

COLLOID CHEMISTRY





Research in the Department of Colloid Chemistry

Scientific Profile

The activities of the Colloid Chemistry Department are a mixture of long-standing strongholds which partly can be traced back to the institute's predecessors, activities stimulated by the director, and new topics independently developed by young researchers. The overall size of the department is 60 people, covering a wide range of research topics.

The effective constituting element of the department are "research groups" or "projects", a functional research structure headed by a senior scientist and which involves technicians, graduate students and post-docs (3 - 8 people). Projects are related to scientists, but usually have a temporal character of ca. 5 years. Then, permanent scientists (including the director) have to redefine their profile. In the case of non-permanent scientists, the projects usually leave the department with the promotion of the scientist to the new academic environment, without competition with the institute.

Incentives for the choice of a new research direction are usually scientific curiosity and promise, but research is sometimes also driven by the demands of industry and society. The strong standing of heterophase polymerization as the base for environmentally friendly coatings and plastic processing, but also the development of better analytical tools are typical examples where stimuli continuously come from the outside.

In detail, the following topics are found in the department:

- Heterophase Polymerization
- Self-organizing Polymers
- Mesoporous Materials & Nanoparticles
- Modern Techniques of Colloid Analysis

Heterophase Polymerization

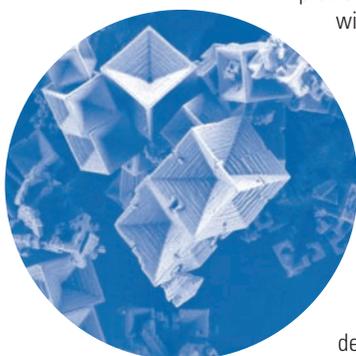
"Heterophase Polymerization" summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization. The solvent is usually water, but heterophase polymerization in organic media is also examined. This class of techniques, although 90 years old, experiences a strong renaissance, since it allows the production of high polymer containing formulations in water as an environment-friendly solvent. Solvent free coatings and glues are just two examples where polymer dispersions are present in daily life.

Central points of interest of the project teams working on heterophase polymerization are a better understanding of the nucleation process and particle formation. For this purpose, new experimental online multidetection techniques are developed and supplemented by theoretical approaches (*Dr. Klaus Tauer*). Other projects strive for the synthesis of complex polymer molecules (e.g. block & graft copolymers) and colloids (e.g. core-shell latexes, reinforced materials) by emulsion polymerization and a rational chemical use of the particle interfaces (*Dr. Klaus Tauer*).

Self-Organizing Polymers

Amphiphilic polymers consist of components which different solubility, e.g. a hydrophilic and a hydrophobic part. Both components can be sensitively adjusted to the dispersion medium as well as the dispersant, and also unusual dispersion problems can be solved. Focal points of interest in this range are:

- The micelle formation and lyotropic liquid crystalline phase behavior of amphiphilic polymers is examined in dependence of molecular parameters as well as the amount of solubilized material (*Dr. Helmut Schlaad*). For that, novel side chain functional copolymers are prepared, e.g. some with sugar moieties.
- The introduction of secondary interactions such as H-bridges, dipole interactions or metal-ligand binding results in superstructures with more complex order (*Dr. Helmut Schlaad*).
- The performance of molecular drugs can be highly enhanced by coupling to a colloidal system with synergistic action. The specific knowledge on functional polymers and colloids is used in cooperation with pharmaceutical/medical partners to generate tailor made colloidal drug carriers and diagnostics (*Dr. Hans Börner*).
- Amphiphilic polymers can step in the precipitation of inorganic and organic matter and control the growth of the particle by biomimetic or polymer-controlled mineralization. So-called double-hydrophilic block co-polymers where one block mediates water solubility and the other interacts with the surface of the particles are examined and enable the design of drugs, fillers and pigments and of new reinforced materials (*Dr. Helmut Cölfen*).
- In biochemistry, complex molecules (proteins and RNA-strands) are made on a technical level by reliable and reproducible automated procedures. The transfer of this technology to polymer and colloid science and its application to non-natural monomers and coupling reactions allows the synthesis of single species polymers (without polydispersity) with specific functionality in the milligram and gram scale. This technology is used to generate blockwise conjugates between peptide and synthetic polymers blocks. Minority peptide blocks are expected to "ordinate" the otherwise disordered world of synthetic polymers. We also expect that such polymers help to address the interface between the biological and technical systems, such as in implants or microstructured diagnostic systems (*Dr. Hans Börner*).



Mesoporous Materials & Nanoparticles

Template synthesis has recently been extended to the employment of surfactant assemblies. Our contribution in this field is the use of more robust and adjustable polymer and colloidal templates which allows a real "nanocasting" of the structure, i.e. a 1:1 replication of the original soft matter template into an inorganic nanostructured replica. Current activities in this field include:

- The synthesis of new well defined nanoparticles with function by solvent and ligand assisted synthetic nonaqueous solgel pathways and their self-assembly into organized 3D superstructures by ligand encoding (*Dr. Markus Niederberger*). This activity has left the institute effective to the 1.1.2007 with the promotion of Dr. Niederberger to the rank of a Professor at the ETH Zürich.
- The synthesis of mesoporous polymers and carbonaceous materials for catalysis and energy applications (*Dr. Arne Thomas*). This work is part of the Max Planck project house "ENERCHEM" (a cooperation of 5 institutes) and is devoted to design new supports, electrode materials and porous systems for energy storage. Highlights in this area are novel fuel cell membrane polymers and the development of a new set of metal free catalysts based on carbon nitrides.
- The synthesis of mesoporous carbon structures by hydrothermal techniques for the sake of Advanced Chromatography and nanoparticles encapsulation (*Dr. Maria Magdalena Titirici*).
- Implementation of experiments within the pore system for "nanochemistry", i.e. the analysis of specific effects of a nanoconfinement on a physical properties and chemical reactions (*Prof. Markus Antonietti*).
- The generation of crystalline thin mesoporous layers by evaporation induced self-assembly (EISA) for electrochemistry and sensing (*Dr. Bernd Smarsly*) This activity will effectively leave the institute to the 1.7.2007 with the promotion of Dr. Smarsly to the rank of a Professor at the University of Gießen.

Modern Techniques of Colloid Analysis

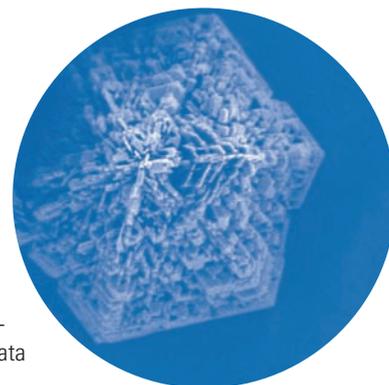
All the work described above is necessarily accompanied by a considerable amount of colloid analysis. This includes fully commercial techniques, but also implies the scientific development of new techniques or methods of data handling, as:

- The development of new ultracentrifugation techniques. Together with industry, a multidetection kit for the ultracentrifuge is developed, e.g. coupling the separation with Raman-, UV- or fluorescence detection. This allows an in-situ chemical analysis within a separating complex colloidal mixture and revitalizes the AUC. (*Dr. Helmut Cölfen, together with the BASF AG*). New gradient techniques for the AUC such as pH-, chirality- or enzymatic activity gradients reveal new information about complex spatio-temporal phenomena and enantiomer-selective crystallization (*Dr. Helmut Cölfen*).
- Special techniques of transmission and scanning electron microscopy on soft, structured matter (*Dr. Jürgen Hartmann*).
- Development of new techniques of dynamic light scattering to colloidal systems, e.g. using optical near fields or a newly developed ellipsometric light scattering technique. (*Dr. Reinhard Sigel*).

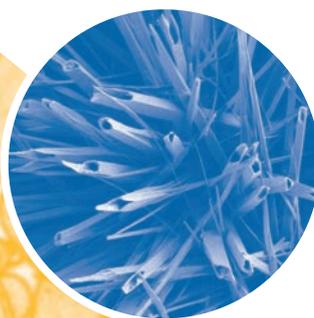
Larger Equipment and Central Service Labs of the Department

Commercial standard techniques which are available in the department are: Transmission and scanning electron microscopy, static and dynamic light scattering, diverse techniques of light microscopy, various chromatographic facilities, reaction calorimetry with online multidetection, analytical and preparative ultra-centrifugation, thermal analysis, DSC, porosimetry, and FT-ATIR for liquid analysis

One laboratory, the electron microscopy lab, is a so-called central service lab, i.e. it belongs and is operated by the department, but is designated to perform scientific routine measurements for the whole institute.



