; d-f) Corresponding field distributions.

As a basis for such an optimization, we established a Figure of Merit for plasmonic sensors, which reflects its ability to detect certain analytes as biomolecules. We introduced small dielectric spheres as benchmark analytes.

Fig. 1 shows the results of a numerical calculation of the resonance shift upon binding of this model analyte. Different analyte positions as shown in a) are considered. Binding of the analyte leads to small resonance shifts as shown in b).

In the first approximation, the shift of a resonance is proportional to the energy density of the near field distribution within the analyte. This becomes obvious when comparing the shifts of three plasmonic resonances (c) with their near field distributions (d,e,f).



**Fig. 2:** Scattering spectrum of an individual crescent-shaped metal particle before (red) and after (black) approaching a dielectric sphere.

To validate this theoretical prediction, the scattering spectra of individual bare crescents was recorded. Then, by nanomanipulation with an atomic force microscope a polystyrene colloid was pushed to the crescent. The inset of Fig. 2 shows a sequence of images before and after the manipulation. From the scattering spectrum of the same crescent after the colloid attachment, the resonance shift was determined and found to be in good agreement with the theoretical prediction.

Further optimized shapes of metal resonators may push sensitivity further down to the ultimate limit of label free real-time detection of single dielectric objects such as biomolecules.

**Crosslinks to other projects:** Scanning Probe Microscopy, Clean Room

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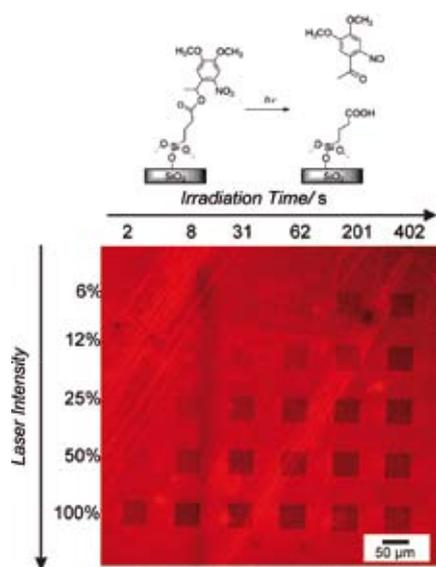
# Two-Photon Nanolithography on Photo-Sensitized Organic Monolayers

M. Kreiter, U. Jonas, K. Koynov

Keywords: Photo-deprotection, two-photon, silane, NVoc

Most resist-based photolithographic processes employed today are based on photo-induced chemical transformations of polymer films with typical thicknesses in the range of ten nanometers to several microns. The photochemical reaction may increase the solubility due to fragmentation or decrease solubility due to cross-linking.

A fundamentally different approach relies on the photolithographic structuring of organic monolayers. The most popular classes of organic monolayers are formed by reactive alkylsilanes (on oxidic surfaces) and thiols (on gold), and can be patterned by exposure to light, x-rays, and e-beams. Functional chloro- and alkoxy-silanes are of particular technological interest since they form very stable siloxane layers by linking covalently to the hydroxyl functions of the substrate.



**Fig. 1:** Light-induced deprotection reaction of a new MeNVoc silane derivative. Pattern written in a monolayer by two photon deprotection after fluorescence staining.

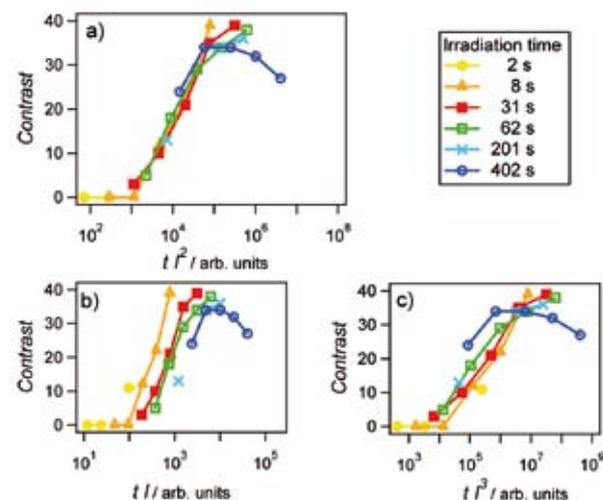
A chemically well-defined approach for monolayer structuring is based on systems with photolabile protecting groups. A popular class of such photolabile protecting groups is based on *o*-nitrobenzyl units, such as the widespread nitroveratryloxycarbonyl (NVoc) derivatives. This compound has an absorption maximum around  $\lambda = 350$  nm, and by irradiation at this wavelength, the bond between the NVoc group and the functional group of the remaining molecular fragment can be cleaved, see scheme in Fig. 1.

In the case of photo-protected monolayers this may yield a reactive group on the substrate which allows further selective chemical functionalization.

We demonstrated two-photon induced photo-structuring of an NVoc-protected polysiloxane monolayer. The main motivation for this work was near-field induced photolithography, which may open the door to photolithography on the nanometer scale. In the blue spectral range high electromagnetic field confinements are very difficult to achieve due to the dielectric response of noble metals. A two-photon process though, can provide the required energy for bond cleavage and thus allows for the use of near infrared light where high field confinements are easy to achieve with noble metal nanostructures.

A fluorescence labeling routine for structured monolayers was developed. It allows for a semi-quantitative determination of the photo-deprotection yield. Based on this, the number of photons required for the cleavage is found by determining the effective dose, where dose-response-curves for different irradiation times collapse. This is shown in Fig. 2 which gives clear evidence for a two-photon process.

We expect this approach to be capable of optical lithography on the scale of a few nanometers and far below the far-field diffraction limit.



**Fig. 2:** Dose-response curves assuming (a) two- (b) one- and (c) three-photon deprotection.

**Crosslinks to other projects:** Materials with Controlled Interface Structure

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# Supramolecular Architectures



# Supramolecular Architectures

K. Landfester, K. Müllen

Molecular chemistry is mainly focussing on the understanding of the behavior of individual molecules and their construction from constituent atoms; strong association forces such as covalent and ionic bonds between atoms are used to assemble the atoms as building blocks.

However, it is obvious that nature not only uses only covalent bonds for structure formation, but many different reversible non-covalent interactions including metal coordination,  $\pi$ - $\pi$  interactions, hydrophobic forces, van der Waals forces, and hydrogen bonding in order to obtain the remarkable properties and functional capabilities of biological systems. A discrete number of molecules organize themselves in a collective manner into longer-range order and higher-order functional structures by comparatively weak forces; such complex systems are considered as hierarchical. The weak interactions play an essential role for the function of the system, one example is a membrane which is built from low lipids.

The idea to imitate nature's supramolecular design motifs to generate robust nanostructured materials in a facile manner has inspired chemists for quite a while to design new architectures as supramolecular assemblies by using not only covalent, but also non-covalent interactions to build new functional, and technologically important materials. Such synthesis approaches of "bottom-up" materials based on supramolecular chemistry can provide a solution to the size limitations of "top-down" approaches which are currently used e.g. in photolithography. Therefore, supramolecular architectures can also be used to assemble active components of miniaturized electronic devices.

A deeper understanding of structure property relationships at a molecular and supramolecular level as well as a combination of molecular and supramolecular design principles allows a great possibility of the design of a large variety of molecules from biological to synthesized, from inorganic to organic, and from monomeric to macromolecular in origin. Different concepts like molecular self-assembly, molecular recognition, guest-host chemistry, mechanically interlocked architectures, and dynamic covalent chemistry are just a few examples of possibilities in current research. They promise to create systems which serve as biocompatible materials, biomimetic catalysts, effec-

tive electronic devices, excellent bio-recognition, chemical sensing, and so on.

Each supramolecular assembly consists of molecular building blocks which can be either small molecules such as molecular liquid crystals, hydrogen bonding molecules, catenanes and rotaxanes, or macromolecules such as block copolymers with incompatible blocks and dendrimers. It is now the interest of current research to design molecules which are suitable for supramolecular architectures. Additionally, a detailed study and characterization of the structure formation and their connected function using the different non-covalent interactions of supramolecular architectures are crucial for the understanding of many processes in materials science. It is the strength of the institute to cover the entire range from the synthesis of the building units, the study of the kinetics and dynamics of the structure formation to the characterization of the systems.

The synthesis and investigation of liquid crystals have been key activities of the institute for years, large efforts have been devoted to the investigation of the dynamics by using NMR, dielectric spectroscopy, scattering, and computer simulation. However, for the application as electronic materials, the intrinsic disk mobility can also influence the charge carrier significantly.

However, the assignment of the slower dynamics was not known. Dipole-functionalized hexabenzocoronenes have now been employed for detailed investigations of the self-assembly behavior, the thermodynamics and pathways of structure formation.

A special interest was in the study of the slow dynamics by a combination of dielectric spectroscopy and site-specific NMR techniques.



For the study of non-covalent hydrogen bonds and hydrogen-bonded aggregates, ultrafast magic-angle spinning proton solid-state NMR is shown to be a useful and sensitive tool. The method allows the investigation of assemblies by different molecules.

There is no doubt that extended  $\pi$ -electron systems belong to the key specialties of the institute. Beside the synthetic approaches which are required to build new molecular architectures (see also synthetic approaches), the arrangement of the systems including the morphologies and electronic states of extended  $\pi$ -electron systems is important for further application as electronic materials.

Multifunctional dendritic molecules can be used in combination with metal particles in order to build hybrid nano-assemblies. The idea is to place the multifunctional molecules with chromophores in the nanosized gap between the metal particle and the metal surface in order to strongly alter the photophysical properties, e.g. to increase significantly the stability and the brightness.

Typical representatives of supramolecular structures are membranes. Biological membranes around a biological cell consist of a lipid layer with many components as transporters or receptors embedded. Since natural membranes are quite complex due to multiple interactions of various components systematic investigations are difficult.

Building units of much higher complexity than lipids in membranes are biological molecules such as peptides and proteins. The secondary structures of the peptides and proteins which play a key role in determining the biological activity describes the arrangement of the monomeric units. It is defined by hydrogen bonds between elements of defined topology and by the primary structure. Tailoring of the chemical structure would allow one to affect the supramolecular architecture and connected with this the activity.

Model membranes can be constructed e.g. with functional ion channel incorporation which allows modeling of the ion transport. The immobilization of proteins in the membrane layer can be investigated by using electrochemically controlled surface-enhanced infrared resonance Raman spectroscopy.

Not only molecules, but also colloidal particles can be used for supramolecular architectures. Using colloidal particles with a high homogeneity in size leads to a defined three dimensional arrangement of the spheres resulting in photonic crystals. The photonic band gap can be tuned in such hierarchical colloid systems, which are also called colloidal crystals.

Supramolecular structures are also utilized in the formation of multiple stable emulsions. Polymerizations in such organized systems can be used for the formation of nanocapsules which can serve as (drug) delivery systems.

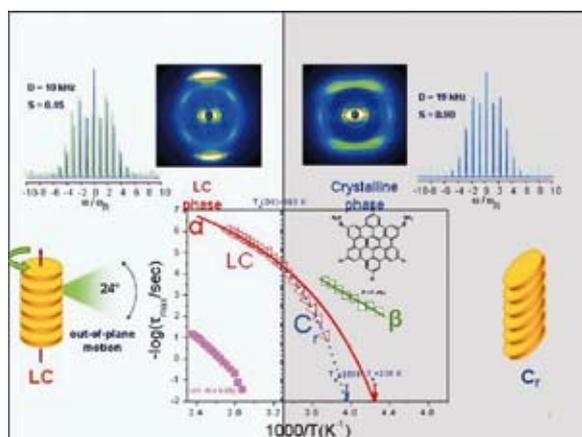
In summary, tailoring structure and function of extended assemblies ranging from small molecules to macromolecular systems and colloidal particles is of special interest in our institute. Here an interplay of chemistry, physics, and biology is important and is demonstrated by the different activities in the institute encompassing significant activities of all groups. The design of functional building blocks to new synthetic systems will lead to materials with more useful ensemble properties originating directly from an interplay of nanoscale and microscale ordering.

## Discotic Liquid Crystals in Motion

G. Floudas, H.-J. Butt, H.W. Spiess, K. Müllen

*Keywords: Self-assembly, dynamics, phase state, metastability, kinetics of structure formation*

Discotic liquid crystals are materials where self-assembly is driven by non-covalent intermolecular interaction. These materials consist of molecules with a flat and rigid aromatic core substituted by flexible aliphatic side chains. The former is responsible for the  $\pi$ -stacking and the latter for the increased solubility, processability and rich thermotropic behavior. During the self-organization process, the disc-shaped molecules organize into columns that further assemble into two-dimensional arrays, whereas the alkyl chains fill the intercolumnar space giving rise to a nanophase separated state. Typical examples include the triphenylene and hexa-*peri*-hexabenzocoronene (HBC) derivatives. Highly ordered columnar structures of the latter are promising active semiconductors in organic field-effect transistors and photovoltaic devices.



**Fig. 1:** Dipole functionalized HBC motional rates and their molecular assignment by combining dielectric spectroscopy with site-specific NMR techniques.

For application in the field of advanced electronic materials, the intrinsic disc mobility can influence the charge-carrier mobility and thus needs to be explored in detail. Earlier efforts by NMR, dielectric spectroscopy, neutron scattering, and computer simulations have shed light on the dynamics. What is still missing, however, is the assignment of the slower dynamics - pertinent to the long range organization - the presence of multiple glass temperatures, as well as the complete phase state.

A systematic investigation of discotic liquid crystals with respect to the nanoscale self-assembly, the molecular dynamics, the thermodynamic phase state and the pathways of structure formation with possible metastable states, requires a combination of model systems bearing dipoles directly attached to the cores and different microscopic techniques that are sensitive probes of the time-scale and geometry of motion. Furthermore, additional thermodynamic variables are needed (i.e., pressure) for constructing the complete phase diagram. For this purpose, a series of dipole functionalized HBCs was employed with dipole moments ranging from 0.25 to 4.55 Debye.

The main effect of dipole substitution was to stabilize the columnar hexagonal liquid crystalline phase ( $Col_h$ ) over a broader temperature range.

Secondly, the core dynamics within the columns were studied by combining dielectric spectroscopy with site-specific NMR techniques. The analysis of the dielectric loss curves provided the exact motional rates, whereas the analysis of the heteronuclear REREDOR NMR spinning sideband patterns provided site-specific information on the mobility. Combined NMR and dielectric spectroscopy investigation has shown unambiguously that the “fast” and “slow” dielectrically active processes are associated, respectively, with the axial disc motion and a collective re-organization of the columns that completely relaxes the dipole moment. The latter is particularly important to understand the alignment of the columns on surfaces in presence of an electric field.

Thirdly, pressure was employed to investigate the stability of the liquid crystalline and crystalline phases by providing the thermodynamic phase diagram.

Lastly, structure formation can be monitored by dielectric means, following a distinct path within the  $T$ - $p$  phase diagram. In this study we were interested in the presence or absence of intermediate states, the possible nucleation sites and the existence of long-lived metastability. The latter study provided glimpses of the exact mechanism for structural re-organization and growth. These results suggested new thermodynamic and kinetic pathways that favor the phase with the highest charge carrier mobility (crystalline).

**Crosslinks to other projects:** Structure and Dynamics of Columnar Photonics via NMR and ab-initio Methods, Organic Electronics: Structure-Property Relations

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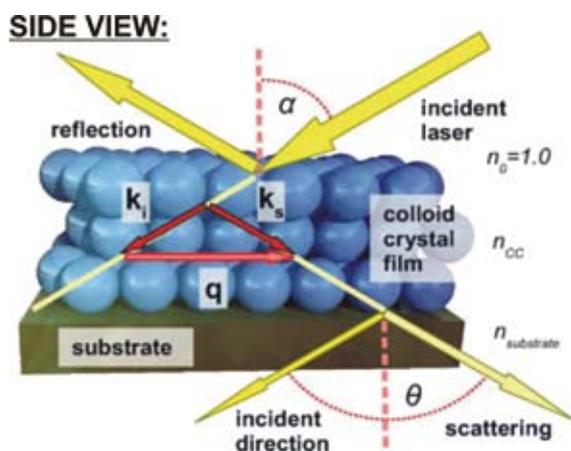
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# Tailoring of Phononic Band Structures in Hierarchical Colloid Systems

G. Fytas, U. Jonas

**Keywords:** Hypersonic phononics, colloid crystal, Brillouin light scattering, band gaps, eigenmodes

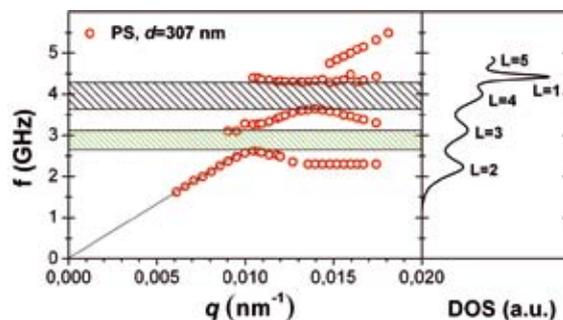
Phonon propagation through condensed matter in the GHz frequency range is best probed by Brillouin light scattering spectroscopy (BLS). It probes the interaction between incident photons and thermally excited phonons with wave vector  $\mathbf{k}$ . For homogeneous systems, energy and momentum conservation requires that the scattering wave vector  $\mathbf{q}=\mathbf{k}$  and the frequency shift  $\omega=\pm c_{l,t}k$ , where  $c_{l,t}$  is the speed of sound with longitudinal ( $l$ ) or transverse ( $t$ ) polarization. For mesostructured materials (hypersonic crystals) (Fig. 1), the introduction of a reciprocal lattice vector  $\mathbf{G}$  modifies the condition,  $\mathbf{q}=\mathbf{k}+\mathbf{G}$  and the phononic band structure is manifested in the dispersion relation  $\omega(q)$ .



**Fig. 1:** Supported opal and scattering geometry with wave vector  $q$  in the (111) plane of the f.c.c. crystalline colloidal film.

The first observation of a hypersonic bandgap was recently reported for PS wet opals (infiltrated with poly(dimethylsiloxane)). This order-related “Bragg” gap (hatched area around 4 GHz in Fig. 2) occurs at wave lengths commensurate to the lattice constant. The strong phonon resonance of the particles in fluids of low elastic impedance was found to open an additional “hybridization” gap (green area in Fig. 2) at the lowest (angular momentum  $l=2$ ) Eigen-frequency. Structural disorder erases the “Bragg” gap, while the hybridization gap remains.

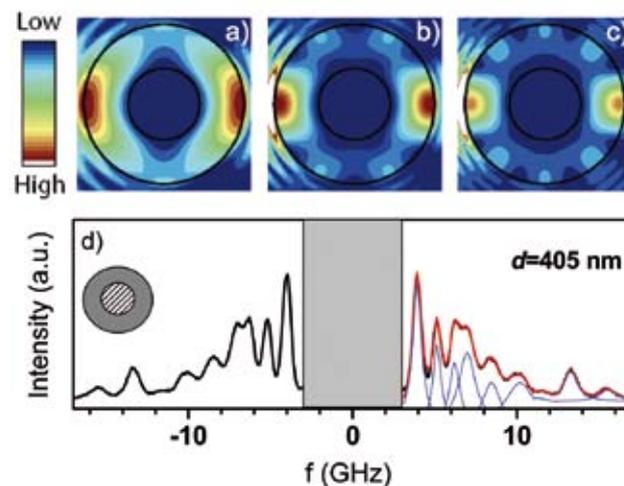
The potential of manipulating the propagation of elastic/acoustic waves in periodic structures can benefit from the complex architecture of submicrometer colloids.



**Fig. 2:** Phononic band diagram for a polystyrene wet opal along with the density of states (DOS) of a PS sphere in PDMS.

The first study of vibrational modes in core/shell particles has demonstrated the biased localization (predominantly in the shell) of the elastic energy (Fig. 3) and allows the non-destructive estimation of nanomechanical properties which can be different from the bulk components.

The rational design of nanostructured colloids with strong resonances and their successful incorporation into crystalline structures is a promising way of controlling the propagation of elastic waves, which presents a rich and challenging research area.



**Fig. 3:** BLS Eigen-mode spectra of a SiO<sub>2</sub>/PMMA particle with 181 nm core diameter and 112 nm shell thickness and displacement field distribution for three resonances.

**Crosslinks to other projects:** Colloidal Lithography for the Preparation of Metallic Nanostructures with Optical Resonances, Elasticity of Hollow Silica Microcapsules, Colloid Probe Technique, Multifunctional Polymer Capsules

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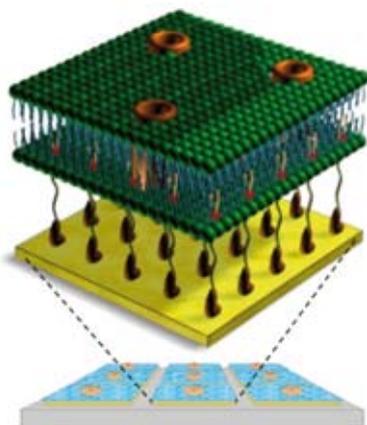
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## Model Membranes

I. Köper, R. Naumann

**Keywords:** *Bilayer lipid membranes, tethered bilayer lipid membranes, membrane proteins, ion channels, ion transport simulations, nano-pore spanning membranes*

The central building block of a biological membrane consists of a lipid bilayer separating the interior of a cell or organelle from the outside. Membranes consist of various types of lipids and they are also the basic support to host membrane proteins, which control transport across the membrane. However, for systematic investigation or the use of membrane architectures in sensing applications, artificial model systems are needed. One of the most promising model systems is the tethered bilayer lipid membrane (tBLM), where the proximal leaflet is covalently grafted to a solid support *via* a spacer group (Fig. 1).



**Fig. 1:** *tBLM with integrated ion channels as biosensing platform.*

### Sensing with channels

The basic sensor concept for a membrane chip requires a highly insulating membrane that can host functional membrane proteins. Upon binding of an analyte to the protein, changes in the protein structure or protein conductivity are detected. In the case of ion channels this can lead to a directly detectable signal.

In order to optimize the membrane architecture for diverse proteins, the molecular structure of the anchor lipids has been adopted and the architecture has been characterized using optical and electrical techniques.

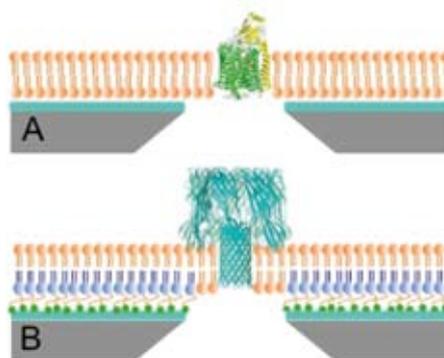
tBLMs show electrical resistances in the same order of magnitude as biological membranes and functional ion channel incorporation can be shown.

### Modeling of ion transport through tBLMs

Ion transport across tBLMs is modeled using a hybrid network description, which combines potential dependent rate equations with passive electrical elements. Passive permeation of ions is described by the integrated Nernst-Planck equation. Simulations based on this model are performed with the network simulation program SPICE (Simulation Program with Integrated Circuit Emphasis).

### Membranes over nanopores

Nanoporous substrates with circular pores of 50-500 nm in diameter are prepared by focused ion beam milling. Bilayers are spanned over the pores by adhesion and rupture of (giant) unilamellar vesicles (Fig. 2). Incorporation of pore-forming peptides into the lipid bilayers can be detected electrically with single-channel resolution.



**Fig. 2:** *Different pore-spanning membranes.*

**Crosslinks to other projects:** Spectro-Electrochemical Investigations of Membrane Proteins in Biomimetic Surface Architectures, BioInterfaces, Focussed Ion Beam, Clean Room

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# Spectro-Electrochemical Investigations of Membrane Proteins in Biomimetic Surface Architectures

R. Naumann

**Keywords:** Surface-enhanced infrared absorption spectroscopy, surface-enhanced resonance raman spectroscopy, time resolution, membrane proteins

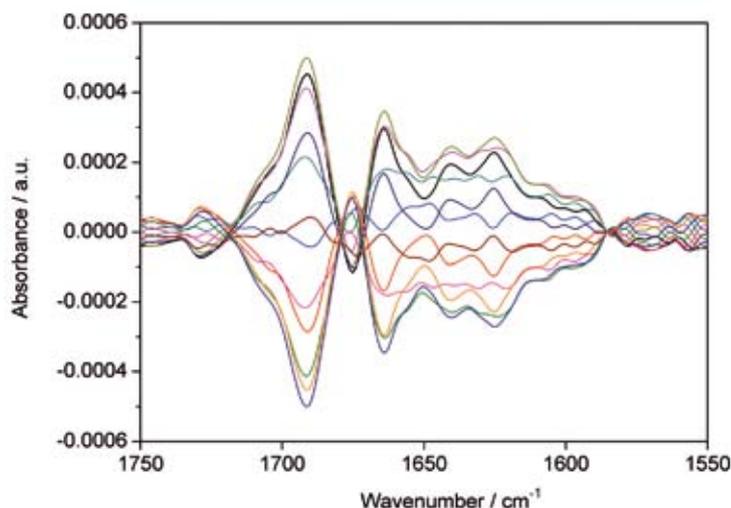
Multi-redox center proteins such as the cytochrome *c* oxidase (CcO) from *R. sphaeroides* were investigated using electrochemically-controlled, surface-enhanced infrared absorption spectroscopy (SEIRAS) and surface-enhanced resonance raman Spectroscopy (SERRS). For this purpose the CcO genetically engineered with a his-tag on SU II was immobilized with the cytochrome *c* binding site directed towards the electrode surface. The immobilization was followed by an *in-situ* reconstitution into a protein-tethered bilayer lipid membrane (ptBLM). Electron transfer was achieved by direct electronic wiring to the gold or silver electrode used for SEIRAS or SERRS measurements, respectively.

## Electrochemically-controlled IR spectroscopy

In the case of SEIRAS a gold film was deposited on the silicon crystal of the IR setup in an ATR configuration. The kinetics of consecutive electron transfer to the Cu<sub>A</sub>, the heme *a* and *a*<sub>3</sub> and Cu<sub>B</sub> centers of the enzyme were followed. Rate constants of electron transfer were obtained by a periodic application of potential pulses and by analyzing the difference spectra of amide I bands assigned to the respective redox centers as a function of time (Fig. 1). The spectral changes were monitored in the step-scan mode. Assignment of site specific vibrational modes was facilitated using phase sensitive detection.

## Electrochemically-controlled SERR spectroscopy

While SEIRAS is designed to register changes of the protein backbone, SERRS is sensitive to vibrations of the porphyrine ring, particularly in the resonance Raman (SERRS) mode. Time-resolved SERRS measurements are thus complimentary to the results of tr-SEIRAS studies.



**Fig. 1:** Time-resolved SEIRA spectra of cytochrome *c* as a model system for more complex heme proteins.

**Crosslinks to other projects:** Model Membranes

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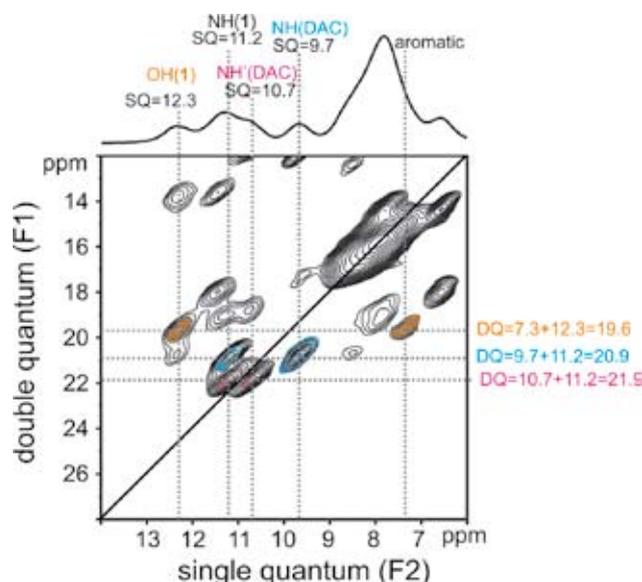
# Hydrogen-Bonded Aggregates

G. Brunklaus

**Keywords:** Supramolecular structures, hydrogen-bonds, solid-state NMR

Currently, much interest is focused on the controlled design of well-ordered structures based on rather weak, non-covalent interactions such as electrostatic forces, van der Waals contacts, aromatic  $\pi$ - $\pi$  interactions as well as hydrogen bonds. In special cases, this approach is referred to as crystal engineering, since a crystalline solid can be regarded as supramolecular network of weak contacts.

Ultrafast magic-angle-spinning proton solid-state NMR is a particularly useful and sensitive tool for the study of hydrogen bonds and hydrogen-bonded aggregates. The proton chemical shift allows for the direct detection of local structural environments and estimation of hydrogen-bonding strengths. Protons involved in hydrogen-bonded structures

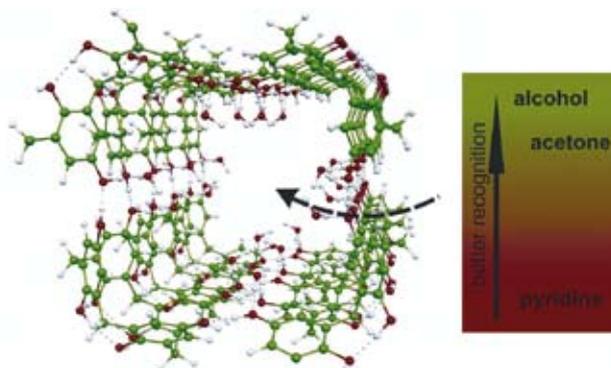


**Fig. 1:**  $^1\text{H}$ - $^1\text{H}$  DQ MAS NMR spectrum of 1-*n*-butyl-5-(4-nitrophenyl) barbituric acid with 2,6-diacetamido-pyridine at 850 MHz and 59524 Hz MAS. The important cross peaks that reveal the structure of the complex are highlighted.

typically exhibit well-resolved  $^1\text{H}$  chemical shifts, mainly between 8 and 20 ppm. Further resolution may be obtained from  $^1\text{H}$  double-quantum  $^1\text{H}$  NMR methods that not only provide precise information on proton-proton distances on length scales of up to 4 Å, but also identify proton positions in arrays of multiple hydrogen bonds. In this way, dynamic processes involving molecular recognition or formation of hydrogen-bonded complexes can be investigated in detail.

Artificial chromophoric receptors for biologically active molecules have attracted considerable attention from the viewpoint of molecular recognition. Indeed, barbiturates show very selective affinities at binding adenine or its derivatives. By means of solid-state NMR and single-crystal X-ray analysis, we obtained detailed insights into the complex formation of 1-*n*-butyl-5-(4-nitrophenyl) barbituric acid that offers multiple binding sites for supra-molecular assemblies with 1,8-bis(dimethylamino) naphthalene and adenine-mimetic 2,6-diacetamido-pyridine.

Other hydrogen-bonded assemblies of interest are calix-[4]hydroquinones and calix[4]arenes, which are hosting suitable guest species, and thus show promising potential for industrial applications within nanotechnology. We have shown, for example, that the calix[4]hydroquinone nanotubes preferably recognize alcohols over acetone, while pyridine does not fit well inside the assemblies, which is derived from characteristic up-field-shifted proton chemical shifts. In addition to molecular inclusion compounds, assemblies of oligoaramides as a model system of polyaramides were investigated. It was found that the resulting hydrogen-bonded packing substantially varied upon changes of the reaction conditions. In most cases, mainly semi-crystalline or amorphous compounds were produced making NMR the choice method for revealing both the structure and dynamics of such supramolecular aggregates.



**Fig. 2:** View into the calix[4]hydroquinone nanotubes. The water molecules that stabilize the structure have one hydrogen-bond donor contact “free” that allows for molecular recognition of alcohols.

**Crosslinks to other projects:** Pushing the Limits of Solid-State NMR, Crystal Engineering of Molecular Architectures, Proton Conductive Polymers for Improved Fuel Cell applications.

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## Hybrids with Biological Components

G. Floudas, R. Graf, H.W. Spiess, H.-J. Butt, K. Müllen

*Keywords: Polypeptide self-assembly in solution, in the bulk and on surfaces, polypeptide dynamics, bio-inspired systems*

The ability to control, predict and manipulate the peptide secondary structure represents a key ingredient in biological systems. The overall goal is to understand how the chemical tailoring of the structure of oligopeptides, polypeptides and oligopeptide-based molecular hybrids affects their self-assembly and activity. Since peptide secondary structure plays an important role in determining the biological activity, the knowledge generated is instrumental in developing novel, biologically-active peptides. The primary outcome is the optimization of such bio-inspired systems for applications that rely on molecular assembly occurring in solution, in the bulk, on surfaces, and at interfaces.

The polypeptides are combined with dendrimers. Such entities with high structural precision, a compact molecular structure and high end-group functionality, can be employed as carriers for controlled drug delivery, in gene transfection, and as novel antimicrobial peptides.

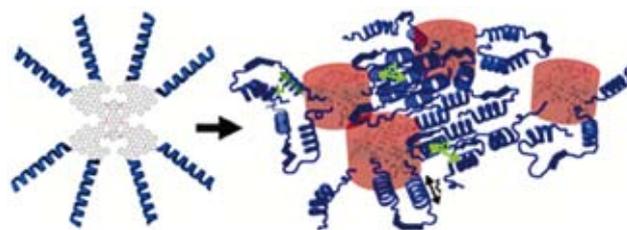
Systems of interest include (i) dendrimers bearing polypeptides with predetermined secondary structures and (ii) block copolypeptides with different architectures.

A key issue in this area is the attachment of several polypeptides, with predetermined secondary structures, to nanoparticles to form synthetic molecules of high immunological value. The combined use of fluorescence correlation spectroscopy (FCS) with  $^1\text{H}$  and  $^{13}\text{C}$  MAS NMR spectroscopy provided the *size* and *type* of peptide secondary structures in a series of poly-Z-L-lysine functionalized polyphenylene dendrimers bearing the fluorescent perylene diimide core in dilute solutions. Furthermore, FCS is a sensitive probe of the core size as well as of the change in the peptide secondary structure. For example, a change in the peptide secondary conformation from  $\beta$ -sheets to  $\alpha$ -helices, detected by  $^{13}\text{C}$  MAS NMR spectroscopy, gives rise to a steep increase in the hydrodynamic radii (FCS).

When similar poly-L-lysine-functionalized polyphenylene dendrimers were studied in the melt as a function of the core size (generation), functionality, and polypeptide length, a striking dependence of the polyphenylene self-assembly on

the poly-L-lysine length was found. In addition, the type of peptide secondary structure ( $\alpha$ -helix/ $\beta$ -sheet) was controlled by the packing restrictions imposed by the polyphenylene core. These studies revealed that constrained poly-L-lysines can adopt different secondary structures from their linear analogues. The dynamic investigation revealed significant mobility associated solely with the polypeptide through three processes: a glass transition, a slower process associated with the relaxation of  $\alpha$ -helical segments, and a glassy mode whose origin could be resolved by site-specific solid-state NMR techniques.

The chain topology, architecture, and the presence of surfaces and interfaces also have a strong effect on the type and persistence of the peptide secondary structure. Polypeptide self-assembly on surfaces, for example, is dictated mainly by the peptide-substrate interactions.



**Fig. 1:** Self-assembly in functionalized polyphenylene dendrimers with long polypeptides. The  $\alpha$ -helical secondary structure prevails (with persistence length  $\xi$ ) that, in addition, displays packing in a hexagonal lattice (with a distance  $d$ ). Notice the absence of correlation between the cores.

**Crosslinks to other projects:** Hybrid Nano-Assemblies, Mechanical, Mechanics, Rheology and Dielectric Spectroscopy Laboratory

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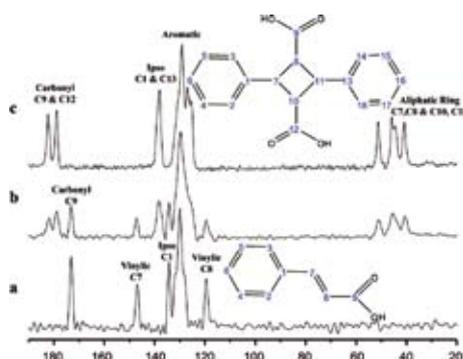
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# Crystal Engineering of Molecular Architectures

G. Brunklaus, V. Enkelmann

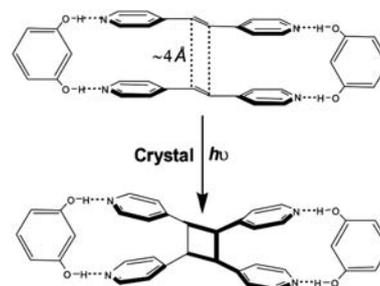
*Keywords: Solid-state NMR, hydrogen-bonds, supramolecular aggregates*

Covalent bond-forming reactions (e.g. of carbon-carbon bonds) constitute the heart of organic synthetic chemistry. Such reactions are commonly used to construct molecules of remarkable complexity. The molecular environment in the solid-state is flexible enough to allow for atoms to move and sometimes to react, but is also sufficiently rigid to facilitate remarkable stereocontrol. The homogeneous nature (i.e. 3D regularity) of a crystal lattice implies that covalent-bond-forming reactions proceed quantitatively. Such reactions are particularly important in the field of green chemistry since highly stereospecific products are obtained from a practically solvent-free medium. The spatial constraints within the crystal packing also enable molecules to adopt geometries that are rarely achieved in the liquid phase. In addition, solid-state reactions that are reversible and driven by light offer possible applications in optical memory storage systems.



**Fig. 1:** Solid-state  $^{13}\text{C}$ -CPMAS spectra of a) *trans*-cinnamic acid, b)  $\sim 25\%$  converted mixture, c)  $\sim 50\%$  converted mixture, and d) *truxillic acid*.

[2+2]-photodimerizations are the most extensively studied organic solid-state reactions and provide access to a large variety of compounds. The photoreaction of *trans*-cinnamic acid (and many of its derivatives) constitutes the classic example of a solid-state reaction that follows topochemical principles. Detailed insights into the reaction mechanism and intermediate products can be obtained from a joint approach of both single-crystal x-ray analysis and solid-state NMR, which have been used to explain the dynamic hydrogen bonding of cinnamic acid and *truxillic acid* obtained by [2+2]-photodimerization.



**Fig. 2:** Reaction scheme for the crystal-engineered [2+2] photodimerization of a 1:1 co-crystal of resorcinol and *trans*-1,2-bis(4-pyridyl)ethylene.

Indeed, peak splittings observed in the corresponding  $^{13}\text{C}$ -CPMAS spectra of *truxillic acid* (Fig. 2) do not result from packing effects, but rather from transient asymmetry of the hydrogen bonds within the crystal that temporarily destroys the photodimer's center of symmetry.

Deeper understanding of packing effects in the solid-state and insights into topochemistry facilitate a more rational design of possibly functional compounds in the solid-state. Efforts have been made to steer olefins for controlled reaction via selective substituents and hydrogen-bonds, respectively. Here, resorcinol (cf. Fig. 2) that has two hydroxyl groups at a distance of  $\sim 4 \text{ \AA}$  is not only an efficient template but also a reliable hydrogen-bonding donor.

Ultimately, such studies serve to provide rules that possibly afford a qualitative prediction of supramolecular structures based on the reactants used. Currently, however, due to the large number of possibly involved interactions and molecular arrangements, this is rather difficult, but with the combined approach of X-ray analysis and solid-state NMR, certain trends can be recognized.

**Crosslinks to other projects:** Hydrogen-bonded Aggregates, Pushing the Limits of Solid-State NMR

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# Hybrid Nano-Assemblies

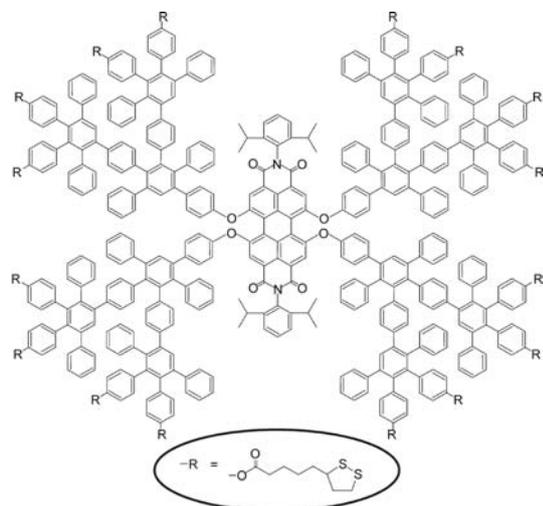
M. Kreiter, W. Knoll, K. Müllen

*Keywords: Hybrid, dendrimer, plasmon, fluorescence, surface-enhanced*

Multifunctional organic molecules can be used as smart building blocks for architectures with typical dimensions on the nanometer length scale and below. In particular, they can be combined with inorganic materials to form hybrid nano-assemblies with specific functionalities.

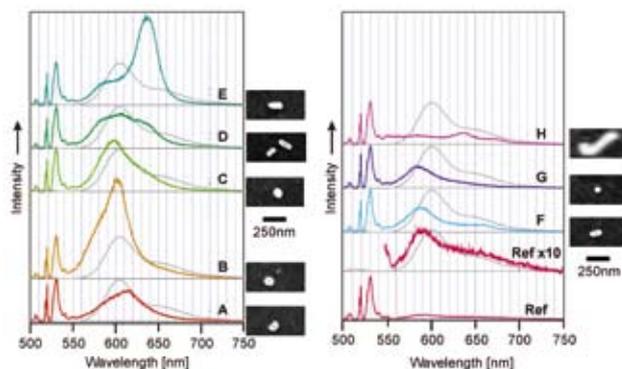
Optical ‘gap resonances’ may occur between a metal particle and a metal surface. Typical length scales are widths of 3 nm and below and particle sizes of 40–100 nm. Here, a coupled optical resonance occurs where the electromagnetic field is tremendously enhanced within the gap in a volume of some cubic nanometers. Chromophores, when placed in this enhanced field, will be strongly altered in their photophysical properties, e.g. stability and brightness may increase significantly. While this effect has been discussed for decades, quantitative experiments have been hampered by the difficulty of placing a chromophore in a defined nanometer-sized gap between a metal surface and a metal colloid.

Fig. 1 shows a dendrimer molecule that combines two functions. First, it carries 16 dithiolane functionalities as anchor groups at its periphery. They attach to the noble metals gold and silver and allow for the formation of a monolayer on such a metal surface. Remaining unbound anchor groups allow for the binding of colloidal noble metal particles in a second step. Secondly, it carries a high-performance organic fluorophore, perylene-diimid, in its center.



**Fig. 1:** Dye-loaded polyphenylene-dendrimer with peripheral dithiolane functionalities.

sequence, the chromophore is placed exactly at the position where the strong interaction with the electromagnetic field occurs.



**Fig. 2:** Fluorescence emission spectra from individual particle-on-plane assemblies. Silver colloidal particles are separated from a silver surface by a monolayer of the dendrimer shown in Fig. 1.

First, an ensemble characterization method for the resonances alone was established. It allows for the quantitative determination of the resonators’ optical response in terms of a complex ability to polarize. It was shown that both the dendrimer shown in Fig. 1 and an analogue structure without chromophore allow for the assembly of well-defined sphere-on-plane structures. A full correlation between the optical response and the sample geometry could be established experimentally. A simple model of a perfect sphere on a perfect plane reproduces the experimentally observed resonances surprisingly well for a gold-on-gold system.

Recently, first experiments on surface-enhanced fluorescence in this defined structure were successful. Fig 2 shows the fluorescence emission from individual sphere-on-plane structures. The dendrimer shown in Fig. 1 is placed between a silver particle and a silver surface. All spectra differ both from each other and from the spectrum of the free chromophore, which is shown as gray curves for comparison. This points to a strong coupling of the dye with the plasmonic sphere-on-plane resonance and will serve as the basis for detailed investigation of the optical effects on molecular length scales.

**Crosslinks to other projects:** Polyphenylene Dendrimers

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# Multifunctional Polymer Capsules

A. Musyanovych, K. Landfester

*Keywords: Biocompatible nanoparticles, interfacial reactions, nanoprecipitation, DNA encapsulation*

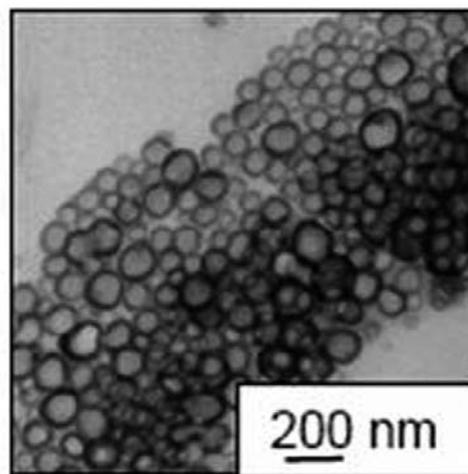
Extensive research activities involving nanocarriers began around forty years ago, when the first example of a liposome was presented in the literature. Over the past two decades interest has focused on core-shell particles consisting of a liquid core (owing to their utilization as sub-micrometer containers) for the encapsulation of biologically active substances. The main advantages of nanocapsules for drug delivery are the efficient protection of therapeutic agents against enzymatic and hydrolytic degradation. The ideal nanocarrier will be one that is size- and morphology-specific, has the ability to encapsulate a variety of compounds, can be functionalized with certain surface targeting ligands, and has the ability to deliver and release the encapsulated material in a controlled way.

Significant benefits of the miniemulsion technique include formation of polymeric nanocapsules with different particle size (50-1000 nm), morphology (single or multi core), and versatility in the polymeric materials and surface functionality. The high stability of the system allows reactions to take place inside the droplets and at their interface. Due to the lack of monomer diffusion processes throughout the polymerization, an efficient encapsulation can be obtained by phase separation inside the nanodroplets throughout the polymerization process, by nanoprecipitation of the polymer onto nanodroplets, or by an interfacial reaction at the nanodroplet's interphase. Moreover, under carefully chosen conditions of miniemulsification, it is possible to entrap different kinds of substances, e.g. Gd complexes for magnetic resonance imaging, Ag particles for antimicrobial applications and also such fragile cargos as DNA molecules, avoiding damage.

Polymeric nanocapsules (size range 250 – 600 nm) with encapsulated dsDNA (790 bp) were produced via anionic polymerization of *n*-butylcyanoacrylate (BCA) carried out at the interface of homogeneously distributed aqueous droplets in the inverse miniemulsion (see Fig. 1). Polyalkylcyanoacrylates are widely used materials in the biomedical field mainly due to their biodegradability, low toxicity, and enhancement of the drug intracellular penetrations. In-

vestigation showed that the average capsule size and polydispersity are mainly determined by the type and concentration of the surfactant(s) used as well as by the viscosity of the continuous phase. The mixture of both hydrophilic and hydrophobic surfactants in the continuous phase with higher viscosity leads to narrow-sized capsules. The capsule morphology (single or multi core) can be controlled by varying the monomer amount. In the case of single core a polymeric shell thickness from 15 up to 40 nm can be obtained. In order to form the polymeric shell with a high molecular weight, the use of low surfactant concentrations and monomer amounts are the best choice. The TEM image of PBCA capsules is presented in Fig. 1. After encapsulation at least 15% of the initially loaded dsDNA molecules, that do not change their structural integrity, could be recovered from the capsules.

In summary, the usage of the miniemulsion technique alone or in combination with other formulation processes enables the production of capsules with the desired properties for a broad range of application.



**Fig. 1:** TEM image of poly(*n*-butylcyanoacrylate) capsules.

**Crosslinks to other projects:** Polymeric Nanoparticles and Interaction with (Stem) Cells: Uptake, Intracellular Trafficking and Cellular Responses, Bio-Responsive Hybrid Nanoparticles, Nanoparticles for Central Nervous System Targeting

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# **Functional Materials and Devices**



# Functional Materials and Devices

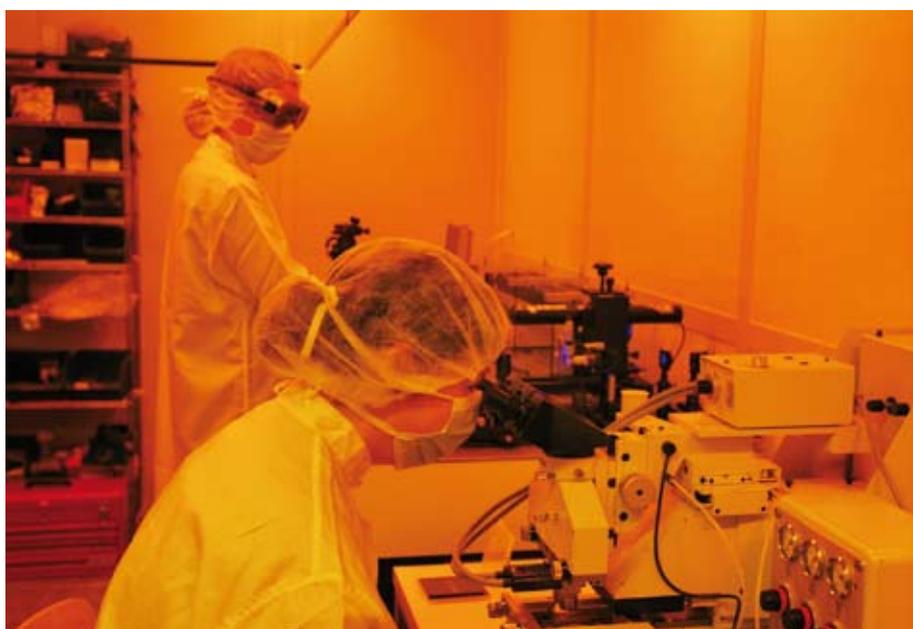
H.-J. Butt, K. Landfester

The aim of the institute is to understand the structure and dynamics of matter at different length and time scales. Ideally, “understanding” implies that from the chemical structure and the process chosen the properties of a material could be predicted. With this knowledge materials with desired functions can be designed. Even though we are still far away from such an understanding the expertise is applied to make functional materials. In this chapter we focus on three fields in which the MPI-P has made substantial contributions: polymer electronics, energy, and drug delivery. These three fields not only demonstrate our awareness of long-term technological developments, but they also show how topics are investigated in an interdisciplinary approach by project leaders with different backgrounds, irrespective of the particular group to which they belong.