By Markus Antonietti,
Director of the Department
of Colloid Chemistry



Polymer Dispersions/Heterophase Polymerizations



Modern developments of polymer chemistry are waiting to be applied to industrially important aqueous heterophase polymerization techniques. Research topics over the last two years were basic investigations regarding the application of new radical polymerization techniques and tools under heterophase conditions and the continuation of our studies on particle nucleation in emulsion polymerization.

Klaus Tauer 27.09.1951

1974: Diploma, Polymer Chemistry

(Friedrich Schiller University, Jena)

Thesis: Dye Sensitization of

Photoconductivity of

Poly(arylene vinylene) Polymers

1978: PhD, Polymer Chemistry

(Friedrich Schiller University, Jena)

Thesis: Investigations of spectral sensitization of photoconductivity of polyarylene-vinylene polymers

1977-1991: Scientific Coworker

(Institute for Polymer Chemistry,

Academy of Sciences, Teltow)

1987: Habilitation, Chemistry

(Academy of Sciences, Teltow)

Thesis: Modelling emulsion

polymerization of vinyl chlorid

Since 1992: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Potsdam)

Since 2004: "Privatdozent" Polymer

Colloids, University of Potsdam

Controlled Radical Polymerization

Dithioesters can be used as reversible addition fragmentation transfer agents (RAFT agents) in batch ab-initio emulsion polymerization to control the polymer growth. The outcome of the polymerization is strongly influenced by the water solubility of both the RAFT agent and the initiator. The highest control inside the latex particles is achieved and the lowest amount of coagulum is formed if a completely water soluble initiator such as potassium peroxydisulfate is employed in combination with moderately water soluble RAFT agents such as benzyl dithioacetate. Compared to the RAFT-free experiment the rate of polymerization is slightly reduced (but complete conversion is achieved in any case), the average molecular weight is reduced, and the molecular weight distribution is considerably narrowed [1]. The crucial step is the sorption of the RAFT agents by the latex particles. The experimentally determined sorption order of the RAFT agents matches very well with the order of the average molecular weights of the polymer inside the latex particles that is the lower the higher the water solubility of the RAFT agent [2, 3].

Control of radical heterophase polymerizations regarding the formation of block copolymer particles is easily possible by seeded polymerization techniques with seed particles functionalized either by RAFT agents or by 1,1-diphenylethylene [4]. The second stage polymerization of the swollen seed particles in the absence of a free monomer phase is an almost perfect realization of the nano-reactor concept. Structured latex particles with average diameters below 50 nm and various morphological features such as core / shell or acorn-like morphologies are accessible (cf. Fig. 1). The block copolymer yield is in all cases larger than 70 % (in most cases above 90 %).

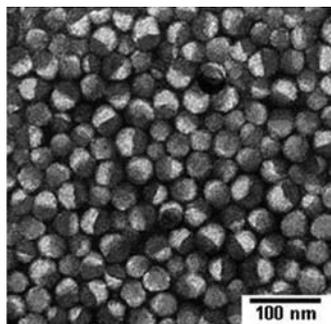


Fig. 1: TEM images of PS(DPE)-b-PtBMA nanoparticles prepared with potassium peroxydisulfate as initiator during the second stage polymerization; multiple staining with phosphor tungstic acid (PTA) and RuO_4 ; darker regions are polystyrene (PS) domains and lighter regions are poly(tert.-butyl methacrylate) (PtBMA) domains.

During these studies two experimental observations of general importance for heterophase polymerizations have been made. First, also hydrophilic radicals stemming from the initiator enter the latex particles [5] and second, latex particles can be modified by sorption even of extremely hydrophobic solids if applied as solution in non-water-miscible solvents (cf. Fig. 2) [6].



Fig. 2: Images of the original 35 nm PS latex (left) and tinted with the hydrophobic dyes Sudan IV (middle) and Solvent Blue (right)

Microwaves as Heating Tool [7-9]

Aqueous radical heterophase polymerizations may be carried out in microwave ovens because the polar nature of the continuous phase allows for efficient microwave coupling. This dielectric heating is extremely fast as the reaction mixture can be warmed up within about 12 seconds from room temperature to $> 90^\circ\text{C}$. Comparable with radiation induced polymerization pulsed thermal polymerizations (PTP) with alternating 'hot' and 'cold' stages as illustrated in Fig. 3 give rise to conditions, in which the cold stages are perfect post-effect situations leading to polymers with extremely high molecular weights (above 10^7 g/mol).

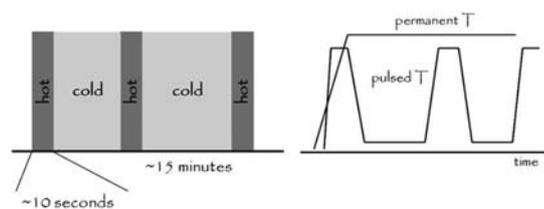


Fig. 3: Illustration of the pulsed thermal polymerization (PTP) procedure (left) with cycles of alternating hot and cold stages and the temperature profiles during polymerizations with pulsed and permanent heating (right)

Compared with 'normal' radical polymerizations PTP of aqueous miniemulsions are characterized by two peculiarities: (1) Medium hydrophobic initiators such as 2,2'-azobisisobutyronitrile (AIBN) and PEGA200 [poly(ethylene glycol)-azo-initiator] lead to largely enhanced conversion rates compared to the much more hydrophilic potassium peroxydisulfate or the much more hydrophobic 2,2'-azobis(2-methyl-butynitrile) and (2) high polymerization rates and extremely high molecular weights can be realized simultaneously.

Particle Nucleation [9]

Thermodynamics requires in any heterophase system an exchange of matter between all phases. Thus, aqueous phase kinetics plays a crucial role even if hydrophobic initiators are employed. In order to study the role of aqueous phase reactions particle nucleation during the surfactant-free emulsion polymerization of styrene has been studied with AIBN as initiator. The initiator was injected either into the monomer phase (mode 1) or into the water phase (mode 2). Surprisingly, polymerization was observed in both phases. Besides the expected bulk polymer in the monomer phase also latex particles were obtained (cf. TEM images of Fig. 4).

Moreover, the reactions in the aqueous phase lead initially to a change in the conductivity and subsequently to the formation of latex particles accompanied by the drop in the transmission (Fig. 5). The shape of the conductivity curve is qualitatively the same as observed for surfactant-free emulsion polymerizations initiated with potassium peroxodisulfate. [10, 11]

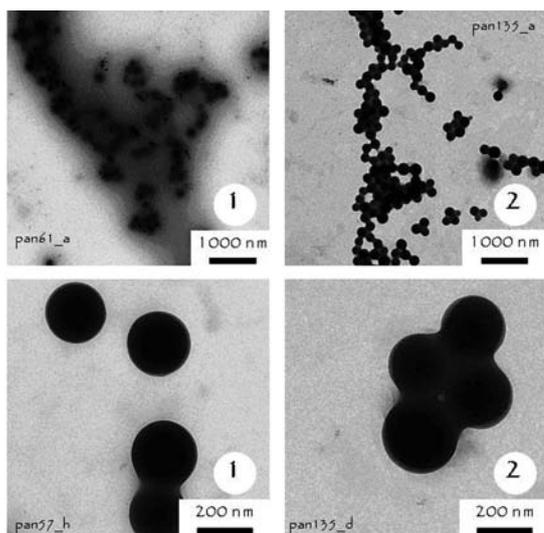


Fig. 4: TEM images of latex particles obtained during surfactant-free emulsion polymerization of styrene initiated with AIBN; 1,2 – AIBN injection modes

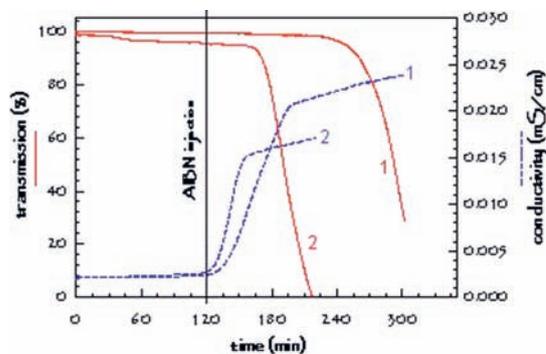


Fig. 5: On-line record of the changes in transmission (red lines) and conductivity (blue lines) during AIBN-initiated surfactant-free styrene heterophase polymerization, 70 °C; the curves represent averages of 5 repeats; 1, 2 AIBN addition into the monomer and the water phase, respectively

The bend of the conductivity curves marks the onset of particle nucleation as conducting species are captured in the diffuse electrical double layer of the particles. These results clearly prove that side reactions of carbon radicals in water lead to conducting species. The zeta-potential of the particles is pH-dependent and negative at pH > 4.

K. Tauer, A. M. I. Ali, M. Antonietti, C. Holtze, J. W. Lee, P. Nazaran, S. Nozari, klaus.tauer@mpikg.mpg.de

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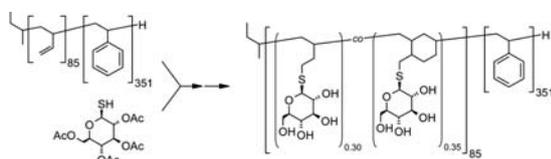
Biohybrid Polymers



Polymer Synthesis

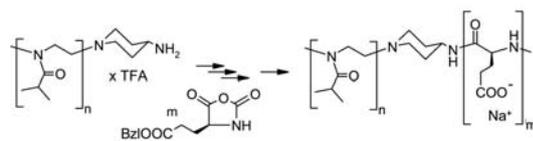
The modification of 1,2-polybutadienes through free-radical addition of mercaptans is a versatile strategy for the generation of a toolbox of functional polymers. However, it was found that the process suffers from a side reaction, namely formation of six-member cyclic units along the backbone. This reaction affects the degree of functionalization but not the molecular-weight distribution of a polymer sample [4, 10].

Functional homopolymers and block copolymers carrying carboxylic acid, amine, ethylene glycol, perfluoroalkyl groups and also biohybrids with pendent amino acid, dipeptide, or glucose units (Scheme 1) have so been prepared [4, 12, 13].



Scheme 1: Synthesis of a glucose-grafted block copolymer (glycopolymer) through the radical addition pathway [12].

A combination of cationic and anionic ring-opening polymerization techniques was applied for the synthesis of well-defined double stimuli-responsive biohybrid block copolymers based on poly(2-isopropyl-2-oxazoline) (responding to a change in temperature) and poly(L-glutamate) (responding to a change in pH). Key steps are the preparation of an ω -(ammonium trifluoroacetate)-poly(2-isopropyl-2-oxazoline) and the subsequent ammonium-mediated polymerization of γ -benzyl L-glutamate N-carboxyanhydride (Scheme 2) [8].



Scheme 2: Synthesis of poly(2-isopropyl-2-oxazoline)-block-poly(sodium L-glutamate) [8].

Structure Formation

Novel biohybrid amphiphiles prepared through the radical addition pathway could be directly dispersed in organic or in aqueous media, leading to the formation of worms and vesicles [12, 13].

The amphiphilic glycopolymer with the chemical structure shown in Scheme 1 self-assembles into sugar-containing polymer vesicles or "glycosomes" (Fig. 1a) being 200-500 nm in diameter [12]. Much larger aggregates are formed by peptide-grafted polybutadiene-*block*-poly(ethylene oxide)s in water. Addition of hydrophobic peptides shifts the morphologies towards lower curvature structures, namely from spherical micelles to giant worm micelles and vesicles (Fig. 1b). Also helical superstructures arise from the chiral peptide interactions inside the hydrophobic core [13].

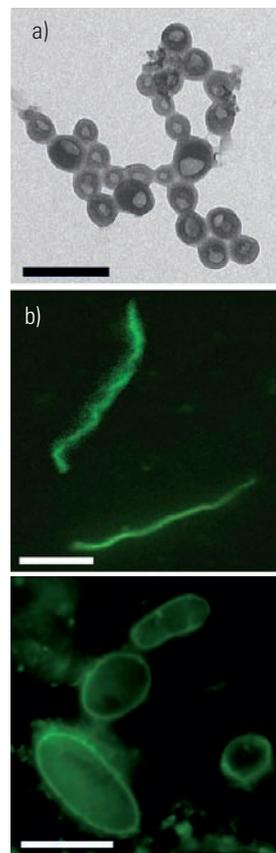


Fig. 1a: Transmission electron micrograph of collapsed glucose-grafted polymer vesicles ("glycosomes") (scale bar = 200 nm) [12], b): confocal fluorescence micrographs of giant peptide-grafted worms and vesicles (scale bar = 5 μ m) [13].

Helmut Schlaad 04.08.1967

1993: Diploma, Physical Chemistry (University of Mainz)

Thesis: Studies of the Anionic Polymerization of Methyl Methacrylate in Toluene in the Presence of Aluminium Alkyls

1997: PhD, Physical Chemistry (University of Mainz)

Thesis: Studies of the Mechanism of the Anionic Polymerization of Methacrylates in the Presence of Aluminium Alkyls in Toluene

1998: Postdoc (University of Massachusetts, Lowell, USA)

Since 1999: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

Since 2004: Senior Scientist (Max Planck Institute of Colloids and Interfaces, Potsdam)

2004: Habilitation, Physical Chemistry (University of Potsdam)

Thesis: Polymer Self-Assembly: Adding Complexity to Mesosstructures of Diblock Copolymers by Specific Interactions

References:

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Unexpectedly, aqueous solutions of poly(2-isopropyl-2-oxazoline)-*block*-poly(sodium L-glutamate)s produce coagulate when heated above the cloud point of poly(2-isopropyl-2-oxazoline) (~40 °C). Micron-sized coagulate particles are spherical in shape, constructed of long fibrils with a diameter of a few tens of nanometers (Fig. 2). Such type of hierarchical structure is also observed for poly(2-isopropyl-2-oxazoline) homopolymers. The mechanism of structure formation is not fully understood yet [15].

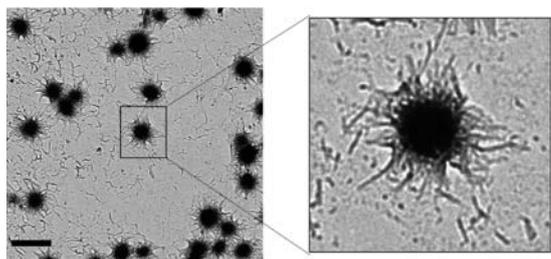


Fig. 2: Transmission electron micrograph of coagulate particles formed by a poly(2-isopropyl-2-oxazoline)-*block*-poly(sodium L-glutamate) (scale bar = 5 μm) [15].

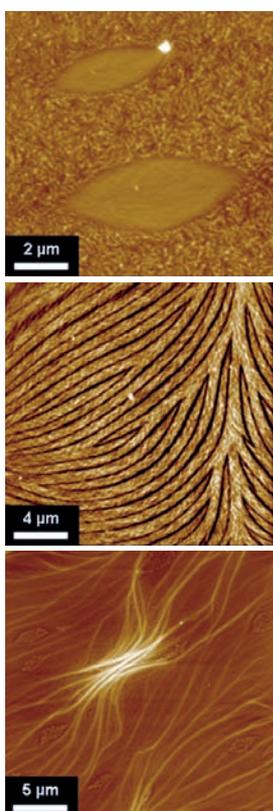


Fig. 3: Scanning force micrographs of a thin film of polystyrene-*block*-poly(γ -benzyl L-glutamate), solvent-annealed for 3.5, 22.5, and 42 hours (from top to bottom) [3].

Solvent-cast films of polystyrene-*block*-poly(γ -benzyl L-glutamate) usually have a hexagonal-in-lamellar hierarchical superstructure. The preferential formation of lamellae (the intersheet spacing being in the range of a few tens of nanometers) is related to the stiffness of the polypeptide layer. Driven by dipole-dipole interactions, the polypeptide helices are usually arranged in an anti-parallel orientation and densely packed into a two-dimensional hexagonal array. Helices are usually folded but can be fully stretched, depending on the hydrogen-bonding ability of the casting solvent [9].

Structures with a higher level of hierarchical ordering were observed for solvent-annealed thin films of polystyrene-*block*-poly(γ -benzyl L-glutamate) on a silicon substrate. On the smallest length-scale, the structure was found to be built of short ribbons or lamellae of interdigitated polymer chains. Depending on the time of solvent annealing, different ordered structures on the micrometer length-scale could be observed (see Fig. 3). So far, a comprehensive picture of the processes involved in the formation of these structures is lacking [3].

H. Schlaad, I. Below, M. Gräwert, A. Greß, Z. Hordyjewicz, J. Justynska, M. Meyer, L. You
helmut.schlaad@mpikg.mpg.de

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SELF-ORGANIZING POLYMERS

Polymer-Bioconjugates as Macromolecular LEGO[®]-Bricks



Controlling interactions in synthetic polymers as precisely as in proteins would have a strong impact on polymer science. Advanced structural and functional control can lead to rationally designable, integrated nano- and microstructures. To achieve this we exploit properties of sequence-defined oligopeptides.

By incorporating these as monodisperse segments into synthetic polymers, we learn how to program structure formation [1], interactions with biosystems [2] and manipulation of crystal surfaces [3, 4].