In the field of organic electronics, the goal is to create processable organic or polymeric materials with an enhanced life duration and an improved performance. This requires a better understanding of the physical processes which lead to the deterioration of device performance. Research is not concentrated on isolated materials, but on the function and performance of a material in its complex device configuration. In addition, a spectrum of processes to be used in device fabrication needs to be developed and improved. This involves the design of molecular and supramolecular structures of organic material. Existing organic or polymeric materials need to be further developed to enhance their usefulness in fast and industrially acceptable processes, e.g. ink-jet printing, roll-to-roll manufacturing. Moreover, their properties in adhesion to metal and/or semiconductor electrodes, corrosion of contacts, undesired migration of dopants etc., need to be considered. For the future ecological use of energy, three different core technologies, to which polymer science can significantly contribute, are developed: Collection of energy, storage of energy, and delivery of energy. For the collection of energy in an environmentally-friendly way, solar cells will play a decisive role. Photovoltaics serves to transform solar light into other types of energy or to generate hydrogen for energy storage. The control of supramolecular ordering in a photovoltaic device is essential for successful development. New technologies are being developed to generate nanostructures with perfect phase separation between the donor and acceptor structures and with a maximized interface for the charge separation. For storage, lithium-ion batteries are commercially available. However, due to the low specific capacity of the electrode materials, batteries small in size and with a high power supply are presently difficult to fabricate. Metal oxides (MOs) yield high specific capacity during reversible redox reactions with lithium, and thus as anode materials are expected to

miniaturize the battery and at the same time significantly improve the battery performance. One major problem with the MO-based batteries is the poor cycling stability. To solve this problem, we developed a concept based on the extensive study of nanographenes. Graphene layers are used for covering the surface of MO nanoparticles to form MO-core graphene-shell structures. The graphene-covered MO displays significantly improved cycling performance. The use of solar energy stored as hydrogen requires the replacement of combustion engines. Therefore, fuel cells will be a core technology in the development of “zero emission” energy production. To rise to this challenge we are developing new proton exchange membranes. Although numerous membranes exist, the demanding criteria for automotive applications have not been satisfied. Long-term temperature stability at a desired working temperature of 130 °C is still not guaranteed. More importantly, due to the production of water during the operation of the fuel cells, the electrolytes in the membranes are diluted. Both processes result in a slow decrease of the performance of the membranes. To solve this problem hybrid materials based on phosphonic acids are developed, which are stable even at high temperatures. Developing drug carriers for directed delivery is another active research area at the MPI-P. In contrast to passive diffusion, directed delivery allows to reduce the amount of drugs that has to be applied. Thus, the total dose and negative side effects can be reduced.

One of our major research interests includes the design of novel bio-hybrid materials for the visualization and initiation of directed drug delivery. Our platform consists of multifunctional oligolysines as well as proteins such as bovine serum albumin (BSA) or human serum albumin (HSA). Up to three different types of functionalities could be attached to both carrier molecules in a spatially organized way.



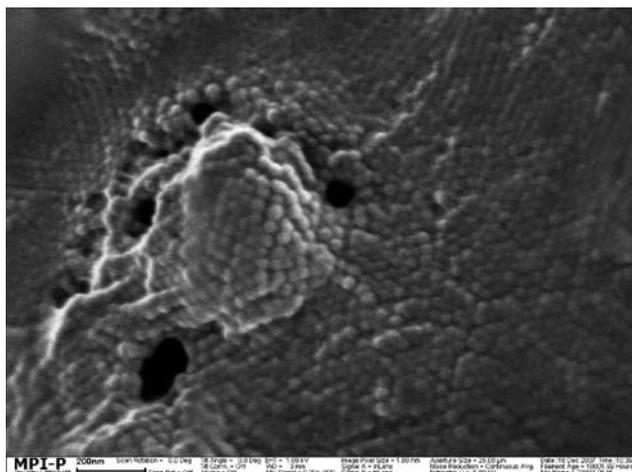
## Advanced Materials for Solar Cell Applications

J.S. Gutmann, R. Berger, C. Li

*Keywords: Block copolymers, hybrid materials, self-assembly, photonic materials, solar cells, scanning conductive microscopy, dye-sensitized solar cells*

The fabrication of organic solar cells is an emerging technology with the potential to replace silicon solar cells in low cost devices. A key issue in the development of all polymer or hybrid organic solar cells is the formation of a hetero-interface between two semiconducting phases originating from a sol-gel process and the other from a conducting polymer. As the photo-generated charges are separated at this hetero-interface, the precise control of its morphology is a key factor that determines the overall performance of the solar cell.

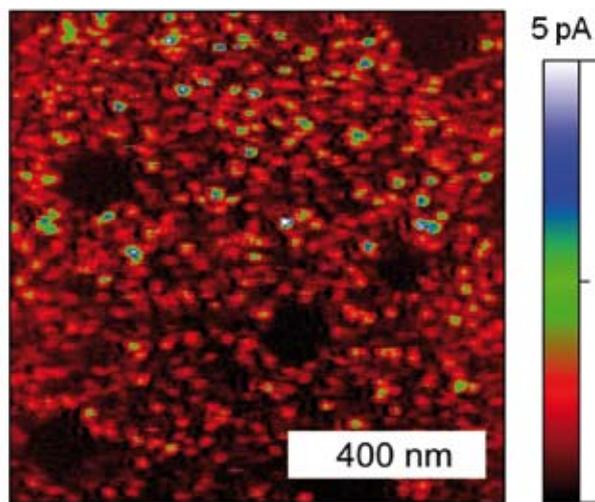
In terms of structure formation in polymeric materials block copolymers provide a versatile route for bottom-up formation of nanostructures. With typical structures in a size range of 10-20 nm, block copolymers are in principle well suited for applications in solar cells. Moreover, block copolymers can not only be used as a self-assembling template, but also to provide an electronic functionality.



**Fig. 1:** Mesostructured titania film in which the pores are filled with a conductive polymer which is part of the templating polymer.

Advanced block copolymers are tested as functional materials in both the photoactive layer of a solar cell as well as in a charge separating barrier layer. In the photoactive layer amphiphilic block copolymers incorporating a hydrophilic block and a semiconducting hydrophobic block are used to act as templates. In connection with sol-gel techniques, which result in crystalline titania at temperatures below 100 °C, the semiconducting block copolymers are used to create semiconductor heterostructures with well defined morphologies (Fig. 1).

For use in barrier layers, poly(ethylene glycol) methylethermethacrylate-block-poly(dimethylsiloxane)-block-poly(ethylene glycol)methylethermethacrylate block copolymers were developed, in which the hydrophobic block consists of siloxane. During templating of a titania sol-gel the gaps surrounding the electrical conducting titania particles are filled with the siloxane polymer chains.



**Fig. 2:** Scanning conductive microscopy of a barrier layer consisting of titania particles enclosed by a silicon-oxycarbide ceramic. The high conductive areas are typically 20 nm in diameter and can be associated to titania particles.

Subsequent ceramization of the siloxane chains leads to a silicon-oxycarbide ceramics.

The electronic properties of the resulting material can be characterized by scanning conductive microscopy (Fig. 2). We observed electrically conductive areas (bright spots) that correspond to titania particles within an insulating matrix of the silicon-oxycarbide ceramics. Initial experiments on integrated blocking layer based hybrid solar cells showed a fifteen fold higher efficiency than cells based on a conventional  $\text{TiO}_2$  blocking layer.

Dye-sensitized solar cells (DSCs) based on nanocrystalline semiconductors have been the subject of intense investigation owing to their potential low cost, easy processing, and good performance. In these cells, a dye monolayer is adsorbed on a mesoporous film of titania. Upon light absorption, the dye injects electrons into the  $\text{TiO}_2$  conduction band, where they are transported to the anode. The neutral dye is regenerated by electron transfer either from an electrolyte containing a redox system or from a solid-state hole conductor. With a closed external circuit and under illumination, the device then constitutes a photovoltaic energy-conversion system, which is regenerative and stable. In this technology, ruthenium complexes maintained a clear lead in performance amongst the thousands of dyes tested, yielding power conversion efficiencies of 10–11%. However, in view of the cost and availability of metals as well as their environmental non-compatibility, many metal-free organic dyes have been developed.

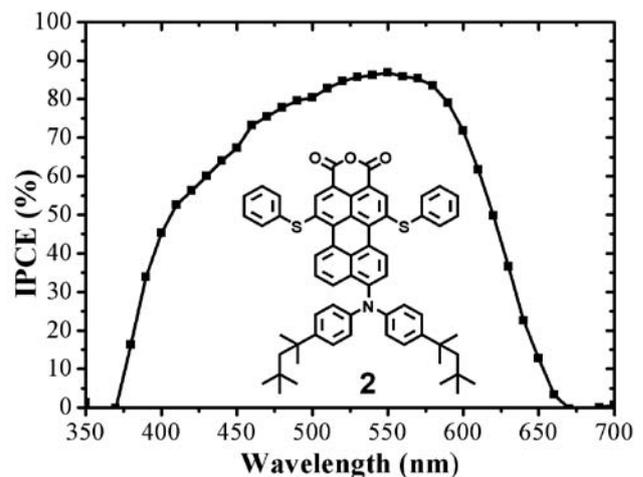


## Rainbow Perylene Dyes

**Fig. 3:** All colors of the rainbow can be realized in perylene dyes through a variation of the substituents  $R_1$ ,  $R_2$ ,  $R_3$ .

As metal-free dyes, perylene derivatives have been widely applied in various optical devices owing to their outstanding chemical, thermal and photochemical stability and non-toxicity. With their large  $\pi$ -conjugated systems, perylene monoanhydrides (PMAs) **1** provide a versatile synthetic basis for functionalization. By using the anhydride group of PMAs as an acceptor/anchor and selectively functionalizing the 1-, 6- and 9-positions with different electronic substituents, our group have constructed a family of “push-pull” type perylenes exhibiting a rainbow of colors, tunable orbitals, spectroscopic and electrochemical properties (Fig. 3). These fine-tunings provide a way to new perylene sensitizers with stronger intramolecular charge-transfer (ICT), more suitable HOMO or LUMO energies, and more favorable light absorption properties for solar conversion.

In these rainbow perylene sensitizers, the best one is compound **2** which delivers an unprecedented incident monochromatic photon-to-current conversion efficiency (IPCE) of 87% and yields a power conversion efficiency of 6.8% under standard AM 1.5 solar conditions (Fig. 4).



**Fig. 4:** IPCE spectrum (top) of compound **1** sensitized solar cell based on volatile electrolyte (active area of  $0.2 \text{ cm}^2$ ). The redox electrolyte was composed of  $0.6 \text{ M}$  1-butyl-3-methylimidazolium iodide,  $0.05 \text{ M}$  iodine,  $0.1 \text{ M}$  LiI, and  $0.5 \text{ M}$  tert-butylpyridine in 15:85 (v/v) mixture of valeronitrile and acetonitrile.

**Crosslinks to other projects:** Functional Dyes and Their Applications, Microfocus GIXAXS Measurements on Micromechanic Structures, Scanning Probe Microscopy

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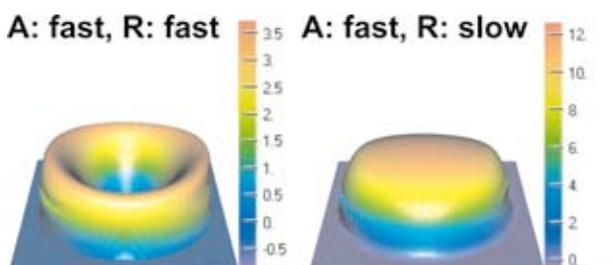
## Microlenses by Evaporation of Drops

K. Graf, E. Bonaccorso, H.-J. Butt

*Keywords: Evaporation of microdrops, structuring of polymer surfaces*

The ink-jet technique is a versatile tool for surface micro-structuring. Usually, drops containing solutes are deposited on solid supports and then evaporated - the solute remains. This way, microlenses of polymers were fabricated with high precision. We use an ink-jet or microdrop-assisted etching technique to directly structure polymer surfaces. Here, microdrops of solvents are deposited on polymer substrates. After evaporation of the drop the originally flat polymer surface is restructured, forming a characteristic 3D topology. With this procedure the contamination of the ink-jet capillary, the time-consuming preparation of solvent/solute mixtures, and the mismatch of the refractive index between solid support and lens can be avoided or minimized.

The resulting surface topology depends on external and intrinsic system parameters. As an example of an external parameter the contact time between droplet and polymer surface was found to have a striking influence (Fig. 1).



**Fig. 1:** Surface structures (width=400  $\mu\text{m}$ ) in PS (284 kDa) after deposition of toluene drops (scale in  $\mu\text{m}$ ), A/R: approach/retraction speed; fast=11 mm/s, slow=10  $\mu\text{m/s}$ .

In this experiment the contact time was triggered via the retraction speed in a microdrop-assisted etching set-up. A pendant drop of toluene was picked up by a moving table with the polystyrene (PS) substrate on top. Thus a liquid bridge is formed. A slow retraction speed results in a long contact time between polymer and solvent drop and thus an increased dissolution/concentration of polymer into/in the droplet: the drop gels as a whole. In contrast, a fast retraction speed leads to a low polymer concentration inside the droplet. It evaporates prior to gelation and a coffee-rim like effect occurs: owing to pinning, solvent and the dissolved polymer are transported to the rim of the droplet during the evaporation.

Thus, polymer is accumulated at the rim leading to a concave surface topology.

As an example of the influence of intrinsic system parameters on the resulting surface structuring, the molar mass of the polymer in the substrate was changed (Fig. 2).



**Fig. 2:** Surface structures (width  $\sim$  400  $\mu\text{m}$ ) on PS of different molar mass after deposition of toluene drops and typical diffraction pattern received with parallel white light from below the concave structure after compensation for light divergence

As for Fig. 1 the deposition of pure toluene on PS with a molar mass of 210 kDa leads to a concave surface structure owing to the coffee-rim effect. In contrast, PS with a low molar mass dissolves and diffuses much faster, especially close to the entanglement molar mass of PS ( $\sim$  20 kDa). Any concentration gradients across the height of the droplet are equilibrated within the time scale of the evaporation: the drop gels as a whole as for the long contact time of Fig. 1.

As a second example of the influence of an intrinsic parameter, the composition of the droplet was changed. Qualitatively, the same sequence as in Fig. 1 or 2 can be observed when a droplet of a solvent mixture is deposited on pure PS. For a droplet with the more volatile solvent and a lower surface tension present in excess, the resulting surface topology after evaporation becomes convex. A tentative explanation assumes a flow of polymer into the center of the droplet, mainly consisting of the less volatile liquid during the last stage of the evaporation.

Since our ink-jet etching technique can be applied in one step on transparent polymers, it is an ideal tool for the use in microfluidic analysis systems.

**Crosslinks to other projects:** Evaporation of Microdrops

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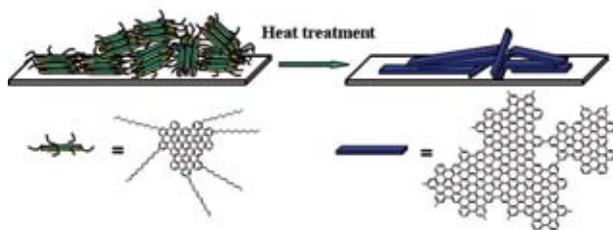
# Transparent Graphene Films for Window Electrodes

X. Feng

*Keywords: Graphene, nanographene, solar cell, indium tin oxide*

Indium tin oxide (ITO) and fluorine doped tin oxide (FTO) have been widely used as window electrodes in optoelectronic devices. These metal oxides, however, appear to be problematic due to the limited availability of the element indium, and the intrinsic chemical and electrical drawbacks. The search for novel electrode materials with good stability, high transparency and excellent conductivity is therefore a crucial goal for optoelectronics.

Graphene forms individual sheets of  $sp^2$ -hybridized carbon bound in two dimensions of which crystalline graphite, the most thermodynamically stable form of carbon, is composed. A great deal of attention has been drawn to its semi-metallic nature, which produces eminent properties such as the quantum Hall effect, ambipolar electric field effect, and transport via relativistic Dirac fermions. Accordingly, all of these unique properties qualify graphene films as one of the prominent electronic materials or components in the area of field-effect transistors, organic solar cells and liquid crystal devices.

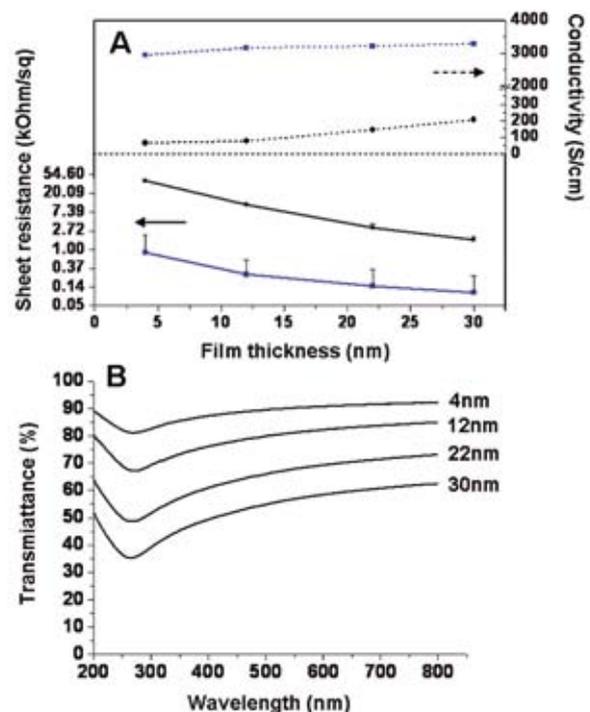


**Fig. 1:** Illustration of the intermolecular condensation of nanographene into graphene film.

A bottom-up chemical approach towards the synthesis of transparent graphene films is achieved by the thermal reaction of synthetic nanographene molecules of giant polycyclic aromatic hydrocarbons (Fig. 1), which are cross-linked and further fused into large graphene sheets. The conductivity is strongly dependant on the substrates, conductivity of  $206 \text{ S cm}^{-1}$  can be obtained for the as-prepared 30 nm thick film on quartz substrate heated at  $1100^\circ\text{C}$ , whereas it is enhanced up to  $3000 \text{ S cm}^{-1}$  by using  $\text{SiO}_2/\text{Si}$  as a substrate (Fig. 2). The transmittance of as-formed graphene films is relatively lower than that of ITO and FTO in the visible region, but bears the advantage of application in the infrared range of wavelengths.

Alternatively, the graphene films can be scalably synthesized by thermal treatment or chemical reduction of graphite oxide. The fabricated graphene films under  $1100^\circ\text{C}$  give conductivities as high as  $730 \text{ S cm}^{-1}$  on quartz substrate (30 nm thickness), comparable to those of polycrystalline graphite, resulting from the effective restoration of conjugated aromatic plane.

Organic heterojunction or dye-sensitized solar cells are fabricated by using of graphene films on quartz substrate as corresponding anode electrodes. Although the performance is still lower than that of ITO and FTO, possibly due to the series resistance of the device and low transmittance, plenty of scope is left for future improvement considering increasing conductivity, transmittance and new fabrication of large-sized graphene films.



**Fig. 2:** A) Sheet resistance (left) and conductivity (right) of graphene film as a function of film thickness; B) Transmittance of graphene film with different thickness.

**Crosslinks to other projects:** Advanced Materials for Solar Cell Applications, Synthesis of Graphene Molecules, Soft Landing and Pulsed Laser Deposition for Thin Films

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# Conjugated Polymers as Semiconductors for High Performance Organic Field-Effect Transistors

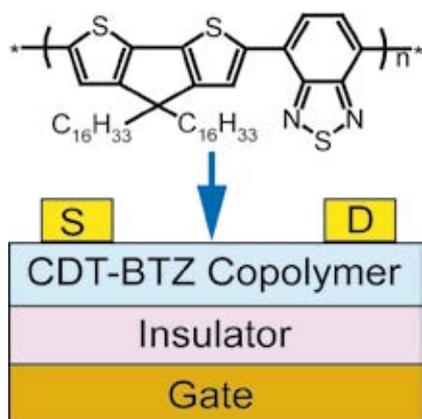
H.N. Tsao, B. Schmaltz, M. Baumgarten

*Keywords: Conjugated polymer, organic field-effect transistor (OFET), dip-coating*

Organic electronics are an attractive alternative to conventional silicon based devices due to its low temperature fabrication and solution processability. Both factors pave the way for flexible, ultra thin, cheap, large area plastic electronics like bendable displays or disposable radio frequency identification tags (RFID) used for information storage and transmission. In this aspect, organic field effect transistors (OFETs) which comprise organic semiconductors play a crucial role and thus have gained increased attention in recent years. For this purpose, small molecules or polymers can be used, but in particularly the polymers are appealing owing to their film forming ability and mechanical flexibility. However, the downturn of polymers is their generally poor molecular order, leading to charge carrier mobilities lower than  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a Figure of Merit quantifying the quality of transistors. For real life applications, a charge carrier mobility higher than this value is required.

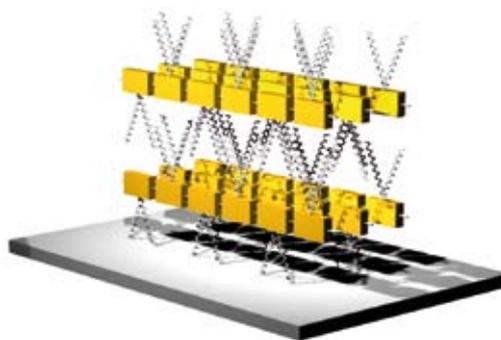
## Donor-acceptor cyclopentadithiophene benzothiadiazole (CDT-BTZ) copolymer OFETs

In order to yield high performance polymer OFETs, a donor-acceptor cyclopentadithiophene benzothiadiazole (CDT-BTZ) copolymer (Fig. 1) was employed, keeping in mind that through interchain donor and acceptor interac-



**Fig. 1:** Chemical structure of  $C_{16}$  substituted cyclopentadithiophene benzothiadiazole (CDT-BTZ) copolymer spin-coated for top-contact OFETs.

tions, a certain degree of order can potentially be achieved by the polymer chains.  $C_{16}$  alkyl chains were introduced to the polymer backbone to guarantee solubility. Solution deposition of this polymer with a number average molecular weight of  $M_n=51 \text{ K g mol}^{-1}$  via simple spin-coating on top contact FET geometry (Fig. 1) resulted in high charge carrier mobilities of up to  $0.67 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Grazing incidence wide angle x-ray scattering (GIWAXS) on this spin-coated polymer layer revealed a lamellar like packing of the polymer chains as schematically presented in Fig. 2.



**Fig. 2:** Schematic presentation of lamellar like packing of the copolymer chains as suggested by GIWAXS.

## Copolymer alignment via dip-coating

Motivated by this excellent transistor performance, the polymer chains were directionally aligned with the aim to even further enhance macromolecular order and charge carrier mobility. This alignment was realized by dip-coating the copolymers. That is, the film was grown by immersing the transistor substrate in the polymer solution and slowly taking the substrate out at a specific rate. An extraordinary charge carrier mobility of  $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was obtained in this way, one of the highest values up to date, rendering this donor-acceptor copolymer system particularly interesting for plastic electronics applications.

**Crosslinks to other projects:** Organic Electronics, Advanced Materials for Solar Cell Applications, Synthesis of Graphene Molecules/Giant  $\pi$ -Conjugated Macrocycles

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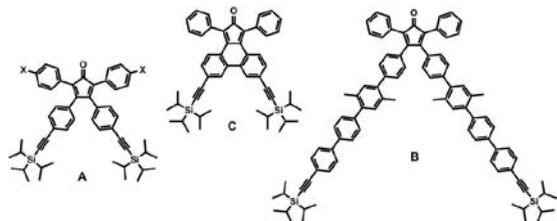
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# Polyphenylene Dendrimers

M. Baumgarten

*Keywords: functional nanoparticles, core-shell, host-guest chemistry, sensing*

Due to their stability, solubility shape persistence, and perfect structure polyphenylene dendrimers are unique three-dimensional macromolecules. Based on the divergent growth of generations, the individual parts as core, branching units, surface, and implemented functional groups they can be adjusted for multiple applications. Besides controlling the shape through multiple core molecules, their size can easily be varied by the different generations or the extension of the branching units. Final surface functionalization can be performed by endcapping with many variable groups, even enabling additional radical polymerization to complex core-shell systems. Furthermore anchored functional groups can be adjusted to set the desired self organization towards defined aggregate or the inclusion of guest molecules. This working principle also allows one to change the polarity of the dendrons and dendrimers and enables the instalment of single or manifold electrolyte functions at the desired place.

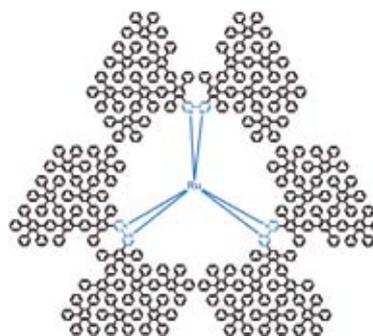


**Fig. 1:** Cyclopentadienone A,B branching units.

Recent achievements have led to size-extended dendrimers by using terphenyl-increased cyclopentadienone (CP) units (Fig. 1 A, B) enabling the synthesis of extended polyphenylene dendrimers up to generation G7 and a molecular weight of 542 000 Dalton.

The classical examples of a core is the tetra(ethynylphenyl) methane, however many more examples of core-functionalized phenylene dendrimers have been realized, like rylene-tetracarboxydiimide or even the aromatic hydrocarbon pyrene. Essential for their use is just the availability of multiethynylated core molecules.

Recently the dendronization of a Ru-bipyridyl complex was achieved (Fig. 2).



**Fig. 2:** Dendronized Ru-bipyridyl complex.

This new synthetic principle introduces positive charge in the core being shielded by the dendrimer shell.

While the polyphenylene dendrimers usually are not fluorescent in the visible range due to the strongly twisted phenylene units, they can be combined with dyes not only in the core, but also at the surfaces or even more interesting in the branching units. A novel approach towards blue emitters for OLEDs was demonstrated by dendrimer growth from the CP unit in Fig. 1C where two neighboring phenyl rings are linked directly in ortho positions. Here the Diels-Alder growth reaction leads to terphenylene units which serve as emitter.

Another approach was to test their function as host particles for inclusion of guest molecules. In cooperation with the University Bonn measurements by microbalance indicated a tendency that aromatic guest molecules can preferable be included. A surprising finding was that with pyridine containing dendrimers the highly explosive trisacetone triperoxide can be detected with a sensitivity of 0.1 ppm. In parallel the precursors hydrogen peroxide and acetone can be detected from such test devices, which may play a crucial role for security in air traffic. The architectural diversification renders these macromolecules as components for the bottom-up fabrication of supramolecular 3D-arrays of nanoparticles with tailored nanoporosity and functionality. Exploitation of the dendritic scaffold for chemical and biological sensing, core-shell systems, hyperbranched carbon-rich polymers, redox-active units, host-guest interactions, and supramolecular assembly are major directions of our scientific work.

**Crosslinks to other projects:** Polyelectrolytes, Electrostatic Self Assembly, BioInterfaces

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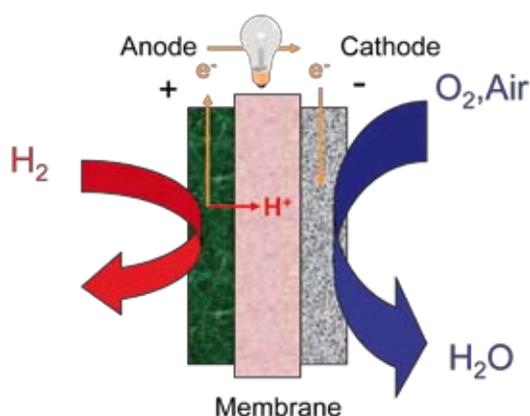
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# Proton Conducting Polymers for Improved Fuel Cell Applications

G. Brunklaus, M. Klapper, W.H. Meyer

*Keywords: Proton conductivity, mobility, membrane, H-bonding, ionomers*

Proton exchange membranes (PEMs) for fuel cells have undergone significant developments during the past decades. Due to a limitation of the operating temperature to about 90 °C, water-based PEMs face several problems including poor carbon monoxide tolerance of the catalyst system, and significant water and methanol transport through the membrane. It has been recognized that these drawbacks may be overcome by increasing the operating temperature to up to 110 °C–150 °C. Great efforts have been made to develop PEMs that provide sufficient proton conductivity at high temperatures and low humidity.



**Fig. 1:** Scheme of a hydrogen powered fuel cell.

A number of projects at the MPI-P aim to improve water-based or phosphoric acid swollen PEMs. In addition, new proton conduction mechanisms are evaluated thus yielding so-called “solvent-free” proton conducting polymers. The latter possibly allows for high-temperature application well above 100 °C provided that the polymeric structure itself is stable enough to tolerate the harsh conditions in a fuel cell.

## Novel approaches to PEMs

The most important factor that significantly influences both the efficiency and performance of a polymer electrolyte membrane within a fuel cell is the appropriate choice of the proton-exchanging polyelectrolyte. An ideal protogenic group should be amphoteric and possess a high dielectric constant. In the case of acid-containing ionomers, the nature of the acid also plays a crucial role while sufficient ordering of the protogenic groups in the bulk compound constitutes another essential requirement for fast proton transport. Indeed, phosphonic acid (PA) based proton conducting polymers fulfill the above requirements.

Moreover, these materials are able to generate acceptable proton transport even at an almost anhydrous state.

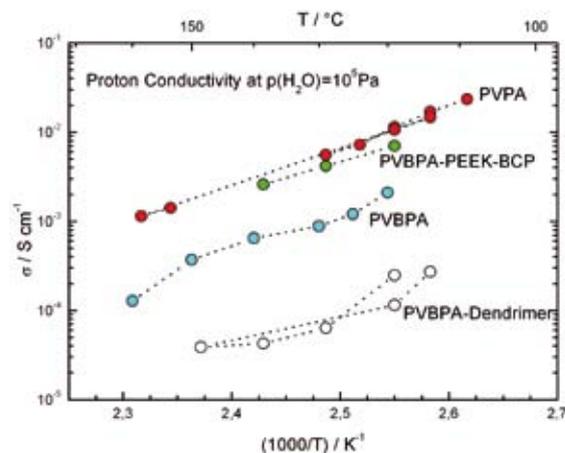
Both the synthesis and characterization of “Solvent-Free Polymeric Proton Conductors” (DryD) are part of a cooperative research project supported by the BMBF within the “PEM Fuel Cells” network.

“Dry” PEMs suitable for high-temperature fuel cell applications based on phase-separated block copolymers, where the protogenic group is tethered to the backbone of one of the polymer blocks, are currently being developed.

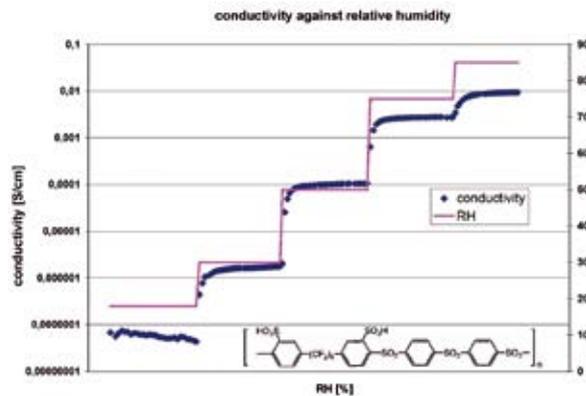
Within the scope of the DryD project, PA-containing polymers with various macromolecular architectures and different spacers that connect the phosphonic acid group to the polymer backbone chain are developed. In particular, linear homopolymers as well as AB- and BAB block copolymers, respectively, are obtained by both free radical- and atom transfer radical processes (ATRP). Compounds such as poly(vinylbenzylphosphonic acid) (PVBPA), its copolymers, as well as well-defined poly(p-vinylbenzyl phosphonate) (PVBPA)-based homo- and AB block copolymers with styrene are prepared. Also, PVBPA/poly(etheretherketone) BAB block copolymers and well-defined PVBPA/poly(2,6-dimethyl-1,4-phenylene oxide) AB block copolymers are synthesized. Indeed, block copolymers of different compositions were obtained in order to study the morphology, thermal behavior and proton conductivities of the corresponding materials (Fig. 2).

Following the so-called “spacer concept”, PA containing ionomers based on a (meth)acrylate structure were proposed. The proton conductors have a more polar structure than the styrene-type phosphonic acids already studied. The polymers exhibited better conducting properties and a minor anhydride formation was observed.

Currently, conducting materials are being studied as a new concept to improve the conductivity in the medium temperature regime (anhydrous state). Actually, the mobility of the chains in poly(vinylphosphonic acid) (PVPA) is limited due to hydrogen bond contacts between neighboring phosphonic acid groups. The introduction of plasticizers in the polymeric membrane should break these hydrogen bonds without decreasing the total quantity of protons in the system. Low molecular weight water insoluble electrolytes,



**Fig. 2:** Proton conductivity above 100 °C under 10<sup>5</sup> Pa water vapour in homo- and blockcopolymers with tethered proton solvents (DryD-Project).



**Fig. 3:** Proton conductivity of sulfonated polysulfones as function of relative humidity (HiPEM-Project).

which can improve the proton conducting properties of the anhydrous proton exchanging membrane once introduced into the system, have been synthesized. The combination of hydrophilic (phosphonic acid groups) and hydrophobic parts should give them the desired properties. This work is mainly performed within the framework of AUTOBRANE, an IP-project funded by the European Commission.

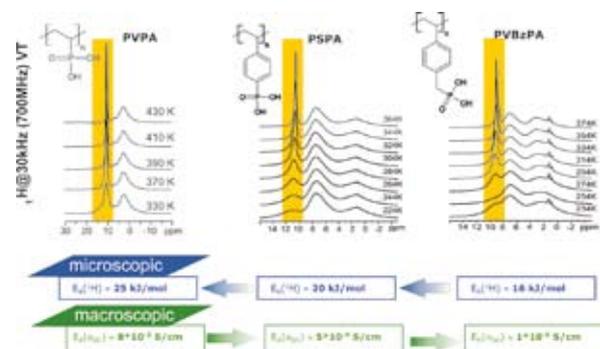
“Optimization of Synthesis and Properties of Sulfonated Polysulfones for PEM Applications”, “HIPEM”, is a co-operative project supported by the BMBF. With partners from the universities of Darmstadt, Dresden and the MPI for Solid State Research in Stuttgart highly sulfonated polymers are being optimized with respect to their synthesis procedures and film-forming properties for use in fuel cell applications. These rather “conventional” materials are proton conductive in the water-swollen state only, but offer the advantage of being more easily processed, more stable and cheaper than typical ionomer membranes like Nafion® (Fig. 3).

### Solid-state NMR characterization of PEMs

Solid-state NMR spectroscopy is a powerful tool with unique selectivity that allows for the determination of local structural arrangements as well as dynamics. Since NMR does not require long-range structural order, it is an exceptionally suitable method for the study of less-ordered or even amorphous but functional materials.

In particular, we highly benefit from the unprecedented resolution offered by our recently obtained high-field 850 MHz magnet and its ultra-fast magic-angle-spinning NMR equipment.

Within the different projects, we use advanced solid-state NMR methods to identify possible mechanisms of proton transport in PEMs on a molecular level. While a presence of “dynamic” hydrogen bonds (fast bond-rupture and (re-) formation) is highly desired, preferably without interfering water or solvent-like molecules, local proton mobilities are not always successful in contributing to a long-range proton transport observable in bulk PEMs. Solid-state NMR also provides insights into the geometry of those motions that possibly govern this long-range proton transport, which is indeed crucial for a systematic improvement of PEMs. In the case of PVPA, PSPA, and PVBzPA, respectively, the corresponding  $^1\text{H}$  chemical shift of the protogenic group decreases from 10.8 ppm (PVPA) to 9.8 ppm (PSPA) and 8.6 ppm (PVBzPA), thus revealing substantial weakening of the hydrogen-bonds while the local proton mobility is unaffected. This clearly demonstrates that though the spacer has a strong impact on the formation of a locally-ordered hydrogen-bonded network, the hydrogen-bond strength is not simply related to local proton mobilities and hence long-range transport.



**Fig. 4:** Variable-temperature  $^1\text{H}$  MAS NMR spectra of PVPA, PSPA and PVBzPA, respectively. Note the decrease of apparent activation energies  $E_A(^1\text{H})$  while the observable bulk proton conductivities  $E_A(\sigma_{DC})$  also decrease (DryD-Project).

**Crosslinks to other projects:** Solid-State NMR, Impedance Spectroscopy, Hydrogen-Bonded Aggregates

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# Lithium-Ion Conductivity in Polymers: Concepts and Novel Materials

W.H. Meyer, G. Wegner

*Keywords: Li-ion solvent, tethering, mobility, conductivity, relaxation*

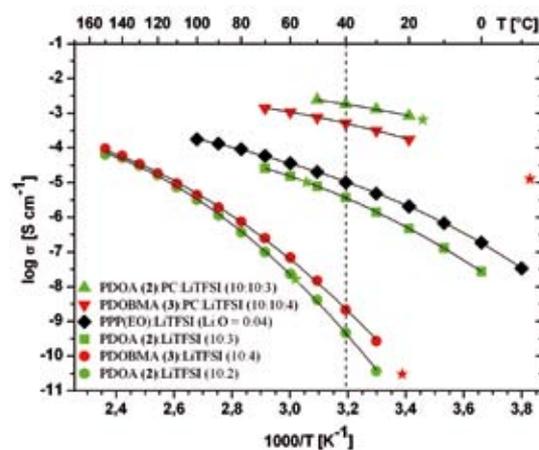
The development of rechargeable lithium batteries is a milestone in the field of energy storage and supply for electrical and electronic devices. In such batteries Li ions are solvated by organic solvents and they diffuse freely between the anode and cathode, which are physically isolated from each other by a separator membrane. Solutions of Li salts in ethylene carbonate (EC) and propylene carbonate (PC) fulfil reasonably well the requirements of safety and market concerns and are thus the solvents of choice for current commercial applications.

However, Li batteries, which contain liquid organic electrolytes, pose potential safety hazards in the case of abrupt leakage or in the case of overheating during sudden and uncontrolled discharge (“short circuits”). The problems encountered with liquid electrolytes could be avoided using polymers as a Li ion solvating matrix. P.V. Wright’s discovery that alkali metal salt complexes of poly(ethylene oxide) (PEO) show substantial ionic conductivity was the starting point for extensive research to develop so-called solid polymer electrolytes (SPEs).

While it was initially assumed that the crystalline domains formed by the PEO-salt complex are responsible for ion transport, it was soon established that it is solely the amorphous phase of the complexes which is responsible for conductivity. The conductivity is thus related to the segmental motion of the polymer, and its temperature and frequency dependence scales with the glass transition phenomena. This restricts the principally achievable magnitude of Li ion conductivity to values of the order of  $<10^{-4}$  S cm $^{-1}$  at 30°C and prevents SPEs from broad commercial application in Li batteries.

Since EC has proven to be an excellent solvent for Li salts we were tempted to tether the structural element of EC to the side chain of a suitable polymer. This approach follows our more general line of “immobilizing” ion solvents, a concept which already proved successful with proton conducting polymers. In order to allow for high local mobility these structural elements should be dynamically detached as much as possible from the main polymer chain; in other words, a spacer should assist in separating the main chain (polymer) dynamics from the motion of the Li solvating elements. We prepared a series of acrylates and methacrylates with 2-oxo(1,3)dioxolane (cyclic carbonate) containing side chains and studied their potential as polymeric solvents of Li salts in the context of the requirements for SPEs in Li batteries.

These polymers have acceptable thermal stability and exhibit glass transition temperatures in the range typical for poly(acrylates) and poly(methacrylates) between 11°C and 93°C, the actual value depending on the structure of the main and side chains. All of these polymers are good solvents for Li salts, e.g. LiN(CF $_3$ SO $_2$ ) $_2$ . Blends of the homopolymers with this salt gave very good ion conductivity. Addition of small amounts of PC caused a further and substantial increase in conductivity up to ca.  $2 \times 10^{-3}$  S cm $^{-1}$  at 40°C. (Fig. 1).



**Fig. 1:** Temperature dependence of conductivity of blends of Li salts with poly(meth)acrylates with tethered EC side chains

The temperature dependence of ion conductivity follows a modified WLF-type with a reference temperature which points toward the ion mobility being controlled by side chain dipole relaxation modes rather than by the main chain relaxations.

## Further Approaches for High Conductivity

Since tethering of the ion solvents usually causes a conductivity loss of about 1-2 orders of magnitude as compared to the liquid electrolyte, we are reaching further approaches to improve ion conductivity:

- tethering ion solvents to low  $T_g$  polymers which themselves are liquids at RT;
- combining these liquid polymer electrolytes with a polymer hard phase in block copolymers;
- introducing oligomeric structures for internal softening;
- combining the advantageous properties of ionic liquids with that of polymers.

**Crosslinks to other projects:** Proton Conductive Polymers for Improved Fuel Cell Applications, Hydrogen-Bonded Aggregates, Pushing the Limits of Solid-State NMR

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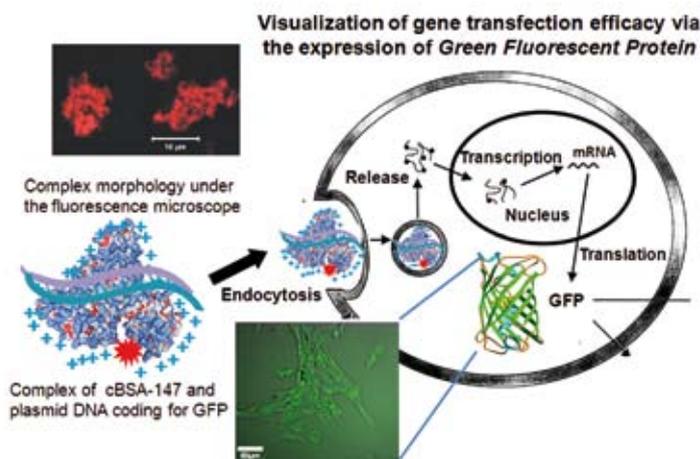
# Chemically Modified and Artificial Proteins

T. Weil

*Keywords: Chemically modified albumins, gene transfection, nano-carrier, unnatural amino acids*

## Proteins as nanoscopic and multifunctional macromolecules

Proteins can be recognized as multifunctional nanoscopic macromolecules bearing a variety of functional groups at distinct locations within their scaffold. Chemical modifications are usually introduced (1) via reaction of accessible amino acids (e.g. lysine, glutamic acid, cystein) with an appropriate reagent. Alternatively, unnatural amino acids bearing a reactive group could be introduced (2) via selective pressure incorporation by feeding them to bacteria cells, which are not able to produce the natural amino acid (auxotrophic strains). In the case of high structural similarity of natural and unnatural amino acids, the unnatural amino acid is recognized by the cellular translation machinery and incorporated into the protein sequence. We usually name proteins according to (1) chemically modified proteins or (2) artificial proteins.



**Fig. 1:** Only stable complexes of BSA-147 with 147 primary amino groups on average and plasmid DNA coding for the expression of green fluorescent protein (GFP) are up taken via clathrin-mediated endocytosis and reveal a high GFP expression in the different cell lines. The morphology of such complexes was studied via fluorescence microscopy and light scattering. In this way, a correlation between the transfection efficacies and complex morphologies was found which facilitated a better insight into the mechanisms involved in gene transfection.

## Albumin polyelectrolytes

Charges play an important role in cell biology. Negatively charged membranes regulate the cellular uptake and efflux of molecules or macromolecules. In the cell nucleus, positively charged histone proteins form highly ordered histone octamers that interact tightly with negatively charged DNA thus forming the nucleosome for storing the genetic material. Important cellular processes, such as the transcription of DNA, are regulated by modifications of the charge density of histone proteins and DNA. To date, the underlying mechanisms and the involved morphological changes of gene storage and gene transcription are still not fully understood. We have achieved the preparation of differently charged albumin species in order to control complex formation with plasmid DNA via chemical coding of the protein surface. In this way, an attractive and efficient non-viral delivery device cBSA-147 was achieved via a

knowledge-driven approach investigating the impact of controlled chemical modifications on the *in vitro* profile of the native protein. Significantly improved expression of the green fluorescent proteins compared to the commercially available, non-viral vector Lipofectamine 2000 displaying a considerably higher cytotoxicity was achieved even in cell lines that are usually difficult to approach.

## Artificial Ribonuclease A (RNaseA)

Ribonuclease A (RNase A) is an endonuclease that cleaves to single-stranded RNA. We have developed an expression system for gaining artificial RNaseA in an auxotrophic strain. Our main goal includes the introduction of positively and negatively charged polymer or oligomer

chains in order to intentionally switch the functional activity of RNase.

Our investigations demonstrate that proteins are attractive shape-persistent, monodisperse and multifunctional building blocks for performing distinct chemical modifications, which significantly affect their functional *in vitro* profile.

**Crosslinks to other projects:** Scanning Probe Microscopy, Polyphenylene Dendrimers, Functional Dyes and their Applications, BioInterfaces

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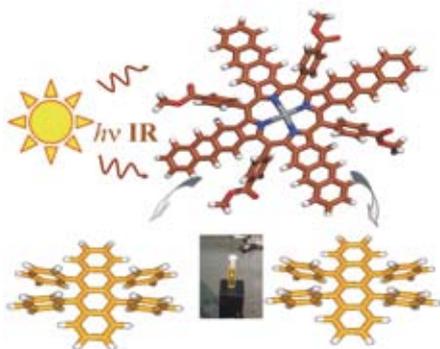
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# Triplet-Triplet Annihilation in Viscous Matrix: Application in Dye-Sensitized Solar Cells and All-Organic Up-Conversion Displays

S. Balouchev

*Keywords: Non-coherent upconversion, all-organic display, sun-light concentrator, solar cells*

The examples of upconversion (UC) described in the literature such as simultaneous or sequential absorption of two or more photons with lower energy, second and higher harmonic generation of the fundamental wavelength and parametric processes have been commonly associated with the use of *coherent* light sources (lasers) and very high excitation intensities. In contrast with all previously described methods the fundamental advantage of the energetically conjoined triplet-triplet annihilation (TTA) photon up-conversion process is its *inherent* independence on the coherence of the excitation light. Another principal advantage of this up-conversion process is the very low intensity (as low as  $100\text{mWcm}^{-2}$ ) and extremely low spectral power density (as low as  $125\ \mu\text{Wnm}^{-1}$ ) of the excitation source needed (it can be the sun).



**Fig. 1:** Palladium complex of the synthesized tetraaryltetraanthraporphyrin was demonstrated experimentally to enable the energetically-conjoined TTA with excitation wavelength in IR-region ( $\lambda \sim 800\ \text{nm}$ ), excited at ultra low light intensity of  $100\ \text{mWcm}^{-2}$ . The upconversion process has a very high quantum yield of 1.2%.

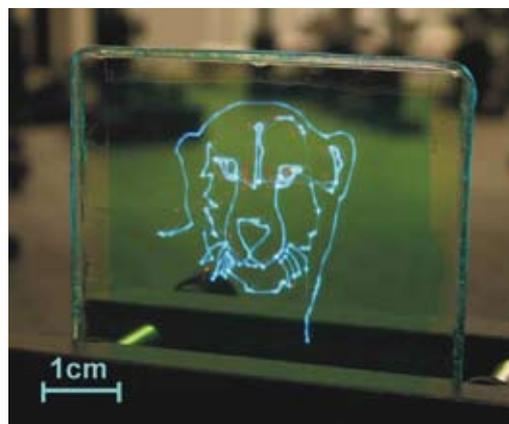
A direct increase in the spectral brightness of the short wavelength region of the solar spectrum by using photons from the longer wavelength region remains a very considerable challenge.

For solar cell applications photons are of great importance, notably spectrally blue shifted to the wavelength of the

excitation photons with an energy shift between 10 kT- 100 kT.

## All-organic UC Display

In Fig. 2 the world's first all-organic, transparent, flexible, versatile color display based upon triplet-triplet annihilation-assisted photon up-conversion is presented. The devices work with ultra-low excitation intensities down to  $10\ \text{mWcm}^{-2}$  red/near-IR light. The displays are based on metallated-porphyrin sensitizers in combination with emitters in a transparent matrix and are driven by galvano-scanned laser diodes. The displays have an external quantum yield as high as 3.2%. The response time can be adjusted to specific application requirements – from  $1\ \mu\text{s}$  to  $100\ \mu\text{s}$  allowing for a kHz-refreshment rate of the displayed information. It is easily possible to tune the optical density of the screens in order to obtain the desired transmittance for the excitation beam. We were able to achieve multicolour emission using only one excitation source. There are practically no display size limitations and it is a very simple, cost-effective method of fabrication.



**Fig. 2:** A CCD-camera image of an all-organic 2D-display. Dimensions –  $60 \times 60\ \text{mm}$ ; polycarbonate substrate; frontal excitation. The excitation intensity is less than  $25\ \text{mWcm}^{-2}$ ,  $\lambda=635\ \text{nm}$ , sampling frequency –  $8\ \text{kHz}$ . The emission is centered at  $\lambda=485\ \text{nm}$ , FWHM  $\sim 40\text{nm}$ . No blocking filters were used, day-light conditions.

**Crosslinks to other projects:** Nanolithography with Nanoparticles, Non-aqueous Emulsions, Bio-responsive Hybrid Nanoparticles, BioInterfaces

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## Porous Oxide Nanoparticles

C.K. Weiss, K. Landfester

**Keywords:** *Inverse miniemulsion, porous nanoparticles, soft templating, confined reactions, sol-gel process*

Gas storage, sorption, separation, or catalysis are only a few examples of research areas where large specific surfaces of metal oxides are crucial for high performance applications. External surfaces can be created by finely dividing macroscopic matter to nanosized entities. Even higher surface areas can be created by giving matter an inner, porous structure. Pore-size tailoring further enhances the specificity and performance of such porous nanoparticles. A well-known way for the generation of pores in the nanometer range is templating with lyotropic phases. The metal oxide is generated during a sol-gel process in the presence of a structure-inducing surfactant. Confining these processes to a droplet of  $< 1 \mu\text{m}$  leads to the formation of metal oxide nanoparticles with an inner, (ordered) porous structure.

This can be realized by creating a miniemulsion of an aqueous solution of water soluble precursors for metal oxide formation and, if desired, a structure inducing surfactant (e.g. CTAB, Pluronic P123), finely dispersed in an organic solvent. A non-ionic block-copolymer is required for droplet stabilization. After particle formation, an optional calcination step can be performed in order to remove residual organic material.

Final particle characteristics such as their morphology, internal structure, crystallinity and specific surface are delicately dependent on the choice and amount of precursor, the reaction parameters, such as temperature, pH, amount of surfactant, etc. This forms a toolbox for fine tuning the particles for the desired application.

Silica particles, for example evolve from solid to porous particles (Fig 1, left) and finally to hollow, porous capsules or structured porous grids according to the chosen reaction parameters.

The application of the water soluble precursor bis(2-hydroxyethyl)titanate leads to aggregates of nanocrystalline titania. While the reaction temperature determines the titania phase (anatase or rutile), the specific surface can be controlled by the amount of surfactant added for droplet stabilization. These anatase nanoparticles have successfully been used as anode materials for Li-ion batteries and as support materials for gold nanoparticles applied in CO-oxidation reactions.

The combination of different water soluble precursors of e.g. titania and zirconia in one miniemulsion droplet yields mixed oxide particles.

These examples demonstrate the potential of this approach. Virtually any water soluble precursor, suitable for sol-gel condensation, can be utilized, permitting the synthesis of a great number of (ordered) porous nanoparticles.



**Fig. 1:** Porous particles prepared with the inverse miniemulsion technique. Left: porous silica particles. Middle: nanocrystalline anatase forming porous aggregates. Right: amorphous  $\text{Zr/TiO}_2$  mixed oxide nanoparticles.

**Crosslinks to other projects:** Reactions in Confined Geometries, Hybrid Nano-Assemblies

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# Polymeric Nanoparticles and Interaction with (Stem) Cells: Uptake, Intracellular Trafficking and Cellular Responses

V. Mailänder, K. Landfester

*Keywords: Nanoparticles, nanocapsules, (stem) cells, endocytosis, drug delivery*

Nanoparticles in biomedical applications have attracted a lot of interest in the last few years. First applications involved submicron particles attached to cells by antibodies in order to sort a specific cell from a cell mixture (e.g. hematopoietic stem cells from bone marrow or blood). Superparamagnetic iron oxide nanoparticles have also been employed for magnetic resonance imaging (MRI) as contrast agents.

Recently, it became clear that nanoparticles are taken up by cells so that homing and migration of cells can be followed. Therefore, we started investigating nanoparticles (commercially available and specially designed) as to how we could enhance nanoparticle uptake into cells. First, we used nanoparticles with specifically designed surface properties. A series of fluorescent nanoparticles from a copolymer (e.g. styrene/acrylic acid, styrene/2-aminoethyl-methacrylate hydrochloride [AEMH]) was synthesized by the miniemulsion technique. In this process a fluorescent dye was also incorporated. Consequently cellular uptake was observed by a fluorescent cell sorter (FACS), confocal fluorescent microscopy as well as TEM and SEM. These surface modifications resulted in an approximately 15x higher uptake of nanoparticles compared with uncharged nanoparticles, when the surface was decorated by carboxy groups (styrene/acrylic acid). A positive charge by amino groups (styrene/AEMH) resulted in ca. 70x higher cellular

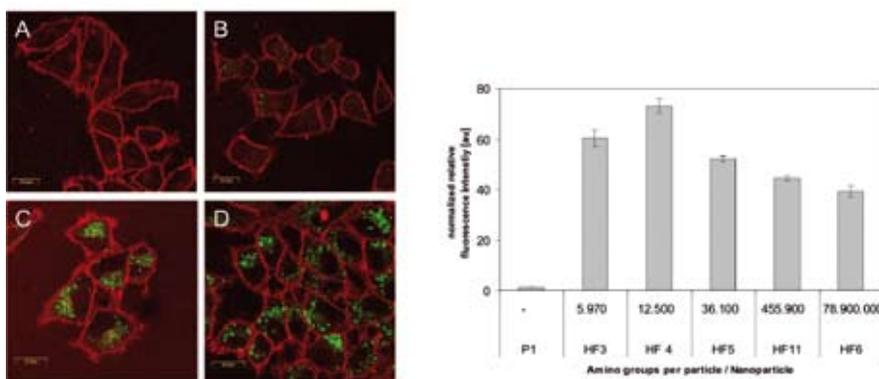
uptake rate. Using the amino acid lysine coupled to the carboxy group resulted in an even higher uptake, hereby mimicking the effect of transfection agents.

By using polyethyleneglycol on the nanoparticle surface, uptake by cells was hindered ("stealth nanoparticles"). Furthermore, we investigated other types of non-biodegradable (polyisoprene, polymethylmethacrylate) and biodegradable (poly-L-lactide, poly-ε-caprolactone) nanoparticles and their uptake behavior.

By using pharmacological inhibitors we dissected the different ways of nanoparticle uptake. These studies are ongoing and are extended to specific surface modifications and polymeric materials.

Uptake of nanoparticles into the brain, i.e. crossing the blood brain barrier with nanoparticles (polybutylcyanoacrylate) has already been achieved in an animal model.

Besides fluorescent labels, superparamagnetic iron oxide particles and gadolinium complexes as reporters, that can be used in a clinical MRI scanner, were also incorporated into these polymeric nanoparticles making them very versatile and flexible tools ("dual reporter nanoparticles"). We have started to investigate nanoparticles as drug carriers and will work on making them responsive to the outer environment (e.g. degradation upon decrease in pH as in lysosomal compartments inside the cells).



**Fig. 1:** On the left confocal laser scanning microscopy images are shown demonstrating intracellular uptake of carboxy functionalized nanoparticles (styrene/acrylic acid NPs). On the right side uptake of amino functionalized nanoparticles is quantified by FACS.

**Crosslinks to other projects:** Particles for Central Nervous System Targeting, Multifunctional Polymer Capsules, Bioresponsive Hybrid Nanoparticles

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# Elucidating Columnar Mesophases of Extended $\pi$ -Electron Systems

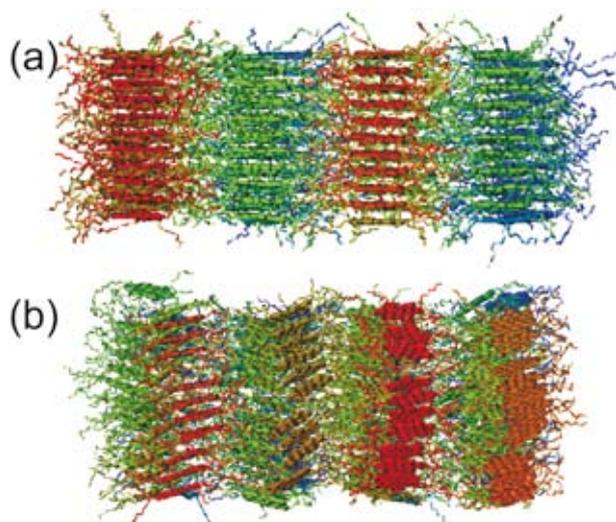
D. Sebastiani, D. Andrienko, R. Graf

*Keywords: Computational chemistry, solid-state NMR, discotic mesophase*

During the last decades the phenomenon of complexity has attracted increasing attention in many areas of science. While the fundamental physical laws that govern the interaction between atoms and molecules are well-established in the framework of quantum mechanics, the concerted motion of extended aggregates is still a formidable challenge due to the complexity of these phenomena.

In a collaborative effort, we have investigated discotic mesophases by means of classical molecular dynamics simulations (the snapshots of a typical discotic liquid crystal with different side chains are shown in Fig. 1), solid-state nuclear magnetic resonance (NMR) spectroscopy, and electronic structure calculations. A unique correlation was established between the molecular structure, the supramolecular morphology, and charge carrier mobility of mesophases made of polycyclic aromatic hydrocarbon (PAH) molecules. Their recent application in organic photovoltaic (OPV) devices relies upon blend films combining a large interfacial area for charge separation with an efficient vertical transport path.

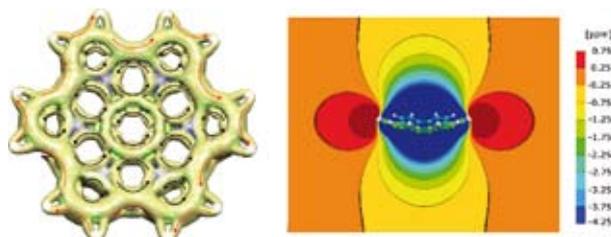
In organic materials, charge transport proceeds by incoherent hopping and depends upon both local molecular ordering and macroscopic percolation.



**Fig. 1:** MD simulation snapshots of columns of HBC molecules with different side chains at  $T=300$  K. Columns are prearranged on a rectangular lattice.

Advanced solid-state NMR methods are applied in combination with molecular electronic structure computations to experimentally probe local molecular packing arrangements in the mesophases.

Variations of the electronic nature of the PAHs, without modifying the structure, can be obtained introducing heteroatoms such as nitrogen to the molecules. This was recently demonstrated in the case of hexapyrrolohexaazacoronenes.



**Fig. 2:** Electronic ring currents and nucleus independent chemical shift maps of a nitrogen-doped PAH.

These were electronically and spectroscopically characterized by means of first-principles electronic structure calculations of the response of the aromatic electron system to external magnetic fields.

This is illustrated in Fig. 2, where the electronic ring currents (left) and the resulting induced magnetic screening of the surroundings of the heterocycle are plotted. It could be demonstrated that the interior nitrogen atoms play an important role in stabilizing higher oxidation states of PAHs, making them specially interesting as electrochromics and as charge-carrier materials.

Further ongoing research efforts attempt to understand the relationships between side chain characteristics and microscopic morphology, in particular the relative pitch angles in the supramolecular stacks. The latter in turn are directly related to macroscopic properties, such as electronic conductivity.

**Crosslinks to other projects:** Solid-state NMR Spectroscopy, Molecular Dynamics Simulations, Electronic Structure Calculations

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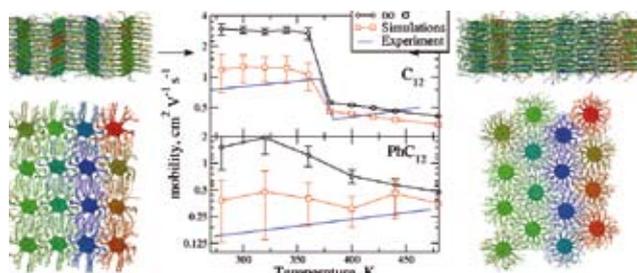
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# Organic Electronics: Structure-Property Relations

D. Andrienko, X. Feng

**Keywords:** Charge transport, molecular dynamics, synthetic chemistry, rational compound design

The quintessence of organic materials lies in the ability of controlling their properties using synthetic methods. Electronic structure, self-organization abilities, stability, ease of processing – all these properties can be adjusted by choosing a suitable chemical structure of a material.



**Fig. 1:** Morphologies of small domains of a discotic material, as simulated with molecular dynamics, in herringbone and hexagonal mesophase. Plot shows experimental and calculated PR-TRMC hole mobility as a function of temperature.

To design a compound with appropriate properties is, however, an extremely challenging task. One can try to systematically vary the molecular architecture, assessing at the same time how this variation affects the performance of a particular device. This strategy is not very successful: small variations in the structure often result in a complete loss of self-assembling properties or inability to transport charge carriers. In other words, it is rather difficult to define a “small variation” in the chemical space. In addition, synthesis of new compounds is time-consuming and requires significant efforts from organic chemists. It is useful to pre-screen the compounds by evaluating their properties prior to actual synthesis. Here computer simulations can help to establish appropriate structure-property relations and aid rational design of compounds.

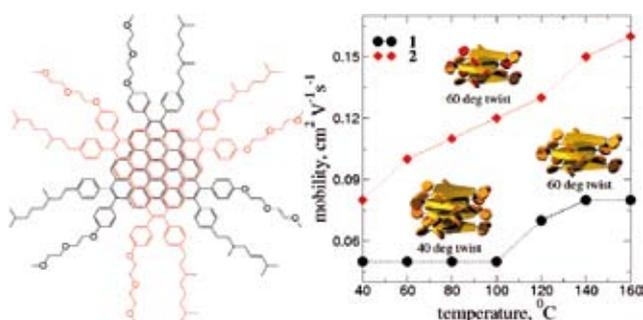
We developed parameter-free methods designed to describe charge transport in molecular solids, which is based on models of nonadiabatic charge transfer between molecules (or conjugated segments in the case of polymers). This approach combines three methods into one scheme: (i) quantum chemical methods for the calculation of molecular electronic structures and reorganization energies (ii) molecular dynamics for simulation of the relative positions

and orientation of molecules, and (iii) kinetic Monte Carlo simulations and Master Equation approach to simulate charge transport.

This method was successfully tested on columnar phases of several discotic liquid crystals, such as derivatives of hexabenzocoronenes, perylene diimides. Excellent agreement with the experimental data (see Fig. 1) made us confident that the developed approach is able to predict charge mobilities without any fitting parameters, and, most important, allowed us to establish a link between the molecular structure and charge mobility. We have also gained an insight into how the electronic structure can be plausibly combined with the mesoscopic morphology of the material in order to maximize the charge carrier mobility of a discotic mesophase.

As a result, a trizigzag-shaped polyaromatic hydrocarbon (see Fig. 2) arranged in a helical fashion has been designed, synthesized, characterized and shown to be superior to hexabenzocoronene in a plastic crystalline mesophase. A helical arrangement of the molecules in the columns maximizes the value of the charge transfer integral; large conjugated core insures smaller reorganization energy. This favors faster Marcus’ hopping rates and hence the higher charge mobility.

The developed simulation software is available online: [csgth.mpip-mainz.mpg.de](http://csgth.mpip-mainz.mpg.de)



**Fig. 2:** Molecular structure (two molecules with a 60° twist are shown) and PR-TRMC mobilities of plastic crystalline mesophases of a trizigzag-shaped PAH.

**Crosslinks to other projects:** Synthesis of Graphene Molecules/Giant  $\pi$ -conjugated Macrocycles, Elucidating Columnar Mesophases of Extended  $\pi$ -Electron Systems

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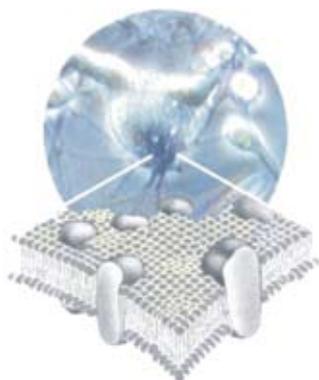
## BioInterfaces

E.-K. Sinner

**Keywords:** Biomimetics, synthetic biosystems, biosensors, membrane protein synthesis

Processes in living nature, such as biochemical pathways, are highly complex; experimental approaches are still compromised by the subtle functional-structural relationship of the “players” involved. Nevertheless, the complexity of a cellular model system tends to “hide” the individual interaction partners, which are interconnected by subsequent biochemical cascades comprising the smallest “living” entity on earth, the cell.

These cascades mostly start with the triggering of a membrane protein receptor, the “antennae” of a cell. For an antenna to perform different signal versions, various receptor-species exist, such as photoreceptors, mechano-receptors, potential-difference receptors, ion-gated receptors and ligand-gated receptors. These protein species underlie the concept of molecular recognition – the structural-functional correlation, which is encoded by the amino-acid sequence, the “building blocks” of these receptors. We transfer these building blocks onto an artificial surface, resembling the membrane of a cell as a matrix, in order to preserve the functionality of certain receptors. Why are we interested in mimicking the bio-membrane? Because we want to understand the underlying concepts of molecular recognition. We aim at using these receptors as functional units of bio-membranes for sensing purposes, such as signal perception, transduction, ligand screening and identification of biological entities, such as bacterial species or even viral particles.

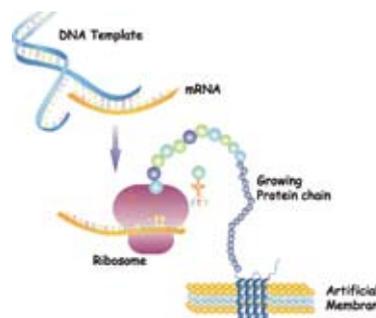


**Fig. 1:** A light-microscopic image of a mammalian cell, with a schematic magnification of the cell-membrane – pointing out the architecture of a membrane, embedding the membrane proteins.

This would have been easy if membrane proteins did not belong to the class of complex amphiphilic entities. Not many membrane proteins have been resolved in molecular

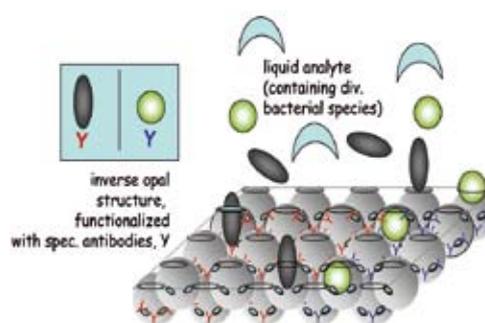
resolution, since crystallization bears intrinsic drawbacks, if it is applied on membrane proteins.

The challenge is how to get these subtle receptors in a format, where they can withstand the synthetic material as surrounding matrix? Our approach is to start on the genetic level, using the basic genetic information of the protein as a template.



**Fig. 2:** Scheme of steps, involved in the *in-vitro* synthesis of membrane proteins in artificial membrane surfaces.

The strategy of *in vitro* synthesis allows synthesis of specific molecules of interest directly in the vicinity of synthetic materials, such as amphiphilic block-copolymers, hydrogels, synthetic lipids and isolated lipids. The resulting protein-functionalized surfaces are the counterparts of cell membranes, still providing the molecular properties of their native background. Our goal is to compile protein-functionalized interfaces in the complex cellular context in order to generate biomimetic, synthetic architecture, relevant in protein-lipid interaction, protein-ligand interaction and signal transduction.



**Fig. 3:** A biofunctionalized surface for bacterial sensing applications. An inverse opal structure (in collaboration with U. Jonas, Q. Li,) is modified with specific antibodies, targeted against bacterial species of interest.

**Crosslinks to other projects:** Chemically Modified and Artificial Proteins, Model Membranes, Optical Single Object Detection

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# Conjugated Polymers for Ultrafast All-Optical Switching

C. Bubeck

**Keywords:** Third-order nonlinear optics, nonlinear optical susceptibility, hyper-polarizability, conjugated polymers, intensity dependent refractive index, two-photon absorption, waveguide, prism coupling

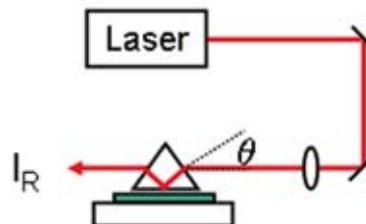
The switching of light by light is based on the intensity dependencies of the refractive index or the absorption coefficient, which are third-order nonlinear optical processes. Conjugated polymers are known to be the most suitable materials as they have the largest nonlinearities due to their highly polarizable one-dimensional  $\pi$ -electron system. Interest in their properties is growing as recent publications show that they can be combined favorably with silicon-based photonic integrated optical circuits offering unprecedented terahertz modulation frequencies, which are needed at telecommunication wavelengths in the range of 1500 nm.

This project involves measurements and model calculations of the intensity dependencies of the refractive index and absorption coefficient of conjugated systems by means of strong picosecond laser pulses tunable in the near-infrared range. In this range the nonlinear optical spectra of conjugated systems are usually dominated by two-photon excitations of electronic states. This causes resonance enhancement of the cubic nonlinearities. Our aim is an improved understanding of relations between chemical structure of conjugated systems, morphology and optical properties of thin film waveguides, which will help us to design appropriate materials to satisfy the application criteria for all-optical waveguide switching.

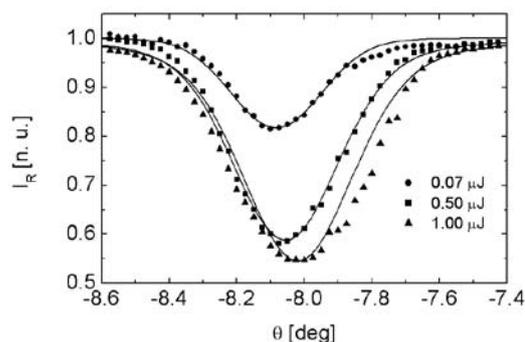
The preparation of thin film waveguides with low mode propagation losses is another challenge, because deleterious light scattering usually happens if sufficiently large aggregates appear in the films. This can be a significant problem with conjugated polymers or dye systems as their structures are rigid and favor nematic-like ordering phenomena, in particular at interfaces. Control of such ordering phenomena is a challenge in other research projects of organic electronics as well.

We use a Nd:YAG laser, which pumps an optical parametric generator-amplifier yielding intense pico-second laser pulses at 680 – 2000 nm for nonlinear optical spectroscopy. In the z-scan technique, the sample is moved through the focal region of a lens, which causes intensity variations to derive sign and magnitude of the nonlinear refractive index. Two-photon fluorescence excitation spectroscopy provides the two-photon absorption spectra of chromophores.

Thin films are studied with third-harmonic generation spectroscopy, and prism coupling of waveguide modes, see Figs. 1 and 2.



**Fig. 1:** Schematic view of prism coupling. The laser beam is totally reflected at the prism base. Its evanescent field couples through the air gap and excites a waveguide mode in the film at an appropriate entrance angle  $\theta$ . This causes a reduction of the reflected intensity  $I_R$  depending on refractive index and absorption coefficient of the waveguide.



**Fig. 2:** Experimental demonstration of intensity-dependent prism coupling using a slab waveguide of the conjugated polymer MEH-PPV. The angular dependencies of the reflected intensities  $I_R$  were measured at various pulse energies. This results in an ultrafast refractive index and absorbance change of the waveguide and causes a fully reversible change of  $I_R$ .

Recently, we showed that waveguides of the conjugated polymer MEH-PPV already satisfy the application criteria for all-optical waveguide switching, however at 1100-1200 nm. We continue to search for conjugated systems which show similar effects at longer wavelengths.

**Crosslinks to other projects:** Optical Spectroscopy and Thin Films, Functional Dyes and Their Applications, Organic Electronics: Structure-Property Relations, Elucidating Columnar Mesophases of Extended  $\pi$ -Electron Systems, Two-Photon Nanolithography on Photo-Sensitised Organic Monolayers

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# Approaches to Synthesis



# Approaches to Synthesis

K. Müllen, K. Landfester

**W**e are living in a material world..." (quoted from Madonna). Indeed, there can be no technological or modern-day progress without new materials – which must be synthesized. Many materials are of a polymeric nature which indicates the key role of polymer synthesis. Competence in synthesis is therefore a cornerstone of our institute.

Although such a synthesis must be practical and provide sufficient quantities, the limitations of the synthetic method with respect to the occurrence of side products and structural defects must be carefully investigated. Polymer synthesis thus plays a dual role: on the one hand the researcher can rely upon established synthetic methods and focus on known polymer structures; on the other hand, he can design novel methods of synthesis and aim for unprecedented targets. The novel methods approach also has a dual character, because the research concept can be significantly different, depending on whether the work is more method- or structure-oriented. Not long ago, the search for new polymers was regarded as obsolete, since most of the important goals of polymer research were supposed to be achievable using classes of compounds then available. Interest in polymer synthesis has since been revived, however, by several events including:

- the utilization of new synthetic methods developed in organic and organometallic chemistry, and this interdisciplinary approach has greatly increased the efficiency and scope of polymer synthesis,
- the introduction of novel polymer topologies made from biopolymers and synthetic polymers or equally important synthetic polymers and inorganic materials,
- the discovery that macromolecules have the potential to form supramolecular assemblies with unique properties.

The focus of polymer research cannot be restricted to molecular structures, but we also have to consider supramolecular ordering at different length scales. While the relevant intermolecular forces may well depend on the conditions of processing, there is the additional challenge for polymer synthesis to prearrange supramolecular effects, e.g. by incorporating units able to self-assemble and thus encode factors for supramolecular structure formation.

Research directed towards electronic materials and devices relies heavily on the synthesis of new structures. Classical chain structures such as polyphenylenes and poly(phenylene vinylene)s do not cover the full scope. New two- and three-dimensional conjugated polymers which we have introduced allow careful tuning of electrical, optical and even magnetic properties. Carbon-rich polymers are of particular interest because of their unique chemical properties and their role as graphite-related electronic materials.

Creative structure design and the use of methods from organic chemistry have produced remarkable results including shape-persistent dendritic polyphenylenes and giant polycyclic aromatic hydrocarbons as processable graphenes. Graphenes are presently one of the hottest topics of solid-state physics due to their outstanding properties such as ballistic charge transport and quantum Hall effect. These single-sheet materials are obtained by exfoliation from graphite. Such methods define an urgent need for a synthetic "bottom-up"-approach toward perfect graphenes, and this becomes possible when using our well-defined polyphenylene precursors.

The so-called nanosciences have recently attracted great attention, since they offer opportunities for visualizing and manipulating single molecules or nano-sized aggregates made from a few molecules.



While sophisticated physical methods are required, synthesis plays an indispensable role: it provides designer-made molecular objects of well-defined size, shape and dimensionality, and it deals with the aspects of processing and pattern formation, which are the ingredients of single molecule detection. The above mentioned 2D and 3D nanoparticles can exhibit complex electronic functions and, thus, may serve as kind of miniaturized devices.

Statements such as "learning from nature" are often used by chemists when selling their results to a broader public. A counter-argument is that we do not construct aeroplanes from feathers. Let us assign the question of "natural" or "synthetic" to the world of propaganda slogans, because it is clear that the technical use of polymeric biomaterials requires synthetic methods for their transformation and that polymer research must include biopolymers as key materials of life. But are there synthetic challenges?

While biodegradation is not a research issue in our institute, new hybrid architectures, e.g. di- and multiblock copolymers, dendrimers, core-shell systems, and bottle-brush macromolecules comprised of a biological and a synthetic part attract great attention. Hybrids containing polypeptide entities are particularly relevant for studying biological functions, including cell adhesion, enzyme mimicking and tissue engineering. The generation of peptide segments does not only rely on ring opening polymerizations of suited amino acid monomers and automated solid phase synthesis, but also on recombinant protein expression, especially when larger peptide units are required.

Progress in polymer synthesis does not only come from the invention of new reactions or new structures, but also from better solutions for "old" processes. While anionic polymerization has recently produced impressive results in the synthesis of, for example, block copolymers or star topologies, controlled radical polymerization, has afforded not only unprecedented amphiphilic block copolymers, but also unique core-shell structures. These have a strong influence on related projects, among which are emulsion polymerization using amphiphilic block copolymers as emulsifiers, and controlled mineralization using block, comb or core-shell copolymers as additives in crystallization from an aqueous solution – so called mineralization. Unique morphologies of titanium dioxide which have long been elusive are now available.

This work receives a special twist by new core-shell systems. Firstly, a fluorophore as a signalling site is encapsulated in its own dendrimer shell and, secondly, functions on the surface are used as initiators for the construction of polyelectrolyte shells by controlled radical polymerization. Depending on the nature and number of charges, drosophila larval tissue can be shown by confocal microscopy to undergo cell-uptake with high specificity.

Further, these polyelectrolytes serve as carriers for efficient DNA transfection. This is monitored not only by suitable assays, but also by AFM, light scattering, and calorimetry.

An even more elegant approach towards functional polyelectrolytes comprises cationization of the bovine serum albumin. Efficiencies in DNA transfection are superior to those of the golden standard which is, again, analyzed in terms of the energetics of polyelectrolyte-polyelectrolyte complexes.

Polymer topologies, which have been long sought after, now become available by innovative methods. A powerful tool is templated and geometry-confined synthesis. Thus, a porphyrin molecule serves to pre-assemble carbazole moieties for the synthesis of giant macrocycles with extended  $\pi$ -conjugation as a model for conjugated polymers of an infinite length. A related process is polymer synthesis in micelles leading to polymer lattices. While often considered as a conventional method, it reveals an undiminished vivacity from both a practical and fundamental viewpoint. A wide breadth of functions, from optoelectronic to biomedical, can thus be obtained.

In many instances, progress in polymer synthesis is fueled by new experimental techniques such as the use of supercritical fluids, high pressure or catalytic processes with specially designed carriers. Not surprisingly, therefore, the relevant research is conducted jointly by chemists and physicists. This holds, in particular, for polymer synthesis in confined geometries, such as surface controlled reactions or latex formation (see above) and the fabrication of organic-inorganic hybrids. New polymer resins have been introduced which serve as remarkably powerful, "responsive" carriers for metallocene catalysts in polyolefin synthesis. Highly dispersed carbon-metal or carbon-metaloxide nanocomposites open up new avenues for lithium storage and catalysis.

The approach described here is comprehensive in that it covers a broad range of polymer molecules and particles with different degrees of complexity. In the first place, established polymer structures are produced more or less routinely for various purposes. Polymer scientists who prefer established chemical methods might consider dendrimers, macrocycles, or chiral polyphenylenes as a somewhat unorthodox species requiring overly sophisticated methods of synthesis. It must be stressed, however, that such synthetic efforts provide access to fundamental questions of polymer science and, as a most welcome spin-off, assist in the solution of long-standing problems of polymer synthesis. Whatever degree of complexity or simplicity is intended within polymer synthesis, structural precision, control of multiple chemical functions as well as combined approaches toward synthesis and processing are indispensable criteria.

# High Performance Polycyanurate Thermoset Networks Based on Cyanate Ester Monomers

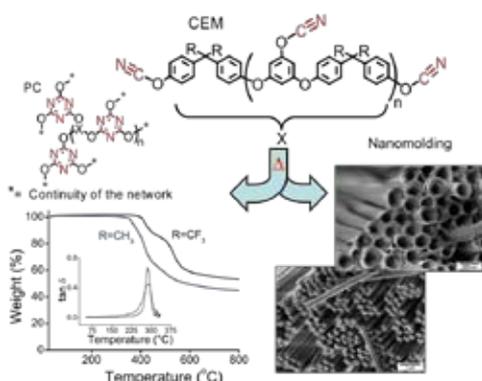
U. Jonas

*Keywords: Thermoset, polycyanurate, cyanate ester*

Resin systems based on cyanate ester monomers (CEM) have been designated as the next generation of thermosetting polymers following the widely used epoxy resins. They are of interest due to their outstanding fire- and moisture-resistance, their good mechanical strength and electric stability at cryogenic and elevated temperatures, high glass transition temperature ( $T_g$ ), low dielectric constant, radiation resistance, excellent metal adhesion, and compatibility with carbon fiber reinforcements. These unique properties of CEM resins make them preferential candidates as structural materials for high-temperature applications in aerospace, insulation, microelectronics, and adhesive industries.

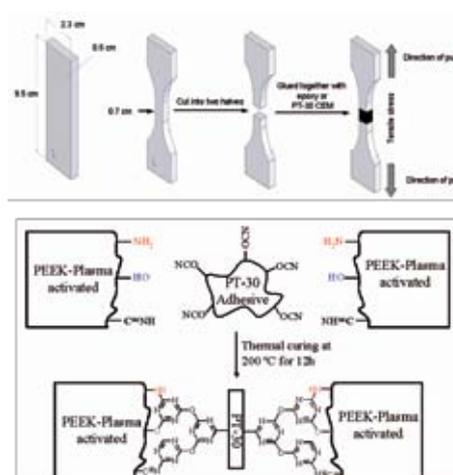
## Multifunctional CEMs

In a standard application scenario the CEM resin is processed and shaped at ambient temperature and then cured at higher temperatures. Upon heating the cyanate ester functions in the CEM resin undergo a formal trimerization reaction leading to cyanurate rings as crosslink points in the polycyanurate (PC) network. Improvement of CEMs for adhesive applications is better processability at room temperature, i.e. low CEM viscosity, while maintaining high-temperature stability of the cured PC.



**Fig. 1:** Generic chemical structure of a CEM and resulting PC network after curing (top), thermal- (TGA) and mechanical (torsional rheology) stability (lower left), and SEM of PC nanorods /-tubes (lower right).

Such improvements are achieved by variation of the molecular architecture, such as: the linear chain with only functional chain ends *versus* a linear chain with functional chain ends and pendant functional groups along the main chain (increased crosslink density), tri-arm architectures, substitution of atoms (F versus H) and main chain blocks. Such optimized CEM resins can even be molded into nanostructures, like nanorods and nanotubes in nanoporous aluminum oxide templates.



**Fig. 2:** Schematics of PEEK specimens glued with a CEM for mechanical testing (top), and the chemistry involved in surface plasma activation and CEM gluing (bottom).

## CEMs as PEEK adhesives

Polyetheretherketone (PEEK) is a high performance polymer for many technical applications with excellent thermal stability and chemical resistance. However, effective joining of PEEK parts presents a problem, which is commonly achieved by gluing with epoxy adhesives with low mechanical stability at elevated temperatures. On the other hand, PC thermosets show outstanding high-temperature performance, but adhesion to PEEK is not satisfactory. This problem can be successfully addressed by surface activation of the PEEK specimens by a wet chemical process or plasma treatment, which substantially improves PC adhesion even at very high temperatures.

**Crosslinks to other projects:** Mechanics, Rheology and Dielectric Spectroscopy Laboratory, Polymer Characterization, Optical and Electron Microscopy

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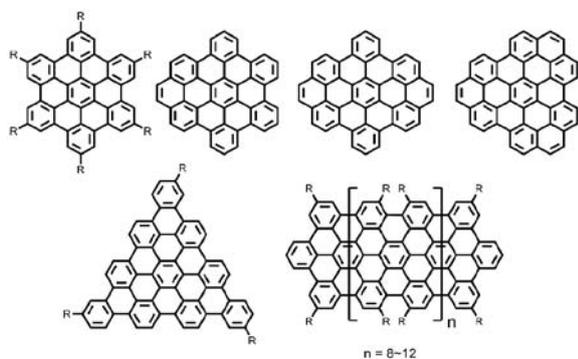
# Synthesis of Graphene Molecules/Giant $\pi$ -Conjugated Macrocycles

X. Feng, B. Schmaltz

**Keywords:** Graphene, nanographene, polycyclic aromatic hydrocarbons, discotic, macrocycle, host-guest

As a bottom-up approach to synthesizing graphene with a 2D aromatic monolayer of carbon atoms, large nanographene molecules of different sizes, shapes and substituents have been synthesized by oxidative cyclodehydrogenation with suitable oligophenylene precursors. A typical example is hexa-*peri*-hexabenzocoronene (Fig. 1) with all-benzenoid rings, showing distinct self-organization propensity via  $\pi$ -interaction and local phase separation between the flat rigid aromatic cores and flexible peripheral substituents. As a result, HBCs and their derivatives belong to the most studied discotic species due to their pronounced stability of columnar mesophases and high local one-dimensional charge carrier mobilities.

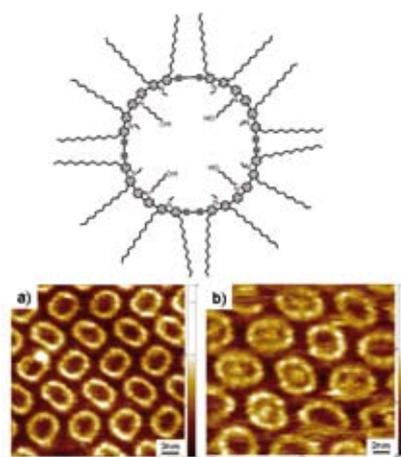
Apart from the synthesis of HBCs with  $D_6$  symmetric substituents, HBCs with  $C_3$  symmetric substituents are synthesized and display unique self-assembly behavior in solution, in bulk, and on the surface. Triangle-shaped nanographenes can self-assemble into a chicken-wire network at the liquid-solid interface, indicating the potential application as a nano-template to host guest molecules. HBC molecules with partially “zig-zag” peripheries, namely zigzagHBCs (Fig. 1), show the different electronic and optoelectronic properties, as well as different electronic and optoelectronic properties from the benzenoid nanographene molecules.



**Fig. 1:** Representative nanographene molecules.

One-dimensional graphene ribbons can be synthesized as a series of oligomers with size of 8 to 12 repeating units of HBC, single graphenes with a length of up to 10 nm were visualized using scanning tunnelling microscopy.

The construction of a  $\pi$ -conjugated macrocycle around a central  $\pi$ -system can self-assemble into a columnar superstructure, giving rise to coaxial-cable charge transport along the columnar direction. Shape-persistent macrocycles composed by large  $\pi$ -conjugated building blocks not only serve as molecular model compared to their linear polymer species, but also provide porous channels along the columnar direction in the bulk or leave hole on the surface, which enables the creation of host-guest complexes. The rigid carbazole based macrocycle is synthesized by a template approach, leaving functional groups at the carbazole nitrogen atoms (Fig. 2). It can self-organize into helical columnar superstructure in the bulk. Other rigid macrocycles built by conjugated fluorene units can also be synthesized by a similar or modified synthetic approach.



**Fig. 2:** Example of a giant  $\pi$ -conjugated carbazole macrocycle. a) 2D STM view of a monolayer with hexagonal packing. b) 2D STM view of host-guest complexes macrocycle + HBC.

**Crosslinks to other projects:** Discotic Liquid Crystals in Motion, Graphene as Window Electrode, Organic Electronics: Structure-Property Relations

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# Organic and Hybrid Spin Networks

M. Baumgarten

*Keywords: High spin molecules, molecular magnets, redox spin switches*

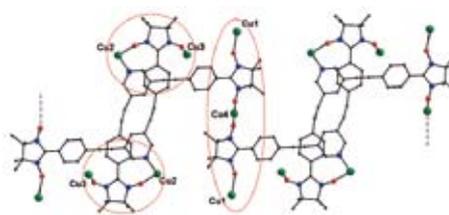
Various approaches toward magnetic properties or molecular magnets with organic spin units have been dealt with experimentally and theoretically. They can be classified into pure organic approaches through synthesis of extended polyradicals, ordering of discrete radical molecules via  $\pi$ -stacking, hydrogen bonding into the organic inorganic hybrid approach combining organic radicals with spin active metal ions, or metal complexes. Therefore, high spin molecules with two or more conjugatively linked biradicals not only help to extend the magnetic structures toward higher dimensions but also overcome the usually uncontrolled antiferromagnetic interactions between chains. Nitronyl- (NN) and iminonitroxide (IN) free radicals have attracted increasing attention. This mainly stems from the use of these stable radical units as building blocks in the design of molecular magnetic materials, such as purely organic ferromagnetically ordered solids, metal–organic exchange coupled complexes, as well as new agents for biomedical applications, e.g. in bioimaging and selective NO scavengers. The challenge in this field consists of assembling functional derivatives such that interaction between spin carriers can be controlled and tailored at will through the rational design of the molecular backbone (CU).



**Fig. 1:** 4-Br-pyridineNN radical forms  $\pi$ -stack and H-bonds.

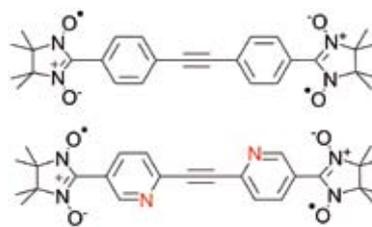
Functionalized monoradicals can even be used for complex structure formation as demonstrated for 5-BromopyridylNN, which underwent  $\pi$ -stacking and hydrogen bonding, including inclusion of water molecules upon crystallization.

Recently we described multiple functional high spin biradicals based on NN and IN and demonstrated how the  $\pi$ -bridging cores influence the exchange interaction between the radical sites. The supramolecular organization and their magnetic properties can even be enhanced through combination with metal complexation and the richness of their bonding opportunities. To this end we prepared a complex spin network of a diphenylacetylenepyridine bridged biradical with  $\text{Cu}(\text{hfac})_2$ . The magnetic properties could only be understood through an in-depth quantum chemical analysis considering all spin subsystems, leading finally to a meaningful fit of the magnetic data.



**Fig. 2:** Spin network of a biradical and  $\text{Cu}(\text{hfac})_2$ . H atoms and hfac fragments omitted for clarity. The red circles show the trimeric and pentameric spin motifs.

In addition to the approaches towards molecular magnets we also focus on quantum computing. For magnetic field-induced Bose-Einstein condensation phenomena in solid state weakly antiferromagnetically coupled diradicals were synthesized as building blocks for spin networks. These diradicals should undergo magnetic field-induced switching between singlet and triplet states in the solid.



**Fig. 3:** Weakly antiferromagnetically coupled NN diradicals.

**Crosslinks to other projects:** EPR Spectroscopy, Hybrid Nano-Assemblies

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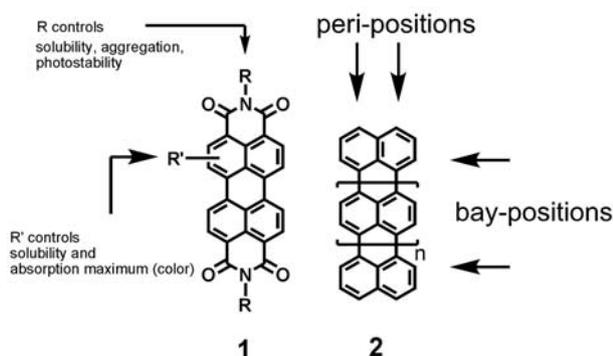
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## Functional Dyes and Their Applications

### C. Li

**Keywords:** Rylene dyes, ultrastable, fluorescent labeling

With the development of science and technology, functional colorants, i.e., dyes or pigments, are no longer used only for their visual appearance but for their intrinsic physico-chemical properties. They are of prime importance in many high-tech applications such as information storage, energy transfer cascades, laser welding processes, heat management systems, organic photovoltaics, light emitting diodes, field effect transistor and fluorescence biolabeling. Perylenetetracarboxydiimide (PDI) **1** and its derivatives are key chromophores in dyestuff chemistry. The solubility, absorption, and emission behavior of this class of materials can be efficiently controlled by functionalization using a variety of different synthetic procedures. New NIR-absorbers have been synthesized by introducing additional naphthalene units to the perylene scaffold to form the higher homologues of the series of poly(peri-naphthalene) **2**, also is named as rylene dyes (Fig. 1). Extension of PDI by one naphthalene results in the terylenediimide (TDI). The next higher homologue in the series of rylene-tetracarboxydiimides is the quaterylenediimide (QDI).

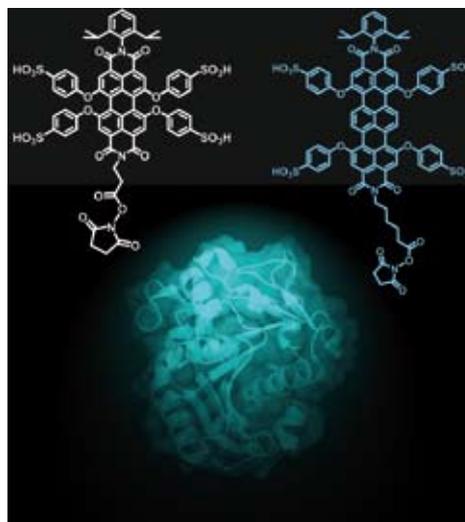


**Fig. 1:** Perylenetetracarboxydiimide and poly(peri-naphthalene).

Recently, our group developed a synthesis for the higher derivatives, pentarylene (5DI), hexarylene (HDI), heptarylene (7DI) and octarylene (8DI). Extending the aromatic  $\pi$ -system with additional naphthalenes induces a bathochromic shift in the absorption spectrum and an increase of the molar absorption coefficient. PDI has a brilliant red color (abs. max. 550 nm), while 8DI is completely colorless in solution and exhibits an absorption maximum at 1066 nm with  $\epsilon$  of 2620000  $\text{M}^{-1} \text{cm}^{-1}$ . For organic NIR-dyes such high absorption coefficients

are unprecedented. In addition to these remarkable photophysical properties, all the presented NIR-absorbers still display excellent chemical, photochemical and thermal stability seen in their smaller counterparts, the PDIs. For this reason the 5DI, HDI, 7DI, and 8DI are very well-suited for use of a new technique for laser welding of polymers. The most striking advantage of the NIR absorbing rylene is that they do not absorb in the visible state, so that the process of laser welding would not be restricted anymore to the use of transparent or colored components.

Another important advantage of PDIs is their quantitative fluorescent quantum yield ( $\Phi_f$ ). Going from PDI to TDI, the  $\Phi_f$  remains almost unchanged at 90%. Due to their outstanding photo-stabilities, perylene and terylene chromophores have been established as key chromophores for single molecule spectroscopy (SMS). Photophysical processes like energy and electron transfer can now be investigated on the single molecule level over long observation times. Monofunctional water-soluble perylene **3** and terylene **4** containing activated groups were synthesized (Fig. 2) These dyes can be attached to a variety of proteins through their reactive functional groups. Beside labeling and visualization of single proteins, terylene dyes have been applied to study activity taking place in living cells.



**Fig. 2:** *N*-hydroxysuccinimide ester functionalized perylene and terylene dyes, model of PLA-I based on crystal structure.

**Crosslinks to other projects:** Advanced Materials for Solar Cell Applications

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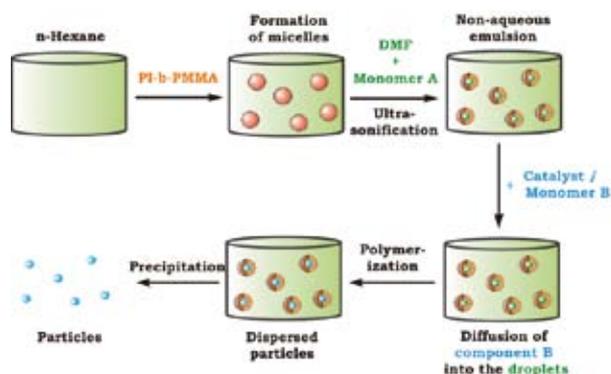
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# Synthesis of Nanosized Polymeric Particles in Non-aqueous Emulsions

M. Klapper

*Keywords: Non-aqueous emulsion, miniemulsion, nanoparticles, water-sensitive reactions*

Strategies to form polymeric nanoparticles usually include a direct synthesis in emulsion, miniemulsion, or dispersion polymerization. Due to the presence of water in these traditional methods, latex preparation using moisture-sensitive reactions or monomers cannot be applied. To overcome this drawback, non-aqueous emulsions, consisting of organic aprotic solvents were developed, exploiting biphasic copolymers such as Polyisoprene-*b*-PMMA (PI-*b*-PMMA) as emulsifiers (Fig. 1)



**Fig. 1:** Polycondensation in a mixture of alkane/DMF.

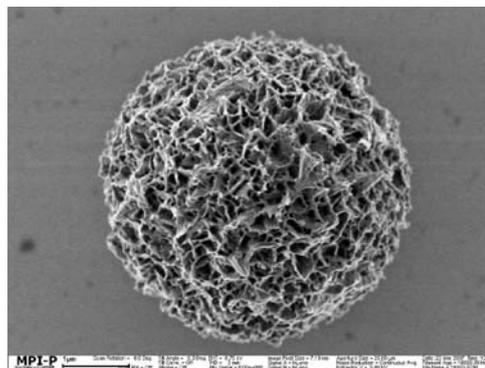
These emulsions dramatically increase the number of applicable monomers and allow the polymerization of acid chlorides or isocyanates. For example, using alkanes as continuous and dimethylformamide as dispersed phases we obtain high molecular weight polyurethanes without urea formation in emulsions from diols and diisocyanates. However, addition of water in a controlled way to the emulsions yields nanoporous spherical particles, which are suitable as supports for catalysts or as additives in composite materials.

This new technique can be further extended to prepare novel polymeric multi-shell structures. For example, architectures containing a polyurethane core and a shell obtained from catalytic ring opening metathesis polymerization (ROMP) have been synthesized.

Unfortunately, the solvents used in these systems are incompatible with more sensitive systems such as metallocene catalysts, and therefore not applicable to metal-catalyzed

polyolefin synthesis. Hence, a second type of emulsion was developed, consisting of a fluorinated continuous phase, and a hydrocarbon dispersed phase. For the stabilization as in the previous cases, polymeric amphipolar copolymers have to be designed containing monomers with an orthogonal solubility in alkanes and perfluoroalkanes. In these emulsions, gaseous monomers such as ethene and propene, and liquid olefins have been used. The resulting polymers obtained are well-defined nanosized spherical particles with high molecular weight.

Due to the non-aqueous conditions, these emulsions allow the versatile fabrication of new types of polymer nanoparticles. Different water-sensitive monomers, reactions, and catalysts can be applied within these systems. Defect-free polyesters, polyurethanes, polyamides, and polyolefins with high molecular weights are accessible in one step under ambient reaction conditions. Currently, the on-going work focuses on the combination of the various polymerization techniques within the non-aqueous emulsions. This offers a versatile access to novel core-shell morphologies in polymer nanoparticles, e.g. by combination of polyaddition and vinyl polymerization. Particles with special material properties, e.g. optimized film forming abilities or adhesion behavior on surfaces necessary for coatings or paints are of interest. Furthermore, defined binding sites which can react with biological macromolecules should be incorporated via the emulsifiers in fluorescence tagged particles.