Hans G. Börner 15.09.1970

1996: Diploma, Chemistry
(Philipps-Universität Marburg)

Thesis: Applying the Concept of Large Counter Cations to Metal Free Anionic Polymerization of Acrylates and Meth Acrylates

1997-2000: Ph.D., Macromolecular Chemistry (Philipps-Universität Marburg)
Thesis: Synthesis of Novel Phosphine Substituted Block Copolymers and Application as Building Blocks for Nano Reactors

2000-2002: Postdoctoral Fellow (Carnegie Mellon University, Pittsburgh, USA)

Since 2002: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

2002: Visiting Researcher
(Department of Biochemistry, Stellenbosch University, South Africa)

References:

[1] Börner, H. G.: Functional Polymer-Bioconjugates as Molecular LEGO[®]-Bricks. *Macromol. Chem. Phys.* **208**, 124-130, (2007).

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Methodologies to Synthesize Bioconjugates

In order to selectively introduce peptides into synthetic polymers, new routes had to be developed, applying two main strategies:

i. Polymerization strategies, in which the polymer segment is synthesized in the presence of the peptide [5]. This approach includes the sequence specific introduction of an initiator or chain transfer functionality to a peptide. The resulting macroinitiator or macrotransfer agent was applied in controlled radical polymerization (CRP) processes, such as atom transfer radical polymerization (ATRP) [6] and reversible addition-fragmentation chain transfer polymerization (RAFT) [7]. This allows the synthesis of well-defined conjugates with controllable molecular weight and polydispersities as low as 1.1.

ii. Coupling approaches including the regio-selective ligation of a polymer that has a defined chain-end functionality with a complementary functionality of a peptide. To diversify this route, different strategies, allowing the introduction of chain-end functionalities into synthetic polymers were investigated. CRP was combined with either protected functional initiators [8] or specific chain-end-group transformations [9]. In addition, different ligation techniques, e.g. the highly specific click-reaction, were applied [10].

Bioinspired Formation of Structure and Function

The resulting bioconjugates allow for the rather direct realization of bio-inspired polymer science. Peptides combine self-assembly properties with the potential to actively interact with biological systems. Hence, peptide-polymer conjugates can be used to program structure formation in polymeric materials.

We exploited the biological concept of peptide-guided structure formation for the organization of synthetic polymers, using different peptide-based organizer units (Fig. 1) [1]. Particularly, the peptide organization in form of the β -sheet secondary structure motif was investigated. Thus, highly attractive, anisometric tape, fibrillar or fiber-like nanostructures can be accessed. These are important structural and functional elements in both native and synthetic materials that provide anisotropic strength and elasticity or directed transport.

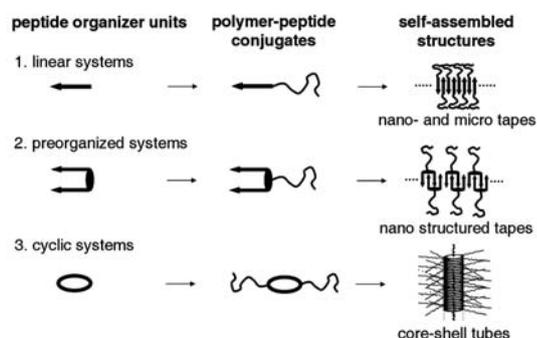


Fig. 1: Illustration of the concept of peptide-guided organization of synthetic polymers.

As outlined in Fig. 1 the peptide organizer segment in a peptide-polymer conjugate induces and controls the microstructure formation. Thus, different peptide organizers result in different structures, ranging from macro- to nanotapes and nanotubes (Fig. 2) [8, 11-14].

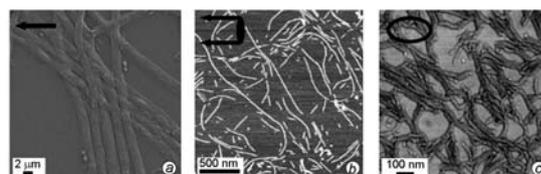


Fig. 2: Peptide-guided self assembly of synthetic polymers: a) PEO-tapes (SEM), b) PEO nanotapes (AFM, height) and c) pBA hollow fibers (AFM, phase).

Representative of the other projects, two examples will be discussed in detail, illustrating the potentials of the peptide-guided organization for materials science:

Linear peptide organizers: The synthesis of extended and robust nanofibres, interesting for material science, requires peptides with strong tendencies to form stable aggregates. These, however, are usually difficult to access. Recently, the SWITCH-strategy of integrating defined defects into the peptide backbone was developed to overcome these obstacles. The defects, referred to as "switch"-segments, temporarily suppress the aggregation tendency of a peptide. The native peptide can be reestablished via a selective rearrangement in the switch segments, restoring the aggregation tendency.

Such switch segments have been shown to be highly useful for the peptide-guided organization of synthetic polymers (Fig. 3a), as the rate of switching can be adjusted to control the aggregation kinetics [11,13]. Using the switch-strategy, PEO-peptide conjugates in water organized into macro-tapes with up to several millimeters in length (Fig. 2a, 3b) [11].

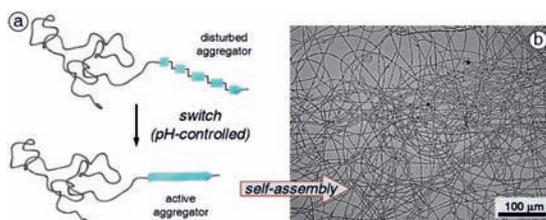


Fig. 3: Schematic presentation of the pH-triggered organization of synthetic polymers (a) and light microscopy of the self-assembled PEO-macro tapes (b).

Moreover, the switch proceeds also in organic solvents, allowing the assembly of poly(butyl acrylate) into helical tapes with a left-handed twist [13]. These protostructures exhibit distinct entanglement into soft organo-gels (Fig. 4). This example shows that structural control provides control over functions, similarly to the constitution of functions in proteins. The helical tapes can be seen as nano-springs and exciting micromechanic properties are expected.

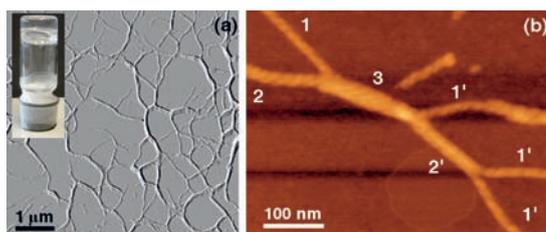


Fig. 4: AFM of the organo-gel, formed by assembly of a poly(butyl acrylate)-peptide conjugate (a); macroscopic gel (a, inset); cross-links in the gel showing single tapes with helical twist (1, 1'), dual tapes (2, 2') and triple tapes (3) (b).

Mimicking Biomaterials

Biological inorganic-organic materials from bones to glass sponges are high performance, fiber reinforced composites, with purpose-adapted properties. For instance, the glass sponge *Euplectella sp.*, one of the most primitive animals in existence, realizes integrated composite materials based on glass with outstanding mechanical properties.

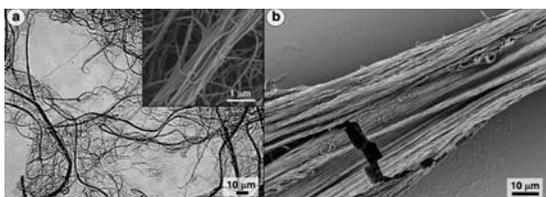


Fig. 5: Self-assembled nanofiber-reinforced silica fibers (light microscopy (a), SEM (a, inset) and continuously produced biomimetic silica fibers exhibiting fracture (b)).

To mimic the biosilification process, peptide-PEO nanotapes (Fig. 2b) [12] were applied in a sol-gel silica synthesis. During a self-assembly-silification process, nanofiber-reinforced silica fibers spontaneously formed (Fig. 5a). Detailed analysis of the material reveals a hierarchical order. The process is still not fully understood. However, apparently, the functionalities

of the PEO-peptide-tapes guide the silification process towards the formation of rather uniform proto-composite fibers that further tend to form bundles (Fig. 5a, inset).

Preliminary experiments show that a continuous spin process can be performed, which results in fiber-bundles whose fracture behavior indicates interesting mechanical properties (Fig. 5b).

Biomedical Applications

The development of defined peptide-polymer conjugates allows addressing pharmacological and biomedical issues [15]. However, to avoid the inherent immunogenicity of peptides, a novel synthesis route to linear poly(amido amines) (PAAs) was developed [2]. This enables one to synthesize monodisperse PAAs with a defined monomer sequence. The cationic character (balance of *tert.*, *sec.*, and *prim.* amine groups) of the PAA segment can be fine-tuned with monomer resolution, making the PAAs – if conjugated to PEO – highly interesting for gene delivery. PEO-PAAs are well-defined model compounds with sharp property profiles allowing for the correlation of e. g. the cationic balance with DNA complexation and compression properties (Fig. 6) as well as membrane translocation and transfection activities.