**Fig. 2:** Nanoporous polyurethane particle obtained in a DMF/hexane emulsion.

**Crosslinks to other projects:** Morphology Control in Polyolefin Synthesis, Reaction in Confined Geometries, Bioresponsive Hybrid Nanoparticles

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# Pyrene as New Building Blocks for Polymers, Macrocycles and Dendrimers

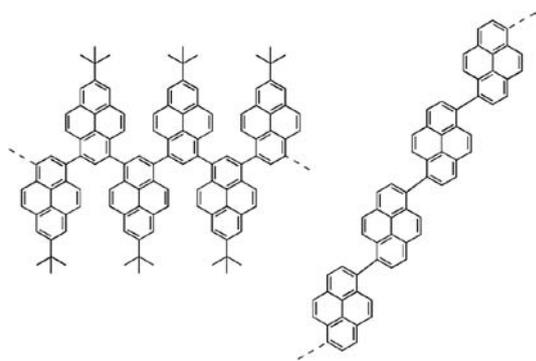
T.M. Figueira Duarte, M. Baumgarten

*Keywords: Pyrene, chromophore, polymers, macrocycles, dendrimers, organic electronics*

The fluorescence properties of pyrene are well-known and characterized by long excited-state lifetimes and distinct solvatochromic effects. Furthermore, pyrene exhibits characteristic excimer formation in concentrated solutions and in the solid state and can be used to study aggregation phenomena. As a large conjugated aromatic system, pyrene not only has the advantages of high photoluminescence efficiency and high carrier mobility, but also exhibits improved hole-injection ability when compared to other molecules. Electronic interaction and intramolecular charge transfer processes in donor-acceptor systems based on pyrene have been studied and potential applications in electronic devices such as light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) were identified. Our goal is to take advantage of the chemical and photochemical properties of pyrene to prepare new pyrene-based systems such as macrocycles, dendrimers, and polymers.

## Pyrene-based polymers

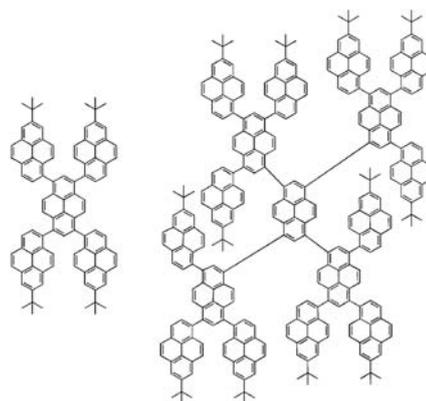
Pyrene combines high photoluminescence efficiency with high carrier mobility. Pyrene-based polymers have received very little attention, although we described oligo-2,7-pyrenylenes and poly-2,7-(4,5,9,10-phenylalkyl)pyrenylenes more than 10 years ago. We have published work on poly-2,7-(4,5,9,10-phenylalkyl)pyrenylenes as blue emitters for OLED application and continue to study the influence on further varying the conjugation pathway and substitution pattern as in poly-1,3-pyrenylenes and poly-1,6-pyrenylenes (Fig. 1).



**Fig. 1:** Two examples of pyrene-based polymers.

## Pyrene-based dendrimers

Our aim was to build up new dendrimers consisting exclusively of pyrene units (Fig. 2). These innovative fully aromatic dendrimers are relevant for artificial light-harvesting in a spatially well-defined three-dimensional architecture constituted by only one type of chromophore.

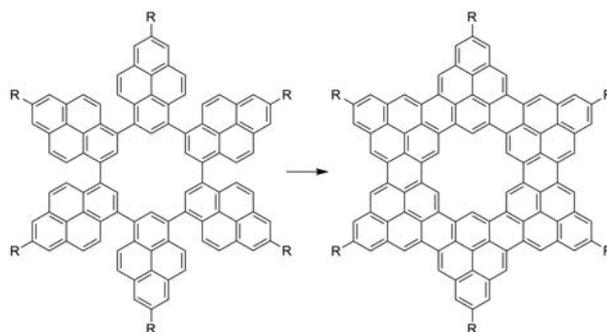


**Fig. 2:** First and second generation of pyrene-based dendrimers.

## Pyrene-based macrocycles

The self-organization behavior of macrocycles into columnar superstructures leads to high charge carrier mobilities along the columnar stacks, resulting in the successful application of such materials in OFETs and photovoltaic devices.

Our motivation for designing pyrene-based macrocycles (Fig. 3) was to combine the photochemical properties of pyrene with self-organization by  $\pi$ -stacking into columnar supramolecular structures for application in OFETs.



**Fig. 3:** Pyrene-based macrocycles.

**Crosslinks to other projects:** Synthesis of Graphene Molecules, Giant  $\pi$ -Conjugated Macrocycles, Organic Electronics, Conjugated Polymers as Semiconductors for High-Performance Field-Effect Transistors

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# Morphology Control in Metallocene Catalyzed Olefin Polymerization

M. Klapper

*Keywords: Catalysis, polyolefins, morphology control*

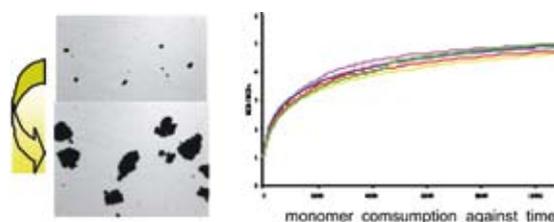
For industrial applications of polyolefins the *in-situ* preparation of nanometer to millimeter sized polymer particles during olefin polymerization is an essential requirement. This aim is mainly achieved by supporting the catalysts on inorganic materials. However, in recent years we have succeeded in developing also organic nanoparticles as catalyst carriers. Loading of the catalysts is performed by an easy non-covalent process in the presence of the cocatalyst methylalumoxane. This approach allows us to introduce different functionalities on the surface such as polyethylene oxide or pyridine moieties, the supports are applicable not only to metallocenes, but also to the very reactive postmetallocenes. The catalyst systems can in fact undergo a controlled fragmentation to nanosized pieces during the polymerization, which is a prerequisite for an excellent morphology control. This reaction can be optimized in terms of the degree of cross-linking, the particle size, polarity, and interaction with the co-catalyst. Leaching of the catalyst is avoided and therefore reactor fouling is not observed. Besides ethylene and propylene, higher  $\alpha$ -olefins, norbornene and even alcohols and acids (using the appropriate protection groups) are copolymerized in different reactors (Fig 1). For a detailed explanation of the polymerization behavior of the support, which is required for the optimization of the morphology control, a number of different tools are available at the MPI-P.



**Fig. 1:** Setup for the polymerization of liquid propylene.

For the characterization of supports, we use in cooperation with different groups within our institute standard techniques *e.g.* elemental analysis, IR, NMR, DLS, GPC as well as TEM, REM, and laser scanning confocal fluorescence microscopy.

Detailed insight into the kinetics can be obtained by monitoring the polymerization in a video microscopy reactor (Fig. 2). This method allows visualization in real time of the polymerization in the gas phase and the study of growth of each single product particle separately. With this data we succeeded in developing a kinetic model of the olefin polymerization.



**Fig. 2:** Monitoring of the polymerization behavior of metallocene catalyst via videomicroscopy; two pictures in the very early and the last polymerization stages of various catalyst particles (left) and statistical evaluation (right) obtained via single-particle analysis.

While the organic supports typically result in polyolefin particles ranging from micro to millimeters in size, nanometer sized particles are still a challenge. To achieve this goal we developed a new type of water-free emulsion, consisting of a fluoruous continuous phase, and a hydrocarbon dispersed phase. These well-defined hydrocarbon droplets serve as nanovessels for metallocene catalyzed olefin polymerizations. As these mixtures are not destroying the catalysts, nanosized spherical polyolefin particles are readily available.

For all the different synthetic approaches we are able to obtain a correlation between the morphology of the obtained polyolefin products and the used catalysts, and supports by studying in detail the reaction kinetics. The broad variety of methods allows us to gain a deep insight into the polymerization processes and to tune the properties of the obtained polymers.

**Crosslinks to other projects:** Reaction in Confined Geometries, Non-Aqueous Emulsions

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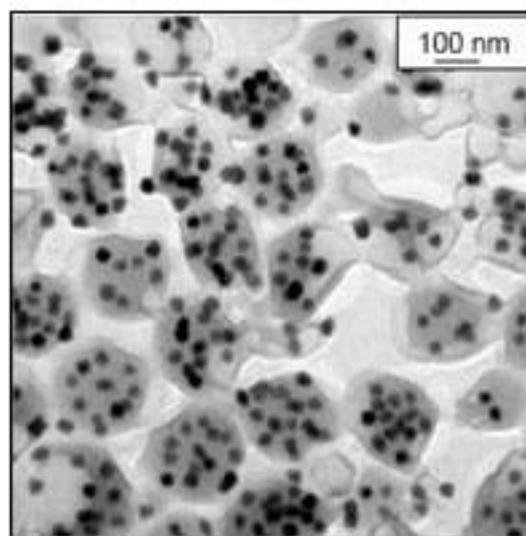
## Bio-responsive Hybrid Nanoparticles

### A. Musyanovych

**Keywords:** surface functionalization, biodegradable polymer, magnetic nanoparticles, stealth effect

In an effort to create particles for each particular application, it is essential and of immense interest to have the ability to control the particle size, morphology, composition, physico-colloidal properties, density of functional groups on the particle surface, and so on. This can be achieved by miniemulsion technique, which is being used widely for the production of many varieties of polymeric dispersions, mainly due to its flexibility in product design and process control. Such flexibility is acquired by adopting different start-up procedures (e.g. type of monomer(s), initiator, surfactant, functional additives, etc.), as well as the possibility to combine various synthetic approaches in one system.

For example, polystyrene and poly(methyl methacrylate) nanoparticles with surface carboxyl-, amino-, epoxy-, phosphate or phosphonate groups were produced by radical copolymerization of styrene or methyl methacrylate and the corresponding functional monomer. The density of functional groups and their distance from the particle surface greatly depends on the properties and the amount of functional comonomer as well as on the type of surfactant (ionic or non-ionic) used during the synthesis. Generally, particles stabilized with non-ionic surfactant are bigger in size and contain higher amount of functional groups as compared with polymer particles obtained in the presence of ionic surfactants. The introduction of a hydrophobic fluorescent dye into the reaction mixture results in composite particles which have found the application as carriers for contrasting or imaging agents. Furthermore, the receptor-specific antibodies could be attached to the functional groups via covalent bonds. The obtained particles were utilized for targeting to the cells of interest. The non-specific particle-cell interaction was reduced by introduction of poly(ethylene glycol) (PEG) chains onto the particle surface. This was achieved either through chemical linkage between amino-modified PEG and functional group on the particle surface or by employing polymerizable PEG as a second comonomer during the synthesis.



**Fig. 1:** TEM image of poly(lactide) particles with encapsulated iron oxide nanoparticles (25 nm, 20 wt% related to the polymer).

Biodegradable nanoparticles with the size of 80-120 nm were formed by effective combination of the emulsion/solvent evaporation method and miniemulsion technique using different biocompatible and biodegradable polymers such as poly(L-lactide), poly(D,L-lactide-co-glycolide), and poly( $\epsilon$ -caprolactone).

Differences between the results of various polymers are found in terms of the particle size and size distribution as well as in the degradation time. Fluorescent polystyrene or poly(lactide) particles with superparamagnetic behavior were obtained by encapsulation of hydrophobic iron oxide nanoparticles inside the polymeric matrix. Using the miniemulsion approach, the magnetite amount as high as up to 40 wt% could be loaded inside the particle. As an example, TEM image of poly(lactide) particles with 20 wt% of iron oxide is shown in the figure.

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**Crosslinks to other projects:** Polymeric Nanoparticles and Interaction with (Stem) Cells: Uptake, Intracellular Trafficking and Cellular Responses, Multifunctional Polymer Capsules

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## Reactions in Confined Geometries

### K. Landfester

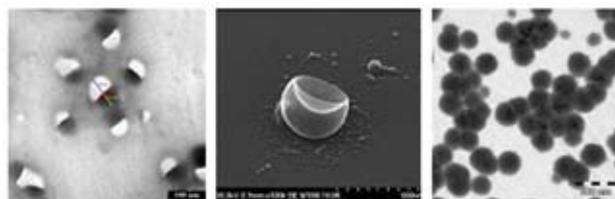
**Keywords:** phase separation in nanoparticles, enzymatic reactions in miniemulsion, polymer reactions in confined geometries, crystallization in nanoparticles

Small, homogeneously distributed and stable nanodroplets are obtained by the miniemulsion process and can serve as small compartments. Various polymer reactions ranging from radical polymerization to polyaddition, polycondensation, enzymatic polymerization, oxidative polymerization, and anionic polymerization can be carried out within the small nanodroplets which can be considered as independent nanocontainers. Nylon 6 (polyamide 6) nanoparticles dispersed in an aqueous phase can also be successfully prepared combining some characteristics of the miniemulsion and the solvent displacement techniques. The principle of the preparation consists of adding nylon 6 dissolved in formic acid to an aqueous phase containing poly(vinyl alcohol) as stabilizer, while ultrasonating the aqueous phase in order to obtain stable nanoparticles. The stability of these particles was studied over a wide range of reaction parameters, such as the temperature, the nature and concentration of the chemicals, the time and amplitude of ultrasonication.

The evolution of phase separation within confined geometries has been studied on polymer blends in nanoparticles by using transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy. The TEM studies show that blend particles formed from two immiscible polymers via the miniemulsion process exhibits biphasic morphologies. The fact that no core-shell type, but Janus-like structures (see Fig. 1 left) were found indicates that the surface energies between both polymers and the solution-water interface (including the surfactant molecules) are similar; therefore the morphology is not driven by the interaction of the polymers with the polymer/water interface. Both the TEM studies and the PL experiments provide strong evidence that phase separation in these particles strictly follows the Flory-Huggins theory. This highlights the applicability of the nanoparticle approach to either fabricate blend systems with well-controllable properties or to study structure-property relationships under well-defined conditions.

As another possibility, nanoexplosions can be performed in nanoparticles. Here, thermally instable azo components can be embedded within a polymer nanoparticle and afterwards quickly decomposed by thermal treatment below the glass temperature of the polymer inside the confined geometry. The resulting nitrogen gas overpressure inside the particles leads to a disruption of the polymer particle (see Fig. 1 middle) and a possible sudden release of encapsulated substances.

The use of polymeric nanoparticles as small template structures for producing inorganic materials is an intriguing approach as it offers the feasibility of synthesizing organic/inorganic hybrid materials for a broad spectrum of applications. Polymeric nanoparticles consisting of gelatin obtained via the miniemulsion process are employed as templates for the biomimetic mineralization of hydroxyapatite in the aqueous phase (see Fig. 1 right). The nanoparticles were subsequently used as templates for the calcium phosphate (CaP) mineralization in the aqueous phase. The nanoparticles were used as confined nano-environment to perform crystallization inside the particle. The formation of hydroxyapatite inside the particles follow Ostwald's rule of stages, where an initially formed amorphous CaP phase transforms into single crystalline hydroxyapatite via an octacalcium phosphate intermediate without any calcination step. These hydroxyapatite/polymer composite nanoparticles have a great potential to be used as a regenerative filler or as a scaffold for nucleation and growth of new bone material.



**Fig 1:** Janus nanoparticles obtained by phase separation within the nanoparticles; middle: particle after controlled nanoexplosion; right: CaP in polymeric nanoparticles.

**Crosslinks to other projects:** Multifunctional Polymer Capsules, Porous Oxide Nanoparticles

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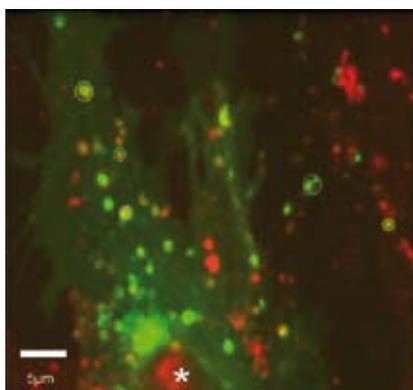
## Crossing Biological Barriers

E.-K. Sinner, T. Weil

*Keywords: Isothermal titration calorimetry, polyelectrolytes, self-assembly*

### Relevance of biological barriers in nature

Membranes and barriers are vital to sustain life. Cell membranes separate a cell's interior from its surroundings and control the traffic, e.g. what moves in and out. The term 'barrier' is often misinterpreted and creating the idea of a rigid fence-like structure. However, biomembranes have a fluidic constitution comparable to a stable oil film. Probably the most important feature of a biomembrane is that it is a selectively permeable structure. Among other factors, specificity of a biomembrane is achieved via proteins and protein receptors embedded in the membrane and controlling the material influx and efflux. Nature has created a number of different barriers containing a varying number of membrane proteins of different kinds. Different membranes were designed which for example can control the transport of particular molecules into the cell, into the cell nucleus or into certain tissues such as brain tissue. Controlling membrane uptake is a challenging task since most fundamental processes are still not fully understood. However, it has a significant impact for several applications ranging from medical applications, such as drug delivery, to technical applications, e.g. biosensors or sensing technologies.



**Fig. 1:** Intracellular transport of highly cationic serum albumin (cBSA-147). Time lapse of 25 min confocal imaging series (4 pictures/sec): PBMEC were incubated for 4 hours with cBSA-147 [1 μM]. Intracellular accumulations of cBSA-147 co-localized with membrane fractions were marked at the beginning of the observation. In 25 min intracellular cBSA-147 vesicles moved ~ 7 μm towards the nucleus while extracellular vesicles moved with an average speed of 900 nm. \*: Nucleus marked interaction.

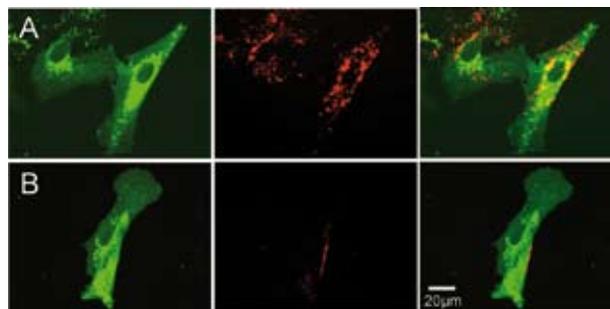
### Understanding membrane interaction

Molecules can either cross membranes via passive diffusion, vesicle formation such as endocytosis, hole formation or through active transport via protein receptors.

We have recently established a relatively new and powerful technique that allows the visualization of cell uptake and cell trafficking of living cells. Such a life cell imaging (LCI) is stressful for the cells since they are studied for several hours under a microscope. Therefore, the conditions for keeping the cells alive have to be adjusted carefully. However, LCI allows online investigation of cellular uptake and trafficking under a confocal microscope. We have successfully studied tailored protein-polycations which displayed rapid and directed movement to the perinuclear region of the cells, which is still not understood (Fig. 1).

### Manipulating cell uptake

Through treatment with different compounds known to block particular cell uptake pathways, we were able to identify the transport mechanism of novel protein-polycations, which were transported via clathrin mediated endocytosis. These results allow a better understanding of protein membrane interaction and pave the way toward improved drug delivery agents.



**Fig. 2:** Pharmacology of cBSA-147 uptake. Before incubating an endothelial cell line for 4 h with cBSA-147, cells were pre-treated with endocytosis inhibitors Filipin (FIL) (1 μg/ml) (A) and Chlorpromazin (CHLP) [50 μM] (B) for 90 min. After pharmacological treatment cells were washed, supplied and incubated with fresh medium containing cBSA-95 [1 μM] for 4 h. Then confocal live cell imaging was performed. Left column shows membrane staining, middle column presents cBSA-147 localization and right column displays the superimposed image. Treatment with CHLP blocks the cBSA-147 uptake efficiently while with FIL no effect was visible compared to untreated cells.

**Crosslinks to other projects:** Polyphenylene Dendrimers, Chemically Modified Proteins

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# Development of Methods



## Development of Methods

H.W. Spiess, K. Kremer

The relationship between the macroscopic properties of polymers and their structure, dynamics, and supra-molecular organization is complex. It involves enormous length- and timescales from the molecular, via mesoscopic to macroscopic dimensions and from picoseconds to years. Bulk-behavior should be compared with surface effects, and electronic, as well as mechanical and transport properties are of interest. Consequently, a considerable variety of techniques is needed in order to unravel the different aspects. In fact, numerous forms of computer simulation, spectroscopy, scattering, and microscopy are used. Advances and modifications of these techniques are needed to cope with new questions associated with new materials, for instance biomimetic systems. Therefore, from its beginning, an important aspect of the institute's work is the development of advanced methods, including the adaptation of techniques for specific polymer problems. Likewise, versatile methods are developed which, by their very nature, can be applied to numerous problems of polymer science. This chapter describes some of these activities.

At the outset of a theoretical description traditionally a model, which is treated in terms of an analytic approach, is studied. This ansatz in the past has been very successful for rather idealized problems, elucidating the very basic principles of polymer physics. These studies then were complemented by computer simulations of rather simple, but already more complex models. This leads to a rather good understanding of scaling properties of macromolecular systems, where the above mentioned many time and length scales were well separated. In order however to take this interplay of scales properly into account and to arrive at truly quantitative predictions of specific chemical systems scale bridging methods have to be developed. Methodology along these lines has been developed in the theory group for more than ten years and nowadays is very fashionable under the name "multiscale modelling". In order to progress here method development has to be pursued not only at the link between methods devoted to specific scales but also on the methods themselves. On the quantum mechanical level mostly ab initio density functional methods (DFT), i.e. the Car Parrinello method (CPMD), are employed. The electron density functionals, which are based on electronic orbitals, are computationally very demanding and thus mark a severe limitation when one wants to study more complicated or larger systems. To improve this situation we contribute to the development of so called orbital free DFT, which eventually should significantly speed up the ab initio DFT. Established quantum mechanical DFT methods are either used for rather small systems or in a hybrid approach, where they are coupled to a classical environment. In this quantum mechanical/molecular modelling (QM/MM) approach a small subsystem is treated by quantum DFT while the surrounding is treated by a classical force field simulation (MM part). A central aspect of improved methodology is the coupling

between the quantum and the classical regime.

This problem is addressed by developing new effective potentials to terminate the dangling chemical bond of the QM region with the special focus to optimize the electronic density and spectroscopic properties. Currently this is used to study proton conducting membranes as they are used in fuel cells. On a larger scale the penetration and solvation of polymers by whole molecules or salt ions is of great interest. Such systems are far beyond the range of applicability of the above described QM/MM ansatz. In a combined approach of a multiscale simulation of the polymeric matrix with a fast growth thermodynamic integration procedure to obtain the excess chemical potential of an inserted particle/molecule one is able to study solvation properties of rather complicated polymeric solvent solute systems. All these methods however use rather different levels of description in a fixed or sequential way. Eventually one would like to perform a simulation of a complex macromolecular system on different levels of resolution in full equilibrium between the different regimes, meaning that we also have a free exchange of particles/molecules between the different levels of resolution.



The AdResS (Adaptive Resolution Simulation) method was developed to achieve this goal on the basis of particle based simulations. In a recent extension also the coupling to hydrodynamic continuum was shown to work properly opening the way to open system simulations. However to study hydrodynamic properties of large systems still requires different methods. To treat macromolecular objects in solution and to properly take hydrodynamic interactions into account a full blown particle based simulations for nontrivial problems can only be performed in very exceptional cases and with the massive use of newest super-computer technology. One way out is given by a discrete lattice description of the hydrodynamics solvent (Lattice Boltzmann method) coupled frictionally to a molecular dynamics simulation of an embedded macromolecule or colloidal particle. In a recent theoretical analysis of this method it was shown how to implement thermodynamically consistently thermal noise via a thermostat and to properly describe Brownian motion. All these activities are needed and often linked together in order to maintain cutting edge modelling activities for soft matter.

On the experimental side, the current trends of science and technology towards further miniaturization calls for ever increasing sensitivity in detection and spatial resolution. Therefore, most of the recent advances in methodology described here deal with these issues. Magnetic resonance (NMR and EPR) are the least sensitive methods, yet provide unprecedented details on structure and dynamics because of the unmatched site-selectivity. Recently, several ways of improving the sensitivity have been implemented in the institute. These include the use of the highest available magnetic fields for solid-state NMR, which now operates at 850 MHz and magic angle spinning at 70 kHz. This also offers unique spectral resolution, improving the possibilities of unravelling complex hydrogen bonding and pi-stacking in supramolecular functional systems such as proton- or photoconductors. High field electron paramagnetic resonance (EPR) now can be applied to sample volumes as small as 2  $\mu$ L, which makes this technique applicable to a significantly larger group of problems, in particular structure of biological macromolecules and the detection of nanoheterogeneities in synthetic systems. Combining NMR and EPR by the technique of Dynamic Nuclear Polarization (DNP) can increase the NMR signals by factors of several hundred and NMR with non-thermal spin polarization by laser irradiation or by spin-conserving chemical reactions with e.g. para-hydrogen, signal enhancements of up to 4 orders of magnitude can be achieved. This offers new applications of magnetic resonance imaging in medicine as well as porous materials.

The sensitivity in optical spectroscopy and imaging is inherently much higher. This offers the possibility to observe single objects and molecules. Indeed, single-molecule fluorescence microscopy has become an established analytical technique during the last ten years or so. The spectroscopic parameters of single molecules, however, also depend on their proximity to metal surfaces, which can be exploited to increase spatial resolution or distinguish different objects in complex superstructures of organic-inorganic hybrids.

Optical plasmon resonances in nanoscopic metal particles offer new routes to manipulation of light on length scales lower than its wave length. This has been successfully exploited to generate highly ordered nanostructures with defined size and spacing. Indeed, evanescent wave optics, exploiting surface plasmon resonance remained an active area of method development. Long range surface plasmon modes enhancing fluorescence intensity were exploited to generate highly sensitive biosensors, and first experiments performing dynamic light scattering close to an interface with surface plasmon polaritons as a source of the scattered light were realized to study motions of particles as small as 10 nm. In a similar fashion, total internal reflection was used to increase the spatial resolution of fluorescence correlation spectroscopy. This allows investigating the diffusion of polymers in an observation volume of order 500 nm in diameter and a height tuneable in the range 70-250 nm.

Laser light can, of course, also be used to manipulate molecules. Along these lines Matrix Assisted Laser Desorption/Ionization - Soft Landing (MALDI-SL) and Pulsed Laser Deposition (PLD) have been applied to deposit thin films of polycyclic aromatic hydrocarbons (PAHs) with up to 222 carbon atoms. PAHs can be regarded as well defined segments of graphite, thus rendering them interesting candidates for electronic applications especially with increasing size. Another unconventional use of light exploits the strong temperature dependences of triplet-triplet annihilation and delayed fluorescence emission in organic phosphorescent molecules dispersed in a polymer matrix to sense temperature with a spatial resolution of 250 nm.

Today's high brilliance synchrotron sources allow focusing X-ray beams down to the  $\mu$ m-scale and thus using them to investigate structure of coatings on microcantilever arrays as the essential parts of scanning probe microscopy, a method widely used in the institute. Decorating the cantilevers with polymers of different nature allows analyzing, e.g., the coil-to-globule transition of macromolecules containing hydrophobic and hydrophilic groups in the repeat unit. Combining transmission electron microscopy (TEM) with nano-area electron diffraction now allows the detection of individual nanoparticles in functional systems to investigate the mechanism of ion storage.

Sensitivity is also a major issue in the study of the mechanical behavior of soft matter, where often only small quantities of materials are available and the samples can be extremely fragile. In a piezoreometer both problems are solved as these devices are extremely sensitive and work with very small deformations in the range of  $10^{-3}$  to  $10^{-5}$ .

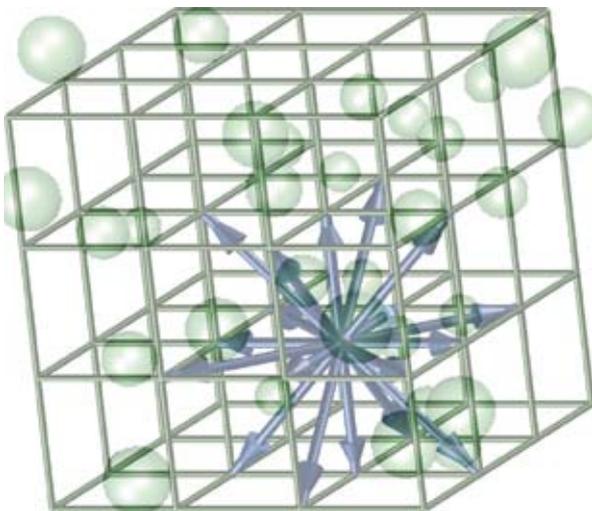
Last, but not least, isothermal titration calorimetry (ITC), a method often used to determine interaction constants, complex stoichiometry or conformational changes of biological macromolecules during assembly, was established at the institute. First results shed light on processes involved in gene transfection, a very complex and still barely understood biological process of high therapeutic relevance. In the future, the method will also be applied to synthetic polymers to study, e.g., polymerization reactions.

# Computational Physics: Advances in Mesoscopic Simulation Methods

B. Dünweg

*Keywords: Lattice Boltzmann method, Poisson-Boltzmann equation*

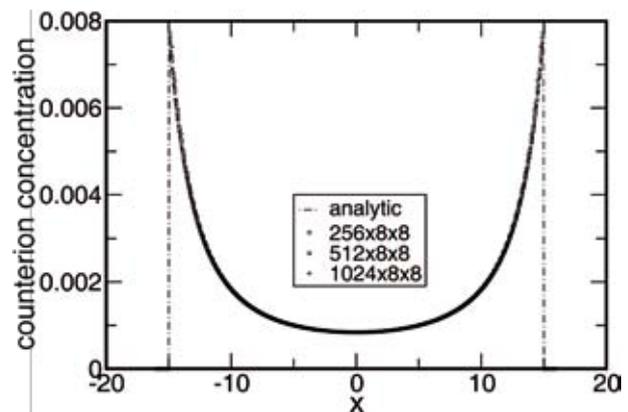
Complex fluids like polymer solutions or colloidal dispersions are characterized by the interplay between degrees of freedom of strongly differing length and time scales. For example, a colloidal dispersion may contain particles of micron size, while the size of the solvent particles is of the order of a few Angstroms. Soft-matter theory is mainly interested in the phenomena which happen on large scales, while still taking the particle character of the solute into account. Therefore, one needs “mesoscopic” simulation approaches, where the solute is treated in terms of particles, while the solvent is just a hydrodynamic continuum. Although there are different ways of doing this, we have found the lattice Boltzmann method, which solves the Boltzmann equation known from the kinetic theory of gases in a fully discretized fashion, a particularly efficient and straight-forward way of simulating hydrodynamic flows. Use of this in combination with a system of particles simulated by Molecular Dynamics was first put forward by A.J.C. Ladd, who spent the first half of 2007 as an Alexander von Humboldt fellow at the MPI-P. For the coupling one may use extended particles with boundary conditions, as in the original version, or a dissipative scheme based upon interpolation, as invented by the MPI-P group.



**Fig. 1:** “Artist’s view” of a system of colloidal particles coupled to lattice Boltzmann. The arrows represent the set of discrete velocities used in the simulation, such that one time step always propagates the lattice Boltzmann particles to a nearby lattice site.

The mesoscopic scales are so small that thermal noise still plays a significant role. In order to simulate Brownian motion, it needs to be included. In the past, there had been some discussion on how to do this consistently within the lattice Boltzmann method. Previous approaches had either only required consistency on the macroscopic scale, or applied rather phenomenological concepts. In essence, the problems could be traced back to the lack of a clear “bottom-up” theory of the statistical mechanics of lattice Boltzmann systems. We have now developed such a theory, from which one can unambiguously conclude what is required for thermodynamic consistency of the implemented thermostat. Essentially, one has to apply the principle of detailed balance, which is well-known from Monte Carlo simulations, to the stochastic collision rules. This opens the way to further improvement of the method, and, hopefully, also to a better understanding of more general lattice Boltzmann models with less trivial interaction.

Another problem which is very important in numerical soft-matter theory is the solution of the nonlinear Poisson-Boltzmann equation which describes the structure of ionic clouds in charged systems. We have recently developed an unconditionally stable method, which is based upon a variational formulation, combined with the representation of electrostatics by Maggs.



**Fig. 2:** Ion concentration profile between two parallel plates, comparing the exact analytical solution with our numerical solver. This is one special case where such a comparison is possible.

**Crosslinks to other projects:** Multiresolution Simulation Methods, Polymers and Colloids in Nonequilibrium Conditions

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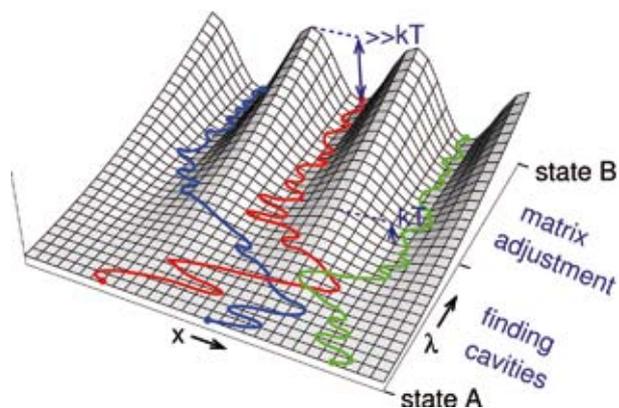
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## Permeation of Polymers – Computational Approaches

N.F.A. van der Vegt

*Keywords: Diffusion and solubility in polymers, free-energy calculations, force field models*

The computational chemistry group develops and uses all-atom and coarse-grained force field models for molecular simulations of polymers. These models, combined with a progress made in development of methods for free-energy calculations, permit modeling chemical potentials and solubilities of additive molecules in high molecular weight polymers with predictive accuracy. We have examined non-equilibrium free-energy calculations methods (Fig. 1) as well as thermodynamic perturbation methods (Fig. 2).



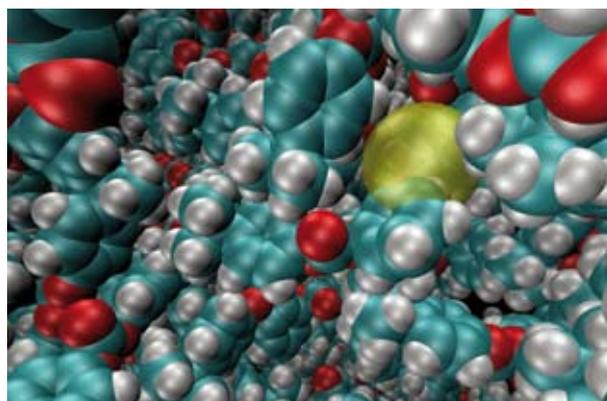
**Fig. 1:** Free energy surface  $F(x, \lambda)$ ; the Cartesian position coordinate  $x$  defines the location of a small molecule (“penetrant”) dissolved in a dense polymer; the coupling parameter  $\lambda$  defines the strength of interaction between the penetrant and the polymer. The penetrant’s excess chemical potential is calculated by moving the system from state A to state B at a finite rate. In state A, the penetrant is a (non-interacting) ideal gas particle; in state B, polymer-penetrant intermolecular interactions are at full strength. The colored “paths” on the free energy surface represent different realizations of the non-equilibrium coupling process.

We applied these computational methods to complex systems including water and aromatic solvents in high molecular-weight polycarbonate and polystyrene melts (obtained by inverse-mapping of equilibrated coarse-grained melts) at low concentrations of the penetrant (infinite dilution) in the polymer. At these concentrations, it

is extremely difficult to obtain accurate experimental data required for optimizing industrial degassing processes for the removal of solvents and monomers at the end of the production process.

Diffusion in polymer-solvent mixtures is studied with coarse-grained molecular dynamics simulations that probe the diffusive (Fickian) time scale with a minimum of computational resources. Tracer diffusion coefficients of ethylbenzene in ethylbenzene-polystyrene mixtures, recently studied by this approach, are in satisfactory agreement with pulse-field gradient NMR data.

These computational approaches to modeling solubility and diffusion are being further developed to characterize permeation in complex polymer-penetrant systems.



**Fig. 2:** Thermodynamic reference state in modeling chemical potentials; an example of a soft-cavity (yellow sphere) in molten polycarbonate. This reference state is perturbed to many, physically realistic, thermodynamic states in which the soft-cavity is replaced by a real molecule. Thermodynamic perturbation theory provides chemical potential differences (and relative solubilities) of various penetrant molecules based on a single simulation of the reference state.

**Crosslinks to other projects:** Multiscale Modelling of Structurally Organized Systems

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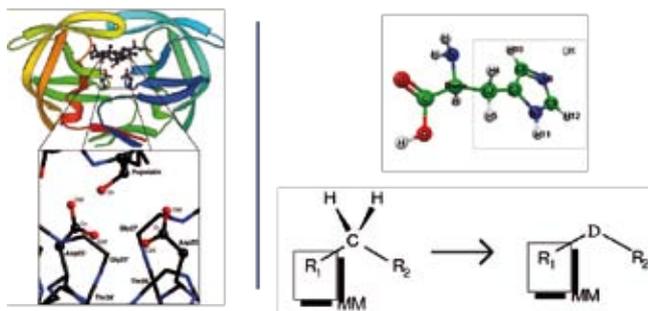
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# Hybrid Quantum/Classical Modeling Methods for Biomolecules

D. Sebastiani

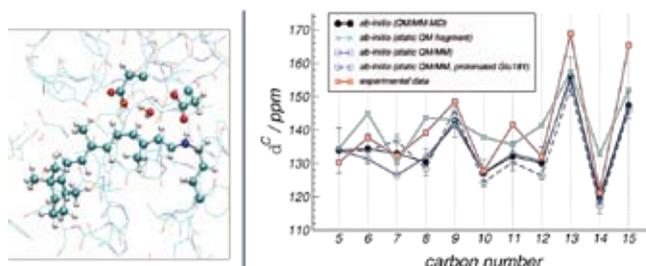
**Keywords:** *Ab-initio electronic structure theory, Car-Parrinello molecular dynamics simulations, QM/MM*

The atomic structure and the electronic and spectroscopic properties of molecules, liquids and solids can be predicted with high reliability from electronic structure theories, in particular density functional theory (DFT). When combined with molecular dynamics simulations, DFT provides an affordable route to observe dynamical disorder and chemical reactions at ambient temperatures. For large systems, however, such numerical calculations require very high computational resources. In this context, it can be sufficient to treat only a smaller part of the system quantum-mechanically (QM), while the remaining part is described using parameterized potentials (MM, molecular modelling). This combined approach is sketched in Fig. 1.



**Fig. 1:** Idea of the combined quantum/classical simulation approach: A (small) part of the (large) molecule is treated using quantum-mechanical methods, while the remainder is described classically with point charges. A special problem occurs if a chemical bond crosses the QM/MM boundary (right).

One of the difficulties of such a hybrid QM/MM approach is the transition between the QM and MM parts. We address these problems by developing novel effective potentials (capping potentials) to saturate dangling chemical bonds from the QM region. This is illustrated in Fig. 1, where the capping potential is represented by “D” atom. These optimized potentials can also be used to improve the non-bonded QM-to-MM contacts. The optimization is done in such a way that the electronic density and the spectroscopic properties of the important quantum region are calculated as accurately as possible.



**Fig. 2:** Spectroscopic properties (NMR chemical shifts, right image) of the rhodopsin chromophore (left), obtained with the hybrid QM/MM simulation approach and from experiments.

With these tools in hand, we are studying technologically relevant materials, in particular proton-conducting membranes (used in fuel cell membranes for the conversion of renewable energy), but also biological systems. The ultimate goal is to understand the relationships between chemical structure and biological functions. This in turn will help to find and to design new drug-related molecules with better properties.

As a complementary aspect, we have combined this quantum-classical molecular dynamics simulations with the calculation of spectroscopic properties, in particular NMR chemical shifts. Such calculations allow us on the one hand to verify computationally predicted structures, while on the other hand they enable the assignment of experimental peaks to specific atoms and conformations. This is an important prerequisite for the understanding of the meaning of such spectra.

Future projects will encompass the QM/MM calculation of large nanostructures in the framework of materials science, for instance functionalized nanotubes and their interaction with other molecules.

**Crosslinks to other projects:** Hydrogen-Bonded Aggregates, Elucidating Columnar Mesophases of Extended  $\pi$ -Electron Systems, Multiresolution Simulation Methods, Modeling and Interactions of Macromolecules and Biomolecules with Surfaces

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## Multiresolution Simulation Methods

M. Praprotnik, L. Delle Site, K. Kremer

*Keywords: Adaptive resolution, multiscale modeling, soft matter*

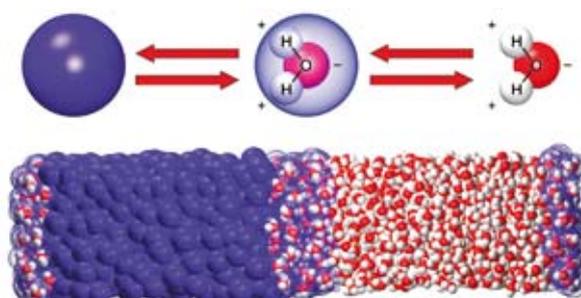
Many processes in soft matter are inherently multiscale, i.e., they involve a range of different time and length scales that are intrinsically interconnected. Due to the many degrees of freedom in these systems all-atom simulations that capture phenomena on the atomic scale are often not computationally feasible or even desirable. The more coarse-grained models or continuum simulations, on the other hand, can cover much larger time and length scales but are unable to provide information at the atomic level. Multiresolution simulation techniques that concurrently couple different length scales hence provide a very efficient way to treat such systems by computer simulation.

In recent years, we have been developing a flexible dual-resolution molecular dynamics (MD) simulation method, i.e., the Adaptive Resolution Scheme (AdResS). The key feature of this particle-based method is that it allows for a dynamical change of molecular resolution by changing the number of molecular degrees of freedom on-the-fly during the course of an MD simulation.



**Fig. 1:** The on-the-fly interchange between the atomistic and coarse-grained levels of description. The middle hybrid molecule is a linear combination of the all-atom and coarse-grained molecules.

Using this method an all-atom molecular system is maintained at thermodynamical equilibrium with a far simpler coarse-grained system. Our approach, which concurrently couples the atomic and mesoscopic length scales of the system, leads to a generalization of the equipartition theorem to fractional degrees of freedom and can be viewed to a certain extent as a geometry induced phase transition. So far we have applied AdResS to molecular liquids.

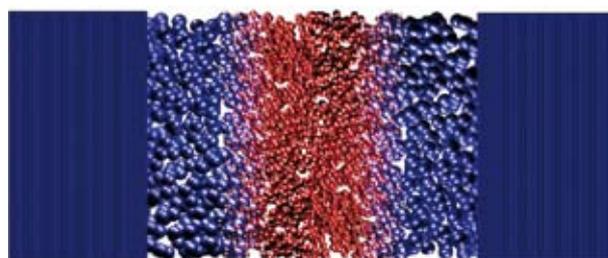


**Fig. 2:** The hybrid liquid water system.

The system is modeled in different domains at different levels of detail while the liquid molecules move freely between the regions. Examples are a simple liquid of tetrahedral molecules, a solvated macromolecule, and liquid water.

In order to cover an even wider range of length scales we have also included the continuum description of a liquid in our model. We performed a triple-scale simulation of a molecular liquid, in which the atomistic, mesoscopic and continuum descriptions of the liquid are concurrently coupled. This multi-resolution approach thus covers the length scales ranging from the micro to macro scale.

The triple-scale method, which correctly describes the hydrodynamics within the hybrid particle-continuum framework, allows us to perform efficient grand-canonical MD simulations of truly open molecular liquid systems.



**Fig. 3:** The triple-scale model of a molecular liquid. The particle-based region is embedded in the hydrodynamics continuum.

**Crosslinks to other projects:** Structure Property Relations, Polymer Dynamics, Multiscale Modelling

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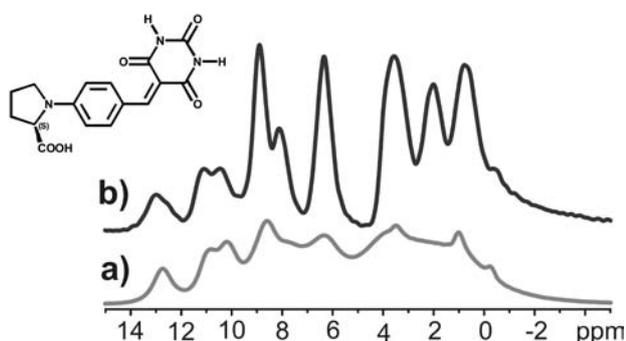
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# Pushing the Limits of Solid-State NMR

R. Graf, G. Brunklau, H.W. Spiess

*Keywords: Supramolecular architectures, hydrogen-bonds, molecular structure and dynamics*

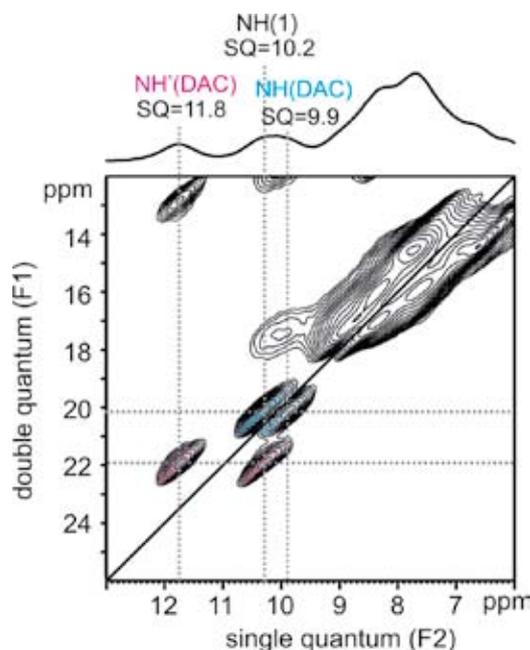
Solid-state NMR spectroscopy is capable of providing valuable and detailed insights into both the structure and dynamics of a broad variety of systems ranging from classical polymers and liquid-crystalline materials to complex supramolecular architectures. In particular, hydrogen bonds, intermolecular packing arrangements and dynamics of molecular segments can be investigated in great detail – in most cases even without the need for special sample preparation. In order to access and exploit the rich variety of information inherent in NMR spectra, the solid-state NMR group devotes considerable effort to the development of new advanced methods and their application to systems of current interest.



**Fig. 1:**  $^1\text{H}$  MAS NMR spectra of the barbiturate dye KS-101. a) 30 kHz MAS at 700 MHz and b) 15 kHz MAS at 850 MHz using windowed phase-modulated Lee-Goldburg (wPMLG) detection. Note the superior resolution in the latter case.

The NMR methods currently developed and applied are based on fast magic-angle spinning (MAS) which allows for an efficient suppression of typical interactions present in the solid state. In this way, site-specific information becomes accessible. The simple and robust  $^1\text{H}$ - $^1\text{H}$  double-quantum (DQ) experiment is particularly useful for studying hydrogen-bonded systems or dynamics of both polymers and liquid crystals. Due to the low chemical shift dispersion of protons, these measurements require high static magnetic fields (up to 20 T) and often very fast MAS (up to 70 kHz) to achieve sufficient resolution. In some cases, multi-pulse suppression of residual dipolar couplings such as phase-modulated Lee-Goldburg can be used to improve the spectral resolution of  $^1\text{H}$  MAS NMR methods, which show excellent performance on modern spectrometer hardware (Fig. 1).

Nevertheless, the spectral resolution can be improved only in special cases of highly crystalline samples with very narrow spectral lines due to the disadvantageous chemical shift scaling factors of the homonuclear decoupling pulse sequences.



**Fig. 2:** Expanded region of the  $^1\text{H}$ - $^1\text{H}$  DQ MAS NMR spectrum of the complex of 1-n-butyl-5-(4-nitrophenyl)barbituric acid with 2,6-diacetamidopyridine in the presence of 1,8-bis(dimethylamino)naphthalene at 59524 Hz and 850 MHz. Notably, the blue-marked peak is unambiguously identified as cross-peak, hence revealing successful complex formation.

However, even at very high static magnetic fields and the fastest MAS, solid-state  $^1\text{H}$  MAS NMR spectra can still be limited with respect to the achievable spectral resolution. This problem can be overcome by heteronuclear multiple-quantum NMR methods, involving nuclei such as  $^{13}\text{C}$ ,  $^{31}\text{P}$  or  $^{15}\text{N}$ , which have recently been developed in our group. For example, based on the resolution of  $^{13}\text{C}$  NMR spectra,  $^1\text{H}$ - $^{13}\text{C}$  recoupling experiments have been designed that allow for the measurement of segmental dynamics of individual  $\text{CH}_n$  groups. In the case of proton-conducting polymeric materials, a new class of  $^2\text{H}$  MAS experiments were particularly valuable facilitating unprecedented site-resolution.

**Crosslinks to other projects:** Hydrogen-Bonded Aggregates, Crystal Engineering of Molecular Architectures, Chain Diffusion in Semi-Crystalline Polymers, Structure and Dynamics of Columnar Photonics via NMR and ab-initio Methods, Proton Conductive Polymers for Improved Fuel Cell Applications, Discotic Liquid Crystals in Motion, Hybrids with Biological Components

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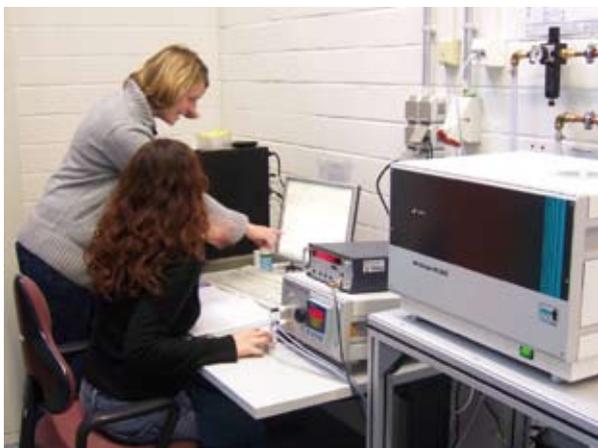
## EPR Spectroscopy

### D. Hinderberger

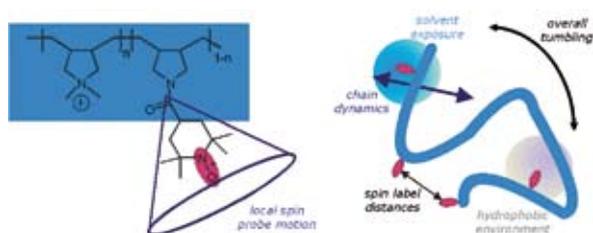
**Keywords:** EPR/ESR spectroscopy, ENDOR, ELDOR, high-field EPR, nanostructure, molecular dynamics

Electron paramagnetic resonance (EPR or ESR) spectroscopy is a magnetic resonance method sensitive to molecular dynamics in the microsecond to picosecond regime and to structures and distances from  $\sim 0.1$  to 10 nanometers. This sensitivity paired with the selectivity of using radicals as probe molecules make EPR spectroscopy an exciting and powerful tool in biophysics and in the emerging interdisciplinary fields of nanoscience and materials science at the molecular level.