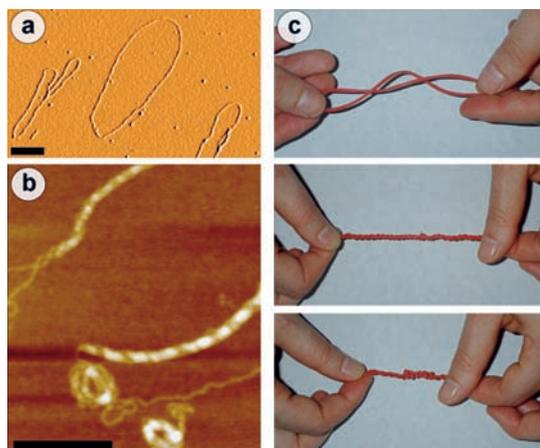


Fig. 6: Induction of super-coiling in plasmid dsDNA (a,b) and illustration of the process by a rubber band (c); (Expanded DNA using PEO-PAAs with tertiary amines (a) and super-coiled DNA using PEO-PAAs with a mixture of *sec.* and *prim.* amines (b)(AFM, scale bar = 200 nm)).

Outlook

It is predictable that polymer chemistry with its inherent molecular weight distributions will evolve to macromolecular chemistry with precisely defined molecules. Hence, the synthesis of fully synthetic, monodisperse polymers with defined monomer sequences will be the upcoming challenge in polymer science. Completely unnatural polymer classes might be developed, which combine novel units capable of specific molecular recognition with new monomer alphabets to fine-tune secondary interactions along linear polymer chains.

H. G. Börner, M. ten Cate, L. Hartmann, Y. Yagci, J. Hentschel, S. Kessel, H. Hahn; J. Brandt, K. Ostwald. hans.boerner@mpikg.mpg.de

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Biomimetic Mineralization



This project investigates polymer additive controlled mineralization in an attempt to apply principles from biomineralization processes. This includes the understanding of crystallization and biomineralization principles as well as their adaptation to synthetic materials. In recent years, it became evident that many crystallization processes do not follow the classical path of atom/ion/molecule assembly to

a single crystal but instead proceed via the self organization of nanoparticles [1-4]. Such self organization processes can be directed in a versatile way by the application of polymer additives. If block copolymers are used, the individual polymer blocks can even be "programmed" to optimally realize a desired function like adsorption on a specific crystal face, temporary stabilization in the solvent etc. It is desirable to work in water as solvent and thus, a useful block copolymer design is to use one water soluble block not interacting with crystal surfaces like poly(ethylene oxide) and another block, which selectively interacts with crystal faces. Especially active for adsorption onto minerals like CaCO_3 or BaCO_3 are acidic polyelectrolyte blocks like polyphosphonates. We have synthesized a variety of such block copolymers using various radical polymerization strategies and successfully applied these molecules as crystallization additive [5].

Especially intriguing structures were obtained when a stiff phosphonated block was applied, which selectively attached to (110) faces of BaCO_3 . In this case, tectonic arrangement of elongated nanoparticles to helical superstructures was achieved, although the polymer was racemic and BaCO_3 not chiral, and the formation mechanism could be revealed [6]. Similar addressing of selected CaCO_3 calcite faces by block copolymers leads to the formation of thin CaCO_3 sheets, which form pancake-like structures [7].

This investigation showed that the epitaxial view of polymer adsorption onto a crystal face is too simplified and that factors like charge density, polymer flexibility etc. also play a role onto which crystal surface the polymer will adsorb. These investigations were extended to the formation of CaCO_3 microrings [8] or ZnO nanorings and disks [9]. If a sophisticated multi-shell polymer particle architecture is used as a template, a single polymer microgel particle could be used to template an entire aragonite nanoparticle super-structure. Not only the synthesis of the aragonite CaCO_3 polymorph is unusual, it is further remarkable that all nanoparticles in the super-structure are crystallographically connected [10].

The self organization of nanoparticles in crystallographic register was of especial interest in this project as it is a non-classical crystallization pathway, by which single crystals can be formed by nanoparticle superstructure intermediates. The underlying mechanism is the so called "Oriented Attachment" in which nanoparticles self organize within crystallographic register. Subsequently, they may fuse at high energy crystal surfaces and a single crystal can be formed gaining energy by elimination of two high energy surfaces. Such mechanism could be identified for CaCO_3 in presence of polymers [11] or even without polymer additives by the adsorption of ammonia ions [12] as well as for BaSO_4 in presence of poly(acrylate) polymer additives [13, 14]. For the BaSO_4 fibers, the formation mechanism was investigated in detail revealing polymer interaction already with the Ca^{2+} ions, formation of amorphous precursor particle aggregates, nanoparticle crystallization and oriented attachment with subsequent nanoparticle fusion to single crystalline defect free nanofibers [13, 14].

The oriented attachment of nanoparticles can not only occur in one [13, 14] or two [11, 12] but also in three dimensions forming so-called mesocrystals, which are nanoparticle superstructures in crystallographic register, single crystalline scattering behaviour and often a faceted morphology [15-18]. DL-alanine proved to be a good model system for mesocrystal formation as the molecule already has a dipole moment and dipole-dipole interactions can be used to structure DL-alanine nanocrystals in crystallographic register to a mesocrystal [16, 17]. In addition, the solubility of an amino acid can be controlled in an easy way by pH variations and the conditions for mesocrystal formation could be identified as those with high supersaturation and thus nucleation burst of a large number of nanoparticle building units, whereas low supersaturation led to molecule mediated crystallization along the classical crystallization pathway [17].

Mesocrystals can also be formed for classical mineral systems like CaCO_3 , however, only in presence of a polymer additive [15, 18 & Figure 1]. Selective adsorption of the poly-acid polymer additive poly(styrene sulfonate) to the charged (001) faces of calcite leads to nanoparticles with positive and negative charges on the opposite faces [18] followed by a self organization of the calcite nanoplatelets in crystallographic register to form the mesocrystal. The transition from single crystal to mesocrystal to polycrystal seems to be continuous and can be adjusted in a simple way via the polymer/ CaCO_3 ratio as shown in Figure 1 with the typical calcite rhomboeder formed at the lowest polymer and CaCO_3 concentration, which are closest to the classical crystallization conditions for CaCO_3 (Fig. 1a, 18)

Helmut Cölfen 24.07.1965

1991: Diploma, Physical Chemistry
(University of Duisburg)

Thesis: Analytical

Ultracentrifugation of Gels

1993: PhD, Physical Chemistry
(University of Duisburg)

Thesis: Analytical Ultracentrifugation of Gels

1993-1995: Postdoc (National Center for Macromolecular Hydrodynamics, University of Nottingham)

Since 1995: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

2001: Habilitation, Chemistry
(University of Potsdam)

Thesis: Biomimetic Mineralisation Using Hydrophilic Copolymers: Synthesis of Hybrid Colloids with Complex Form and Pathways towards their Analysis in Solution

Since 2004: Private Docent;
University of Potsdam

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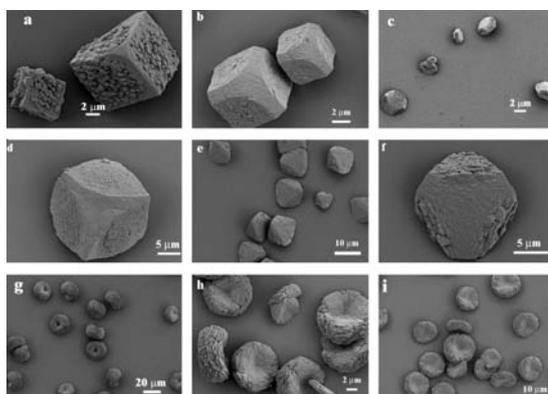