By using spin probes, such as nitroxides or transition metal ions, it is possible to obtain site-specific information on the structure and dynamics of almost any material that contains soft matter. We use conventional continuous-wave (CW) EPR and advanced pulsed EPR and pulsed double resonance techniques, all of them available at high field (3.4T) and frequency (94.2 GHz), for the characterization of very diverse soft matter systems. Most of these techniques can now be applied with sample volumes as small as  $2\mu\text{L}$  at spin concentrations down to 100 or even  $10\mu\text{mol L}^{-1}$  in a temperature range between 6 and 350 K, and at even higher temperatures, if sample volumes of  $50\mu\text{L}$  are available. For routine CW EPR measurements and teaching purposes, an easy-to-use benchtop CW EPR spectrometer operating at 0.34 T (X-band) is the newest addition to the EPR equipment.



**Fig. 1:** An easy-to-use benchtop CW EPR spectrometer for routine measurements and student training is available.



**Fig. 2:** Schematic picture of the information available from CW EPR and pulse EPR of spin-labeled macromolecules.

We have developed methods to determine nanostructures and their dynamic behavior, in particular in such materials that exhibit a relatively low degree of order or high complexity in their structures. The topics of interest are broad-ranged and include ionically self-assembled systems (small ions, synthetic polyelectrolytes, DNA-polyamine interactions), nanoinhomogeneities of functional polymeric systems such as hydrogels, and membrane-bound proteins.

Using more sophisticated models, it was possible to show by analysis of conventional CW EPR spectral line shapes that in solutions of cationic Poly(diallyldimethylammoniumchloride) (PDADMAC) polyelectrolytes the radial counter-ion distribution can be described by a charged cylindrical cell model. Furthermore, we could characterize the nanoinhomogeneities in thermoresponsive Poly(N-isopropylacrylamide) (PNIPAAm)-based hydrogel systems and show how dendrons of polyamines interact with DNA.

Pulse EPR methods that probe the hyperfine interaction of the electron spin with surrounding nuclear spins can be used to study not only the electronic and geometric structure of novel main-group (Pb- and Sn-based) radicals, but also how accessible radicals in self-assembled systems are towards solvent molecules. Furthermore, using high-field pulse electron-nuclear double resonance (ENDOR) it was possible to directly probe the solvation sphere around small inorganic radicals in mixtures of methanol and water and to show that methanol and water indeed have preferential positions when surrounding and solvating these ions.

**Crosslinks to other projects:** Structure Formation by Ionic Interaction, Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels, NMR Signal Enhancement by Dynamic Nuclear Polarization

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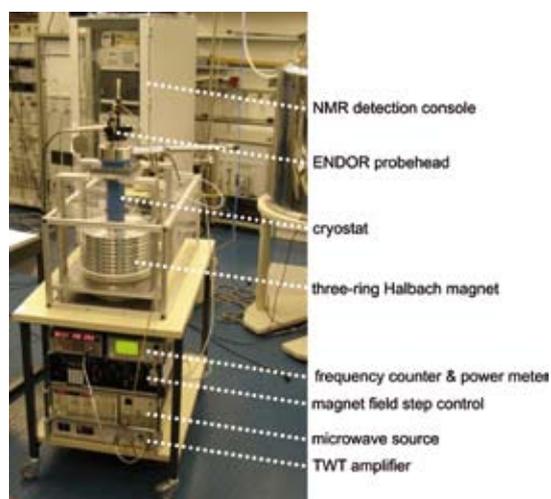
# A Mobile Polarizer for Dynamic Nuclear Polarization

K. Münnemann, D. Hinderberger

*Keywords: DNP, hyperpolarization, radicals,  $T_1$  relaxation*

The application of  $^{13}\text{C}$  (or other low  $\gamma$  nuclei) NMR spectroscopy and imaging for material science and especially clinical diagnosis has been constrained by the extremely long imaging and spectroscopy acquisition times that are required to obtain high signal-to-noise ratio (SNR) under ambient conditions (low natural abundance of  $^{13}\text{C}$ , low concentration of  $^{13}\text{C}$ -compounds, physiological temperature etc.). However, this obstacle could be overcome by *in vitro* hyperpolarization of a  $^{13}\text{C}$  containing molecule with long spin lattice relaxation time by Dynamic Nuclear Polarization (DNP) or Parahydrogen Induced Polarization (PHIP) and subsequent transfer of the hyperpolarized compound into the spectrometer or tomograph used for investigation. One major issue of this approach is the limited lifetime of the hyperpolarized state, which restricts the application and detection of the hyperpolarized molecules to roughly 3 times  $T_1$ . This problem is even more pronounced if the hyperpolarization process can not take place in the vicinity of the used MR tomograph due to safety restrictions or space limitation as it is often the case in hospital MR facilities.

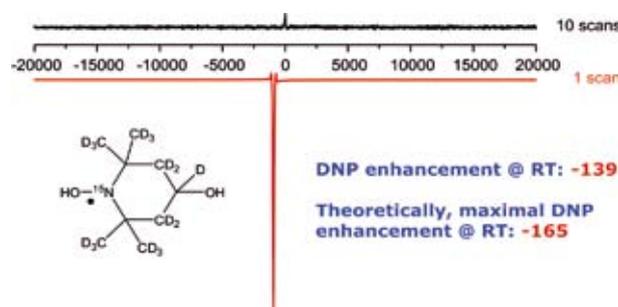
To overcome this problem we developed a mobile DNP polarizer based on a Halbach magnet operating at intermediate fields of 0.1 to 0.35 Tesla. The use of a mobile permanent magnet design enables us to minimize the transport time from the hyperpolarization site to the



**Fig. 1:** Mobile DNP polarizer. The complete polarizer is mounted on one rack. The tuneable Halbach magnet with cryostat and probehead can be seen on the upper tray, the microwave source & amplifier and the control electronics for the stepper motors are placed on the lower tray.

MR tomography, resulting in efficient use of the non-equilibrium magnetization regardless of which scanner has to be used.

DNP takes advantage of the very high Boltzmann polarization of unpaired electron spins that can be transferred by dipolar or scalar coupling to nuclear spins thereby drastically enhancing the NMR signal. For DNP experiments free radicals have to be added to the sample and the electron paramagnetic resonance (EPR) transitions of the electron spins have to be saturated by microwave irradiation resulting in the transfer of the electron spin magnetization to nuclear spins.



**Fig. 2:**  $^1\text{H}$ -NMR spectra of water doped with the free radical Tempol ( $^{15}\text{N}$  enriched and perdeuterated) at room temperature (black: reference spectrum; red: DNP enhanced spectrum with 8 W CW microwave irradiation).

One of the major advantages of DNP is that virtually every nuclear spin species ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  etc.) in arbitrary molecules can be polarized, which underlines the general applicability and importance of the DNP effect for NMR and MRI. We are able to perform reliable DNP experiments in this mobile apparatus and obtain reasonably high  $^1\text{H}$ -DNP enhancement. Our next steps are aimed at the polarization of heteronuclei ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ). In addition, the cooling of the sample should significantly increase the DNP efficiency, which led us to the implementation of a cooling system for temperatures as low as 4 K. With this add-on we should be able to significantly increase the thermal polarization of the electron spins resulting in much higher DNP enhancement.

**Crosslinks to other projects:** Parahydrogen Induced Polarization, EPR Spectroscopy, NMR with Non-Thermal Spin Polarization

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# NMR with Non-Thermal Spin Polarization

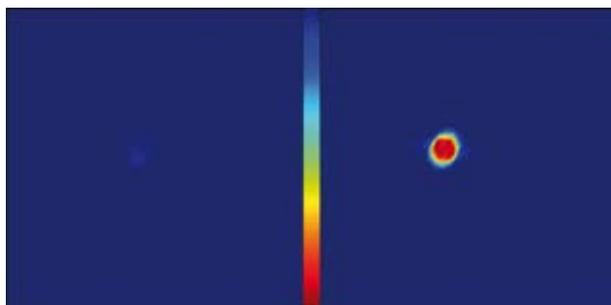
A. Koch, K. Münnemann

*Keywords: PHIP,  $T_1$  relaxation, hyperpolarized gases and liquids, distant dipolar fields in gases*

## Parahydrogen Induced Polarization (PHIP)

PHIP is a way to achieve hyperpolarization of spin ensembles by a chemical route. It makes use of the parahydrogen symmetry breaking during homogeneously catalyzed hydrogenation of unsaturated substrates, creation of non-equivalent product protons and the re-insertion of parahydrogen spin information into the substrate molecule.

Parahydrogen, the thermodynamically preferred spin isomer of the hydrogen molecule (as opposed to orthohydrogen), can be enriched to > 98% by cryo-cooling under the effect of active charcoal. After a subsequent homogeneous parahydrogenation reaction, PHIP NMR experiments lead to absorption and emission signals and a theoretical signal increase of up to  $10^4$ , which is in practice limited by relaxation processes.



**Fig. 1:** Comparison of an MRI slice at thermal (left, barely visible) and PHIP (right) polarization levels (1-hexyne, FLASH sequence, matrix  $128 \times 128$ , resolution  $0.7 \times 0.7$  mm, single shot).

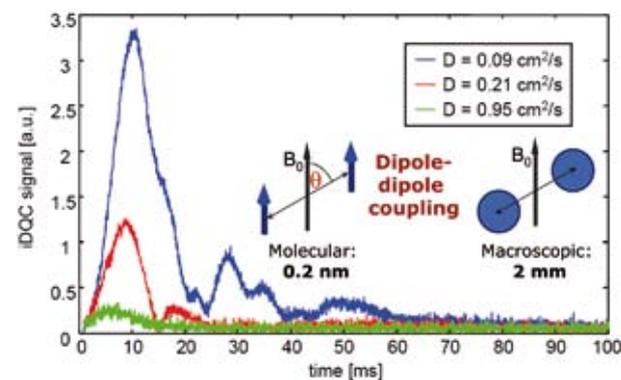
Imaging experiments on a model compound show a substantial advantage in contrast and imaging time. At 1.5 Tesla a  $^1\text{H}$  signal enhancement of 2000 was achieved. The large proton magnetization can be transferred to heteronuclei by PHIP-INEPT and PHIP-INEPT+ pulse sequences, which led in our recent experiments at 7 Tesla to a  $^{13}\text{C}$  NMR signal enhancement of 3900. The next step will be to transfer these promising results to physiologically relevant substrates that might be of diagnostic importance. Experiments along these lines are performed in our laboratory and in cooperation with the University hospital in Mainz.

## Hyperpolarized gases in MRI

Conventional  $^1\text{H}$  pulmonary Magnetic Resonance Imaging (MRI) applications are restricted by low sensitivity and contrast due to the low proton density in the lung. Therefore, clinical lung MRI is increasingly employing hyperpolarized (HP) gases as functional contrast agents. While inhaled HP  $^3\text{He}$  is particularly well-suited for ventilation measurements and depicting lung morphology, HP  $^{129}\text{Xe}$  can be of great benefit for perfusion measurements because of its higher solubility in liquids, e.g. in blood.

Our group conducts basic research with both,  $^{129}\text{Xe}$  and  $^3\text{He}$ . Both nuclei have spin=1/2 and can be laser-polarized. This means that angular momentum from a circular polarized laser beam is transferred to the nuclei. We are able to polarize  $^{129}\text{Xe}$  with a home-built polarizer (developed and built by S. Appelt et al.; FZ Jülich). The polarized  $^3\text{He}$  is provided by Prof. Heil's group (Institute of Physics at the University of Mainz).

During the last few years several topics of hyperpolarized gas imaging have been investigated by our group. The main results concern “simultaneous NMR-Imaging of hyperpolarized  $^3\text{He}$  and  $^{129}\text{Xe}$ ”, “direct molecular solution of hyperpolarized gases through hollow fibre membranes”, “detection of pseudo spin echoes in gases” and “observation of distant dipolar fields in HP gases”.



**Fig. 2:** Intermolecular double-quantum coherences arising from distant dipolar fields in HP  $^3\text{He}$  measured for different diffusion coefficients.

**Crosslinks to other projects:** A Mobile Polarizer for Dynamic Nuclear Polarization

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# Optical Single Object Detection

M. Kreiter

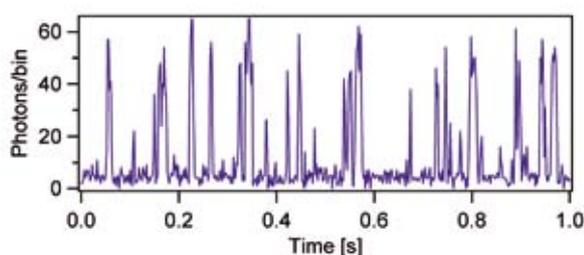
*Keywords: Confocal microscopy, fluorescence, scattering, single-molecule, dynamics*

Single-molecule fluorescence microscopy and spectroscopy has become an established analytical method in the last ten years. In two important classes of experiments it can reveal information that is not accessible by ensemble measurements.

## Time-dependent fluctuations

The first class of experiments deals with identical objects that show some uncorrelated changes as a function of time.

Fig. 1 shows, as a prominent example, the intensity of a single organic fluorophore. Successive bright and dark periods are seen, the dark periods are assigned to excursions of the molecule into the long-lived triplet ground state. Clearly, this blinking can not be seen in an ensemble experiment since the bright and dark periods of different dyes are uncorrelated and add to a constant average intensity.



**Fig. 1:** Time trace of the fluorescence intensity of a single fluorophore.

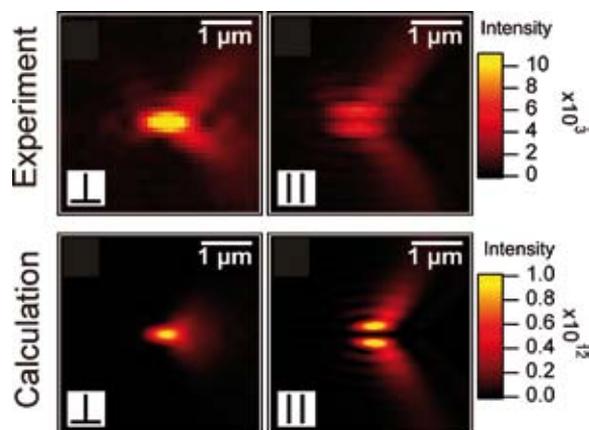
Next, two examples of physical systems are briefly discussed where this technique was applied. The triplet dynamics of organic chromophores is strongly influenced in the vicinity of a metal surface. It could be shown that the duration of the dark periods is reduced while the duration of the bright periods increases due to the presence of the gold. Taken together, these two effects lead to a considerable increase in chromophore brightness. Colloidal semiconductor quantum dots show bright and dark states which at first sight are very similar to the triplet blinking. A closer analysis of the blinking statistics, though, implies that a

fundamentally different physical mechanism must be responsible for the bright and dark periods in this case. We could show that this blinking is highly insensitive to external parameters like excitation intensity and quantum dot surrounding. Furthermore, a memory effect of this blinking was discovered.

## Inhomogeneous ensembles

A second class of experiments where single-molecule techniques are very useful are investigations of ensembles of non-identical objects. Such techniques can be of great importance for the investigation of complex superstructures like macromolecular assemblies or organic-inorganic hybrids.

For example, a technique was developed to record the optical scattering spectrum of objects through thin metal films. The appearance of individual scatterers in this 'plasmon-mediated dark field' mode is displayed in Fig. 2. Spectroscopy on individual objects using white-light illumination reveals substantial differences between the optical resonances of these scattering entities.



**Fig. 2:** Measured and calculated appearance of individual scattering objects through a thin gold film for two different linear polarizations of the incident electrical field.

**Crosslinks to other projects:** TIR-FCS Studies of Diffusion and Flow Near a Liquid-Solid Boundary, Optical and Electron Microscopy

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# Colloidal Lithography for the Preparation of Metallic Nanostructures with Optical Resonances

M. Kreiter, U. Jonas

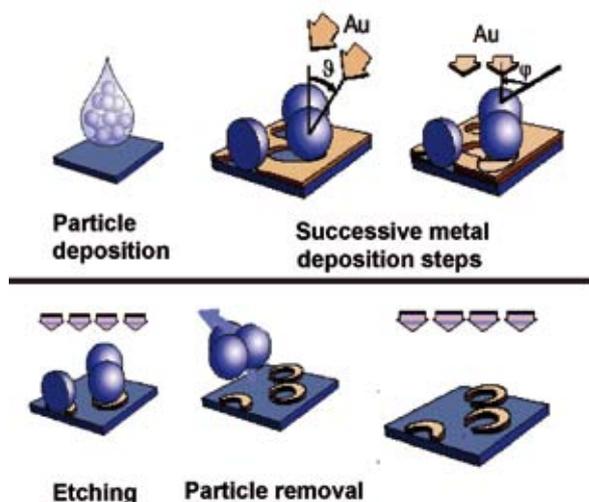
*Keywords: Colloidal lithography, plasma etching, plasmon, metamaterial*

Nanoscale metal particles with nontrivial shapes support optical (plasmon) resonances making them interesting for the manipulation of light on the sub-wavelength scale.

While almost arbitrary shapes can be realized by sequential structuring methods using electron beams or focused ion beams, these approaches suffer from two severe drawbacks. Firstly, maximum sample areas with typical dimensions of only some 100  $\mu\text{m}$  can be structured within reasonable time scales. Secondly, both techniques suffer from contamination degrading the chemical purity and the optical response of these structures.

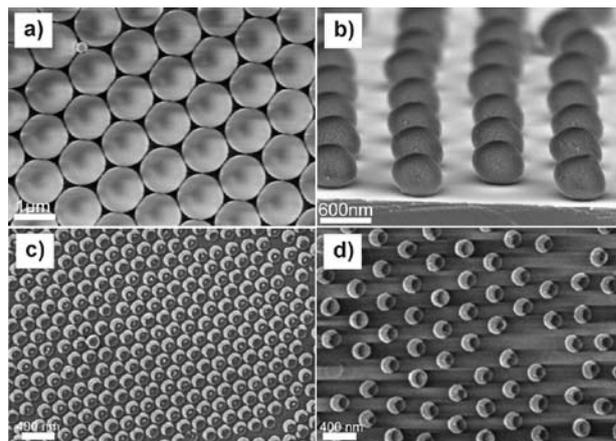
An alternative method that allows for the parallel structuring of macroscopic areas utilizes colloids as shadow masks for material deposition and etching. This technique, called 'natural' or 'colloidal' lithography, allows for the parallel structuring of macroscopic areas. At the same time, contamination of the metal is almost completely avoided.

Fig. 1 shows as an example the preparation of crescent-shaped metal particles by using isolated colloids as a mask that were established in 2005.



**Fig. 1:** Preparation of metal nanocrescents by colloidal lithography.

A common limitation of this technique, like other schemes relying on isolated colloids, is the very low surface coverage that can be realized, on account of geometrical reasons the process requires a minimum distance between the colloids. Furthermore, the distance between resonators is not defined.



**Fig. 2:** a) Ordered monolayer of polystyrene colloids on a silicon wafer. b) after plasma etching. c,d) ordered arrays of gold nanocrescents with varying size and spacing.

Fig. 2 shows the individual steps of a novel approach to obtain surfaces decorated with oriented arrays of metal structures with a maximum packing density and tuneable distance. It is based on the deposition of highly monodisperse polystyrene colloids on a substrate in a monolayer with very low defect density (Fig. 2a). Next, a two-step plasma process reduces the colloid size. Both their position and a smooth surface are retained (Fig 2b). They can be used as masks for the preparation of ordered nanostructures with defined size and spacing (Fig. 2c, d).

The transfer of this methodology to the assembly of metal structures in three dimensions is of current interest, e.g. it is needed to build optical metamaterials. With this goal, the as-prepared layer has been covered with a thin silica film in a sol-gel process. On top of this film another layer of particles could be prepared, resulting in a three-dimensional ordered arrangement of these plasmonic resonators.

**Crosslinks to other projects:** Nanolithography with Nanoparticles, Tailoring of Phononic Band Structures in Hierarchical Colloid Systems

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# Evanescent Wave Optics

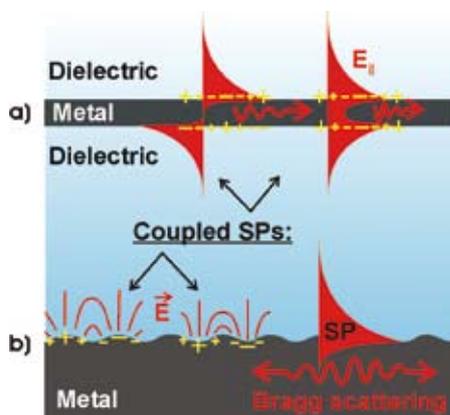
J. Dostálek, B. Menges

*Keywords: Surface plasmon resonance, thin films, optical sensors, biosensors*

Surface plasmon resonance (SPR) is a phenomenon associated with the resonant excitation of surface plasmons (SP) – evanescent waves originating from oscillations of electron plasma on a metallic surface. SPs can be used to probe processes occurring at interfaces between a metal and a dielectric. SPR is a technique used in the material sciences for the characterization of thin films, biomolecular interaction analysis (BIA) and biosensors for detection of chemical and biological species.

## Coupled surface plasmon modes

Surface plasmon propagating along thin metallic films or along periodically modulated metallic surfaces can become coupled giving rise to new SP modes, see Fig. 1.



**Fig. 1:** Coupled surface plasmon modes a) propagating along a thin metallic film and b) formed by the Bragg scattering on periodically modulated surface.

Characteristics of coupled SPs can be tailored for specific applications. For instance, a thin metallic film embedded between dielectrics with similar refractive indices supports a SP mode with an anti-symmetric component of electric intensity that is parallel to the metallic surface. This coupled mode is referred to as long range surface plasmon (LRSP) and can propagate along the surface with lower orders of damping than conventional surface plasmons.

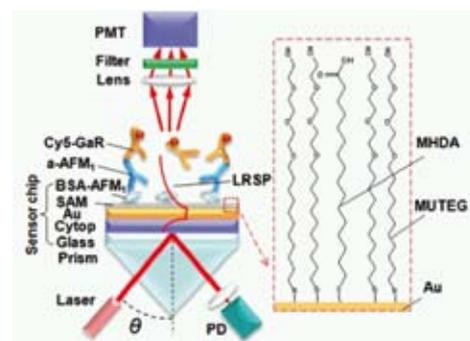
## Implementation of SPFS biosensors

The excitation of LRSP leads to an improvement of biosensors based on surface plasmon-enhanced fluorescence spectroscopy (SPFS). In these devices, target molecules contained in the sample of interest are captured by bio-recognition elements immobilized on a metallic surface.

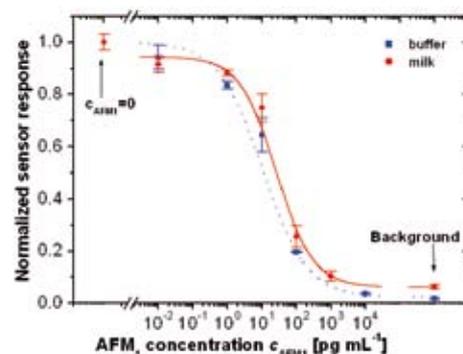
The binding of fluorophore-labeled molecules to the surface is observed via the induced fluorescence signal, which is greatly increased by the strong enhancement of the electromagnetic field on the sensor surface upon the resonant excitation of SPs. The excitation of LRSPs provides an even greater enhancement of the electromagnetic field ( $|E/E_0|^2$  larger than 100 is possible) and thus enabling a further increase in the sensitivity of the SPFS method.

## Detection of aflatoxin M<sub>1</sub> in milk

LRSP-enhanced fluorescence spectroscopy was implemented in a highly sensitive biosensor for detection of aflatoxin M<sub>1</sub> in milk. These biosensors employed an optimized layer structure for the excitation of LRSPs on the sensor surface and an inhibition immunoassay, see Fig. 2. The sensor allowed for fast detection of AFM<sub>1</sub> at sub pg/mL levels.



**Fig. 2:** Scheme of the SPFS-based biosensor exploiting inhibition competitive immunoassay and the excitation of LRSPs.



**Fig. 3:** Calibration curve of a LRSP-FS biosensor for detection of AFM<sub>1</sub> in milk (red curve) and a buffer (blue curve).

**Crosslinks to other projects:** Functionalized Surfaces for Optical Biosensors, Size and Interaction Dependent Mobility in Hydrogels

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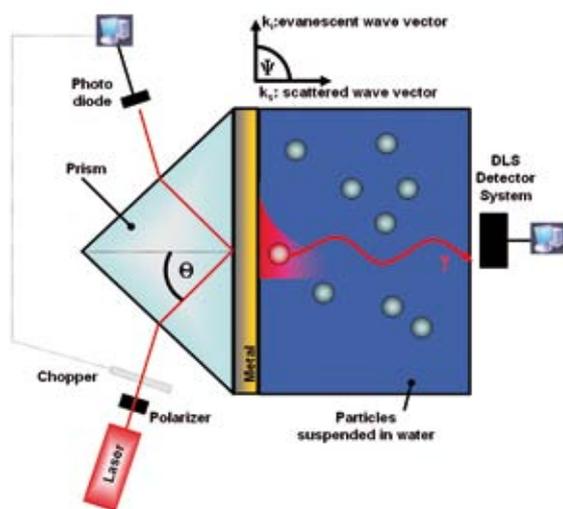
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# Field Enhanced Dynamic Light Scattering at Interfaces

B. Menges, W. Steffen, G. Fytas

*Keywords: Field enhancement, evanescent wave optics, surface plasmon polaritons, dynamics at interfaces, transport phenomena*

The study of motion on the nanometer scale close to a surface is of paramount importance for the understanding of dynamic behavior, e.g. of particles or polymers at interfaces, transport phenomena to and from surfaces, thin films or membranes. Local structure and properties of material in the immediate vicinity of a solid surface often differ from those in the bulk state due to the physical and chemical influence of the interface. These effects extend to fractions of a micrometer only. Observation of the near-interface region requires very sophisticated techniques to obtain information within such a thin layer.



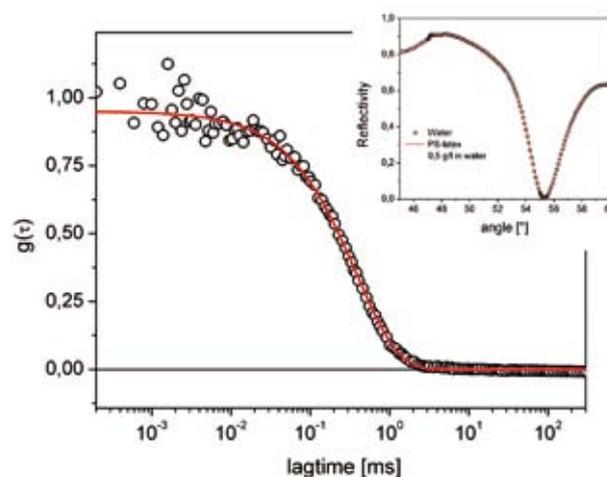
**Fig. 1:** Scheme of SPR-PCS set-up for field enhanced dynamic light scattering.

The combination of Surface Plasmon Resonance and Photon Correlation Spectroscopy (SPR-PCS) is a means to achieve this goal. With an adapted detection system and a modified SPR setup we were able for the first time to perform such an experiment.

Although the evanescent wave generated by total internal reflection has attracted a great deal of interest in recent years as a probe with high spatial resolution, our approach is to utilize a surface plasmon as the incident electromagnetic field instead of the evanescent field generated from total internal reflection. The surface plasmon polariton delivers a much greater enhancement of the evanescent field. It thus opens the possibility of studying the diffusion on surfaces at very low levels of laser power and for example low concentration of particles in solution.

In addition the SPR supplies a highly sensitive detection of the optical properties and conditions of and near the interface. Every change during the SPR-PCS experiment like alteration of the surface or adsorption of molecules to the surface would be detected.

Here we describe the first experimental realization of a dynamic light scattering experiment close to an interface with surface plasmon polaritons as a source of the scattered light. As a proof of concept the diffusion of polystyrene-latex particles close to the metal surface was studied. The particle radii can be extracted from relaxation function  $g(q, \tau)$  within certain limits.



**Fig. 2:** SPR-PCS data and fit of a  $R=30$  nm PS-Latex at a scattering vector  $q=0.019$  nm<sup>-1</sup>. The inset shows the surface Plasmon reflectivity scan of this system. The PCS data were obtained at the minimum.

So far we are able to probe particles with radius  $R$  as small as 10 nm. The scattering volume in this experiment is limited to the space between the solid surface and 200 nm above.

This novel combination of experimental techniques opens up new possibilities in materials science as well as in biophysics. The metallic interface in the SPR-PCS will lead to new insights in electro- and surface chemistry.

**Crosslinks to other projects:** Evanescent Wave Optics, Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels, Polymer Characterization, Matter Diffusion in Nanoporous Media and Dense Polymer Systems by FCS

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## TIR-FCS Studies of Diffusion and Flow Near a Liquid-Solid Boundary

K. Koynov

**Keywords:** Fluorescence correlation spectroscopy, evanescent wave, diffusion, flow, interface, dynamics, polymer brushes, boundary slip

In recent years fluorescence correlation spectroscopy (FCS) has emerged as a powerful tool to measure the diffusion of fluorescent molecules, macromolecules or nanoparticles in various environments. The method is based on detecting fluctuations in the fluorescent light intensity caused by the diffusion of the fluorescent species through a small observation volume ( $<1 \mu\text{m}^3$ ), formed by the focus of a confocal microscope. We have successfully used the method to address a broad range of research questions:

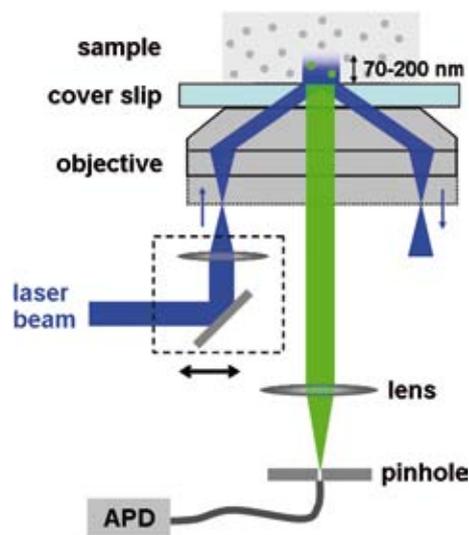
- Size and diffusion properties of various dendrimers, proteins and DNA-based macromolecules.
- Tracer diffusion in undiluted polymer solutions and bulk polymers.
- Dynamics of swollen crosslinked polymer networks of micron sizes e.g. poly(N-isopropylacrylamide) hydrogels or polystyrene microbeads.

Despite its high sensitivity and versatility the classical confocal FCS is not a very suitable tool for addressing the diffusion close to surfaces. This limit is due to the fact that the interfacial region typically reaches only few nanometers away from the bulk while the focus extends over typically  $1 \mu\text{m}$ . To overcome this limitation we have developed and implemented a new FCS scheme, namely Total Internal Reflection Fluorescence Correlation Spectroscopy (TIR-FCS). The principle of TIR-FCS is based on the phenomenon of total internal reflection at the interface between two media with different refractive indices. Under the conditions of TIR, a standing evanescent (vanishing) wave is produced in the medium having a lower refractive index. This wave can be used for excitation of fluorophores in close proximity to the interface. The basic principle of our TIR-FCS setup is to excite the evanescent wave through the same microscope objective which is used for collection of the fluorescent light (Fig. 1). The excitation laser beam is focused onto the periphery of the back focal plane of the objective. This results in a parallel beam, propagating at a certain incident angle towards the cover slip/sample interface. By changing the position at which the excitation beam enters the microscope objective, the angle of incidence

and therefore the penetration depth of the evanescent wave can be continuously tuned. The emitted fluorescent light is focused on a pinhole and further detected with an avalanche photo diode. In this way a disc shaped observation volume is created with a diameter in the order of  $500 \text{ nm}$  and height tunable in the range  $70\text{--}250 \text{ nm}$ .

Using this extremely small observation volume we can measure the diffusion of fluorescent species in the close proximity of the glass/sample media interface. In such a way we can address the near-wall hindered diffusion of fluorescent nanoparticles, dynamics of polymer chains near solid surfaces, adsorption/desorption kinetics or tracer diffusion in polymer brushes.

Furthermore, by modifying the scheme shown in Fig. 1 through introducing a second pinhole/APD channel, that monitors a laterally shifted observation volume and performing spatial cross-correlation, we are able to directly measure flows in the  $\sim 100 \text{ nm}$  proximity of the interface. This allows investigation of the boundary slip phenomenon as well as transport processes in polymer brushes.



**Fig. 1:** Sketch of a total internal reflection fluorescence correlation spectroscopy setup.

**Crosslinks to other projects:** Matter Diffusion in Nanoporous Media and Dense Polymer Systems by FCS, Field Enhanced Dynamic Light Scattering at Interfaces, Colloid Probe Technique, Modeling and Interactions of Macromolecules and Biomolecules with Surfaces

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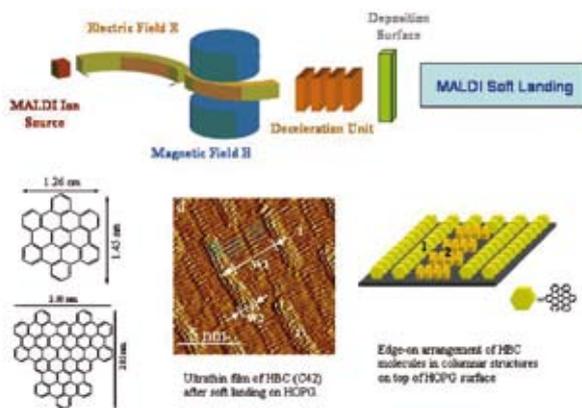
# Processing Molecules Beyond Traditional Limits: Soft Landing and Pulsed Laser Deposition for Thin Films

H.J. Räder

**Keywords:** MALDI, PLD, insoluble and non-volatile molecules, thin layers, STM, OFETs

Thin films are important in various applications, such as corrosion protection, surface compatibilization or molecular electronics. Traditional methods for thin film preparation require samples which can be processed either from solution or from the gas phase, therefore suitable molecules must be soluble or volatile. Large molecules like Polycyclic Aromatic Hydrocarbons (PAHs), however, are neither soluble nor volatile. PAHs can be regarded as well defined segments of graphite, thus rendering them interesting candidates for electronic applications especially with increasing size. Therefore we developed new processing techniques, which overcome the existing limitations: Matrix Assisted Laser Desorption/Ionization - Soft Landing (MALDI-SL) and Pulsed Laser Deposition (PLD). Both methods allow one to “evaporate” huge molecules much beyond their thermal evaporation limit and in both cases, the phase transition from the solid state to the gas phase is achieved with the help of a nitrogen laser.

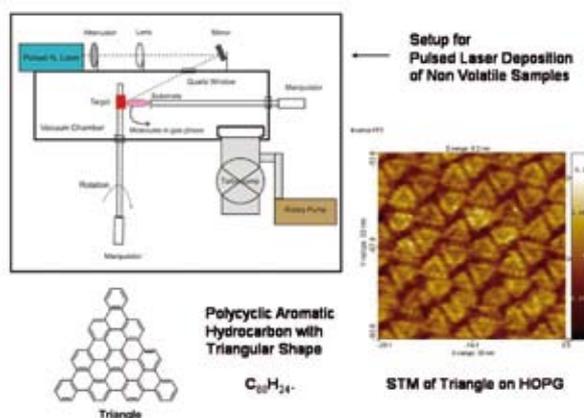
Soft landing (Fig. 1) makes use of a modified sectorfield mass spectrometer and a special method of MALDI sample preparation for insoluble molecules developed by us.



**Fig. 1:** MALDI-soft landing of molecular ions.

MALDI-SL enables not only the intact phase transition and ionization of molecules, so far considered as intractable, but also their direct purification due to their mass-to-charge ratio. Furthermore, MALDI-SL has virtually no upper molecular weight limit. So far crystalline 2 D structures on top of Highly Oriented Pyrolytic Graphite (HOPG) could be prepared and characterized by Scanning Tunneling Microscopy (STM) with PAHs like hexabenzocoronene (C<sub>42</sub>, HBC) being at the borderline of solubility and volatility and the superphenalene (C<sub>96</sub>) being well above the conventional processing limits.

As opposed to MALDI-SL which handles the non-volatile and insoluble molecules in form of their ions, pulsed laser deposition employs the neutral molecules in the gas phase, produced by direct absorption of laser light (Fig. 2). With optimized experimental parameters, the size of applicable molecules for PLD is much higher than the thermal decomposition limit. Fig. 2 shows the STM picture of a triangular PAH molecule (C<sub>60</sub>) with sub molecular resolution which could not be obtained by traditional sample preparation methods for STM. Hitherto PAH molecules with up to 222 carbon atoms could be deposited successfully.



**Fig. 2:** Pulsed laser deposition.

**Crosslinks to other projects:** Scanning Probe Microscopy, Optical and Electron Microscopy, Synthesis of Graphene Molecules/ Giant  $\pi$ -Conjugated Macrocycles, Graphene as Window Electrode, Conjugated Polymers as Semiconductors for High-Performance Field-Effect Transistors

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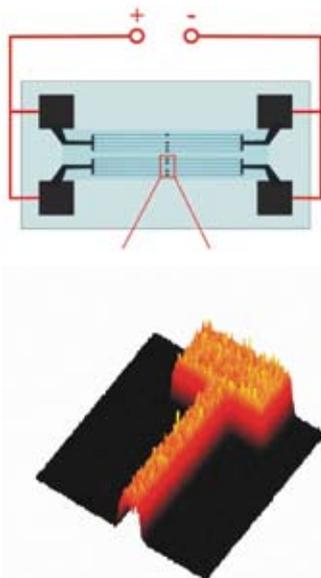
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# All-optical Ultrahigh Spatial Resolution Temperature Mapping of 2D-Objects on Microscopic Scale

S. Balouchev

*Keywords: All-optical temperature sensing, triplet-triplet annihilation, microscopic objects*

Rapid progress in the synthesis and processing of materials with a structure of nanometer length has created a demand for greater scientific understanding of thermal transport in nanoscale devices, individual nanostructures, and nanostructured materials. The direct quantitative sensing of local temperature and the definition of two dimensional spatial and temporal temperature profiles in ultra thin (sub-100 nm) films and small (sub-micrometer) objects is still a considerable challenge. The challenge for getting quantitative information about the local temperature distribution increases drastically when the thin films are included in complicated multilayer structures and / or are locally heated – typical examples being the process of optical addressing in memory devices, where diffraction limited spots are used.

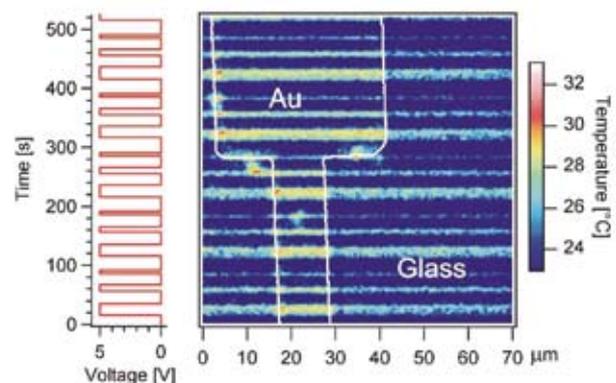


**Fig. 1:** Sample geometry. (a)–Electrical connection, (b)–reflection image in confocal geometry. The scan area  $65\mu\text{m}$ , resolution  $250\text{ nm}$ .

Here we present a novel all-optical method to sense temperature with a spatial resolution of more than  $250\text{ nm}$ . We studied the temperature dependence of the process of triplet-triplet annihilation (TTA) in organic phosphorescent molecules dispersed in a polymer matrix (“solid solution”) in a broad temperature range. We show that the TTA process in these systems, as a diffusion controlled process, is strongly temperature dependent. Moreover, it results directly in a strong temperature dependent delayed fluorescence

emission for the investigated class of metallated porphyrin molecules. Therefore, the ratio between the intensities of the delayed fluorescence and the prompt phosphorescence emission at different temperatures represents a real-time temperature probe with ratiometric response for a broad temperature interval.

The resulting temperature distribution obtained by feeding a series of  $50\text{ mA}$  current pulses of different duration is shown in Fig. 2. The white contour defines the position of the gold stripe. The temperature measurement consisted of two successive scans. The first scan is in the reflection mode, exciting the sample with a HeNe laser in order to precisely locate the gold and glass regions. During the second scan the sample luminescence is registered with the two avalanche photodiodes and suitable filters. Then, defining the specific calibration curve (material depending) and using the measured ratio of  $I_f/I_p$  for each pixel the local temperature was obtained. The reported lateral spatial resolution is the highest for non-contact methods of temperature determination. We combined the advantages of using of the confocal geometry for wavelengths from the visible region with the ratiometric optical response of the sensing molecules. The heat capacity of the thermal sensing layer is small in comparison to those of the objects under investigation. The calibration curve is material dependent, but the calibration procedure is simple and highly reproducible.



**Fig. 2:** Steady-state 2D-temperature profile of the microcircuit shown in Fig. 1. Observed part of the sample  $\sim 70 \times 70\ \mu\text{m}^2$  ( $300 \times 300$  pixels,  $2\text{ ms/pixel}$ ). Current pulses (left) of  $5\text{ V}$  with duration of  $20$ ,  $10$  and  $5\text{ s}$  were applied during the acquisition of the image. Right: temperature scale. Lateral spatial resolution of the temperature profile  $\sim 250\text{ nm}$ .

**Crosslinks to other projects:** Organic Electronics: Structure-Property Relations, BioInterfaces

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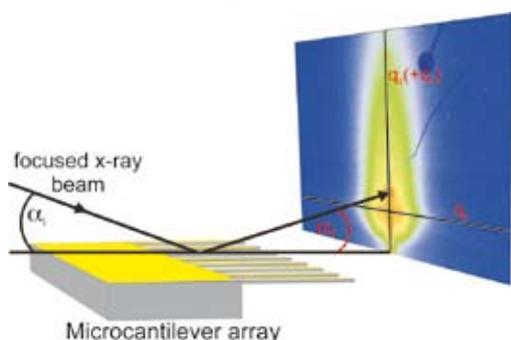
# Microfocus GISAXS Measurements on Micromechanical Structures

J.S. Gutmann

**Keywords:** Scattering techniques, microfocus beams, microcantilever arrays

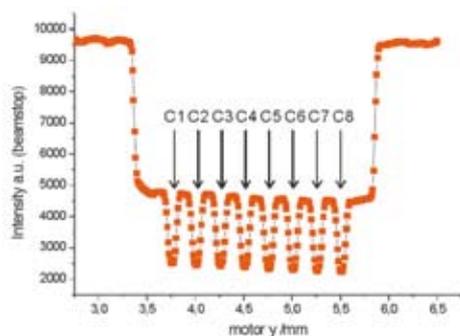
Modern high brilliance synchrotron sources allow the focussing of x-ray beams to  $\mu\text{m}$  size without the incurrance of a prohibitively high beam divergence. We used the microfocus option at the BW4 beamline of the HASYLAB at DESY to yield a microfocus beam of  $17\mu\text{m}\times 32\mu\text{m}$  size. Such small beams allow us to investigate the structural properties of materials on selective positions on the sample.

We used the small beam size to investigate the structure of coatings on microcantilever arrays. In sensor applications micromechanical structures, such as cantilever arrays, are used to transduce the binding event in a sensing layer into a mechanical response, which can be used as a detection signal. To analyze the structure of the sensing layer the cantilever array was illuminated under grazing incidence angles of less than  $1^\circ$  (Fig. 1).



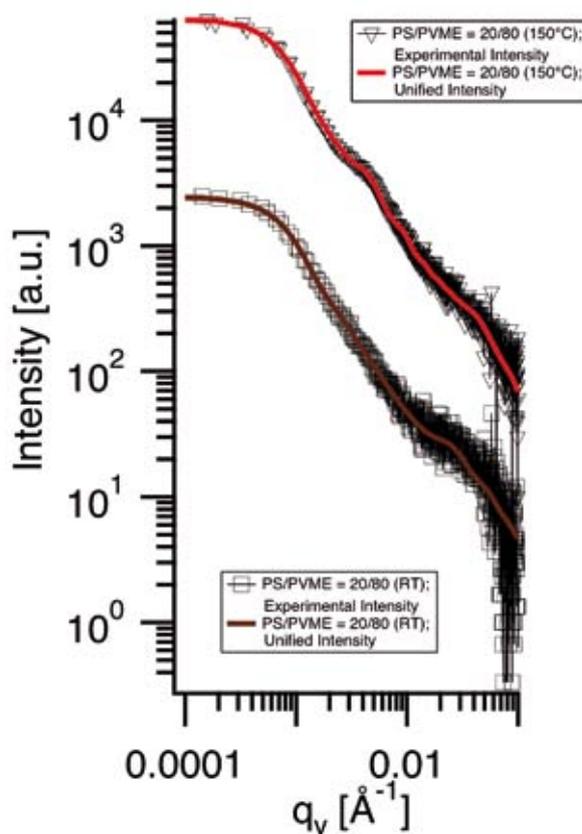
**Fig. 1:** Microfocus GISAXS setup with a typical 2D scattering image obtained from a single gold coated cantilever.

The cantilever array may be freely moved with respect to the beam and the small beam size allows projection of the X-ray beam exclusively onto a cantilever, which makes it possible to address individual cantilevers (Fig. 2).



**Fig. 2:** All 8 cantilevers within a microcantilever array may be individually addressed with a microfocussed x-ray beam.

In a GISAXS geometry the accessible resolution is only limited by beam size, divergence and the size of the detector pixel. This allows us to investigate lateral film structures in the range of 10 nm to 1  $\mu\text{m}$  within a single scattering experiment. In the  $q_z$  direction data analysis is complicated by the presence of refraction effects. In  $q_y$  direction refraction effects are negligible, which allows the analysis of weakly correlated films with conventional approaches known from small angle scattering experiments in transmission (Fig. 3).



**Fig. 3:** Scattering curves obtained from a microfocus GISAXS experiment on a mixed poly(styrene) poly(vinyl methyl ether) brush layer. The fit to a unified scattering model shows the formation of  $\sim 130$  nm droplets.

**Crosslinks to other projects:** Materials with Controlled Interface Structure, Polymer Brushes on Nanomechanical Cantilever Sensors

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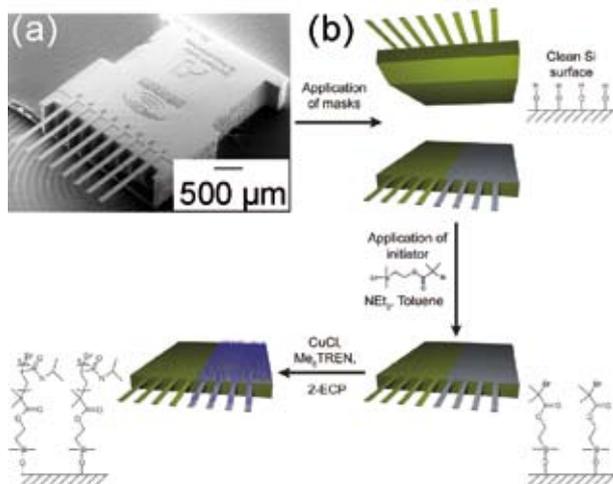
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# Polymer Brushes on Nanomechanical Cantilever Sensors

J.S. Gutmann, R. Berger

*Keywords: Nanomechanical cantilever, ATRP, switchable polymers*

An essential part of scanning probe microscopy is a nanomechanical cantilever sensor (NCS), which transduces forces acting on the tip into a deflection. Forces of pico-newtons can be measured which correspond to a sub-nanometer deflection of the NCS end. However, not only forces acting on the tip lead to a deflection, but also expansive or contractive forces acting on one side of the cantilever surface result in bending. For example this is the case in a swelling or a phase change of thin polymer films situated only on one side of a NCS.

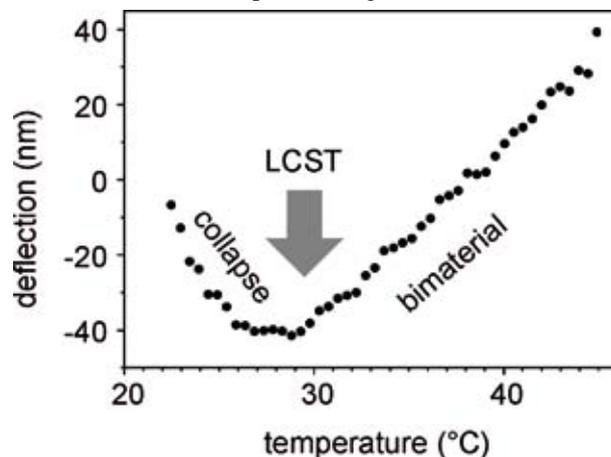


**Fig. 1:** (a) Scanning electron micrograph of a nanomechanical cantilever sensor array. (b) ATRP synthesis of poly(NIPAM) brushes on a nanomechanical cantilever sensor array.

The NCS is made from silicon and is very small; typically 0.5  $\mu\text{m}$  thick, 50  $\mu\text{m}$  wide and 500  $\mu\text{m}$  long (see Fig. 1a). The small size enables arrangement of several NCS sensors in an array on a single chip. Hereby, experimental noise can be reduced by averaging signals as a response to an analyte solution (e.g. mixture of substances). In addition, the response of differently functionalized NCS sensors to the analyte solution can be recorded. Owing to the small size, the NCS technique is suitable for studying tiny amounts of materials that are expensive when produced in large quantities.

In order to study the response of polymer materials in liquids we have developed a synthetic strategy to coat selected surfaces with covalently bonded polymer brushes: In a first preparatory step all interfaces not to be coated with brushes are protected with a gold layer. The remaining  $\text{SiO}_x$  surface is coated with a starter for atom transfer polymerization (ATRP). Then a dense brush layer is grown using ATRP at room temperature (see Fig. 1b).

In this way a wide variety of polymeric brushes can be synthesized. We recently applied NCS to study structural changes in ultrathin PMMA and PS layers. Other polymers like N-isopropylacrylamid (NIPAM) result in a thermal responsive surface coating. At temperatures around 32  $^\circ\text{C}$  poly(NIPAM) undergoes a coil-to-globule transition in water. Thus heating of a poly(NIPAM) brush layer results in a mechanical response owing to the coil-to-globule transition at the lower critical solution temperature (LCST). Fig. 2 shows the measured temperature dependent deflection indicating a LCST-transition temperature of  $\sim 30$   $^\circ\text{C}$  for a 7 nm thick poly(NIPAM) layer that was grafted by ATRP selectively onto a NCS-surface. Below 30  $^\circ\text{C}$  the NCS response is dominated by the collapse of the poly(NIPAM) brush layer. Above 30  $^\circ\text{C}$  the NCS bends owing to the mismatch in thermal expansion coefficients of the silicon and the poly(NIPAM) brush layer leading to a bimaterial behavior upon heating.



**Fig. 2:** Coil to globule transition of a 7 nm thick poly(NIPAM) brush layer measured by NCS.

**Crosslinks to other projects:** Microfocus GIXAXS Measurements on Micromechanic Structures, Scanning Probe Microscopy, Tailored Mechanical Properties of Plasma Deposited Polymers, Ordering of Polydisperse Systems in the Presence of Interfaces, Evaporation of Microdrops

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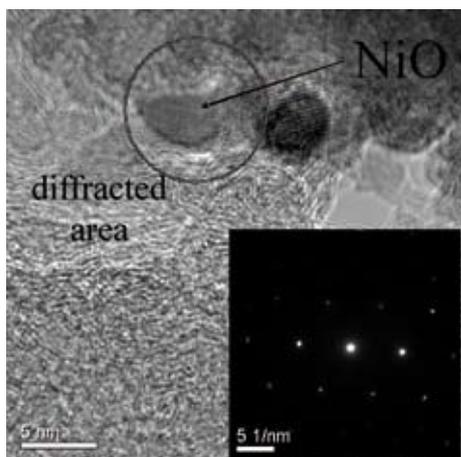
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# Local Li-Storage Mechanism as seen by EELS

## I. Lieberwirth

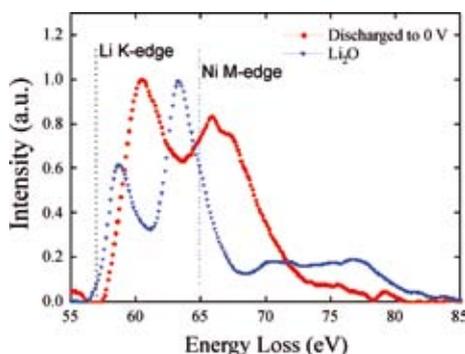
**Keywords:** Li-ion battery, electron microscopy

On account of their high energy storage capacity, lithium-ion batteries are one of the most popular types of battery for portable consumer electronic devices. Basically, a lithium-ion battery is composed of four primary functional components; the anode and the cathode serve as storage for lithium ions, the electrolyte provides the necessary Li-conductivity and a separator membrane prevents electrical contact between the electrodes. On discharging, the Li-ions migrate from the cathode to the anode and vice versa during the charging process.



**Fig. 1:** TEM micrograph and NAED pattern of lithiated NiO.

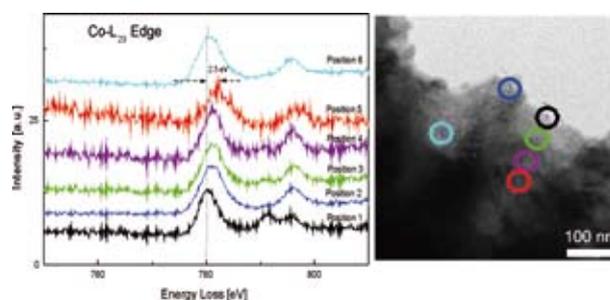
In commercial batteries graphite is the common functional anode material, which has a significantly lower specific capacity compared to that of  $\text{LiCoO}_2$ , being the usual anode material. Hence, the specific capacity of the anode material limits the performance of the battery.



**Fig. 2:** EEL spectrum of lithiated NiO (red) and  $\text{Li}_2\text{O}$  (blue).

Metal oxides are potential candidates to replace the graphite as anode material. In order to optimize the overall performance of the battery, one has to understand the mechanism of how Li is reversibly stored in the respective material. For metal oxides one potential process is the reduction of the host oxide under simultaneous formation of lithium oxide (conversion mechanism  $\text{MeO} + 2 \text{Li} \rightarrow \text{Me} + \text{Li}_2\text{O}$ ).

However, exploring the storage mechanism requires, amongst other things, the identification of light elements (e.g. Li) on the nanoscale. Transmission electron microscopy (TEM) in combination with electron energy loss spectroscopy (EELS) provides the lateral resolution needed and yields information on the electronic structure.



**Fig. 3:** EEL spectra of Co core loss (left) from different positions on a partly discharged  $\text{LiCoO}_2$  particle (TEM micrograph on the right part).

During the first discharge cycle Li-ions are inserted into the formerly micron-sized metal oxide, usually leading to its disintegration and formation of nano sized crystallites. Fig. 1 shows a NiO anode material from a battery which has been discharged completely. The corresponding EEL spectrum (Fig. 2) reveals the presence of Li through the significant peak at 60 eV. Moreover, from the observed peak position one can deduce information on the valence, showing, that in this case the lithium does not exist in form of  $\text{Li}_2\text{O}$ , as expected from the conversion mechanism. Consistent with this, nano-area electron diffraction (NAED) identifies the individual nano-particles as NiO. Moreover, EELS can provide very local information as shown in Fig. 3. Here the individual spectra were taken at different positions on a partly lithiated  $\text{LiCoO}_2$  particle. Only an area of approx 20 nm diameter contributes to the respective spectra. With increasing distance from the edge of the particle one can observe that the Co core loss peak shifts to higher energies, indicative of an increasing valence of the Co, corresponding to a decrease of Li content.

**Crosslinks to other projects:** Optical and Electron Microscopy

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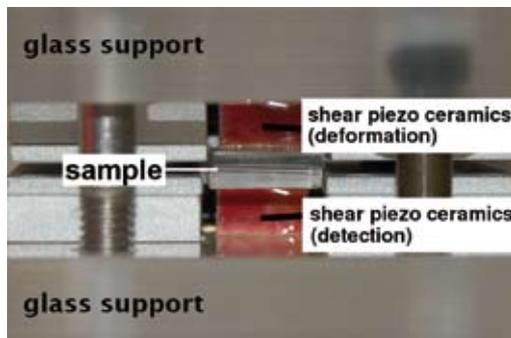
# Piezorheology: Rheoptics on the Microscale

G.K. Auernhammer, D. Vollmer

*Keywords: Rheology, small deformations, microscopy*

Scientists studying the frequency-dependent mechanical behavior of soft matter are often confronted with special challenges such as small sample quantities or extremely fragile samples (e.g. during gel formation). Furthermore, as with most complex systems, the principle of time-temperature superposition is no longer valid. Several groups have designed piezorheometry devices that deal with these challenges better than classical rheometers.

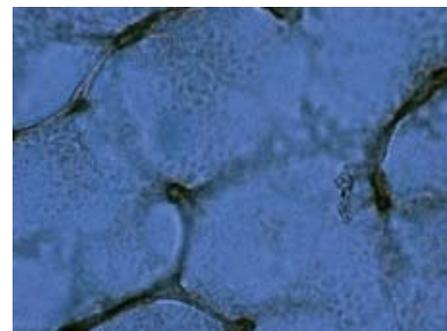
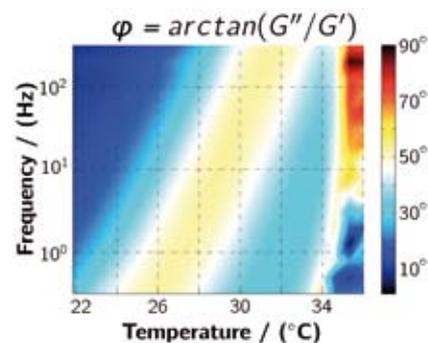
In a piezorheometer, both mechanical deformation  $\epsilon$  as well as detection of the mechanical stress  $\sigma$  transmitted through the sample is implemented with piezoceramics using plate-plate geometry. These highly sensitive devices work with very small deformations (typically  $10^{-5} - 10^{-3}$ ), low sample volumes ( $<100 \mu\text{l}$ ), and sample thicknesses of tens to hundreds of micrometers. Our home-made piezorheometer (see Fig. 1 for a side view) is designed for a frequency range from  $10^{-1}$  Hz to 1 kHz and a dynamic range of  $G = \sigma/\epsilon = G' + iG''$  from 10 Pa to  $10^7$  Pa. With deformation amplitudes below optical resolution, the glass construction of the sample cell support enables observation of the sample with an optical microscope while taking rheological measurements. This device allows for correlation of real-space structural information with the frequency-dependent mechanical properties of the sample.



**Fig 1:** Side view of the set-up showing the glass support, the piezoceramics and the sample plane.

The small deformation even permits the study of aggregation dynamics of highly fragile structures (e.g. colloid aggregates in a carrier fluid) without influencing their formation by the measurement. Colloid aggregation can be induced by phase transition of the suspension medium: While colloids are readily suspended in isotropic

media, they are expelled from the medium when it undergoes phase transition to the nematic state. As a result, at sufficiently high colloid concentrations rigid sponge-like colloidal networks are formed in the nematic phase although the isotropic suspension was fluid-like. In Fig. 2, we followed up the shear response of such a system throughout the phase transition. The phase shift  $\phi$  between excitation and detection signal reflects the relationship between storage and loss modulus (elastic and dissipative components of the mechanical response). Fig. 2 (above) shows a sharp transition from liquid-like behavior above the isotropic-nematic phase transition temperature to solid-like behavior below it, the latter corresponding to network formation as depicted in Fig. 2 (below).



**Fig. 2:** Above: At the phase transition temperature ( $35^\circ\text{C}$ ) the mechanical signal changes from liquid-like (below sensitivity and thus having a random phase) to solid-like (well defined phase). Color changes indicate viscoelastic behavior (intermediate  $\phi$ ) that is gradually replaced by elastic behavior (low  $\phi$ ) further below phase transitions. Below: The phase transition creates a network structure with a characteristic mesh size depending on the thermal history of the sample (typically tens of  $\mu\text{m}$ ).

**Cross-links to other projects:** Mechanics, Rheology and Dielectric Spectroscopy Laboratory, Colloid Probe Technique

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# Theoretical Development of Electronic Functionals

## L. Delle Site

*Keywords: Many-electron theory, electron correlations, kinetic functionals*

The development of electronic functionals for Density Functional Theory (DFT) has been for long a field of intense activity. In general, research during the last decades has focused on the so-called exchange and correlation functionals, which are then used in computer approaches based on the Kohn-Sham (KS) derivation. The KS approach is based on electronic orbitals and is computationally rather demanding. Recently the so-called Orbital Free DFT (OFDFT) approach, which circumvents the problem of solving the KS equations, has gained popularity. In this method the electron wave function is no longer required, nor the diagonalization of the electronic Hamiltonian or the reciprocal space sampling is needed. Thus, this technique allows for studies of relatively large systems compared to those treatable with the standard KS method. The central point of OFDFT is the quality of the kinetic functional, and the current functionals are still too simple to provide the same accuracy of the KS approach. This makes the development of kinetic functionals of central importance for the OFDFT method and leads to a challenging field of research. We have investigated the theoretical aspects of many-body electron systems which are connected to the derivation of a kinetic functional.

Our approach is based on the representation of the many-body electron wave function as a product of a three dimensional (standard) electron density and a  $3N-3$  dimensional conditional probability density (CPD) (being  $N$  the number of electrons). This formalism allows us to derive a simplified variational problem for the CPD, whose solution leads to a formally rigorous kinetic functional. Unfortunately the CPD is unknown, however it can be built on the basis of rigorous mathematical requirements and basic physical principles. We proposed a functional form for the CPD and later used a Monte Carlo procedure (MC) for calculating the multidimensional integrals in the variational principle. Applying this procedure we have been able to obtain a kinetic functional for the simple case of a spinless, interacting, almost uniform electron gas. The relevance of this method is that it is internally consistent, and the stricter the physical principles used to build the CPD are, the more rigorous is the kinetic functional obtained. Future work will focus on including the physics of the spins into the functional form of the CPD and of testing the functionals obtained for atoms of the periodic table, whose properties are well-known.

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**Crosslinks to other projects:** Elucidating Columnar Mesophases of Extended  $\pi$ -Electron Systems, Organic Electronics: Structure-Property Relations

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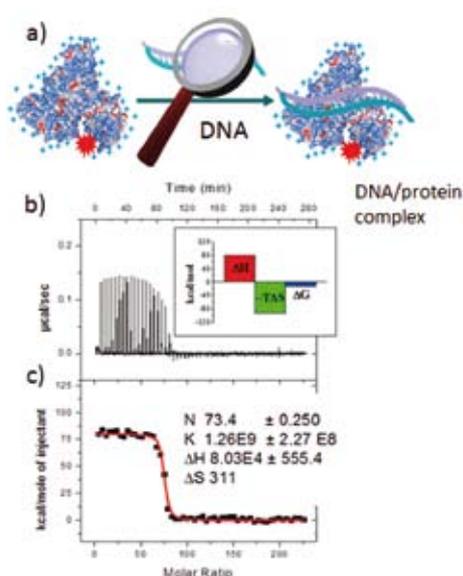
# Isothermal Titration Calorimetry: A Powerful Technique to Quantify Intermolecular Interaction

T. Weil, M. Klapper

*Keywords: Isothermal titration calorimetry, polyelectrolytes, self-assembly*

## Background of isothermal titration calorimetry

Isothermal titration calorimetry (ITC) is a biophysical technique for studying the thermodynamic parameters of non-covalent interactions. In most cases, ITC is used to investigate the binding of small molecules to larger macromolecules such as proteins or DNA. As successive amounts of the ligand are titrated into the cell, the quantity of heat absorbed or released is in direct proportion to the amount of binding occurring.



**Fig. 1:** a) Titration of a positively charged albumin protein to negatively charged plasmid DNA; b) raw titration curve; the enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and the Gibbs energy ( $\Delta G$ ) of the interaction are plotted in the inset; c) integrated heat for each injection and the determined thermodynamic data of the interaction. The red line represents the best data correlation obtained using the one binding site model.

The ITC instrument monitors the heat released upon the interaction ( $\Delta H$ , Fig. 1a) over time. When the system reaches saturation, the signal diminishes until only the dilution heat is observed (Fig. 1a). By plotting the recorded heat of each injection against the ratio of the ligand we

are able to calculate the corresponding binding parameters (e.g. binding constant, stoichiometry) of the complexes formed (Fig. 1b). Accordingly, ITC is a quantitative technique which allows us to measure the binding constant, enthalpy changes ( $\Delta H$ ), and binding stoichiometry ( $n$ ) of an interaction between two or more molecules in solution. Individual experiments usually last between one to four hours.

## Current application of the ITC at the MPI-P

During the past two years the ITC technique has been established and successfully applied to investigate the interaction of protein as well as dendritic polyelectrolytes with negatively charged DNA or positively charged nuclear proteins. The qualitative *in vitro* observation that dendritic core-shell macromolecules with multiple negative charges selectively stain the cell nucleus was explained by a high affinity interaction with positively charged nuclear proteins, so-called histones. In the same context, the chemical coding of albumin proteins allowed the preparation of different albumin species with varying numbers of positive charges within the protein scaffold. Several ITC binding experiments of each protein species and plasmid DNA of a defined length facilitated the calculation of the approximate number of positive charges of the respective albumin protein, the complex stoichiometries in solution as well as their binding constants. Based on these results, we were able to shed light on processes involved in gene transfection, a very complex and still barely understood biological process of high therapeutic relevance.

## Impact on polymer chemistry?

In the past, ITC was mainly used to determine interaction constants, complex stoichiometries or conformational changes during assembly. Nowadays, this technique is also used to consider classical polymer chemistry related questions. Recently, the mechanism of chiral recognition processes in molecularly imprinted polymers, or different polymerization reactions under real process conditions, have been studied. We are now actively involved in the investigation of polymerization reactions by applying the ITC technique.

**Crosslinks to other projects:** Polyphenylene Dendrimers, Chemically modified Proteins, Structure Formation by Ionic Interaction

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# Scientific Infrastructure



## Scientific Infrastructure

W.H. Meyer

The interdisciplinary nature of the institute, in particular the cooperation between chemists who synthesize new polymers, and physicists, who characterize their properties, calls for strong support from scientific service groups.

Analytical chemistry includes the detailed characterization of the chemical structure of the macromolecules. Here, various spectroscopic techniques are used, in particular IR-, UV-, mass-, and high resolution NMR spectroscopy. Furthermore, polymer analysis has to characterize the macromolecules themselves. This includes the determination of molar mass, molar mass distributions, branching, shape in solution, etc. It is clear that attempts to correlate macroscopic and molecular parameters with the macroscopic behavior of polymers are bound to fail if this polymer-specific information is not to hand. Therefore, extended scientific service is provided in this area. Likewise, the packing of macro-molecules in the solid state raises a number of polymer-specific questions. Since synthetic macromolecules are often non-uniform, they typically form amorphous solids. Even stereo-regular polymers in general cannot crystallize completely, but form semi-crystalline structures. The packing in the solid state, the phase behavior, and the morphology are checked by various physico-chemical methods, in particular thermal analysis, x-ray diffraction and electron microscopy.

In solution, polymers are very often not simply dispersed as single macromolecules but form aggregates sometimes with rather complicated architectures. The analysis and characterization of macromolecular aggregates in solution is the domain of various light scattering techniques and other optical methods which are offered in corresponding service projects. A number of projects are concerned with research on surfaces, surface interaction and ultrathin layers of polymers. This made it necessary to establish a clean room.

The characterization of polymers surfaces and the manipulation of macromolecules at surfaces have been developed very pronouncedly at the institute. This has led to the establishment of a Scanning Probe Microscopy service group. Here, a variety of different instruments working under various environmental conditions are provided for surface analysis. Besides optical microscopy the visualization of materials and their surfaces at high resolution with electron microscopy has become a powerful tool. A number of transmission electron microscopes with specialized equipment is operated at the MPI-P within the framework of the *Electron Microscopy Center Mainz* (EZM) together with the Mainz University.

Even in cases where the optical or electrical properties of polymers are of primary interest, their mechanical behavior must be characterized, because very often their applicability depends on mechanical and thermal properties. Therefore, an up-to-date laboratory for mechanical measurements covering the whole range of properties from viscous liquids to glassy solids has been installed.

Dielectric spectroscopy gives complementary information on relaxation phenomena in solid polymers and also serves to characterize conductive properties of polymers designed as either ionic or electronic conductors. Conductivity measurements under well-defined humidity conditions is a speciality which serves the needs of characterizing materials for fuel cells and batteries.

Research today cannot do without hard- and software development concerning the control of experiments, data collection and analysis, as well as theoretical interpretation and simulation. Consequently, the institute has installed a group offering computer services in all fields from personal computers to remote access to supercomputers and modelling of polymers on all length scales.

### Service Groups

The corresponding service groups are headed by staff scientists who are supported by technicians.

“Service groups” are linked to scientific projects and very often are major partners in a collaborative scientific project and thus significantly contribute to the research of the institute. “Service Groups” also means that students and scientists are trained in specific methods to carry out their own measurements, and also that methods are further developed to improve the quality of data produced.



# Mass Spectrometry

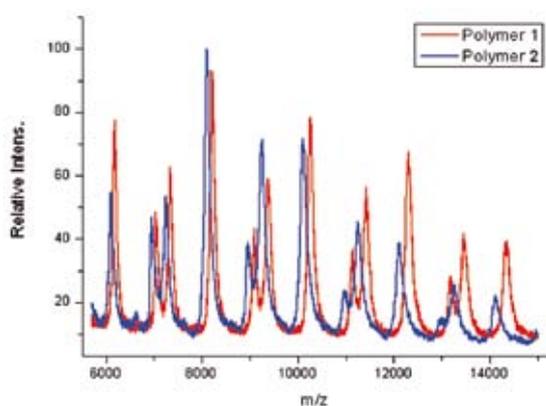
H.J. Räder

**Keywords:** Molecular weight determination, end groups, electron impact, field desorption, MALDI-TOF

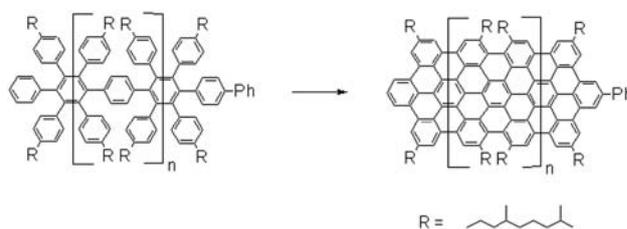
Determination of molar mass is an essential step to identify and characterize new chemical structures. The molar masses of organic molecules cover several orders of magnitude from a few hundred g/mol up to several million g/mol. Moreover, organic molecules have a broad range of different structures and properties. For this reason, molar mass determination requires different mass spectrometers and different ionization techniques. In the department of mass spectrometry the emphasis is placed on soft ionization techniques to characterize intact macromolecules with minimized fragmentation. Frequently used methods are Field Desorption (FD) and Matrix-Assisted Laser Desorption/Ionisation Time-of-Flight (MALDI-TOF) mass spectrometry. FD is measured on a high resolution magnetic sectorfield instrument with a mass range up to 15000 g/mol, whereas MALDI is coupled with a time-of-flight analyzer and has an unlimited mass range in principle. Both methods allow for the measurement of labile samples,

mass distributions of polymers and compounds in reaction mixtures. It is possible to resolve even single molecules in polydisperse samples, providing information about end groups, macrocycles, side products or impurities. An example of polymer characterization before and after a polymer analogous reaction is shown in Fig. 1.

The corresponding structure of the poly para phenylene type educt polymer can be converted into the nanographene type product polymer via cyclodehydrogenation (Fig. 2). The mass difference of both polymers, as obtained from the mass spectrum, is a direct measure of the cyclodehydrogenation efficiency. As opposed to most other techniques MALDI is also capable of analyzing insoluble macromolecules. Samples such as polythiophenes, polyfluorenes or giant polyaromatic hydrocarbons (PAHs) can thus be characterized in detail and valuable chemical and structural information is obtained where traditional methods fail.



**Fig. 1:** MALDI-TOF mass spectra of a polymeric educt (1) and product (2) of a polymeranalogous cyclodehydrogenation reaction.



**Fig. 2:** Synthesis of a polymeric nanoribbon by cyclodehydrogenation.

**Crosslinks to other projects:** Polymer Characterization, Soft Landing and Pulsed Laser Deposition for Thin Films, High Resolution NMR, Synthesis of Graphene Molecules/Giant  $\pi$ -Conjugated Macrocycles, BioInterfaces

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## Optical Spectroscopy and Thin Films

C. Bubeck

**Keywords:** UV-Vis-NIR spectroscopy, reflectometry, fluorescence, Raman, FTIR, prism coupling, waveguide, spin-coating, Langmuir-Blodgett technique, profilometry, contact angle

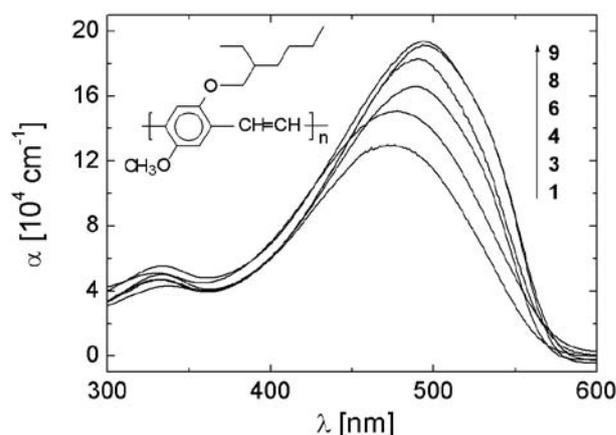
Preparation of thin films and their optical characterization are basic methods applied in many areas of polymer research. Layer thicknesses ranging between a monolayer and several micrometers are required depending on the research topic. The optical spectroscopy of polymers yields information on the chemical structure and orientation of molecular units, electronic and vibronic excitation and relaxation, and optical materials constants such as the absorption coefficient and refractive index of thin films. Experienced staff engineers are involved in the technical development of these methods and keeping updated on the know-how of the instrumentation. Access to the methods is provided either as a service or by training scientists who need the techniques frequently to enable their own use of the instruments. The group is involved in the following major activities:

The thin film laboratory comprises all technological steps from substrate cleaning, fabrication of inorganic and organic thin films, to thickness measurements by surface profilometry and contact angle measurements. Major film preparation techniques are: thermal evaporation and sputtering of inorganic materials (metals, semiconductors or dielectrics), spin-coating of polymers at laminar flow and inert gas conditions in a so-called glove-box, the Langmuir-Blodgett technique for multilayer films of amphiphilic materials, film drawing and dipping techniques.

The optical spectroscopy laboratories are involved in transmission and reflection spectroscopy of the whole range from ultraviolet to infrared light, fluorescence and Raman spectroscopy. Supplementary instruments are microscopes for the FTIR- and Raman-spectrometers, cryo- and thermostates to provide specific sample temperatures between approximately 100 K and 500 K, and high-intensity lamps combined with filters for photochemical reactions.

The development of measurement techniques is frequently required for special projects in the institute, for example:

- IR transmission and reflection spectroscopy at grazing incidence is used to evaluate the orientation of molecular units of thin polymer films and even monolayers.
- Reflections at interfaces cause frequent problems in the transmission and reflection spectra of ultrathin films. Quantitative reflection and absorption spectroscopy in the visible and near-infrared range is used in combination with model calculations to solve this problem. This allows us to determine the optical constants of thin films i.e. intrinsic absorption coefficient (see Fig. 1) and the refractive index.
- A prism coupler setup is used to study planar waveguides. The refractive index, and attenuation loss of thin film waveguides and their anisotropies can be determined at many laser wavelengths.



**Fig. 1:** Spectra of the intrinsic absorption coefficient of thin films of MEH-PPV (inset) with different molecular weights between 1:  $M_w = 9.3$  kg/mol and 9:  $M_w = 1600$  kg/mol.

**Crosslinks to other projects:** Conjugated Polymers for Ultrafast All-Optical Switching, Synthesis of Graphene Molecules/Giant  $\pi$ -Conjugated Macrocycles, Functional Dyes and Their Applications, Organic Electronics: Structure-Property Relations, Model Membranes

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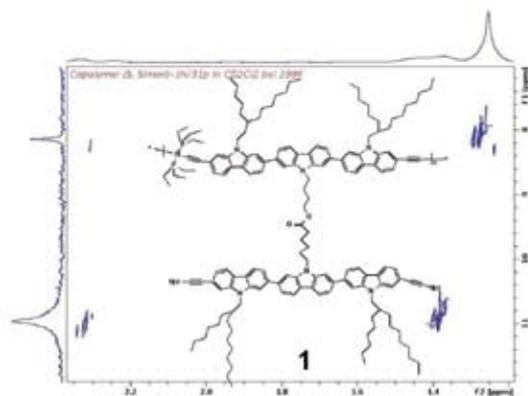
# High Resolution NMR Spectroscopy

M. Wagner

**Keywords:** Hydrodynamic radius, copolymerization characterization, one- and two- dimensional NMR, high- and low-temperature measurements, heteronuclear investigation

High resolution Nuclear Magnetic Resonance (NMR) has become an indispensable and routine tool for organic and polymer chemists. Both one- and two-dimensional methods (such as NOESY, COSY, TOCSY, ROESY, HMBC, HSQC) in homonuclear and heteronuclear experiments provide quick access to the structural information of novel organic molecules. Inverse broad band probes utilizing gradient techniques allow for the observation of nuclei other than carbon and hydrogen. Therefore the structural elucidation of many organic compounds containing  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{29}\text{Si}$ ,  $^{11}\text{B}$  etc. can be simplified.

As an example of hetero nuclear NMR coupling measurements, we investigated the precursor structure 1, which was polymerized to a double strand copolymer. For long range coupling between  $^1\text{H}$  and the  $^{31}\text{P}$  atoms in the structure 1, we used inverse gradient NMR in order to demonstrate the existing AB structure in the polymer (Fig. 1).

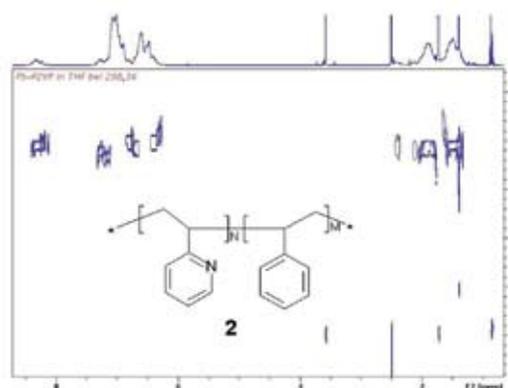


**Fig. 1:** Compound 1, 500 MHz in  $\text{CD}_2\text{Cl}_2$  at 298.1 K.

To go deeper inside the microstructure of copolymers, another new method in the NMR field is being developed in our group called the diffusion NMR technique. In many cases, it would be interesting, to discern if a targeted block copolymer is in fact chemically linked, or if it is

rather a homogenous mixture of homopolymers, as both cases have similar NMR spectra. One example is shown in Fig. 2. The signals at 8.1 ppm are correlated to the pyridinium ring and show the same diffusion coefficient value as the benzene ring of the styrene polymer at 6.6 ppm in the DOSY (diffusion ordered spectroscopy) NMR measurement. Homopolymers of different sizes show different diffusion values; very rarely these coefficients can be the same if the homopolymers themselves are of the same size. The consequent proof of the same-sized homopolymer mixtures can be shown with the coupled LC (liquid chromatography)-NMR technique.

An investigation of NMR DOSY was also performed on Precursor 1 to prove the complete copolymerization of the monomers. It shows the same diffusion coefficient value for all protons of the platinum complex and for those of the multi-carbazole derivative offering structural proof for precursor 1. These measurements also allow us to calculate molecular sizes (hydrodynamic radius) of a particle, which we have done on dendrimers with Ruthenium atoms in the center.



**Fig. 2:** Compound 2, 500 MHz in  $\text{CD}_2\text{Cl}_2$  at 298.1 K.

**Crosslinks to other projects:** Solid-State NMR Spectroscopy, Mass Spectrometry, Polymer Characterization, Biologically-inspired Materials, Functional Materials from Discotic Mesophases

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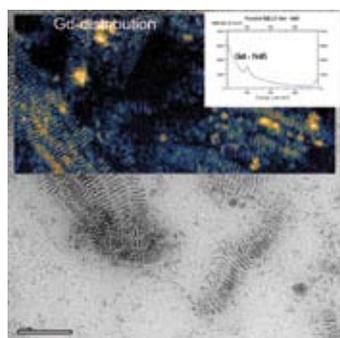
# Optical and Electron Microscopy

## I. Lieberwirth

*Keywords: Analytical TEM, structure analysis, morphology*

Determination of morphology and texture and the degree of order and orientation of chain molecules require imaging instrumentation appropriate for a wide range of length scales. Optical microscopy in reflected and transmitted light together with associated techniques cover the regions down to roughly 1  $\mu\text{m}$ . In addition, polarization microscopy is a powerful tool providing evidence of mutual orientation of macromolecules. The cost of sample preparation for light-optical microscopic observations is modest.

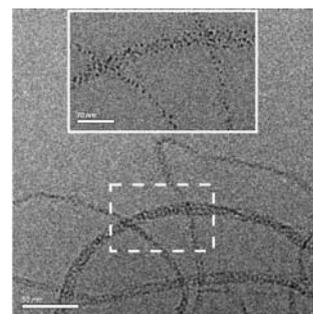
Imaging of morphologies at dimensions down to several  $\text{\AA}$  requires higher microscopic resolution. Their visualization is the domain of transmission electron microscopy (TEM) which generally requires appropriate preparation necessary to provide very thin (50 nm) and thus electron-transparent samples.



**Fig. 1:** TEM micrograph and Element Specific imaging (ESI, upper part) of Gd-hybrid structures.

The electron microscopy group operates 3 TEMs providing a resolution down to 1.5  $\text{\AA}$  with a wide range of analyzing capabilities. Equipped with an integrated electron energy loss spectrometer (EELS) the LEO 912 TEM can be applied to differentiate phases containing distinct heteroatoms. In addition, the Tecnai F20 offers the possibility of scanning TEM (STEM) together with an energy dispersive x-ray analysis (EDX) and a high angular annular dark field (HAADF) detector. The first supplies local information on the elemental composition of the sample whereas the latter provides STEM dark field information with an element of specific contrast depending on the atomic number. Furthermore, many scientific questions are concerned with the molecular structure and self-assembly in a liquid surrounding.

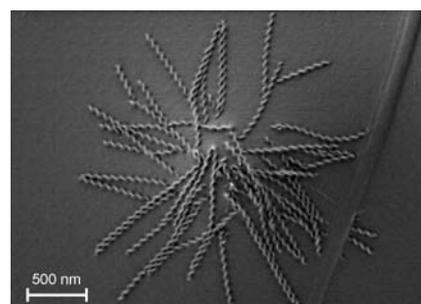
These are usually only accessible by methods using scattering techniques since common imaging methods need a dry sample, which might change the native structure of the objects under examination. However, with special equipment it is possible to vitrify the sample solution as a thin film and to examine the sample by cryo-TEM in its native environment.



**Fig. 2:** Cryo-TEM micrograph of poly(para-phenylene) sulfonate micelles with Ba as counter ion.

The investigation of surfaces in a medium resolution-range down to some nm is the domain of scanning electron microscopy (SEM). Imaging using low acceleration voltage (< 1 kV) supersedes any additional coating of the sample for conductivity reasons. Thus, SEM examination requires plain sample preparation only.

Moreover, the electron microscopy group is an integral part of the Electron Microscopic Center Mainz (EMZM). In this center the electron microscopy groups of the University of Mainz and the MPI-P are integrated in order to gain synergetic effects in sharing expertise and equipment.



**Fig. 3:** SEM micrograph of polydiacetylene rods on a silica surface.

**Crosslinks to other projects:** Local Li Storage Mechanism as seen by EELS, Structure Formation by Ionic Interaction, Synthesis of Graphene Molecules/Giant  $\pi$ -Conjugated Macrocycles, Morphology Control in Polyolefin Synthesis

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## Polymer Characterization

W.H. Meyer

*Keywords: Routine characterization, development of methods*

**Polymer analysis** offers many routine characterization methods as a service to all research groups in the institute.



**Viscometry** is a tool to determine the intrinsic viscosity which can be used to estimate the molecular weight.

**Liquid chromatography** (GPC, HPLC) is a common method used to provide the molecular weight distribution.

**Vapor pressure osmometry** determines the absolute number-averaged molecular weight.

Using **static light scattering** the absolute weight-averaged molecular weight and information about the shape and size of the macromolecule can be obtained. Diffusion coefficients and hydrodynamic radii of polymers in solution can be measured by **dynamic light scattering**.

Characterization work of samples is usually done by the researchers themselves in close collaboration with the skilled technicians of the group.

Another main activity of the polymer analysis group is the development of new analytical tools:



**Fig. 1:** *The Polymer Analysis Group at work.*

A **scanning interferometer** was developed in order to achieve accurate values of the refractive index derivatives with respect to concentration and temperature which are essential, e.g. for light scattering measurements. A setup was constructed suppressing multiple scattering which enables the study of turbid and highly concentrated polymer solutions and colloidal systems. Experiments are in progress to check the suitability of capillary electrophoresis as a tool to separate and characterize polymers.

Further equipment of the group includes 2-dimensional chromatography, **HPLC coupled with GPC**, allowing the measurement of more complicated molecules and online **GPC-MALLS** providing the absolute weight-average molecular mass, molecular weight distribution and the radius of gyration of polymers.

**Thermal analysis** includes a group of analytical methods by which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature and atmosphere.

With **differential scanning calorimetry** (DSC) a small sample is heated or cooled using a controlled temperature program in a controlled atmosphere and the heat flow to or from the sample in comparison to a reference is determined. With DSC the melting temperature and melting enthalpy, the glass transition temperature and specific heat change, the temperature and enthalpy change of other phase transitions and related variables like the degree of crystallinity of a polymer sample can be determined.

**Thermogravimetric analysis** (TGA) permits the continuous determination of sample weight as a function of a temperature / time program and in various atmospheres. Typically, only a few milligrams of a polymer sample is heated with 10 or 20  $\text{Kmin}^{-1}$  in  $\text{N}_2$  or  $\text{O}_2$  to determine its decomposition onset temperature, or the loss of low molecular weight components like residual solvent, plasticizer, etc.

The **TGA coupled mass spectrometry** allows for the direct analysis of the species driven out of the sample in the course of a TGA program.



**Fig. 2:** *The Thermal Analysis Group at work.*

**Crosslinks to other projects:** Mass Spectrometry, High Resolution NMR, Optical Spectroscopy and Thin Films, X-Ray Structure Analysis

**Hardware:** Viscometer, GPC, HPLC, vapor pressure osmometry, light scattering, Michelson scanning interferometer, capillary electrophoresis, 2-dimensional chromatography, GPC-MALLS, DSC, TGA, TGA-MS-Coupling

# X-ray Structure Analysis

V. Enkelmann

*Keywords: Structure determination, supramolecular chemistry, molecular structure*

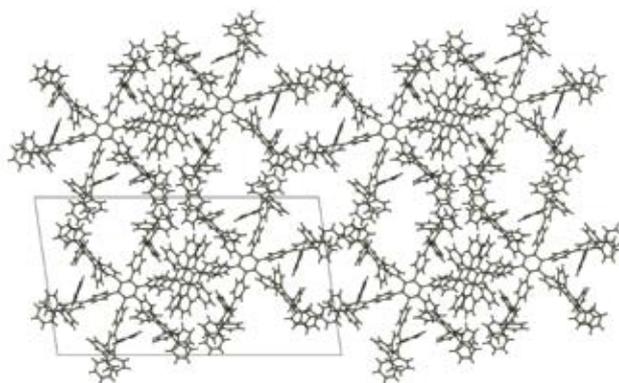
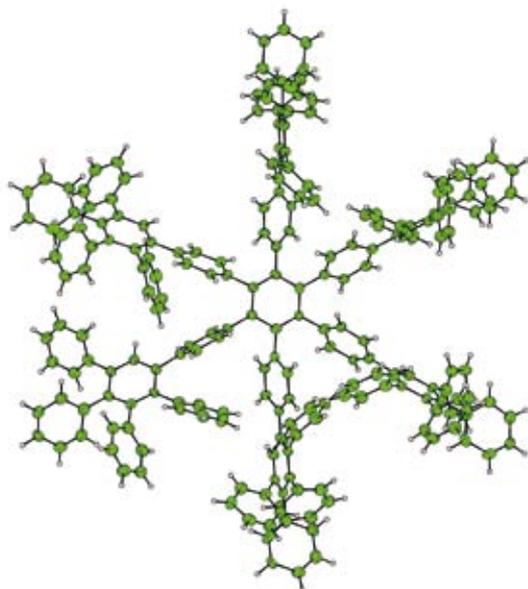
A key question for many studies performed in our institute is the exact knowledge of the state of order or the crystal structure of the sample. Depending on the origin or quality of the sample and the information requested a large variety of experiments can be performed. These range from the fast characterization of crystallinity in a powder diffractometer to characterization of polymer textures, fiber diagrams, small angle scattering and to crystal structure analyses of single crystals.

The x-ray analysis group offers experimental techniques and develops new ones which cover this range. The laboratory is organized in such a way that most experiments are accessible within a few days either on staff-operated or self-service basis. The service also includes help or advice in sample preparation techniques, e.g. crystallization.

Structure determination can be used as analytical tool, complementary to NMR spectroscopy in the field of supramolecular chemistry, e.g. characterization of chemical structure, conformation, intra- and intermolecular interactions as well as the characterization of solid-state reactions.

In order to study large molecules and unstable samples, emphasis is put on the development of methods for fast data collection at temperatures ranging between 90 K to room temperature. The time necessary for a complete data collection of single crystals can be reduced to a few hours using area detectors.

In many cases, however, single crystalline samples are not available owing to the insolubility of the substance or its polymeric nature. Here alternative methods for the investigation of the structure or state of order are necessary. Methods for data acquisition, e.g. goniometers for texture analysis and powder diffractometers equipped with one- and two-dimensional detectors have been developed and are available. However, in many cases the interpretation of the data (model building and refinement) is still a challenge and requires an interdisciplinary approach combining diffraction and spectroscopic data with the results of modelling calculations.



**Fig. 1:** Crystallization of polyphenylene dendrimers still remains a challenge. The crystal structure of  $C_{222}H_{150}$ , which is the largest dendrimer for which good crystals are available exhibits channels in which 24 molecules tetrachloroethane per dendrimer are located.

**Crosslinks to other projects:** Crystal Engineering of Molecular Architectures, Polyphenylene Dendrimers, Solid-State NMR

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## Computer and Network Service

### V. Macho

*Keywords: Network infrastructure, computer*

The computer service group provides, organizes and manages the IT infrastructure of the institute and offers support for the operation of computers and peripherals. At present we have 680 registered users operating 1800 network components.

The local network offers a bandwidth of up to 100 MBit/s from desk to desk which can be increased to 1 GBit/s if needed. The backbone consists of a star-like network of HP Procurve 5300 and 5400 edge switches. The backbone is constructed redundantly by using two interconnected core switches and two separate uplink connections from each edge switch.

Our internet access, which we share with the Max Planck Institute for Chemistry, has a bandwidth of 150 MBit/s. Provider is the "Deutsches Forschungsnetz" (DFN).

Wireless LAN is available within the building in all public areas such as seminar rooms, the lecture hall, meeting points, the entrance lobby and the guest-house. It provides guest network ensuring direct access to the internet. Our WLAN is controlled by a set of two redundant controllers, which take care of a uniform IP-address (roaming access) within the whole building and which allow user-based authentication by means of a Radius server (NAC).

Virtualization techniques based on VMware Infrastructure (ESX 3.5) have been utilized to improve quality and performance. All infrastructure services like e-mail, www, file services, together with their associated networks (internal, external, DMZ), are provided by virtual machines and virtual networks (VLANs). The physical hardware behind the scenes is a HP blade system with 5 dual- or quad-core servers and a Storage Attached Network (SAN) on a HP EVA4000 with a capacity of 15 TB located in a single 19" cabinet (Fig. 1). Virtualization not only saves money, because of improved usage of hardware resources and less electric power consumption, but also improves the quality of our infrastructure services, since all virtual machines can easily be moved from one physical server to another without interrupting the running processes on these machines. This is essential for load balancing and high availability.

Security and especially the firewall play a key role in every IT service infrastructure. Our firewall consists of a pair of Astaro Security Gateway Appliances (ASG) configured as a cluster in the active-active mode. It controls and supervises our traffic from and to the internet by packet filter rules as well as by content filtering of e-mails, ftp and http downloads. Furthermore it acts as an Intrusion Prevention System (IPS) by providing means against attacks from the internet. For the majority of our office computers, which are running under Microsoft Windows, we provide a regular update service from one of our servers, which can be configured to run automatically without user intervention. Likewise, antivirus protection is organized by supplying new antivirus patterns at regular intervals.



**Fig. 1:** By means of virtualization our data center fits into a single 19" cabinet with the blade servers on top and the storage system in the middle.

## Scientific Computing

T. Stühn, N. van der Vegt

*Keywords: Computing services, simulation, visualization, ESPResSo*

Research in the field of computational physics and chemistry requires a high level of expertise, both in science as well as in modern computer technologies. The aim of the scientific computing project is to provide an easy-to-use framework of hard and software that complies with the needs of the theory group in these fields.

Apart from installation and maintenance of standard hardware systems such as desktop PCs, laptops and printers, the provision of high-performance computing power to the group members is one of our tasks. This is accomplished in close collaboration with the Max Planck Society's computing center in Garching and by managing several high performance computing clusters (e.G. IBM Regatta cluster with 40 CPUs, mixed AMD Opteron / Intel Xeon cluster with 440 Cores (see Fig. 1) at the MPI-P itself. Several storage and backup systems (~40 TB) can be used to maintain the huge quantity of data that is produced in the simulation runs.



**Fig. 1:** Local Linux cluster for medium-sized simulations, also used as a test and development system for simulation software.



### Visualization

The interpretation and analysis of computer simulation data can be tremendously eased by visualization and appropriate representation of the simulation data. This includes the creation of high-quality images and movies used for presentations. A fully equipped modern graphics workstation provides all the tools and programs to accomplish this important task.

### ESPResSo – Extensible Software Package for Research on Soft Matter

The increasing complexity of computer simulations in soft matter gives rise to the need of a simulation package that is easy to use and highly expandable. Unlike existing programs for atomistic systems (e.G. GROMOS, GROMACS), packages for coarse-grained simulations that provide a high degree of flexibility were not existent to date. Therefore the “Extensible Simulation Package for Research on Soft matter” (ESPResSo) has been designed and developed in the theory group to perform numerical MD/MC simulations for a broad class of soft matter systems in a parallel computing environment. The ESPResSo package is maintained in the scientific computing project and it is also freely available to other groups and institutions outside the Max Planck Society.

Through joint collaboration the MPI-P and the Fraunhofer Institute for Algorithms and Scientific Computing (SCAI) have developed a new simulation package ESPResSo++, which is based on ESPResSo. The advantage of the new package is much more flexible programming and user interface that allow scientists to implement new simulation methods not handled by the predecessor.

**Hardware:** Linux Cluster (440 Cores), IBM Regatta (40 CPUs), Net App Filer (1 TB), NAS-Server (3 TB), 50 Linux PSs, IBM Blade Center (28 CPUs), Infiniband Opteron Cluster (RZG, 40 CPUs), Backup: TSM, Overland Library (40 TB), Graphics/Video Workstation (Apple PowerPC)

### References

GROMOS: <http://www.igc.ethz.ch/gromos>; GROMACS: <http://www.gromacs.org>, ESPResSo: <http://www.espresso.mpg.de>, SCAI: <http://www.scai.fhg.de>; ESPResSo: <http://www.espresso-pp.de>

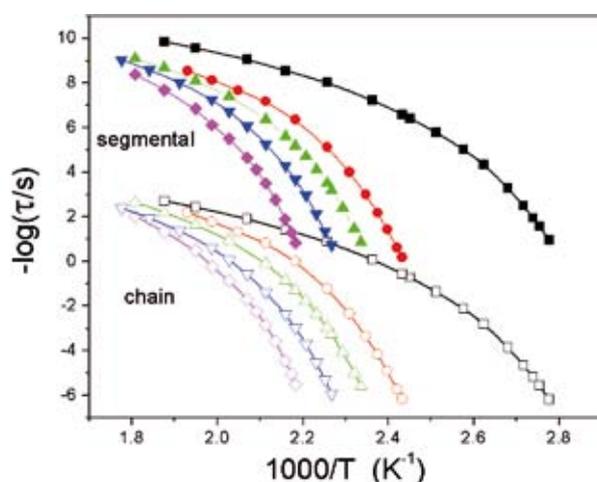
# Mechanics, Rheology and Dielectric Spectroscopy Laboratory

K. Koynov, G. Floudas

*Keywords: Dynamic testing, mechanical relaxation, dielectric relaxation, rheology, viscoelasticity, local and chain dynamics, phase transitions, topology*

A broad spectrum of mechanical properties ranging from hard solids to low viscosity liquids can be measured in the laboratory. Studies are performed taking into account various aspects of mechanical and rheological testing:

- Mechanical spectroscopic measurements are applied to detect molecular motion or structural rearrangements in a polymer. Information from other methods (e.g. NMR, DSC, x-ray diffraction, dielectric relaxation, etc.) are combined aiming at the assignment of particular microscopic motions to the macroscopically observed relaxation of the material.



**Fig. 1:** Segmental (filled symbols) and chain (open symbols) relaxation times for the different cycloolefin copolymers of ethylene and norbornene with increasing norbornene content; (squares): 36, (circles): 50, (up triangles): 51.8, (down triangles): 56.5 and (rhombus): 61.5 mol%. The lines are fits to the VFT equation.

- Rheological measurements are performed in order to characterize flow properties of polymer melts and polymer solutions. Of particular interest are heterogeneous polymer systems like copolymers, gels, or polymers with liquid crystalline properties, in which the flow induced structural changes or instabilities under flow still constitute unsolved problems. A second topic is a better understanding of the mechanical response of complex macro-molecules like stars, comb polymers, or microgels.

- Large deformations of polymers in solid or rubbery states are studied in order to deduce deformation mechanisms leading to highly oriented states.

- Pressure-Volume-Temperature (PVT) measurements are performed to provide the equation of state. When the equation of state is combined with the segmental relaxation times, it provides the thermodynamic variable that controls the liquid-to-glass transition.

- Material constants like elastic modulus, viscosity, compressibility, specific volume (temperature and pressure dependent) are characterized.

In addition, dielectric relaxation spectroscopy can be performed in the laboratory, which is an extremely effective method for characterizing the molecular dynamics over a large range of time scales. The technique is sensitive to orientational motions of permanent dipoles, to translational contributions of ions as well as to surface and interfacial polarization effects. The range of accessible frequencies extends from  $10^{-5}$  to  $10^7$  Hz. Dielectric spectroscopy is used to study the local and global (chain) relaxation of homopolymers, the dynamic miscibility in polymer blends, polymer and ion dynamics in polyelectrolytes, dynamics in normal and super-cooled liquids as well as conductivity contribution in ion-containing systems.