Fig. 1: Typical SEM images of calcite mesocrystals obtained on a glass slip by the gas diffusion reaction after 1 day in 1 mL of solution with different concentrations of Ca^{2+} and polystyrene-sulfonate: a) $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$, $[\text{PSS}] = 0.1 \text{ g/L}$; b) $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$, $[\text{PSS}] = 0.5 \text{ g/L}$; c) $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$, $[\text{PSS}] = 1.0 \text{ g/L}$; d) $[\text{Ca}^{2+}] = 2.5 \text{ mmol/L}$, $[\text{PSS}] = 0.1 \text{ g/L}$; e) $[\text{Ca}^{2+}] = 2.5 \text{ mmol/L}$, $[\text{PSS}] = 0.5 \text{ g/L}$; f) $[\text{Ca}^{2+}] = 2.5 \text{ mmol/L}$, $[\text{PSS}] = 1.0 \text{ g/L}$; g) $[\text{Ca}^{2+}] = 5 \text{ mmol/L}$, $[\text{PSS}] = 0.1 \text{ g/L}$; h) $[\text{Ca}^{2+}] = 5 \text{ mmol/L}$, $[\text{PSS}] = 0.5 \text{ g/L}$; i) $[\text{Ca}^{2+}] = 5 \text{ mmol/L}$, $[\text{PSS}] = 1.0 \text{ g/L}$. (From Ref. 18)

Another target of our research is the investigation of biomineralization principles. In the field, amorphous precursor phases are recently reported for an increasing number of biominerals. Even liquid precursors are discussed and we investigated for amino acid model systems, under which conditions, liquid precursors can be formed and how they can be applied to generate crystals with complex shape in a very easy way [19]. In addition, unstable amorphous CaCO_3 could be synthesized with a simple phosphorylated sugar molecule (phytic acid) and kept stable in aqueous environment for weeks demonstrating the use of amorphous precursor phases as material reservoir [20].

Applying amorphous precursor particles as precursors in a biomimetic mineralization reaction inside the organic demineralised matrix of nacre as a scaffold, the platelet-like mineral structure of the original nacre was obtained (Fig. 2, 21). This suggests this system as suitable model system to study the details of the mineralization process and to learn about the natural nacre archetype [21].

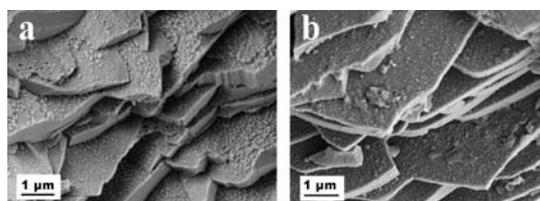


Fig. 2: SEM micrographs of fracture surfaces of (a) synthetic nacre; (b) original nacre from *Haliotis laevis*. (From Ref. 20)

Indeed, a high resolution TEM investigation of natural nacre revealed an amorphous layer on top of the aragonite platelets [22] similar to synthetic aragonite [10] supporting amorphous precursor phases in the synthesis of nacre.

The role of amorphous precursor phases in the morphosynthesis of crystals was also investigated for the DL-alanine model system. Here, hollow alanine needles could be obtained by a dissolution-recrystallization process of amorphous precursor nanoparticle aggregates [23]. In addition, we introduced an improved method for slow CaCO_3 crystallization without ion contamination [24] as it turned out that ammonia ions can act as active additive in CaCO_3 crystallization [12].

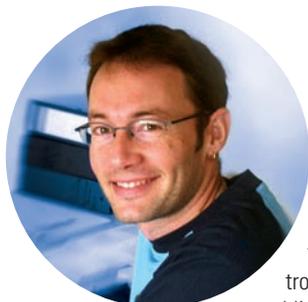
Also, dynamic pattern formation in crystallization was investigated. When phosphonated block copolymers [5] were used as additives for the crystallization of BaCO_3 , a reaction-diffusion system could be established under certain experimental conditions leading to a concentric ring pattern typical of a Belousov-Zhabotinsky reaction. This reaction was described here first, for a two phase system implementing self organizing nanocrystal structures. The key step was the autocatalytic formation of a Ba-polymer complex as a precursor to amorphous nanoparticle formation, which was followed by particle crystallization and self organization [25].

Overall, our research has revealed that polymer controlled crystallization is useful to study basic crystallization mechanisms, generate crystals with complex structure and form or mimic and understand biomineralization principles. Especially the non-classical particle mediated crystallization paths are highly interesting for future studies, as so far, only little is known about these self organization mechanisms.

H. Cölfen, M. Barth, N. Nassif, T. Wang, A.W. Xu, Y. Ma, M. Page, N. Gehrke, D. Gebauer
Coelfen@mpikg.mpg.de

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Organic Chemistry Meets Inorganic Materials Synthesis



1. Introduction

Sol-gel routes to metal oxide nanoparticles in organic solvents under exclusion of water represent a versatile alternative to aqueous methods. In comparison to the complex aqueous chemistry, nonaqueous processes offer the possibility to better understand and to control the reaction pathways on a molecular level, enabling the synthesis of nanomaterials with high crystallinity and well-defined and uniform particle morphologies [1].

Markus Niederberger 10.06.1970

1996: Diploma, Chemistry

[Swiss Federal Institute of Technology (ETH) Zürich, Switzerland]

2000: PhD in Chemistry (ETH Zürich)

Thesis: Synthesis and Characterization of Novel Micro- and Nanostructured Vanadium, Molybdenum, and Iron Oxides

2001-2002: Postdoc

(University of California at Santa Barbara)

2002-2006: Group Leader

(Max Planck Institute of Colloids and Interfaces, Potsdam)

2007: Assistant Professor

(ETH Zürich, Department of Materials)

2. Synthesis

The most popular metal oxide precursors are metal halides, metal acetylacetonates, and metal alkoxides, and mixtures thereof for multi-metal oxides. The solvents vary from alcohols to amines, nitriles, ketones and aldehydes, and also include mixtures of these solvents [1]. Depending on the reactivity of the metal oxide precursor with the respective solvent, the synthesis temperature typically ranges from about 50 °C to 250 °C. Procedures at temperatures higher than or close to the boiling point of the organic solvent are performed in steel autoclaves with Teflon liners.

These nonaqueous and surfactant-free sol-gel procedures gave access to a wide variety of metal oxide nanoparticles including TiO₂, CeO₂, ZrO₂, HfO₂, In₂O₃, Ga₂O₃, Nb₂O₅, Ta₂O₅, SnO₂, ZnO, WO_x, FeO_x, BaTiO₃, SrTiO₃, (Ba,Sr)TiO₃, BaZrO₃, Pb(Zr,Ti)O₃, LiNbO₃, NaNbO₃, NaTaO₃, or BaSnO₃ [1].

As selected examples **Fig. 1** displays TEM overview images of indium oxide, tin oxide, indium tin oxide and zinc oxide nanoparticles. The indium oxide nanoparticles in **Fig. 1a** were obtained from indium acetylacetonate in benzylamine at 200 °C. The same process can also be used for iron, gallium and zinc oxide nanoparticles [2]. Fairly monodisperse tin oxide nanocrystals in the size range of 3-6 nm were prepared from tin tetrachloride and benzyl alcohol at 100-110 °C (**Fig. 1b**) [3]. The high dispersibility of these nanoparticles made it possible to assemble them into mesoporous materials (**Fig. 1b**, inset) by applying block copolymers as templates and the evaporation-induced self-assembly process [3]. Indium tin oxide was obtained from indium acetylacetonate and tin *tert*-butoxide in benzyl alcohol at 200 °C [4]. Obviously the reactivity of these two precursors in benzyl alcohol matched each other in a way that formation of solid solution takes place. The nanoparticles are crystalline with diameters of 5-10 nm (**Fig. 1c**). Without further annealing they show good electrical conductivity [4]. Another low-temperature route to metal oxides involves the solvothermal reaction of metal acetylacetonates with acetonitrile at 100 °C. Using this approach, indium and zinc oxide nanoparticles were synthesized [5]. Whereas In₂O₃ consisted of individual nanoparticles with a spherical morphology and a small size distribution of 3-6 nm, the ZnO nanoparticles had sizes of 15-85 nm (**Fig. 1d**) and were sometimes composed of a highly oriented arrangement of smaller nanocrystallites forming hexagonal, well-faceted mesocrystals (**Fig. 1d**, inset).

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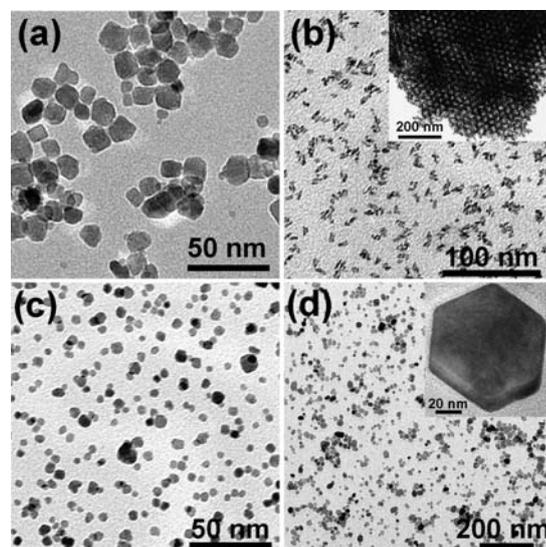
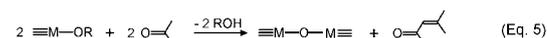
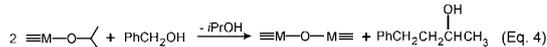
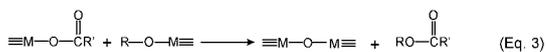
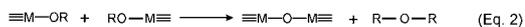
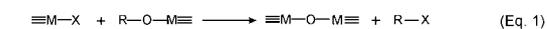


Fig. 1: TEM overview images of selected metal oxide nanoparticles. a) Indium oxide, b) tin oxide (inset: mesoporous SnO₂), c) indium tin oxide, d) zinc oxide (inset: ZnO mesocrystal).