**Hardware:** advanced rheometric expansion system (ARES, Rheometrics) with rheo-optical and rheo-dielectric units, torsional mechanical spectrometers (Rheometrics RMS 800 and Bohlin), universal materials testing machine (INSTRON 6022), PVT Apparatus (Gnomix), broadband impedance spectrometer (Novocontrol Technologies)

**Crosslinks to other projects:** Matter Diffusion in Nanoporous Media and Dense Polymer Systems by FCS, Discotic Liquid Crystals in Motion, High Performance Polycyanurate Thermoset Networks Based on Cyanate Ester Monomers, Piezorheology: Rheo-optics on the Microscale, Polymer Characterization

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# Scanning Probe Microscopy

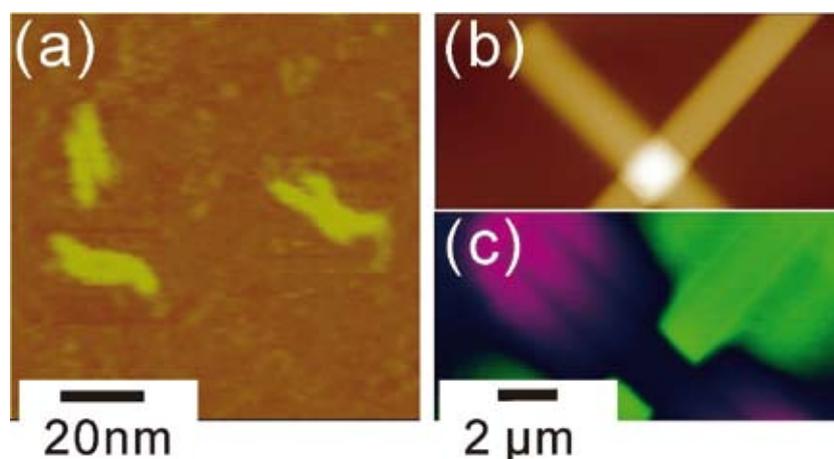
R. Berger

*Keywords: Surface properties, blockcopolymer, structuring of surfaces, electrical properties of surfaces*

In daily life we obtain information about material properties by touching surfaces with our fingers. In addition to the roughness of a surface we can feel other properties such as elasticity, friction, hardness, temperature, and granularity. These properties can be analyzed at a million times smaller scale by means of scanning probe microscopy (SPM). An atomically sharp probe is scanned over a sample and the interaction between the probe and the sample is measured. The interaction strength depending on the tip position is converted into a 2-dimensional map of surface properties. Often SPM is used routinely to study surface topography. However, specific probes can be used to probe lateral variations of frictional, elastic, thermal, electrical and magnetic properties. As a result a map of the lateral variation of these properties is obtained with nanometer resolution. The interaction strength between the tip and the sample is controllable, which allows for the local alteration or manipulation of surface properties. Objects, such as colloids can be moved to a desired position on the surface. Functional probes that allow a controlled heating of surfaces on a nanometer scale can be used to characterize thermal properties of the surface and can be applied for thermal treatment of structures.

Complementary to scanning electron microscopy, SPM allows investigating surfaces in their natural environment. For example, the molecular assemblies of a DNA template with blockcopolymers composed of single stranded DNA and polypropyleneoxide (PPO) are shown in Fig. 1a. These studies were performed in DNA buffer solution while operating the SPM in the soft tapping mode.

Electrical properties of sample surfaces can be mapped by applying an electrical potential between the SPM-tip and a surface. Either the electrostatic force (electrostatic force microscopy) or the current flow (scanning conductive microscopy) between the SPM-tip and the surface is measured. Furthermore, the work function (Kelvin potential microscopy) can be measured by operating the SPM in close vicinity to the surface. As an example, strip lines of electrically insulating  $\text{SiO}_x$  on top of conductive Pt were made by focussed ion beam deposition. While the topography does not allow distinction of both materials, the Kelvin potential microscopy shows a clear difference (Fig. 1b and c). Electrical measurements on a nanometer scale play an important role in characterizing materials that play a role for polymer electronics.



**Fig. 1:** (a) Scanning force microscopy of the structures obtained from base pairing of DNA blockcopolymer with long DNA templates. The Watson-Crick motif aligned the hydrophobic polymer segments along the DNA double helix, which resulted in dimer formation. (b) Topography of strip lines obtained by scanning force microscopy and (c) Kelvin probe microscopy. The Kelvin potential of Pt corresponds to green and that of  $\text{SiO}_x$  to pink colors.

**Crosslinks to other projects:** Detuning of Individual Plasmonic Antennae by Attachment of Dielectric Colloids, Advanced Materials for Solar Cell Applications, Polymer Brushes on Nanomechanical Cantilever Sensors, Focused Ion Beam

## References

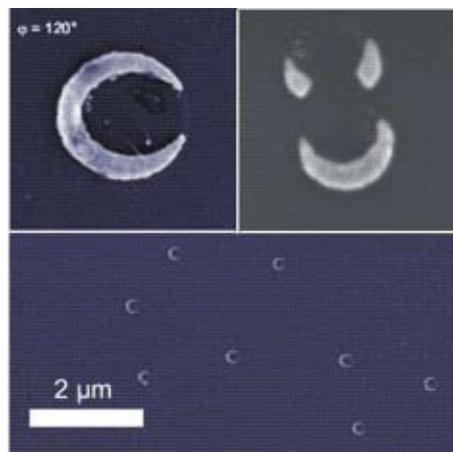
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## Clean Room

### B. Menges

**Keywords:** Micro- and nanostructures, evanescent wave optical sensors, grating coupler, photolithography, reactive ion beam etching

Nanostructured materials and small assemblies in nanophotonics, microelectronics or in microsystems technology are of great interest to interdisciplinary research at the institute.



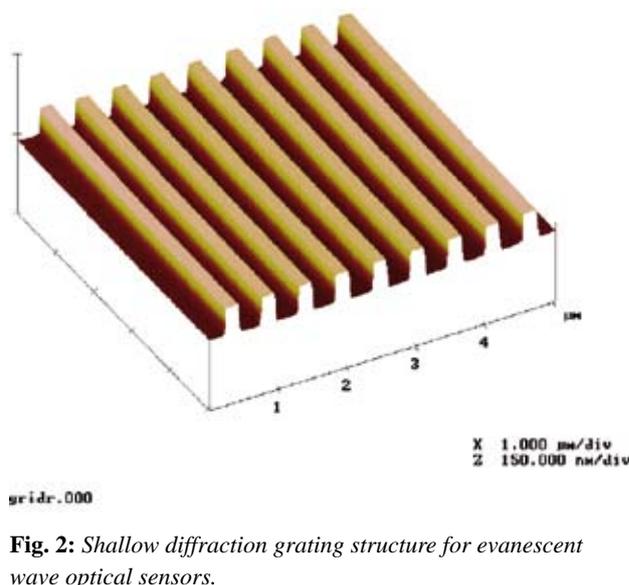
**Fig. 1:** Crescent-shaped metal structures for nano optics.

Shallow diffraction gratings are an elegant way of exciting surface bound electromagnetic waves in integrated optic devices like surface plasmon polaritons or optical waveguide sensors. The preparation of these submicron structures requires a holographic grating setup, which is an interference pattern caused by a laser beam.

The clean room class 100 specification-laboratory is an essential requirement for micro- and nanostructuring as well as for sample preparation under particularly dust free conditions. Micro- and nanostructuring of polymeric or inorganic materials can be done by established techniques such as optical lithography and Reactive Ion Beam Etching (RIE). The infrastructure allows for complex preparation of integrated optics and sensors including specific functionalization. For the preparation of ultra-thin layers or supra molecular architectures different techniques are available such as a Langmuir trough or a spin coater.

#### Two examples of cross-linking projects:

Metal structures with the typical dimensions of the wavelength of light and lower, support optical resonances – the particle plasmons. Preparation of these highly versatile crescent-shaped metal objects is achieved by ion beam milling.



**Fig. 2:** Shallow diffraction grating structure for evanescent wave optical sensors.

**Crosslinks to other projects:** Optical Single Object Detection, Evanescent Wave Optics, Structural and Dynamic Inhomogeneities in Thermoresponsive Hydrogels, Detuning of Individual Plasmonic Antennae by Attachment of Dielectric Colloids

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## Focused Ion Beam

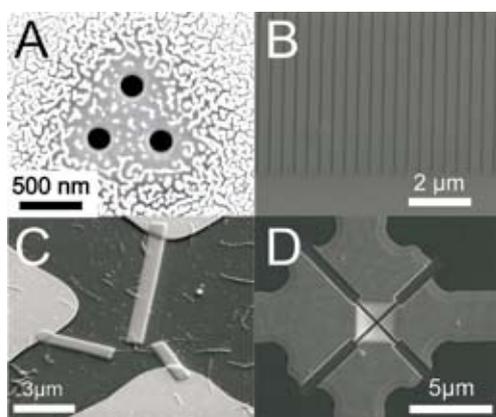
M. Kappl

*Keywords: Nanostructuring, EDX, cryo-SEM, TEM sample preparation*

With the increasing importance of nanotechnology, analytical as well as preparative tools that work on such length scales are in high demand. A very versatile instrument is the focused ion beam, where a beam of ions is focused onto the surface and raster scanned by means of ion optics. This allows the removal of material by ion sputtering (“milling”) with a resolution of  $\sim 10$  nm.

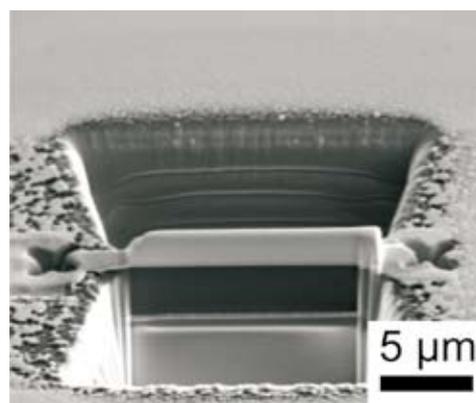
The FEI Nova 600 Nanolab FIB instrument at the MPI-P is a so-called dual-beam instrument that combines a focused ion beam with an SEM that allows simultaneous imaging of the sample. This combination is especially important for the preparation of delicate samples, where sample alignment is done under SEM control without the need of ion beam imaging. Our system is equipped with 3 gas injection systems that can be used for ion beam induced material deposition of Pt, Au or  $\text{SiO}_2$  layers. Further options include an EDX detector for elemental analysis, a nanomanipulator for the lift-out of TEM-lamella (see below) and a cryo-system for investigation of “wet” samples such as cells or hydrogels at temperatures down to  $-140$  °C. The main application of the FIB at the MPI-P are nanostructuring of surfaces, cross sections of samples, TEM sample preparation and cryo-SEM.

The main application of FIB at the MPI-P is the nanostructuring of surfaces. Fig. 1 shows examples of nanostructures prepared by FIB milling.



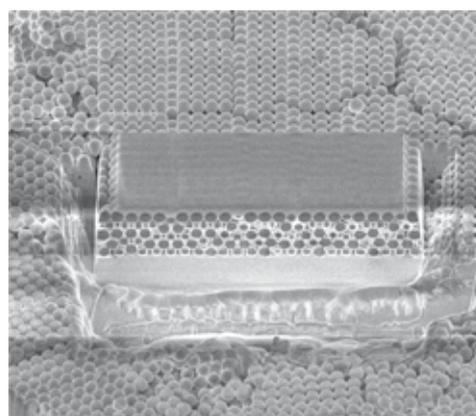
**Fig. 1:** (A) 180 nm diameter holes in a silicon nitride membrane for use in electrophysiological measurements of membrane proteins. (B) optical grating to improve coupling of laser light into a waveguide (C) part of an electrode array for four point probe testing of conductive polymer colloids (D) electrical contacting of single nanofibers for electrical characterization.

Where FIB opens completely new possibilities is the preparation of TEM lamellae, i.e. the site directed preparation of  $\sim 50$  nm thin slices out of bulk samples that are not or hardly accessible by other means. Fig. 2 shows the first step in the preparation of a TEM lamella from a pixel of an OLED display. The lamella that contains the region of interest is already visible but has still to be cut out and lifted out with the nanomanipulator.



**Fig. 2:** Preparation of a TEM lamella from a single pixel of an OLED display.

Using the so-called “slice and view” protocol, a 3D tomography of samples is possible. In this mode, slices of typically 10-100 nm thickness are removed by ion beam sputtering from a small block of the sample. After each slice, a SEM image of the newly exposed sample face is taken (Fig. 3). From such a set of slice images, a 3D reconstruction of the sample can be obtained by image analysis.



**Fig. 3:** SEM image of a colloidal crystal made from  $1 \mu\text{m}$  polystyrene spheres during a “slice and view” run to reconstruct the 3-D crystal structure.

**Crosslinks to other projects:** Scanning Probe Microscopy, Optical and Electron Microscopy, Model Membranes

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# The Institute



## **Board of Directors**

## Prof. Dr. Hans-Jürgen Butt



Hans-Jürgen Butt joined the Max Planck Society in September 2002 as one of the directors at the MPI for Polymer Research. After a physics education at the Universities of Hamburg and Göttingen, he received his diploma in 1986. His master thesis was on high energy physics. In 1986 he moved to Frankfurt/Main to work in Ernst Bamberg's group at the Max Planck Institute for Biophysics on light induced proton transport of bacteriorhodopsin.

In 1989 he received his PhD from the Johann Wolfgang Goethe University of Frankfurt. As a postdoc in Santa Barbara, California, with Paul Hansma, he got into contact with the newly developed atomic force microscope. In 1990, back in Germany at the Max Planck Institute for Biophysics, he studied biological objects with the atomic force microscope. In this period the work on surfaces in particular on surface forces became a central issue. He habilitated in 1995.

In 1996 he went to the institute for physical chemistry at the Johannes Gutenberg University of Mainz as Associate Professor. There he focused on the physics and chemistry of interfaces and on polymer physics. Three years later he followed a call to the University of Siegen as full professor for physical chemistry. Here, the interest in nano- and microchemistry started.

Since 2007, Hans-Jürgen Butt chairs the German Colloid Society.

### Specific areas of research are

- surface and interparticle forces
- nano- and microchemistry: developing
- evaporation and condensation of microdrops
- atomic force microscopy
- wetting phenomena
- colloids in external fields

### The following staff scientists interact closely with Professor Butt

- Dr. G.K. Auernhammer (microrheology)
- Dr. R. Berger (atomic force microscopy, cantilever sensors)
- Dr. E. Bonaccorso (evaporation of microdrops)
- Dr. J.S. Gutmann (composite materials, thin films)
- Dr. M. Kappl (surface and interparticle forces)
- Dr. K. Koynov (confocal microscopy)
- Dr. D. Vollmer (kinetics of phase transitions)



Regina De Hoogh and Claudia Reitz are assistants to Prof. Butt

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## Prof. Dr. Kurt Kremer



Kurt Kremer joined the Max Planck Society in September of 1995 as the sixth director of the Max Planck Institute for Polymer Research, heading the new theory group. He studied physics at the University of Cologne. In 1983 he received his PhD degree in theoretical physics from the University of Cologne under the supervision of Prof. Binder at the National Research Center KFA Jülich. He performed computer simulations for dynamic and static properties of polymers in bulk and near surfaces. After spending another year at Jülich as a scientific staff member he moved for a post doctoral stay to Exxon Research and Engineering Co., Annandale, New Jersey, USA. There, he started working on molecular dynamics simulations of polymers and on charge stabilized colloids in collaboration with Drs. Grest, Pincus, and others. In 1985 he came back to Germany becoming a member of Prof. Binder's group at the University of Mainz as an Assistant Professor of theoretical physics. There he got his habilitation in Theoretical Physics in 1988. After that he returned to the solid state laboratory of the KFA Jülich as a senior scientific staff member joining the Department of Prof. Villain. In 1992 his habilitation was transferred to the University of Bonn and in fall of 1995 back to Mainz. He spent several extended periods as visiting professor/scientist at Exxon Research and Engineering Co. (Dr. Grest), UC Santa Barbara (Materials Dept., Prof. Pincus), and the University of Minnesota (Dept. Chem. Engineering and Materials Science, Profs. Davis, Bates, Tirell, and others). In spring 1995 he stayed for a period of three months at the central chemical engineering department of the Bayer AG, Leverkusen, looking into the applicability of current theoretical results to industrial problems.

Prof. Kremer was awarded the "George T. Piercy Distinguished Professorship of Chemical Engineering and Materials Science" of the University of Minnesota, Minneapolis, in 1991, and the "Walter Schottky Preis der Deutschen Physikalischen Gesellschaft" in 1992. He was Whitby Lecturer of the Akron University in 1999 and Nakamura Lecturer at the University of California, Santa Barbara in 2006. Since 2005 he is a Fellow of the American Physical Society.

### Specific areas of research are

- multiscale description of macromolecular systems
- computational physics methods/applications
- computational chemistry methods/applications;
- statistical mechanics of soft matter (polymers, colloids, membranes)
- polymer networks and gels
- polyelectrolytes, liquid crystalline polymers, semi-flexible polymers
- structure property relation of soft matter,
- surface and interface properties
- hierarchical structure formation in soft matter
- coupling on conformational and electronic properties

### The following staff scientists interact closely with Professor Kremer

- Dr. D. Andrienko (electronic materials)
- Prof. Dr. B. Dünweg (computer simulation methods, statistical mechanics)
- Dr. L. Delle Site (multiscale modeling, quantum-chemical calculations)
- Dr. Ch. Peter (multiscale modeling of biomolecules)
- Prof. Dr. H. Pleiner (macroscopic theory of complex fluids, nonlinear dynamics)
- Prof. Dr. T.A. Vilgis (analytic theory, networks, polyelectrolytes)
- Dr. N.F.A. van der Vegt (computational chemistry)

### Collaborations with former group members include

- Dr. M. Deserno (analytic theory, computer simulations, biological membranes)
- Prof. R. Everears (polymer melts and networks)
- PD Dr. Ch. Holm (computer simulations, polyelectrolytes)
- Prof. F. Müller-Plathe (multiscale modeling)
- Prof. H. Schiessel (biopolymers)
- Prof. F. Schmid (amphiphilic systems)



Doris Kirsch is assistant to Prof. Kremer

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## Prof. Dr. Katharina Landfester



Katharina Landfester joined the Max Planck Society in September 2008 as one of the directors of the Max Planck Institute for Polymer Research. She studied chemistry at the Technical University of Darmstadt. Her diploma thesis was undertaken at the Ecole d'Application des Hautes Polymères in Strasbourg (Prof. M. Lambla). In 1995 she received her doctoral degree in physical chemistry from the Johannes Gutenberg University in Mainz after working with Prof. H.W. Spiess at the Max Planck Institute for Polymer Research on the synthesis and characterization of core-shell latexes by transmission electron microscopy and solid state NMR. After spending another year as a group leader at the institute, she moved to the Lehigh University (Prof. M. El-Aasser) as a post-doctoral scientist, where she first came in contact with the miniemulsion technique. She returned to Germany in 1998 joining the group of Prof. M. Antonietti at the Max Planck Institute of Colloids and Interfaces in Golm. There, she led the miniemulsion group working on new possibilities in the synthesis of complex nanoparticles. In 2002, she was awarded her *Habilitation* degree in physical chemistry at the university of Potsdam. In 2003, she accepted the chair (C4) of macromolecular chemistry at the University of Ulm. Here, she started her activities in the field of biomedical applications in cooperation with several medical groups working on the interaction of nanoparticles with different cell compartments, the labeling of cells and the delivery of substances to specific sites.

In 1992 and 1994 she obtained DAAD stipends for her research activities in Strasbourg. For the research in the USA in 1996 she received a stipend by the DFG. In 1998, she received the Liebig stipend of the Fonds der Chemischen Industrie (FCI).



Rita Schäfer and Dagmar Stiep are assistants to Prof. Landfester

In 2001 she was awarded the Reimund Stadler prize of the Gesellschaft Deutscher Chemiker (GdCh) as well as the prize of the Dr. Hermann Schnell Stiftung.

From 2002 to 2007, she was a member of the Young Academy (Junge Akademie) of the Berlin-Brandenburgischen Akademie der Wissenschaften und Deutschen Naturforscher Leopoldina; in 2003/2004 she was the spokesperson for the Young Academy.

### Specific areas of research are

- heterophase polymerization, esp. miniemulsion polymerization
- complex hybrid nanoparticles
- functionalization of nanoparticles
- polymerization and crystallization in confined geometries
- interaction of nanoparticles with cell compartments
- structure formation in (polymeric) nanoparticles
- surface and interface properties
- hierarchical structure formation in soft matter

### The following staff scientists interact closely with Professor Landfester:

- Dr. A. Kröger-Brinkmann (polymer characterization)
- Dr. F. Laquai (optical spectroscopy)
- Dr. I. Lieberwirth (electron microscopy)
- Dr. V. Mailänder (particles and cell interaction)
- Dr. W.H. Meyer (ion containing polymers, physical chemical characterization)
- Dr. A. Musyanovych (nanoparticles for biomedical applications)
- Dr. C. Weiss (inorganic and hybrid nanoparticles)

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## Prof. Dr. Klaus Müllen



Klaus Müllen joined the Max Planck Society in 1989 as one of the directors of the Max Planck Institute for Polymer Research. He obtained his Diplom-Chemiker degree at the University of Cologne in 1969 in Professor E. Vogel's group. He was granted his PhD degree by the University of Basel (Switzerland) in 1972 where he undertook research with Professor F. Gerson on twisted  $\pi$ -systems and EPR spectroscopic properties of the corresponding radical anions. In 1972 he joined Professor J. F. M. Oth's group at the Swiss Federal Institute of Technology in Zurich, where he worked in the field of dynamic NMR spectroscopy and electrochemistry. He received his Habilitation degree from the ETH Zurich in 1977 and was appointed "Privatdozent". In 1979 he became a Professor in the Department of Organic Chemistry, University of Cologne, and accepted an offer of a chair in Organic Chemistry at the University in Mainz in 1983. He received the offer of a chair at the University of Göttingen in 1988, and at the University of Cologne in 1992. In 1993 he was awarded the Max Planck Forschungspreis and in 1997 the Philip Morris Forschungspreis. He received the Nozoe Award in 2001, the Foundation Award of the University of Kyoto in 2002, the Science Prize of the "Stifterverband für die Deutsche Wissenschaft" in 2003 and the International Award of the Belgian Polymer Group in 2005/2006. In 2007 he received the Otto Bayer Lecture Prize. In 1999 he became a member of the German Academy Leopoldina. He obtained a Honorary Professorship from the East China University of Science and Technology, the Institute of Applied Chemistry, Changchun, of the Chinese Academy of Sciences and the Institute of Chemistry, Beijing, Chinese Academy of Science.

In 2001 he was awarded an Honorary Doctorate degree from the University of Sofia. He has been a visiting scientist at the Universities of Osaka (JSPS), Jerusalem, Cambridge, Rennes, Leuven (SMETS Lecture), Illinois at Champaign-Urbana (Lane Lecture), Nice and Bordeaux. In 2006 he became Associate Editor of the Journal of the American Chemical Society and in 2008 President of the German Chemical Society. In 2008 he received the Nikolaus Otto Award and the Innovation Award of Northrhine Westphalia and in 2009 the International Award of the Society of Polymer Science, Japan. In 2009 he became honorary member of the Israel Chemical Society.

### Specific areas of research are

- synthetic macromolecular chemistry
- supramolecular chemistry and materials science

### The following scientists interact closely with Professor Müllen

- Dr. M. Baumgarten (organic magnets, EPR spectroscopy)
- Dr. M. Klapper (synthetic macromolecular chemistry)
- Dr. H.J. Räder (mass spectrometry of polymers)
- Dr. M. Wagner (high-resolution NMR spectroscopy)



Petra Rapp and Angelika Altherr-Liewald are assistants to Prof. Müllen

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## Prof. Dr. Hans Wolfgang Spiess



Hans Wolfgang Spiess joined the Max Planck Society in 1984 as one of the directors of the Max Planck Institute for Polymer Research. He received his doctoral degree in physical chemistry in 1968 from the University of Frankfurt with Prof. H. Hartmann. After a postdoctoral stay at Florida State University (Prof. R. K. Sheline) he returned to Germany in 1970 joining the Max Planck Institute for Medical Research, Department of Molecular Physics in Heidelberg, headed by Prof. K. H. Hausser. The work there on molecular motions in liquids and solids was also the topic of his habilitation in physical chemistry (1978) at the University of Mainz, where he worked in the group of Prof. H. Sillescu. In Mainz he changed his research interests to the study of molecular structure and dynamics in polymers and developed pulsed deuteron NMR techniques that opened up new possibilities in this area. From 1981 to 1982 he held a professorship of physical chemistry at the University of Münster and in 1983 he accepted a chair of macromolecular chemistry at the University of Bayreuth. Prof. Spiess served as the chairman of the European Polymer Federation (1991-92), as the chairman of the Capital Investment Committee of the German Science Foundation (DFG) (1994-96); and as the chairman of the Committee for Electronic Data Processing of the MPS (1997–2006). From 2000-2006 he served as President of the Groupement AMPERE and from 1999 to 2005 he was a Member of the Scientific Council of the Federal Republic of Germany. Since 2008 he is Vice President of the International Society of Magnetic Resonance.

In 1987 he received the Leibniz Award of the DFG. Honorary lectureships he delivered include the Washburn Lecture, University of Nebraska, USA (1995), Barrè Lectures,

University of Montreal, Canada (1996), Kolthoff Lectures, University of Minnesota, USA (1998), University of California, Berkeley (2000), Gomberg-Lecture University of Michigan, USA 2001. He is doctor honoris causa of the Technical University of Cluj-Napoca, Romania (1997) and of the Adam Mickiewicz University, Poznan, Poland (1998). In 2000 he received the Eastern Analytical Symposium NMR Award, USA. In 2002 he was honoured by the AMPERE Prize, the Liebig Medal of the German Chemical Society (GDCh) and the Presidential Medal of Cornell University, USA. He received the Award of the Polymer Society, Japan in 2003 and the Walther Nernst Medal of the Bunsen Gesellschaft for Physical Chemistry in 2005. He applies magnetic resonance and other methods to study new polymer and supramolecular materials in order to relate their microscopic and macroscopic behavior.

### Specific areas of research are

- two- and three-dimensional NMR methods for studying molecular dynamics
- high-resolution multiple quantum NMR spectroscopy of solids for studying molecular structure and organization in bulk and at surfaces
- spin diffusion techniques for determining the phase behavior of multicomponent systems
- NMR imaging with hyperpolarized gases
- hyperpolarization by dynamic nuclear polarization and parahydrogen
- pulsed EPR to study molecular dynamics and defect radicals in polymers

### The following staff scientists interact closely with Professor Spiess

- Dr. G. Brunklaus (solid-state NMR)
- Dr. R. Graf (NMR structure and polymer dynamics)
- Dr. D. Hinderberger (EPR spectroscopy)
- Dr. A. Koch (chemistry)
- Dr. V. Macho (IT department)
- Dr. K. Münnemann (hyperpolarized gases)
- Dr. D. Sebastiani (ab initio molecular dynamics, ab initio calculation of NMR shifts)

### Collaborations with former group members include

- Dr. P. Blümler (NMR imaging)
- Prof. G. Jeschke (EPR spectroscopy)
- Prof. U. Wiesner (organic-inorganic hybrids)
- Prof. M. Wilhelm (Fourier-Transform rheology and polymer characterization)



Corinna Probst and Brigitte Kulen are assistants to Prof. Spiess

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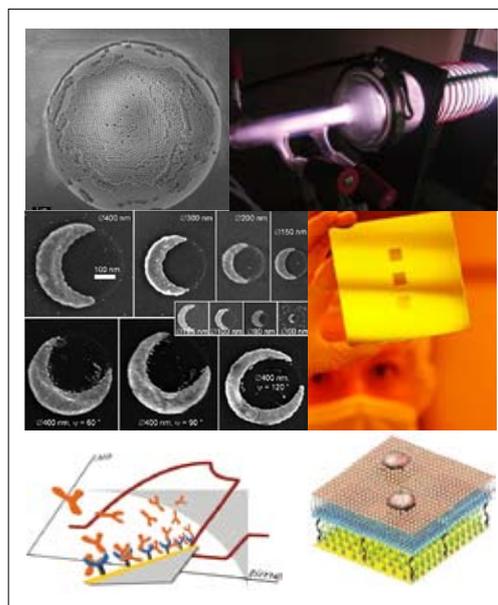
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## Materials Science Group



The group is composed of eight subgroups run by staff scientists. The general research topic is to investigate relations between structure, molecular order and physical, chemical and biological properties of polymeric or organic systems in thin films and at functionalized surfaces. Strong emphasis is put on optical and electrochemical techniques to elucidate the structural and functional characteristics of supramolecular assemblies and nano-materials.

The films can be composed of various materials, ranging from functionalized hydrogels, conjugated polymers, plasma polymerized molecules to biomimetic membrane systems. Special emphasis is given to the interface to biological samples, e.g. proteins, DNA or lipid membranes. This interdisciplinary approach is complemented by developments of novel optical detection methods using integrated optics, especially (localized) surface plasmons and waveguide analysis methods as well as nonlinear optical studies of thin films. Specially designed and functionalized surfaces can be used as sensing platforms to probe the binding of selected compounds to the interface.

### Specific areas of research are

- structural engineering of functional polymers at the molecular level
- organic supramolecular architectures at interfaces including membrane-mimetic approaches
- thin films, including self-assembly and Langmuir-Blodgett multilayers
- interfacial and thin film physics (structure, dynamics)
- linear and nonlinear optical properties of polymers
- integrated optics (plasmonics, waveguide architectures)
- micro- and nanostructures (nano optics, plasmonics)
- dynamics at interfaces (field-enhanced dynamic light scattering)
- biofunctional interfaces and sensor development

### Staff scientists

- Prof. Dr. C. Bubeck (thin films, optical spectroscopy, nonlinear optics)
- Dr. R. Förch (surface functionalization, plasma polymerization)
- Dr. U. Jonas (polymer surface structuring)
- Dr. I. Köper (tethered biomolecular lipid membranes)
- Dr. M. Kreiter (near-field and nano-optics)
- B. Menges (evanescent wave optics, integrated optics and sensors, clean room)
- Dr. R. Naumann (membrane proteins at surfaces)
- Prof. Dr. E.-K. Sinner (biomimetic systems, biointeractive surfaces)

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**Emeriti**

## Prof. Dr. Erhard W. Fischer



Erhard W Fischer is one of the two directors who were appointed to establish the institute in June 1983.

He obtained his doctoral degree in physics from the Technische Universität Stuttgart in 1957 working there since 1956 as a research assistant with Prof. H. A. Stuart at the Institute of Physical Chemistry at the University of Mainz. There he studied the crystallization of polymers, the formation of polymer single crystals and the physical properties of semicrystalline polymers by means of electron microscopy, X-ray diffraction, and mechanical and calorimetric measurements. His work for habilitation in physics (in 1962) was concerned with these investigations including the role of chainfolding during crystallization. In 1963 he worked as Research Fellow at the Research Triangle Institute in Durham, N. C. with A. Peterlin and in 1965 as an Associate Professor at the Polytechnic Institute of Brooklyn, N. Y.

He was appointed to a chair in Chemical Physics at the University of Mainz in 1966, where he stayed until 1983. During this time, he went to the USA, Great Britain and China as a visiting professor. His scientific work was honored by the award of the Polymer Physics Prize of the American Physical Society (1979), the election as a member of the Austrian Akademie der Wissenschaften (1984), the French-German Alexander v. Humboldt Award (1987) and the Award of the Japanese Society of Polymer Science (1990).

He was elected as an Honorary Member of the Society of Polymer Science of Japan (1997) and a Fellow of the American Physical Society (1998). In 1999 he received the Doctor Honoris Causa degree from the Universidad del Pais Vasco, San Sebastian, Spain.

E. W. Fischer served as Chairman and founder of the Polymer Physics Section of the European Physical Society (1969-75), Chairman of the Polymer Physics Group of the Deutsche Physikalische Gesellschaft (1969-73), and member of the Macromolecular Division of IUPAC (1970-75) and of the scientific Council of the ILL, Grenoble (1974-78).

Professor Fischer retired in 1997. However, his current research activities are still dedicated to the relationship between molecular parameters and macroscopic physical properties of polymers. In addition he is especially interested in the relaxation processes and the dynamics of supercooled molecular liquids.

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## Prof. Dr. Gerhard Wegner



Gerhard Wegner joined the Max Planck Society in 1983 as one of the founders of the present Max Planck Institute for Polymer Research. He holds a doctoral degree in chemistry from the University of Mainz (1965). In 1966-69 he worked as a research staff chemist with Prof. H.G. Cassidy at Yale University, Conn., USA. Returning to the University of Mainz, he joined the group of Prof. E.W. Fischer in the Institute of Physical Chemistry. His Habilitation in physical chemistry (1970) concentrated on solid-state polymerization of diacetylenes and showed how macroscopic single crystals of polyconjugated macromolecules can be made. From 1974 to 1984 he had the chair in Macromolecular Chemistry at the University of Freiburg (Germany). He was a visiting professor at Poona, India (1974), Amherst, Mass., USA (1979), Tucson, AZ, USA (1986), Milan, Italy (1987), Leuven/Louvain, Belgium (1988), Midland, Mich., and Storrs, Conn., USA (1990), Helsinki, Finland (1991), Pisa, Italy (1992), Université de Montreal, Canada (1992), Cornell University (Baker Lecture-ship) (1994), University of Akron, Ohio, USA (1995).

He received the Otto Bayer Award in 1984, the Philip-Morris-Technologie-Preis in 1989, the Hermann Staudinger Medal of the German Chemical Society in 1990, the Rolf Sammet Lectureship (1997), the ACS Award in Polymer Chemistry (1998), the Award of the Society of Polymer Science Japan (1998), the Xerox-Lectureship, Halifax Kanada (1998), the Butler-Lectureship, Gainesville, Florida (1999), the Honorary Doctorate from the University of Massachusetts at Lowell, USA (2000), FEMS-European Materials Medal, Lausanne (2003), Federal Cross of Merit (Bundesverdienstkreuz) Germany (2003), Honorary Doctorate

of Engineering Science, University Erlangen, Germany (2004), Honorary Member of Society of Polymer Science Japan (2004), Marin-Drinov Medal, Bulgarian Academy of Science (2004), Honorary Professorship Nankai University, China (2004), H.F. Mark Medal, Österreichisches Forschungsinstitut, Wien (2004), Honorary Member of the A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (2004), Honorary Doctorate Technical University of Lodz, Poland (2005), Honorary Member of the Society of Polymer Science, Japan (2005), Solomon Lecture, Brisbane, Sidney, Melbourne, Adelaide, Australia (2005), Honorary Doctorate University of Patras/Greece (2007), the Verdienstorden des Landes Rheinland Pfalz (2008).

He served as the chairman of the Chemistry, Physics & Technology Section of the Max Planck Society from 1991 to 1994 and was Vice President of the Max Planck Society from 1996 to 2002. Prof. Wegner was the chairman of the International Max Planck Research School for Polymer Materials Science in Mainz.

### Specific areas of research are

- chain-stiffness as a structural principle in the design of novel macromolecular materials
- solid polyelectrolytes and ion conductors
- polymers as semiconductors and optical materials
- synthesis and evaluation of polymer surfactants
- mineralization processes controlled by polymers
- characterization of polymer structures by quantitative methods (X-ray scattering, electron microscopy, light scattering)

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**Independent Junior Research Group and Minerva Programme**

## Dr. Frédéric Laquai



Frédéric Laquai joined the Max Planck Society in 2008 as head of an Independent Junior Research Group. He studied chemistry at the University of Oldenburg and at the University of Marburg from 1999 to 2003. During his studies he undertook a 6-month research project in Synthetic Polymer Chemistry in the group of Professor Andrew B. Holmes at the University of Cambridge (UK). In May 2003 he received a *Diplom-Chemiker* degree from the University of Marburg after completing his diploma thesis with Professor Heinz Bässler in physical chemistry. He moved on to the Max Planck Institute for Polymer Research and joined the group of Professor Gerhard Wegner. In April 2006 he received a PhD degree from the University of Mainz for his experimental research on energy transfer processes and charge carrier transport in conjugated polymers for optoelectronic applications. He then became a Research Fellow in the Optoelectronics Group of Professor Sir Richard Friend at the Cavendish Laboratory of Physics in Cambridge (UK). There he worked on ultrafast transient absorption spectroscopy of excited states in conjugated polymers and blends. In August 2008 Frédéric Laquai rejoined the MPI for Polymer Research as an Independent Junior Research Group Leader. He is currently setting up his new group which will study the dynamics of excited states in conjugated materials by time-resolved optical spectroscopy. The main focus of his research is to investigate the processes that lead to charge carrier generation and recombination in organic solar cells, in particular to gain an understanding of the loss mechanisms that currently limit the efficiency of organic photovoltaics.

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In 1999 Frédéric Laquai was awarded 1<sup>st</sup> prize in the nationwide competition “*Jugend forscht*” for work on Organic Light Emitting Diodes (OLEDs). He also received the prize for the best interdisciplinary research project awarded by the German Science Foundation (DFG) and an award from the minister of the Federal German State Niedersachsen for outstanding scientific achievements in 1999. His PhD work was supported by a Kekulé scholarship from the *Fonds der Chemischen Industrie*. He received a postdoctoral research fellowship from the German Science Foundation (DFG) for his research on ultrafast spectroscopy at the Cavendish Laboratory in Cambridge. From 2007-2008 he was a Research Fellow in the Sciences of Clare Hall College in Cambridge and is now life member of Clare Hall.

### Specific areas of research are

- time-resolved photoluminescence spectroscopy of conjugated organic materials
- ultrafast transient absorption spectroscopy (pump-probe spectroscopy)
- steady-state and time-resolved photo-induced absorption (PIA) spectroscopy
- charge carrier transport in disordered organic solids and charge carrier mobility measurements using the time-of-flight technique
- amplification of light in optical waveguide structures and organic lasing
- organic electronic devices, especially light emitting diodes and organic photovoltaics

### Collaboration with other scientific groups includes

- Prof. R. Friend, Optoelectronics Group, Cavendish Laboratory, Cambridge (ultrafast optical spectroscopy)
- Prof. Th. Basché, Physical Chemistry, University of Mainz (single molecule spectroscopy)
- Prof. R. Zentel, Organic Chemistry, University of Mainz (IRTG Optoelectronic Materials)
- Dr. D. Hertel, University of Cologne (time-resolved photoluminescence spectroscopy)

## Dr. Aránzazu del Campo



Aránzazu del Campo joined the Max Planck Institute for Polymer Research in February 2009 and is heading the research group “Active Surfaces and Materials”. She studied chemistry at the *Universidad Complutense* (Madrid, Spain) and received her MSc degree in 1995. In 2000 she obtained her PhD degree from the *Instituto de Ciencia y Tecnología de Polímeros* (Madrid) for experimental research on ferroelectric liquid crystalline polymers. Parallel to this she studied materials science and engineering at the *Universidad Politécnica de Madrid*. After completion of her PhD, she moved to the Max Planck Institute for Polymer Research as a Marie Curie Fellow and joined Prof. H.W. Spiess’ department to work on surface patterning and colloidal assembly. During this time she spent some months at Berkeley National Lab (USA) in Prof. Miquel Salmerón’s group to acquire experimental experience in X-Ray Photoelectron Spectroscopy and Atomic Force Microscopy. In September 2003 she was appointed Senior Research Fellow by the University of Greenwich (London, UK) to work at the *Università degli Studi di Urbino* (Italy) within the framework of an European Research Project. She worked on surface tailoring of magnetic nanoparticles for applications in magnetic separation and purification of biomolecules. In December 2004 she moved to the Max Planck Institute for Metals Research (Stuttgart) as group leader in Prof. E. Arzt’s department. In 2007 she became head of the department “Functional Surfaces” at the *Leibniz Institut für Neue Materialien GmbH* (Saarbrücken).

Her group at the MPI for Polymer Research works on the development of surfaces and materials with tunable properties. These are based on novel photochemical and micro- and nanofabrication concepts and conceived to understand and/or reproduce mechanisms by which biomolecules, cells, or even animals (geckos) interact during locomotion with solid surfaces.

Three main research lines will be established from the beginning: (i) bioactive caged surfaces with selective response to different irradiation wavelengths that allow dynamic and multi-parametric studies in biology, (ii) responsive hydrogels with photo-tunable stickiness, and (iii) bio-inspired reversible adhesives for dry and wet environments mimicking gecko and tree frog locomotion mechanisms.

In 2007 Aránzazu del Campo was awarded the Federation of European Materials Scientists (FEMS) Lecturer Award for Excellence in Materials Science and Engineering. She also received the Marie Curie Post-Doctoral Fellowship during her stay at MPI for Polymer Research and the Ramón Areces Fellowship for her PhD. She is currently finishing her *Habilitation* degree at the faculty of Biophysical Chemistry at the University of Heidelberg.

### Specific areas of research are

- Responsive surfaces and materials
- Photochemistry: wavelength dependent photo-activation
- Adhesion phenomena: gecko- and tree-frog inspired adhesives
- Micro- and nanostructuring approaches
- Interaction of biomolecules and cells with synthetic surfaces
- Polymer materials: synthesis, structure-properties relationships, liquid crystalline behavior

### Collaboration with other scientific groups includes

- Prof. J. Piehler, University of Osnabrück
- Prof. M. Goeldner, University Strasbourg (France)
- Prof. A. García, GeorgiaTech (USA)
- Prof. H. Finkelmann, University of Freiburg
- Prof. E. Arzt, Leibniz Institut für Neue Materialien, Saarbrücken
- Prof. J. Mano, University of Minho (Portugal)
- Dr. J. Barnes, University Glasgow (UK)
- Prof. J. Spatz, MPI for Metals Research, Stuttgart
- Prof. H.-J. Butt, MPI for Polymer Research, Mainz
- Prof. H.W. Spiess, MPI for Polymer Research, Mainz
- Prof. A. Bello, Instituto de Ciencia y Tecnología de Polímeros, Madrid (Spain)

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## **External Scientific Members**

## Prof. Dr. Kurt Binder



Kurt Binder has served as an external scientific member since 1989. He obtained his doctoral degree in physics from the Technical University of Vienna in 1969. There he studied spin correlation functions of ferromagnets near the critical point. From 1969 to 1974 he joined Prof. Dr. H. Maier-Leibnitz's and Prof. Dr. H. Vonach's group at the Technical University of Munich working on the computer simulation of phase transitions, in the bulk and at surfaces. After a year as an IBM postdoctoral fellow in Switzerland he completed his thesis in physics, based on his development of computer simulation methodology in the study of critical phenomena considering the finite size effects. In 1974 he worked at the Bell Laboratories in New Jersey USA, and was appointed professor at the University of Saarbruecken where he stayed until 1977. From 1977 to 1983 he served as director at the Solid State Laboratory (IFF) of the National Research Center at Jülich, while simultaneously holding the position of full professor at the University of Cologne. He was mainly working in the field of the kinetics of phase transitions (nucleation, spinodal decomposition), simulation of structure and of diffusion in alloys and adsorbed layers, and on the phase transition of spin glasses. In 1983 Kurt Binder received a full professorship for theoretical physics at the University of Mainz. His main fields of research are physics of the glass transition (from 1987 to 2001 he was Speaker of a "Sonderforschungsbereich" on glass research sponsored by the German National Science Foundation (DFG)), computer simulation of polymers and other complex materials. He also served as a member of the Technology Board of Rhineland-Palatinate and as chair of the Materials Science Research Center (MWFZ) at Mainz University. In 1993 he was awarded the Max Planck Medal, in 2001 the B. J. Adler CECAM Award of the EPS, and in 2003 the Staudinger-Durrer Medal of the ETH Zurich and in 2007 the Boltzman Medal of IUPAP. In October 2007 he was awarded the Gutenberg Research Fellowship by the University of Mainz. In addition Kurt Binder received an Honorary PhD in chemistry from the Maria Curie Skłodowska University, Lublin, Poland in 2007.

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## Prof. Dr. George Fytas



George Fytas has been an external scientific member of the MPI-P since 1998. He obtained his doctoral degree in physical chemistry from the Technical University of Hannover in 1975 for his work on Brillouin spectroscopy of liquids. From 1978 to 1980 he was a post-doctoral associate at the Department of Chemistry SUNY at Stony Brook in Prof. B. Chu's group, working on photon correlation of bulk polymers. He returned to Prof. Dr. Th. Dorfmueller's group in the Department of Chemistry at Bielefeld University, where he finished his Habilitation degree in 1983. His research was based on the application of laser light scattering techniques to study molecular motion in polymers. In 1983 he was appointed visiting Associate Professor in Salt Lake City, USA; in 1984, he worked as a visiting scientist at the MPI-P in Prof. Dr. E.W. Fischer's group. In 1985 he was appointed Professor at the University of Crete. Since 1988 he has been an affiliated researcher and head of the Polymer Group at FO.R.T.H.-Institute of Electronic Structure and Laser (I.E.S.L.). From 2004 to 2007 he was Professor in the Department of Materials Science at the University of Crete and Chairman. In 1999 he was awarded the FORTH prize for basic research, in 2002 he received a Humboldt Research award and in 2004 he was named as a fellow of the American Physical Society.

### His current research activities include

- collective dynamics and self-assembly of soft materials with an emphasis on block copolymers, persistent polymers and colloids
- polymer and particle dynamics near surfaces and in confined geometries
- the dynamic nature of glass transition in multi-component systems
- new applications of dynamic laser light scattering techniques and laser interaction with condensed soft matter
- elastic wave propagation in periodic and quasi-periodic polymer and colloid-based structure (phononics)

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[www.materials.uoc.gr/en/general/personnel/fytas.html](http://www.materials.uoc.gr/en/general/personnel/fytas.html)

## **Partner Groups**



**Rodolfo Acosta** studied physics at the Universidad Nacional de Córdoba. He received his doctorate in 2002, under the direction of Prof. Daniel Pusiol for research on thermotropic liquid crystal dynamics via fast field cycling Nuclear Magnetic Resonance. In 2002 he moved to Mainz for a postdoctoral stay at the Max Planck Institute for Polymer Research under the direction of Prof. Hans Wolfgang Spiess. At the MPI-P he participated in building up a laboratory dedicated to the study of laser polarized noble gases by NMR, in particular the influence of fast diffusion of  $^3\text{He}$  atoms on imaging of the lung. On 2004 he returned to Córdoba and was appointed as CONICET Researcher at the Facultad de Matemáticas, Astronomía y Física (FaMAF) of the National University of Córdoba. During a stay of three months at the MPI-P in 2005 a new research line dealing with nonlinear effects due to rapid diffusion and high spin polarization of laser polarized gases was established. In 2006 he was promoted to Professor at the FaMAF. His current research interests include the study of decoherence phenomena as determined by NMR with applications to quantum information, the determination of relaxation behavior in model polymer networks, and the

determination of structures via diffusion measurements in confined geometries, for instance in carbon nanotubes. In 2008 an agreement was signed between the MPI-P and FaMAF to establish a Partner Group for NMR Spectroscopy with High Spin Polarization. He is currently setting up a laboratory for hyperpolarization of different nuclei using parahydrogen. Results benefiting from the Partner Group collaboration have been published in several joint papers, among them two papers in Physical Review Letters.

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**Omar Azzaroni** studied chemistry at the Universidad Nacional de La Plata, Argentina. He received his PhD in 2004, under the direction of Prof. Roberto Salvarezza, for research on the development of new alternative nanofabrication methods using self-assembled monolayers at electrochemical interfaces. In 2004 he was awarded a Marie Curie Fellowship and joined the Melville Laboratory for Polymer Synthesis at the University of Cambridge (United Kingdom) to work in the field of “soft nanotechnology” under the supervision of Prof. Wilhelm Huck. He moved to the Department of Materials Science at the MPI-P as an Alexander von Humboldt Research Fellow in 2007, conducting research into the design and applications of functional supramolecular bioconjugates. After his stay at the MPI-P he was appointed, in 2008, CONICET Researcher at the Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA). He is currently setting up a Soft Matter Laboratory at INIFTA devoted to the study of different physicochemical aspects of soft matter-based systems, with particular emphasis on self-assembling architectures. His current research interests include recognition-driven molecular assembly, supramolecular bioconjugates, smart and tunable

macromolecular materials, soft nanotechnology and electron transfer at soft interfaces. In 2008 the MPI-P and INIFTA established a Partner Group for Functional Supramolecular Bioconjugates supported by the Max Planck Society. At present, the partner group is actively working in close collaboration with different groups at the MPI-P on different aspects of the molecular recognition- mediated assembly of interfacial architectures.

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**Mehmet Sayar** received his MSc degree at the University of Illinois Urbana-Champaign in 1999 as a Fulbright Scholar. He received his PhD in Materials Science and Engineering at Northwestern University in Prof. Samuel Stupp’s research group. His PhD thesis was on computational modeling of self-organization of organic materials. In 2003 he received the Marie Curie Intra-European Fellowship for Postdoctoral Research and continued his academic career as a postdoctoral research associate at the MPI-P in Prof. Dr. Kurt Kremer’s Theory Group. During his postdoctoral studies he worked on the aggregation of like-charged polyelectrolyte chains into finite size bundles. Since 2005 he has been working as an associate professor at the College of Engineering at Koç University, Istanbul, Turkey. In 2007 he received the TUBITAK Career Award (Turkish Scientific and Technical Research Foundation).

In 2006 a partner group agreement was signed between the MPI-P and Koç University and supported by the Max Planck Society. He is currently the active director of the partner group “Self-Organization of Charged Peptide Amphiphiles” at Koç University. His current research interests focus on computational materials science. He is working on computational modeling of both biological and synthetic soft matter. His research interests also include modeling of the self-assembly of peptide based synthetic molecules into nanostructures. Part of this research is done in collaboration with Dr. Christine Peter and Prof. Dr. Kurt Kremer. In collaboration with Prof. Dr. Alkan Kabakcioglu, he is working on the supercoiling and melting behavior of the DNA molecule. He is also continuing his research on aggregation of polyelectrolyte molecules.

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## **Scientific Staff**



**Denis Andrienko** did his Master degree in the University of Kiev, Ukraine and obtained his first PhD in optics/structural transitions in liquid crystals from the Institute of Physics, Ukraine in 2000. In 1999 he joined the group of Prof. M. P. Allen, then at Bristol, UK, where he obtained a second PhD on computer simulations of complex fluids (2001). He then moved to MPI as a Humboldt Fellow (2002-2003) doing theoretical studies of slippage effect, mechanical properties of polyelectrolyte microcapsules, bridging forces in colloidal systems, nematic colloids, and stressed liquid crystals. In 2004 he joined the group of Prof. K. Kremer as a postdoctoral fellow working on multiscale simulation of static and dynamic properties of polycarbonate melts. Since 2005 he is a project leader at the Theory Department and is responsible for the development of multiscale simulation techniques for conjugated polymers and small molecular weight materials used in organic electronics.

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**Günter K. Auernhammer** studied physics in Bayreuth, Germany and Paris, France. He obtained his diploma degree and PhD under the supervision of Prof. Brand at the University of Bayreuth with theses in the field of hydrodynamics of soft matter. In 2003 he joined the MPI-P working on phase separation kinetics of binary mixtures. As a Marie Curie Fellow he joined Dr. Martinoty's group at the Institute de Mécanique des Fluides

et des Solides (Strasbourg, France) for two years, working on a project on magnetic colloids embedded in polymeric matrices. At the MPI-P he is focusing on dynamics of soft matter. His current research interests include the influence of external fields, instabilities, and micro-rheology in soft matter systems.

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**Stanislav Balouchev** studied Laser Physics at the Sofia University "Saint Kliment Ochriski", Bulgaria, where he received his M. Sci. in 1990. In 1995 he finished his PhD in the field of dark spatial solitons at the Quantum Electronics and Laser Physics Department, Sofia University. In 1996, he was granted a DAAD- research fellowship and spent a

year in the group of Prof. Welegehausen, Hannover University. Since 1995 he has also been affiliated as assistant professor in the Technical University Sofia, Bulgaria. In 1997 he was visiting scientist at the Institute of Experimental Physics, Technical University of Graz, Austria in the group of Prof. Windholz. In 1999 he was granted a Feinberg Research Fellowship at the Department of Complex Systems, Weizmann Institute of Science, Rehovot, Israel in the group of Dr. Davidson. In 2000 he started

his Maria-Curie fellowship in the group of Prof. Riehle at PTB, Braunschweig. In 2001, he joined the group of Prof. Wegner at MPI-P. His current research interests include nonlinear optics, atomic physics and optical properties of conjugated polymers, especially upconversion in multimolecular organic systems.

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**Martin Baumgarten** received his PhD in organic chemistry at the Freie Universität Berlin after working with Prof. Dr. H. Kurreck and Prof. Dr. W. Lubitz in 1988. From 1988-1990 he held a postdoctoral position at Princeton University with Prof. G.C. Dismukes studying the Photosystem II, the water splitting enzyme and Mn model complexes. In 1990 he joined the Max Planck Institute for Polymer Research in Mainz as

a project leader. In 1996/97 he achieved his habilitation and was appointed Privatdozent at the University of Mainz. From 1999-2002 his group participated at the graduate college on "kinetics and mechanisms of ion reactions" of the Technical University of Darmstadt. For 2 semesters 2001/2002 he was guest professor at the Universität des Saarlandes, Saarbrücken, teaching organic chemistry. In 2004 he was appointed visiting professor of northeast normal university in Changchun, China. Since 2006 he represents the MPI-P at the www.matcor.de graduate school. His primary interests focus on synthesis of novel conjugated polymers and dendrimers, organic high spin molecules and molecular magnets, organic and hybrid spin networks.

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**Rüdiger Berger** studied physics at the University of Erlangen-Nürnberg. In 1994 he received his diploma degree from the Institute of Physics in the field of high temperature superconductivity. In 1997 he received his doctoral degree in physics from the University of Basel for his research on micromechanical cantilever sensors. These studies were performed in collaboration between the

University of Basel and the Nanoscale Science department of IBM Zurich Research Laboratory in Rüschlikon (Switzerland). In 1998 he moved to the Analysis Laboratory & New Projects at IBM Speichersysteme Deutschland GmbH in Mainz, where he worked as a specialist in the field of storage component analysis, storage tester projects and patterning of magnetic media. In 2002 he joined Prof. H.-J. Butt's group at the MPI-P where he is working in the field of nanomechanical cantilever sensors and scanning probe microscopy.

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**Elmar Bonaccorso** studied Electronic Engineering at the University of Genova (Italy) from 1992 to 1998. His master thesis was on ISFET-based pH sensors. From 1998 to 2000 he stayed at the Institute of Microtechnology in Mainz and mainly worked in the clean-room facilities. In 2000 he joined the group of Prof. H.-J. Butt at the University of Mainz and at the University of Siegen.

He received his PhD in 2001 with a

thesis on hydrodynamic and electrokinetic interactions between colloids. As a Max Planck postdoctoral fellow in 2002 he worked on the microstructuring of polymer surfaces by plasma and solvents. As a Marie-Curie fellow in 2003-2004 he worked on the evaporation of microdrops from solid surfaces. He spent part of his fellowship in the Biophysics and Nanotechnology Group at the University of Genova investigating mechanical properties of biological specimen by means of Atomic Force Microscopy. In 2005 he rejoined the group of Prof. H.-J. Butt at the MPI-P as a project leader and presently works on the evaporation of microdrops from soluble and non-soluble surfaces and on nanoflows at liquid/solid interfaces.

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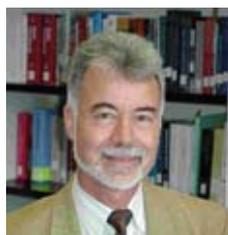


**Gunther Brunklaus** studied chemistry at the University of Münster, where he received his diploma in 1999. His PhD thesis in the group of Prof. H. Eckert concentrated on the application and development of solid-state NMR methods suitable for connectivity studies in solid electrolytes, e.g. copper-ion conducting phosphochalcogenides. After obtaining his PhD from the University of Münster

in 2003, he continued his work on self-assembling supramolecular coordination compounds in the group of Prof. H. Eckert. In 2004/2005 he was a post-doctoral fellow in the group of Prof. S. J. Opella at the Department of Chemistry and Biochemistry of the UC San Diego, where he investigated peptides and transmembrane proteins in lipids using NMR methods. After his return to Germany in 2005 he joined the group of Prof. H.W. Spiess at the MPI-P in Mainz. His current research interests focus on advanced solid-state NMR techniques applied to supramolecular systems and ion conductors.

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**Christoph Bubeck** studied physics and received his PhD from the University of Stuttgart in 1979 for work on EPR investigations of diacetylene single crystals. After a post-doctoral year at the IBM Research Laboratory in San Jose, USA, he joined Prof. Wegner's group at the University of Freiburg and studied

optical properties of Langmuir-Blodgett multilayers. Since 1984 he has been a member of the scientific staff of the MPI-P.

He received the *Habilitation* degree in Experimental Physics in 1993 for his work on spectroscopy and nonlinear optics of ultrathin layers. He is currently lecturing at the physics department of the University of Mainz, where he was appointed Professor in 2001. His current research interests focus on optoelectronic properties of conjugated polymers, especially the linear and nonlinear optical properties of thin polymer films.

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**Luigi Delle Site** studied mathematical physics at the the University "La Sapienza" of Rome. He obtained his Master degree in 1995 with Prof. R. Ruffini working on the mathematical model to describe the ground state of fermions in gravitational interactions. In 1995 he was awarded of a university grant to continue the research activity at the International Center of Relativistic As-

trophysics of the University of Rome "La Sapienza". In 1996 he moved to Belfast as a PhD. student at the School of Mathematics and Physics, of the Queen's University of Belfast where he worked on ab initio description of solvation properties with the supervision of Prof. R. M. Lynden-Bell and Dr. A. Alavi. In 1999 he obtained his PhD degree in physics with a thesis entitled "Ab initio Study of Water". He then moved as a postdoc to the MPI-P in the Theory Group of Prof. K. Kremer, where he became a project leader in 2004.

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**Jakub Dostálek** received his PhD degree in physics in 2006 from Charles University, Faculty of Mathematics and Physics, Prague (Czech Republic). From 2000 to 2006, he stayed at the Institute of Photonics and Electronics in Prague (Czech Republic) as a research assistant. In 2000 and 2001 he was a visiting scientist in University of Washington in Seattle (USA). In 2006, he joined the

MPI-P as a post-doctoral researcher and worked here as project leader since 2007. Jakub Dostálek left the institute in 2009. His research interests include guided-wave optics, plasmonics, fluorescence spectroscopy and optical sensors and biosensors.

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**Burkhard Dünweg** studied physics at the Technical University of Munich and at the University of Mainz, where he received both his diploma (1987) and his PhD (1991), working in the group of Prof. K. Binder on Monte Carlo and Molecular Dynamics. From 1991 to 1993 he joined the Center for Simulational Physics, Athens, Georgia (USA) as a Humboldt fellow, working with Prof. D. P. Landau on elastic alloys. From 1993

to 1996 he worked as an assistant in Prof. Binder's group, and joined the theory group of the MPI in 1996 as a project leader. In 2000 he received his habilitation in Theoretical Physics at the University of Mainz. His main research interests are computer simulation methodology, theory of polymer dynamics, and phase transitions. In January 2008, he was appointed as Extraordinary Professor at the University of Mainz.

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**Volker Enkelmann** studied chemistry at the University of Mainz gaining his PhD in 1974. After one year of post-doctoral studies at the Case Western Reserve University at Cleveland, he joined the Institute of Macromolecular Chemistry at the University of Freiburg where he received his habilitation in 1983. Since 1984 he has been head of

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**Xinliang Feng** received his Bachelor's degree in analytical chemistry from the Chinese University of Geosciences in 2001. In 2004 he obtained his Master's degree in organic chemistry from Shanghai Jiao Tong University, where he worked on the synthesis of fluorinated ion-exchange resins and polymer-

supported catalysis. In 2004 he moved to Prof. H. Mayr's group at the University of Munich for a short period of research on the ionization in solvolysis reactions. In September 2004, he joined Prof. K. Müllen's group at the Max Planck Institute for Polymer Research for his PhD research on the synthesis and supramolecular chemistry of novel polycyclic aromatic hydrocarbons. In April 2008 he was awarded his PhD degree. In December 2007 he was appointed project leader in charge of the graphite subgroup of Prof. K. Müllen. His scientific interests include the synthesis and self-organization of extended discotic nanographene materials, conjugated oligomers and polymers, testing for applications in organic electronic devices, fabrication of solution-processable graphene sheets for window electrodes, and nanostructured functional carbon materials for energy storage and conversion.

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**Renate Förch** studied chemistry at King's College, University of London, England (1984) and received her PhD at Queen Mary College, University of London, London, England (1987). She began her activities in the area of plasma assisted modification of polymeric surfaces as a post doctoral fellow at Surface Science Western, University of Western Ontario in London, Canada.

In 1992 she returned to Germany and started as a research scientist at the IMM Institut für Mikrotechnik in Mainz investigating the plasma treatment of textiles, the development of barrier coatings and surface functionalization. In 1996 she joined the Material Science Group of Prof. W. Knoll at the MPI for Polymer Research, where she is project leader in the area of thin film plasma assisted deposition processes. She is project leader for several third party projects and coordinator of a three year FP7 funded project to develop antimicrobial coatings using plasma assisted- and wet chemical processes. Since 1/2009 she is Managing Editor for Plasma Processes and Polymers for Wiley-VCH, Weinheim, Germany.

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**Karlheinz Graf** studied chemistry at the Friedrich-Alexander University of Erlangen-Nürnberg and at the Johannes Gutenberg University in Mainz. He was awarded his Diploma degree in Prof. Helmuth Möhwald's group at the Institute of Physical Chemistry in Mainz. Here he also obtained his PhD 1997 for work on wetting of solid substrates by lipid monolayers. From 1997 to 1999

he worked as a post-doc researcher on physicochemical aspects of MS (Multiple Sclerosis) and RDS (Respiratory Distress Syndrome) in Dr. Cynthia Husted's group at the Neuroscience Research Institute and Prof. Zasadzinski's Chemical Engineering group in Santa Barbara, California. From 1999 to 2000 he joined Prof. Christiane Helm's group, University of Greifswald, investigating nanostructures in ultrathin layers of lipopolymers. He started work on his *Habilitation* in Prof. Hans-Jürgen Butt's group at the University of Siegen, moving to the MPI-P in Mainz in 2002. His research is focused on model systems for microsystem technology such as microfluidic devices. Since October 2008 he has been an interim professor at the University of Siegen.

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**Robert Graf** studied physics at the Johann-Wolfgang-Goethe University in Frankfurt am Main where he obtained his diploma in the field of solid-state physics with Prof. B. Lüthi on the study of phase transitions induced by the interaction of localized and delocalized electrons in the rare earth compounds. In 1994 he joined Prof. H.W. Spiess's group at the MPI-P and in 1998 he

gained his PhD from the Johannes Gutenberg University in Mainz for his research on the application of double-quantum NMR spectroscopy to amorphous polymers under fast magic angle spinning (MAS) conditions. Subsequently he was appointed a staff member at the MPI-P.

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**Franziska Gröhn** studied chemistry at the University of Cologne, where she obtained her diploma in the group of Prof. D. Woermann in the department of Physical Chemistry. In 1995 she moved to the Max Planck Institute for Colloids and Interfaces working with Prof. M. Antonietti on "Spherical polyelectrolyte microgels as model polyelectrolytes and nanotemplates" and received her PhD in Physical Chemistry from the University of Potsdam in 1998. Afterwards she spent two years as a guest researcher at the National Institute of Standards and Technology (NIST), Maryland, USA, in the Polymers Division with Prof. E. J. Amis. Main research topic was the study of dendrimers as templates for inorganic nanocrystals. In October 2000 she joined the MPI-P and the Physical Chemistry Department of the University Mainz. Present research interests include interactions of polyelectrolytes, the controlled design of nanostructured materials based on macroions and scattering methods. In 2004 she was awarded the Reimund Stadler Award of the German Chemical Society (GDCh).

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**Jochen Gutmann** studied chemistry at the Technische Hochschule Darmstadt and spent one year as a ERASMUS student at the University of Bristol, England, where he obtained a M.Sc. in Colloids and Interface Science. In 1996 he received his diploma in chemistry working with W. Haase on the NIR spectroscopy. 1997 he joined M. Stamm's group at the MPI for Polymer

Research in Mainz, where worked on his PhD thesis investigating the structure formation in thin polymer blend films with surface sensitive scattering and scanning probe microscopy techniques. Following post-doc stays at the IPF Dresden and Cornell University, USA, he joined the MPI-P's physics groups in 2002. In 2005 he was appointed professor at the Institute of Physical Chemistry at the University of Mainz.

His research focuses on X-ray scattering techniques for the structural characterization of complex multicomponent polymer composite materials and chemistry in confined geometries. His current area of interest centers on the synthesis and investigation of structured polymer/inorganic hybrid materials as well as surface functionalization with polymers.

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**Dariush Hinderberger's** scientific career started in 1999/2000 at the University of Washington in Seattle (USA) with work on electrooptic materials with high dipole moments. He subsequently received his diploma in chemistry from the Technische Universität Berlin in 2001. His PhD thesis at the MPI-P led to new

insights into polyion-counterion interactions in polyelectrolytes. Before becoming a project leader in the MPI-P's spectroscopy department in August 2006 he was a postdoctoral fellow at the Laboratory of Physical Chemistry at the ETH in Zürich from 2004-2006. In Zürich he joined an ongoing international research project on the explanation of the catalysis of methane formation in archaea microorganisms, which are major contributors to the atmospheric release of this potent greenhouse gas. His research focuses on elucidating how non-covalent interactions (e.g. electrostatic, hydrophobic) govern the structure and dynamics of synthetic and biological soft matter. His main research tool is electron paramagnetic resonance (EPR) spectroscopy, a magnetic resonance method that is sensitive to molecular dynamics in the microsecond to picosecond regime and to structures and distances from ~0.1 to 8 nanometers.

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**Ulrich Jonas** studied chemistry at Mainz University and the University of California, Santa Barbara, in Prof. H.-W. Schmidt's and Prof. P. Smith's groups. In 1992 he joined Prof. H. Ringsdorf's group in Mainz working on amphiphilic fullerene derivatives and completed his Diploma in 1993. He continued investigating amphiphilic

fullerene derivatives during his dissertation and expanded the research on triphenylenes and quaternary nitrogen compounds. After a stay in Prof. F. Diederich's group at the ETH Zurich, Switzerland, he received his PhD in 1996 from Mainz University. From 1996 to 1998 he worked as a post-doctoral Feodor Lynen fellow with Dr. D. Charych at the Lawrence Berkeley National Laboratory in Berkeley, California, on polydiacetylene biosensors for the detection of DNA hybridization. He joined Prof. H.W. Spiess's group at the MPI-P in 1999, in 2004 Prof. W. Knoll's group. In 2007 he was appointed as affiliated scientist of FORTH (Foundation for Research and Technology - Hellas) in Crete, Greece, active in the Polymer & Colloid Science Group, and in 2009 he was elected director of research at the Institute of Electronic Structure and Laser, heading the newly founded Bio-Organic Materials Chemistry Laboratory.

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**Michael Kappl** studied physics at the University of Regensburg and Technical University of Munich where he got his diploma working in the group of Prof. Michel-Beyerle on photosynthetic reaction centers. During his PhD work in the group of Prof. Bamberg at the MPI of Biophysics in Frankfurt he studied the transport kinetics of the Na-Ca exchanger membrane protein. He received his PhD from the University of

Frankfurt in 1996. He stayed for one year of postdoctoral research on surface forces in the group of Prof. Butt at the University of Mainz. From 1998 – 2000 he worked as a consultant for the Pallas Soft AG in Regensburg. In 2000 he joined the group of Prof. Butt at the University of Siegen. Since 2002 he is active at the MPI-P as a project leader. His current research interests are the adhesion and friction of single microcontacts, confined liquids and micro- and nanomechanics of polymers, and the development of new AFM-related techniques. Since 2007 he also runs the Focused Ion Beam lab of the MPI-P.

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**Markus Klapper** studied chemistry at the University of Mainz and received his PhD in 1990 under the supervision of Prof. R. C. Schulz for work on the synthesis and topochemical polymerization of aminodiacetylenes. Subsequently, he joined the MPI for Polymer Research and became project leader in the Synthetic Chemistry Department. His research interests include new polycondensation

and polymerization methods, as well as polymer analogous reactions towards the synthesis of functional polymers and block copolymers. These materials are especially designed for fuel cell applications or for the hydrophobisation of inorganic nanoparticles. In recent years his work has also focused on the polymerization of olefins in the heterogeneous phase. Here he has developed new organic supports and studied their polymerization behavior. Another central topic of interest is the development of non-aqueous emulsions suitable for the polymerization of water-sensitive monomers.

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**Achim Koch** studied chemistry at the University of Mainz. In 2000 he joined Prof. Dr. Hans Wolfgang Spiess's group at the MPI-P, where he received a Dr. rer. nat. in 2003 for his work on synthesis and characterization of models for photoswitches and electronic valves. He was subsequently made project leader and head of the chemistry lab of the spectroscopy department in 2004.

His research interests are focused on parahydrogen induced polarization (PHIP) as a method for NMR and MRI sensitivity enhancement, as well as synthesis and characterization of photoactive compounds and conjugated systems to investigate electronic communication effects.

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**Ingo Köper** studied chemistry at the University of Dortmund and received his diploma in 1998. He carried out his PhD research at the Laboratoire Léon Brillouin, CEA-Saclay, France. In 2002 he received his PhD degree in chemistry from the University of Paris VI for his work on neutron scattering experiments on the interactions between a sugar and

a protein, undertaken in the group of M.-C. Bellissent-Funel. Afterwards, he joined the group of Prof. W. Knoll as a post-doc and in 2003 was appointed a project leader, working on biomimetic model membrane architectures. Currently, he is pursuing his *Habilitation* in the biology department of the Johannes Gutenberg University in Mainz.

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**Kaloian Koynov** studied physics at Sofia University. In 1993 he completed his diploma at the Institute of Electronics in Sofia, investigating the optical nonlinearities of GaInSb semiconductors. In 1997 he received his PhD from the Faculty of Physics, Prof. S. Saltiel's group at Sofia University for work on cascaded nonlinear optical processes and

their application for all-optical switching. After a post-doctoral year at the Institute for Fundamental Electronics, University Paris Sud, France, studying grating couplers into semiconductor waveguides, he joined the MPI-P as a post-doc and EU Marie Curie Fellow in 2000. His research focused on optoelectronic properties of conjugated polymers and the flow velocity profiles in micro-channels and boundary slip phenomena. In 2006 he joined Prof. Hans-Jürgen Butt's group at the MPI-P. His current research interests focus on structure-dynamics-properties correlations in polymer systems with complex architectures. Such systems are studied using a variety of experimental methods, including dielectric and mechanical spectroscopy, confocal microscopy and fluorescence correlation spectroscopy.

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**Maximilian Kreiter** received his Diploma (1997) and PhD (2001) degrees from the University of Mainz for work on photothermal effects and the optical response of metallic gratings. After a post-doctoral stay in 2000-2001 in Prof. U. P. Wild's group at the ETH Zürich, where he worked on single-molecule fluorescence spectroscopy, he returned to the MPI-P as a group leader. His

main fields of research focus on optical plasmonic resonances on nanoscopically structured metals, single-molecule fluorescence microscopy and scanning tunneling microscopy. He is co-author of 45 articles in peer-reviewed journals. He was involved in several national projects and industrial collaborations. He received the 'Otto-Hahn-Medaille' for his PhD work and was awarded the 'Nachwuchswettbewerb Nanotechnologie' by the German Ministry of Science and Education.

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**Chen Li** studied chemistry and completed his diploma thesis under the supervision of Prof. H. Tian at the East China University of Science and Technology in 2003. In 2004 he joined the group of Prof. K. Müllen at the Max Planck Institute for Polymer Research in Mainz to work on functional rylene dyes for dye-sensitized solar cells.

He received his PhD in 2008 from the University of Mainz. He is currently working in Prof. Müllen's group and his research interests focus on functional dyes and their applications.

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**Ingo Lieberwirth** studied physics at the University of Dortmund. He obtained his diploma in 1997 with a thesis on selected metallization of polymer surfaces under the supervision of Prof. J. Petermann. During this work he came into contact with electron microscopy of polymers for the first time. In 2001 he finished his PhD at the Technical University of Eindhoven in the group of Prof. P. Lemstra on orientation induced crystallization of semi-crystalline

polymers. Subsequently he joined the group of Prof. Wegner at the MPI-P. Besides his work in the electron microscopy group, his research activities include the polymer controlled crystallization of anorganic minerals and the structure formation of self assembled polyelectrolytes in aqueous solution.

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**Volker Macho** studied physics at the University of Münster and at the Free University of Berlin, where he gained his Master degree in 1977 on the theory of dynamic hyperfine interactions of highly ionized atoms, and his PhD on optical nuclear polarization studies in molecular crystals. He then spent a year at IBM in San Jose, California, working on magic angle spinning  $^{13}\text{C}$ -NMR at

very low temperatures. After returning to Germany he worked with Siemens in the field of NMR imaging. He joined the MPI-P in 1985 and built up the EPR laboratory. His research interests include NMR imaging and lineshape analysis in  $^2\text{H}$ -NMR and EPR spectroscopy. Since 1985 Volker Macho is running the Computer Service Group, which is planning, organizing, coordinating and supporting the IT infrastructure at the institute.

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**Volker Mailänder** studied medicine at the University of Ulm supported by a stipend from the *Studienstiftung des Deutschen Volkes* and was in the graduate program "Molecular Biology". He joined the Blume/Negrin lab in Stanford, California, working on natural killer cells and bioluminescent imaging in mice. After completing his medical studies and his doctoral thesis he worked in the Charité hospital in Berlin,

receiving training in internal medicine (haematology/oncology). There he was involved in studies for leukaemia vaccination and stem cell treatment. After relocating to the Institute for Clinical Transfusion Medicine, University Clinic of Ulm, he worked on stem cell collection and manipulation and new stem cell types and was board certified in transfusion medicine. He focused on using polymeric nanoparticles for labelling or manipulation of stem cells and other cell types and is since 2008 leading a joint research group between the University Clinic Internal Medicine III, Mainz, and the MPI for Polymer Research. Current research topics include cell labelling with nanoparticles, detecting pathways of endocytosis and harnessing nanoparticles for use in biomedical applications like manipulating cell functions.

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**Bernhard Menges** studied physical engineering at the University of Applied Sciences in Wiesbaden. He finished his Diploma degree in 1993 on Langmuir–Blodgett films for a second harmonic generation in cooperation with the Hoechst AG in Frankfurt. In 1993 he joined the Central Research and Development Section of Bosch in Stuttgart and worked on optical devices in the MIGA technique for sensor and telecommunication applications.

Since 1994 he has been working at the Max Planck Institute for Polymer Research in the materials science group. Besides his work on the cleanroom project his current research interests are evanescent wave optics for sensors, imaging and characterization of structure and dynamics at inorganic-organic interfaces, thin films anomalies and supramolecular architectures on surfaces.

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**Kerstin Münnemann** studied chemistry at the Heinrich-Heine University Düsseldorf and the Technical University of Aachen. During her PhD she worked on applications of hyperpolarized  $^{129}\text{Xe}$  NMR and MRI in Prof. Blümich's group at the ITMC in Aachen in close collaboration with the research center at Jülich. In 2006 she joined Prof. Schreiber's group

at the University Medical School Mainz, section for Medical Physics as a post-doc. Here, she worked on myocardial perfusion imaging and the hyperpolarization of liquids via DNP and PHIP. In 2008 she became a project leader in Prof. Spiess's group at the MPI-P in Mainz, continuing her research on various kinds of hyperpolarization methods. She holds a joint position at the MPI and the group for Medical Physics combining basic research and medical applications.

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**Anna Musyanovych** studied biochemistry at the National University "Lvivska Politechnika" in Lviv, Ukraine. In 1994 she received her diploma (with honours) in biotechnology for her thesis on the synthesis of monomodal microspheres for immunoassays, supervised by Prof. S. Voronov and Prof. V. Kolesnikov. From 1994 to

2000 she worked as a research assistant in the department of Macromolecular Chemistry in Prof. S. Voronov's group. Her work focused on the elaboration and characterization of environmentally resistant polymeric coatings based on aqueous dispersions. In 2000 she joined Prof. H.-J. Adler's group at the TU Dresden, where she obtained her PhD in 2003 for her work on the synthesis of amino-functionalized latex particles in the

presence of surface active hydroperoxide-containing initiators. Afterwards, she moved to Ulm University, first working as a post-doc, and then as a project leader in the group of Prof. K. Landfester. Since 2009, she has been a project leader in Prof. K. Landfester's group at the MPI-P. Her main research interests are composite nanoparticles/nanocapsules, multiresponsive surfaces, single molecule reactions.

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**Renate Naumann** studied chemistry at the Humboldt University of Berlin where she was awarded her doctorate. She subsequently worked for the Merck company in Darmstadt, Germany, where she specialized in the field of electrochemistry. As a senior scientist she supervised a project on 'tethered lipid bilayer membranes', in the context of which she started a cooperation with the Max Planck Institute for Polymer

Research. Since 1997 she has been working as a senior scientist and project leader in the Material Science group at the MPI-P in the field of proteins incorporated in biomimetic membrane systems on planar substrates.

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**Christine Peter** studied chemistry and mathematics at the University of Freiburg and received her diploma in chemistry in 1999 on solid-state NMR spectroscopy. In 2003 she obtained her PhD at the ETH Zurich working in Prof. W.F. van Gunsteren's group researching biomolecular simulation. After post-doctoral research in Dr. G. Hummer's group at the National Institutes of

Health, she joined the Theory Group at the MPI-P as a post-doctoral researcher working on the development of multi-scale simulation models for photo-switchable liquid crystals. Since August 2008, she has been in charge of an Emmy Noether junior research group at the MPI-P working on the "Development of coarse grained simulation models to study structure formation and self assembly in peptide systems". Her research interests are (bio)molecular simulation, development of multi-scale simulation methods, thermodynamics, biological and bio-inspired materials, and structure formation in biological systems.

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**Harald Pleiner** got his physics diploma at the University of Stuttgart in 1974 with a diploma thesis on the role of nonlinear fluctuations at the Benard instability. He finished his doctoral thesis on the hydrodynamics of the superfluid phases of  $^3\text{He}$  in 1977 at the University Essen (with R. Graham). Habilitation in theoretical physics was granted by the University Essen in 1983 for work on

broken symmetries and hydrodynamics of liquid crystals. As a Heisenberg fellow he went abroad for several years staying at the Lab. Physique des Solides, Orsay (M. Kleman), Dept. of Physics, CU Boulder (N.A. Clark), and ITP and Materials Dept, UC Santa Barbara (P. Pincus). In Germany he worked as a substitute professor for theoretical physics teaching at the Universities Essen and Augsburg. In 1993 he was appointed apl. Professor by the University Essen. He joined the new Theory Group (K. Kremer) at the MPI-P in 1995 as a senior scientific staff member. Currently, he is the representative of the institute's co-workers in the CPT Sektion, ombudsperson of the institute, and one of the *Schlichtungsberater* of the CPT Sektion. His interest is still focused on the macroscopic description of the dynamics of complex fluids and soft matter including rheology, instabilities, defects, surface waves and phase transitions.

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**Hans Joachim Räder** studied chemistry at the University of Mainz. He obtained his diploma in 1987 with Prof. K. Müllen on a synthetic approach to new heterocyclic fulvalene-type donor structures which can be transformed into conducting organic metals. From 1988 to 1991 he worked on his doctoral thesis in the field of electrochemistry. Using cyclic voltammetry, he investigated the

redox behavior of extended  $\pi$ -systems which can be used as model compounds for conjugated polymers. In 1990 he moved with Prof. K. Müllen's group to the MPI-P, where he was responsible for projects on redox chemistry and heterocyclic donors. He currently heads the mass-spectrometric division, which he established in 1991. His present research involves methodical development of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) in the analysis of synthetic polymers. Special research interests are desorption and ionization mechanisms, soft landing and pulsed laser deposition of insoluble and non-volatile macromolecules, as well as manipulation of self-organization and crystallization by strong electric fields.

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**Silke Rathgeber** received her diploma in physics from the Heinrich Heine University, Düsseldorf in 1993. During her PhD (1994-1997) she worked with Prof. Dr. Richter at the Forschungszentrum Jülich (FZJ) on the dynamics of polymers in melts using neutron scattering techniques. During her post-doctoral stay (1998-2000) at

the National Institute for Standards and Technology, Gaithersburg (MD), USA, she was responsible for building and commissioning a neutron spin-echo spectrometer. Back at the FZJ (2000) she set up and ran a rheology laboratory and focused on the combination of scattering experiments and microscopy with rheology. Her research focused on the structure, dynamics and structure-property relationships of highly branched polymers, e.g. in external shear field. In 2005 she joined the MPI-P. Her current research focuses on the correlation between structure formation kinetics in polymeric systems (e.g. conjugated polymers) and the driving forces, which can be external stimuli, but also internal forces such as excluded volume interactions. To cover a large length and time-scale range she further broadened her methodical repertoire to time and space-resolved static scattering methods, fluorescence correlation spectroscopy and dielectric spectroscopy.

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**Daniel Sebastiani** studied physics at the University of Karlsruhe and the Ecole Normale Supérieure de Lyon, where he graduated in 1997 with the *Diplôme d'Etudes Approfondies de Physique Théorique*. He then joined the group of M. Parrinello at the MPI for Solid State Research in Stuttgart. For his PhD in 2001, he developed an *ab-initio* method to compute NMR

parameters from electronic structures under periodic boundary conditions and received the Otto Hahn Medal of the MPS. After joining the group of H.W. Spiess at the MPI-P, he spent two sabbaticals as a visiting staff scientist with U. Rothlisberger at the ETH Zurich and with R. Car at Princeton University. In 2006, he was awarded the *Habilitation* degree. His present research field is *ab-initio* electronic structure calculations and first-principle MD simulations mainly focused on the calculation of structural and spectroscopic properties in condensed matter systems under realistic thermodynamic conditions.

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**Eva-Kathrin Sinner** studied biology at the University of Hannover and received her PhD in 1998 under the supervision of Prof. R. Hedrich for her work on 'Immobilization and Characterization of Membrane Proteins in Artificial Planar Lipid Membranes'. From 1998-1999 she worked in Dr. M. Hara's and Prof. W. Knoll's group at the RIKEN Institute,

Tokyo, Japan, working on 'In-situ Detection of Membrane Proteins with Surface Plasmon Enhanced Fluorescence Spectroscopy'. 2000 -2006 she completed her *Habilitation* with Prof. D. Oesterhelt, MPI-B, Martinsried. In 2006 she rejoined the MPI-P as a project leader heading the Synthetic Biosystems group. In 2008 she was awarded a full professorship in molecular biophysics at the University of Mainz. Currently she is working in Singapore, starting a pilot research project with the Institute of Materials Research Engineering (IMRE) collaborating in the cross council initiatives between the A-star Institute and the university. Her research activities include application and implementation of synthetic materials into biomimetic systems for biosensing applications and new approaches in the field of membrane protein analysis.

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**Torsten Stühn** studied physics at the Johannes Gutenberg University in Mainz and at the Université de Provence Aix-Marseille I, France (Thesis: "Hydrodynamics on cellular automata"). He received his diploma in 2000 in the Condensed Matter Theory Group of Prof. Kurt Binder in Mainz for his computer simulations on "Methods to equilibrate supercooled liquids". He continued his

work on supercooled liquids under the supervision of Prof. Walter Kob (Montpellier, France) and Prof. Binder in Mainz, where he received his PhD in theoretical physics in 2005. Already in 2003 he moved to the Max Planck Institute for Polymer Research as scientific support for computational physics in the group of Prof. Kremer, where he joined the team of the ESPResSo project (Extensible Simulation Package for Research on Soft Matter) and the system administration group. Since 2006 he is also a member of the development team of ESPResSo++ which is a complete rewrite of the simulation software and will be the successor of ESPResSo. Since February 2009, he has been responsible for the scientific computing project at the MPI-P.

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**Nico van der Vegt** studied chemical engineering at the University of Twente Enschede, The Netherlands. He obtained his PhD in 1998 at the same university under supervision of Prof. W.J. Briels and Prof. H. Strathmann with a doctoral thesis on Molecular Dynamics simulations of gas sorption and diffusion in rubbery and glassy polymer matrices. In 1998 he became assistant

professor at the University of Twente. There, he worked on synthetic membranes for technical separations including polymer- and carbon-molecular-sieve membranes for gas separation, bipolar membranes for acid/base electro dialysis, and porous polymer nanofoams produced by carbon dioxide expansion. In 2002 he moved to the department of physical chemistry at the ETH Zürich, working with prof. W.F. van Gunsteren studying aspects of hydrophobic hydration in water/co-solvent mixtures and

energy-entropy compensation in aqueous solvation thermodynamics. He joined the MPI-P in 2003 where he is responsible for Computational Chemistry and Molecular Simulation. His current interests include atomistic and multiscale modelling of polymer in bulk and at interfaces, polymer permeation, aqueous solutions, and biopolymers at solid surfaces. In 2009, he was awarded a full professorship in computational methods at the Technical University of Darmstadt.

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**Thomas A. Vilgis** studied physics and mathematics at the University of Ulm, where he achieved his PhD in 1984. In 1984 and 1985 Vilgis post-doctored at the Cavendish Laboratory, Cambridge, UK in the group of Sir Sam Edwards about the theory of the glass transition, polymer networks and the statistics of entanglements. In 1985 Vilgis joined the

MPI-P as a staff member. Thomas Vilgis accomplished his habilitation on the statistical mechanics of condensed polymer systems. In 1996 he became professor at the University of Mainz. In between he took several research stays in Cambridge, London (Imperial College) and Strasbourg (Université Louis Pasteur, Institut Charles Sadron). His main research interests are statistical mechanics of strongly interacting polymer systems such as blends, copolymers, and polyelectrolytes, elasticity and interactions in soft solids, like polyelectrolyte networks, filled rubbers, and theoretical materials science. He is working also in the field of glass transition of polymers and amorphous systems. Quite recently Vilgis extended his research to molecular food physics and molecular gastronomy including also experimental work.

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**Doris Vollmer** studied physics at the University of Bielefeld, the ETH Zürich and the University of Utrecht, where she received her Master's Diploma. She was awarded her PhD at the University of Basel in 1994 for research on structural and thermodynamic transitions in microemulsion systems. The *Habilitation* degree in physical chemistry was granted by the University of Mainz in

2001 for work on phase transitions in microemulsions and their dynamics. As a Marie Curie fellow she went to the University of Edinburgh to investigate phase separation and network formation in suspensions of liquid crystals and colloids. In 2002 she joined Hans-Jürgen Butt's group at the MPI-P. Her current research is focused on the kinetics of phase transitions of soft condensed matter, especially simple binary mixtures and colloidal suspensions. This includes investigating instabilities due to external driving as well as studying the dynamics of colloids in external fields and liquid crystals.

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**Manfred Wagner** studied chemistry at the University of Mainz. He received his diploma in 1988 in Prof. K. Müllen's group. In 1993 he obtained his doctorate at the MPI-P for his work on the synthesis of band structures and their physical properties. Since 1988 he has been head of the High-Resolution NMR Spectroscopy Service Group. His research

interests include the clarification of small molecules and polymeric structures by using multi-dimensional NMR methods. His current research activities concentrate on 1) the use of gradient-field NMR to study the diffusional behavior of oligomers and polymers in solution, 2) heteronuclear NMR investigations such as  $^{31}\text{P}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ ,  $^{11}\text{B}$  etc. measurements in order to understand the microstructures of copolymers and 3) the LC-NMR for the compositional dependence of copolymers as a function of molecular weight.

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**Tanja Weil** studied chemistry at the Technical University of Braunschweig in Germany and at the University of Bordeaux I in France. After receiving her *Diplom-Chemiker* degree with Prof. Hopf in 1998, she moved to the MPI-P, where she was awarded her PhD in 2002 for work on Biologically Inspired Polyphenylene Dendrimers with Prof. Müllen, which was awarded the Otto

Hahn Medal of the Max Planck Society. Between 2002 and 2008 she held different positions from section head of medicinal chemistry to Director of Chemical R&D at Merz Pharmaceuticals in Frankfurt, Germany. In 2005 she rejoined the MPI-P working on polymers for medicinal applications. Recently, she accepted an Associate Professorship in chemistry at the National University of Singapore. Her current scientific interests include biohybrid materials and artificial proteins.

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**Clemens Weiß** studied chemistry at the Universities of Constance and Ulm. He received his diploma in 2001 with Prof. A. Lentz in Ulm on the preparation of stable maghemite sols. He continued his PhD research in Prof. Lentz's group, working on the crystallization and magnetic properties of multinary oxide phases grown from KOH-melts. He received his PhD in 2004. In 2005 he joined Prof. Landfester's group at the

University of Ulm as post-doctoral researcher focussing on the preparation of nanoparticulate, polymeric drug delivery systems capable of entering the central nervous system (CNS). Since August 2008 he is a project leader in Prof. Landfester's group at the MPI-P. Besides CNS-targeting nanoparticles his research interests include the synthesis and properties of porous metal oxide nanoparticles and metal(complex)/polymer hybrid nanoparticles as well as the preparation of polymers with enzyme-cleavable blocks.

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## Scientific Technical Coordinator



**Wolfgang H. Meyer** received his PhD from the University of Freiburg, Germany in 1977 for his work on "Solid State Polymerization of Diolefins". From 1978 to 1984 he worked as a researcher at the Laboratories RCA Ltd. in Zurich, Switzerland. His focus during that period was on electronically conducting conjugated polymers and high resolution photoresists. In 1984 he

joined the newly founded MPI-P and was responsible for "Ion-Containing Polymers and Networks", "Polymer Surfactants" and "Thermoanalysis". Since August 2001 he has been the institute's Scientific Technical Coordinator and his research has focussed on "Lithium- and Proton-Conducting Polymers".

The position of the institute's Managing Director rotates every two years among the directors. The MD is supported by two principal members of staff who help him conduct current business: The Head of Administration and the Scientific Technical Coordinator.

The Scientific Technical Coordinator stands in as the Managing Director's deputy in everyday business matters and is responsible for the institute's technical and building services as well as for operational safety. He coordinates all scientific activities and events which concern the institute. Additionally, the Scientific Technical Coordinator is responsible for the press and public relations department and for providing information on external funding.

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## Facts and Figures

### The Max Planck Society

The Max Planck Institute for Polymer Research (MPI-P) is an institute of the Max Planck Society for the Advancement of the Sciences e.V. - an independent, non-profit research organization which was founded in 1948. In 2008, the Max Planck Society employed about 13,600 people, including approximately 4,400 scientists and 6,400 student assistants, PhD students, postdoctoral students and guest scientists. Around 82 % of Max Planck Society expenditure is met by public funding from the Federal Government and the German States. The remaining 18 % comes from donations, members contributions and from funded projects.

### The Max Planck Institute for Polymer Research

In 2008 the total budget of the Max Planck Institute for Polymer Research amounted 25.3 million Euro, from which 20 % came from external funds. The main expenses went into the personnel (57%), consumables (31%) and investments (12%).

In early 2009, 541 people have worked at the Max Planck Institute for Polymer Research with about three quarters of them being researchers (directors, staff scientists, international fellows, PhD and master students and student assistants). The personnel currently consists of 184 scientists - thereof 72 visiting scientists, 185 PhD, diploma and Master students as well as 172 technical and administrative employees and student assistants. Women accounted for over a third of the staff accounting for both scientific and non-scientific employees. Almost 40 % of all employees are foreign nationals. The number of international co-workers has remarkably increased in recent years reaching a total of 212 people in early 2009.



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## Library and Publication Services

### Library

The Max Planck Institute for Polymer Research accommodates its own library including a reading room. The library's staff support the institute's scientific work by providing scientific information and media. The library collections contain interdisciplinary literature covering the subjects polymer physics, chemistry as well as biology and mathematics. The MPI-P library contains a portfolio of approximately 75 print journals, 6,000 monographs, various thematic encyclopedias and dictionaries and collects all MPI-P diploma and PhD theses. Within the framework of the Max Planck Digital Library's project electronic access to more than 20,000 current online journals and backfiles as well as to numerous electronic resources is provided. The library offers an online catalogue that can be accessed at [www.mpip-mainz.mpg.de/bibliothek](http://www.mpip-mainz.mpg.de/bibliothek)



### Publications

The institute has a considerable output of scientific publications. Annually MPI-P scientists publish around 300 papers in numerous well-known journals. Since 1998 the bibliographic data of all papers published by MPI-P researchers have been collected and maintained with the help of eDoc, an electronic documentation server. eDoc provides access to all scientific output of Max Planck researchers and is part of the Max Planck Digital Library (MPDL) - a central scientific service unit within the Max Planck Society. The eDoc Server is accessible at <http://edoc.mpg.de>

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## Training Programs for PhD Students



The programs aim to provide the fellows with thorough expertise in most modern research instrumentation, to teach the development and handling of software tools for polymer materials science, to develop understanding of the necessary theoretical background to solve the complex problems of polymer materials research both at the academic level and as a tool for industrial use.

The necessary diversity of the PhD study is provided by an obligatory training program - in the form of seminars, the teaching of soft skills such as learning how to handle research tasks by teamwork, presentation and writing skills, language training, intellectual property protection, networking with a scientific community and weeklong workshops. All these activities support on-site and "at the bench"-training in the course of the PhD students' research projects.

Up to now 129 students from 23 countries were trained and sponsored by these programs.

Within the scope of the German Federal "Excellence Initiative", which aims to support excel-

lent research and enhance the quality of universities and research institutions, the IMPRS and Mainz University's graduate programs POLYMAT and MATCOR decided to join forces. They established the graduate school MAINZ - MATERIALS science IN mainZ. Since 2008, MAINZ has officially been a Graduate School of Excellence and is funded by the German Research Foundation and the state Rhineland Palatinate.

The new Max Planck Graduate Center (MPGC) provides innovative opportunities for outstanding PhD students. Within this center PhD students and junior professors from the MPI-P, the MPI for Chemistry and the Johannes Gutenberg University Mainz work on interdisciplinary topics in the natural and life sciences.

Educating young scientists is of crucial importance for the future of science, research and innovation. Therefore, the Max Planck Society established in cooperation with German universities a programme to promote junior researchers: the International Max Planck Research Schools. Founded in 2000, the International Max Planck Research School for Polymer Materials Science (IMPRS) in Mainz is a joint initiative of the Max Planck Institute for Polymer Research and the Department of Chemistry at the Johannes Gutenberg University in Mainz. It addresses PhD students working in the field of polymer science.

From 2004 to 2008, the institute hosted the Marie Curie Host Fellowship for Early Stage Research Training (EST) for "Analytical Methods in the Development of Science and Technology of Polymers" - a training program funded by the European Union.

Both the EST and the IMPRS have offered extraordinarily well-qualified international students the chance to carry out research at the MPI-P and the cooperating university's departments within the framework of the IMPRS-PMS and EST programs.



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## Public Relations and Knowledge Transfer

Publicly funded research relies upon the population's acceptance and appreciation. To make the scientists' work and their results transparent to the public, the Max Planck Institute for Polymer Research has actively engaged in public relations work for several years.

Hereby, the press and public relations is the interface between scientists of the institute and the public as well as partners in industry and politics. The first and foremost goal is to popularize the institute's research and its results, to rise public interest for scientific topics and thus contribute to public discussion.

Annually, the institute participates at Science Market in Mainz. Interesting talks and exciting experiments allow the public to put their hands on basic research performed by the MPI-P. In cooperation with the *Verein zur Förderung der Polymerforschung - Mainz e.V.* (Association for the Promotion of Polymer Research – Mainz), the institute holds a semi-annual series of lectures called [polymer populär] presenting popular scientific evenings with information from science and culture related to the MPI-P.

The institute also regularly opens its gates to give the residents of Mainz the opportunity to have a look behind the lab doors and talk to scientists on the Open Day.

Additional activities comprise, for example, organizing guided tours for school classes and art exhibitions. In 2008, the Max Planck Institute for Polymer Research, the Johannes Gutenberg University, universities of applied sciences, academies, museums and researching companies from Mainz and surrounds formed the "Mainzer Wissenschaftsallianz" (Mainz Science Alliance). The task of this initiative is to call attention to the scientific potential in Mainz and to further improve the networking among the partners of the alliance which represents the scientific performance in Mainz with almost 4,000 researchers.

Knowledge transfer covers interactions between the institute and its external partners. It creates benefits that flow in both directions as the community gains from the expertise of the institute and the institute becomes better informed by ideas and experiences from beyond its boundaries.



MPI-P researchers offer lectures and laboratory courses for undergraduates and graduate students mainly at the University of Mainz. In addition, PhD students act as tutors in many of the mandatory curricula of the students in the departments of physics, chemistry and biology, both beginners and advanced.

The Max Planck Institute for Polymer Research is not only well-known for educating and training international junior researchers. For more than twenty years, the institute has offered apprenticeship positions in three different professions. School graduates can choose between the following three workplaces: the precision mechanical workshop, the laboratory or the administration. Guided by experts and supported by the institute's excellent infrastructure, apprentices are trained to become industrial mechanics specialized in precision mechanics, laboratory assistants or office management assistants. Additionally, the Max Planck Institute for Polymer Research allows senior students to gain a first insight in the work of a research institution during their compulsory industrial placements.

The MPI for Polymer Research also adopts schools in the Mainz region and provides them with material for lessons in chemistry and physics. Regularly, MPI-P researchers hold lessons at Mainz schools. Furthermore, the institute participates in the *Girls' Day* - a day organized throughout Germany to support and encourage young women interested in typical male professions and acquaint them with science. Finally, the institute offers projects on polymer research within the Mainz University's Student Lab ([www.nat-schuelerlabor.de](http://www.nat-schuelerlabor.de)).

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## How to Reach Us

The Max Planck Institute for Polymer Research is located at the main car entrance of the Johannes Gutenberg University in the southwest of the city of Mainz.

Max Planck Institute for Polymer Research  
Ackermannweg 10  
55128 Mainz  
Germany

Make your way...

### ... by car

From the south via the Autobahn A60. Take the exit *Mainz-Lerchenberg*. Turn right onto *Koblenzer Straße* and keep the left lane. Just before the fifth traffic light, onto *Ackermannweg* and follow the signs "Max-Planck-Institut für Polymerforschung".

[www.mpip-mainz.mpg.de](http://www.mpip-mainz.mpg.de)  
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From the north via the Autobahn A60. Take the exit *Mainz-Finthen* and follow the sign *Innenstadt*. After passing the roundabout "Europaplatz", take the next right in the direction *Bretzenheim* and *Universität*. Turn left at the traffic lights onto *Koblenzer Straße* and then left again turning onto *Ackermannweg* and follow the signs "Max-Planck-Institut für Polymerforschung".

### ... by train

Take any train or the S-Bahn (line S 8 direction Mainz/Wiesbaden) to *Mainz Hauptbahnhof* (central railway station). Then take the bus or a taxi. The taxi fare from *Mainz Hauptbahnhof* to Ackermannweg 10 is approximately 10 Euro.

### ... by bus

At Mainz central railway station proceed to bus stop *F*. Take bus no. 69, which is a circle line running from the central railway station (Hauptbahnhof) to the university campus (Universität/Campus) and back. The nearest stop for the MPI-P is *Duesbergweg*.

Alternatively proceed to bus stop *G* at Mainz central railway station.

Take bus no. 68 (direction Klein-Winternheim) and get off at bus stop *Ackermannweg* or take either buses no. 54, 55 or 58 (direction Lerchenberg, Finthen or Wackernheim) and get off at bus stop *Friedrich-von-Pfeiffer-Weg*. Then cross the *Saarstraße* on the pedestrian bridge, turn right and follow *Duesbergweg* until you cross *Ackermannweg*.

Bus tickets can be purchased from the driver.

### ... by airplane

Take any train or the S-Bahn (line S 8, direction Mainz/Wiesbaden) from Frankfurt Airport ("RheinMain") to Mainz main station or go by taxi (approx. 40 mins.) to the institute.

**For a detailed description and maps please check our website at [www.mpip-mainz.mpg.de](http://www.mpip-mainz.mpg.de)**



## **Imprint**

### **Publisher**

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