3. Formation and Crystallization Mechanisms

In aqueous sol-gel processes, the oxygen for the oxide formation is provided by the water molecules. In nonaqueous systems, where intrinsically no water is present, the oxygen comes either from the organic solvent or from the organic constituent of the metal oxide precursor [1]. The most common condensation steps leading to a metal-oxygen-metal bond, the basic "molecular" unit of metal oxides, are summarized in **Scheme 1**. Eq. 1 displays the condensation between metal halides and metal alkoxides (formed *in situ* upon the reaction of metal halides with alcohols) under release of an alkyl halide. Ether elimination (Eq. 2) is the result of the reaction between two metal alkoxides, ester elimination between metal carboxylates and metal alkoxides (Eq. 3). In selected cases a more sophisticated pathway was found, where the M-O-M bond formed upon reaction of benzyl alcohol with the isopropoxy ligand of the metal isopropoxide (Eq. 4) [1]. Ketones as solvent release their oxygen typically by aldol condensation reactions (Eq. 5).



Scheme 1: Selected condensation steps in nonaqueous sol-gel processes resulting in the formation of a metal-oxygen-metal bond. Alkyl halide elimination (Eq. 1), ether elimination (Eq. 2), ester elimination (Eq. 3), C-C bond formation between benzylic alcohols and alkoxides (Eq. 4), aldol condensation reactions (Eq. 5).

Although the investigation and classification of these organic reaction mechanisms represent an important progress in nanoparticle synthesis, the ultimate goal of a rational synthesis strategy for inorganic nanomaterials is still far away. The big question of finding a relationship between a particular synthesis system and the final particle morphology remains unanswered. One of the reasons is the poorly understood crystallization process of nanoscale materials. In addition to the classical crystallization mechanism based on the attachment of ions, atoms or molecules to a growing nucleus, particle mediated growth and assembly mechanisms seem to be important, too. These non-classical crystallization pathways involve processes like oriented attachment and mesocrystal formation [6]. The complexity of crystallization is nicely represented in the case of indium tin oxide nanoparticles. They do not crystallize in a simple nucleation and growth process during solvothermal treatment, but first form an intermediary phase consisting of aligned nanocrystallites embedded in an organic matrix (Fig. 2a and b), followed by the transformation into the bixbyite structure with larger crystallites (Fig. 2c) and accompanied by the disappearance of both the organic phase and the superstructure [7].

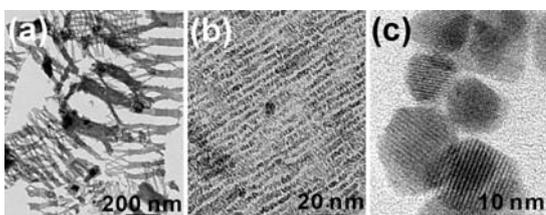


Fig. 2: TEM images of indium tin oxide nanoparticles after different reaction times. a) After 3h, b) after 6h and c) after 24h.

4. Role of the Organic Species: Tungsten Oxide as Case Study

The organic species in the reaction system strongly influence the composition, size, shape, surface properties and even the crystal structure of the inorganic products. Consequently, the organic side bears the potential to control the structural and morphological characteristics. However, this goal can only be achieved, if the role of the organic species is understood on a molecular level and at all stages of the synthesis process. To make first steps in this direction, the influence of different organic solvents and ligands on the particle morphology and assembly behavior of tungsten oxide was investigated. The reaction of tungsten chloride with benzyl alcohol leads to the formation of tungstite nanoplatelets (Fig. 3a). If the same process is carried out in the presence of the bioligand deferroxamine, the particle morphology drastically changes, leading to bundles of assembled nanowires (Fig. 3b) [8]. The nanowires are highly crystalline and exhibit a uniform diameter of about 1.3 nm (Fig. 3c). Similar nanowires can be prepared without any additional organic templates by reacting tungsten isopropoxide with benzyl alcohol (Fig. 3d) [9]. Tungsten chloride and 4-*tert*-butylbenzyl alcohol result in highly ordered ribbon-like structures, composed of parallel columns of stacked nanoplatelets (Fig. 3e) [10]. It is also possible to get stacks of nanoplatelets in the tungsten chloride-benzyl alcohol system. But in this case, 4-*tert*-butylcatechol has to be added to induce the assembly process (Fig. 3f) [10].

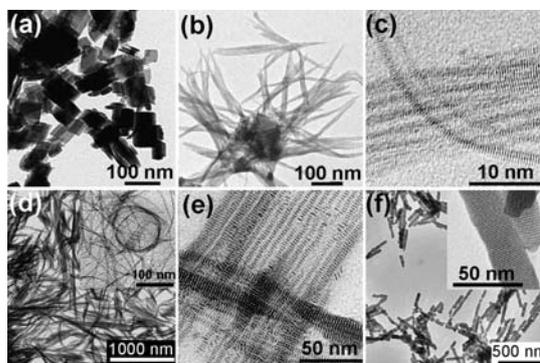


Fig. 3: TEM images of a) tungsten oxide nanoplatelets, b) tungsten oxide nanowire bundles, c) tungsten oxide nanowires, d) tungsten oxide nanowire bundles (inset: individual tungsten oxide nanowires), e) and f) stacks of tungsten oxide nanoplatelets. Details see text.

M. Niederberger, J. Ba, J. Buha, M. Cao, I. Djerdj, G. Garnweitner, R. Rothe, L. Zhang, S. Zhou
markus.niederberger@mpikg.mpg.de

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Mesoporous “Non-Oxidic” Materials



Nanostructured mesoporous materials have a broad scope of prospects and applications and were extensively studied in recent years. Our research is focused on the development of new or improved “soft” mesoporous materials composed of carbon, carbon nitrides, polymers or organosilicas, in contrast to the recently more often described “hard” mesoporous inorganic metal oxides.

Arne Christian Thomas 07.04.1975
2001: Diploma, Chemistry (Philipps-Universität Marburg)
 Thesis: Synthesis of cholestric cellulose derivatives with covalently bonded chromophores and investigation of their optical properties
2003: PhD, Chemistry (Universität Potsdam)
 Thesis: Mesoporous silicas by nanocasting – from chiral templates to a new chemistry in pores
2004-2005: Postdoc (University of California, Santa Barbara, USA)
Since 2005: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)

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The sustainability of a technical innovation is always accompanied by the question of costs, environmental constraints and accessibility of the required scaffold. Therefore new materials are not only required to have an exceptional performance for the desired application, but also a low cost, non-toxicity and overall environmental compatibility of the respected materials. For many applications, such as catalysis this practically excludes most of the so far used transition metals or metal oxides. Therefore our research goal is the synthesis of nanostructured organic materials from abundant precursors using self-assembly, templating or nanocasting techniques and their application as catalysts, electrode materials, gas storage devices, membranes and separation media.

Carbon

The search for new synthetic strategies for generating nanostructured carbon or carbon-hybrid materials is an exciting topic in material chemistry, motivated by the natural abundance and therefore cost-efficiency of carbon precursors and on the other hand promising applications of the resulting materials. The synthesis of carbon materials, as performed today, always relies on very harsh conditions (e.g. pyrolysis), which makes modifications of the surface functionality especially difficult. In contrast we use a mild hydrothermal route to produce μm -sized, colloidal carbon spheres, distinguished by a hydrophilic surface of the particles (see Fig. 1a) [1]. The resulting carbon structures can be further controlled when suitable templates are introduced in the synthesis. Hydrothermal carbonization for instance can be carried out in the pores of porous silica beads yielding porous carbon spheres with a hydrophilic surface area (see Fig. 1b) [2]. These carbon spheres can act as templates on their own and were successfully used for the direct synthesis of metal oxide hollow spheres by addition of metal salts into the hydrothermal reaction mixture [3].

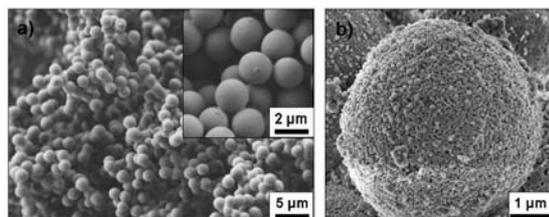


Fig. 1: Hydrothermal carbonisation of carbohydrates: a) direct production of colloidal carbon spheres b) mesoporous carbon particles via hydrothermal carbonization inside porous silica beads

Carbon Nitrides

Many of today's catalytic systems are not sustainable solutions, because they are based on rare elements (e.g. noble metals). Therefore the replacement of these materials by catalysts derived from abundant elements or, as the most elegant possibility, a “metal-free” catalyst is a valuable object for future catalyst research. Such a catalyst is provided by graphitic carbon nitride, $g\text{-C}_3\text{N}_4$. Graphitic Carbon Nitride ($g\text{-C}_3\text{N}_4$) is a material, which is easily obtained through thermal condensation of cyanamide, dicyandiamide or melamine. Following a reaction/condensation scheme the resulting materials adopt a very special architecture, with a graphitic stacking and individual layers composed of condensed melem units, yielding a material which combines lewis-acidity with interesting electronic properties. A mesoporous graphitic C_3N_4 (mpg- C_3N_4) can be produced using colloidal silica particles as templates (see Fig. 2) [4].

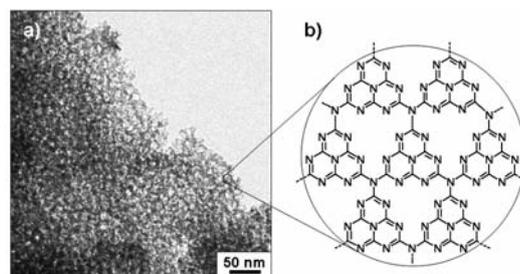


Fig. 2: a) TEM-micrograph and b) chemical structure of the pore walls of mesoporous graphitic carbon nitride (mpg- C_3N_4)

Mesoporous graphitic carbon nitride was shown to be a versatile heterogeneous, metal-free catalyst for the Friedel-Crafts acylation of benzene, which proceeds via the activation of the aromatic ring [4,5], the cyclotrimerizations of substituted nitriles and alkynes [6] and for an unusual activation of CO_2 [7].

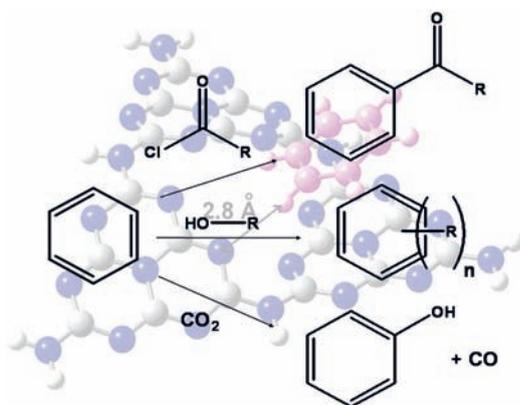


Fig. 3: Chemical reactions with benzene catalyzed by mpg C_3N_4

In another application, mpg-C₃N₄ can be used as a nanoreactor for the preparation of metal nitride nanoparticles. In this approach the carbon nitride acts, firstly as a confinement for nascent nanoparticles and then, during decomposition, as a nitrogen source, generating metal nitride nanoparticles of various compositions [8].

Polymers

Poly(benzimidazole) (PBI) has a good proton conductivity in a wide temperature window when doped with acids. PBI has therefore high potential for applications in proton exchange membrane fuel cells (PEMFCs). New nanostructured polymer membranes based on poly(benzimidazole) with enhanced properties in terms of conductivity and thermal stability were synthesized by a casting approach via a monomer adsorption/polycondensation process inside the pores of selected mesoporous silicas [9] or using colloidal silica as templates (see Fig. 4) [10].

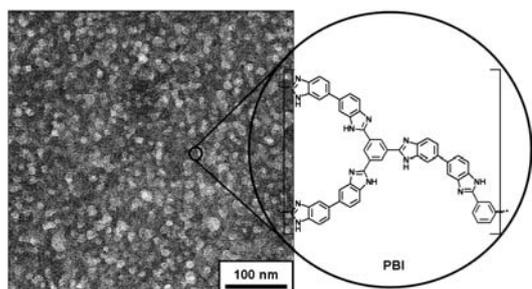


Fig. 4: TEM picture and chemical structure of a mesoporous poly(benzimidazole)

The porosity and surface area of the resulting mesoporous polymers can be tuned by the amount of the silica template but also by varying the cross-linking density of the polymer frameworks. The so obtained mesoporous PBIs show improved proton conductivity at temperatures above 100°C when doped with phosphoric acid [11].

Organosilicas

Mesoporous organosilicas (MOs) represent a promising class of organic-inorganic nanocomposites because they combine the unique features of porous glasses, such as high surface areas and defined pore structures, with the chemical functionality and physical properties of organic materials. Their distinct feature is the presence of organic groups incorporated into the channel walls of a mesoporous structure.

We introduced an “all-in-one approach” controlling functionality and porosity of organosilicas by using a specially designed monomer, combining the features of a surfactant and a silica precursor (see Fig. 5) [12].

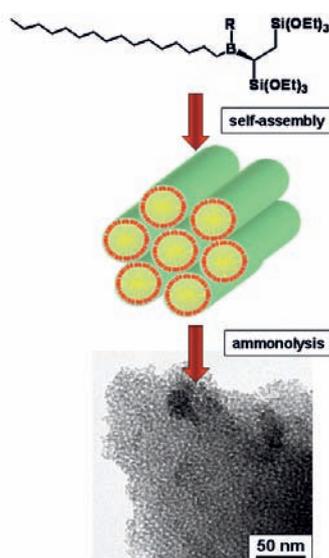


Fig. 5: All-in-one approach for the synthesis of functional mesoporous materials

These monomers self-organize when hydrolysis of their inorganic part takes place via an aggregation of their organic parts into hydrophobic domains. Porous materials are made from these monomers via a condensation/ammonolysis sequence, while the monomer architecture ensures an exclusive arrangement of functional groups along the channel interfaces. Recently this approach was extended to the preparation of chiral mesoporous organosilicas [13].

A. Thomas, M. Bojdys, R. D. Cakan, A. Fischer, F. Goettmann, A. Ide, P. Kuhn, P. Makowski, F. Roohi, M. M. Titirici, J. Weber, M. Antonietti
arne.thomas@mpikg.mpg.de

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Synthesis and Characterization of Self-assembled Inorganic Materials



Bernd Smarsly 21.12.1971

1998: Diploma, Physical Chemistry
(University of Marburg, Germany)

Thesis: Structure investigations of phenylalkyl-substituted poly-(p-xylylene)s

2001: PhD, Physical Chemistry
(University Potsdam)

Thesis: Characterization of porous materials by small-angle scattering techniques

2002-2003: Postdoc
(University of New Mexico, Albuquerque, USA)

Since 2003: Group Leader
(Max Planck Institute of Colloids and Interfaces, Potsdam)

Various “classical” inorganics are supposed to possess advanced properties if scaled down to the nanometer region. If prepared in the form of materials with pores on the nanometer scale (“mesopores”, pore size 3-50 nm), especially carbonaceous materials and metal oxides offer attractive fields of applications requiring strong interaction with other molecules or ions, e.g. in catalysis, sensing, chromatographie and electrochemical processes. Meanwhile, different sol-gel strategies, based on self-assembly of surfactants, are known to obtain such materials in form of powders. However, a lot of devices require crack-free thin coatings of such mesoporous metal oxides. Our research in this project is dedicated to the generation of such mesoporous layers and also the development of suitable characterization methods (pore size, pore shape and arrangement, etc.). Finally, we aim to understand if the porosity and down-scaling to nanometer-sized crystals indeed results in better physico-chemical properties, e.g. in terms of the sensibility of sensing, storage of electric energy, etc. Recently, we described a general methodology for the generation of diverse metal oxides as homogeneous coatings with highly ordered 3D mesopores of ca. 14 nm in diameter, taking advantage of evaporation-induced self-assembly in combination with novel types of block copolymers [1]. Such films usually have to be prepared in the crystalline modification, because the physico-chemical functionality (sensing, catalysis, etc.) is only exhibited by a highly crystalline oxidic matrix. Here we present exemplarily mesoporous WO_3 (tungsten oxide) films, which is industrially used for the coloration of glass. WO_3 is an ideal model system, because it exhibits a reversible color change (transparent-blue) upon reversible electrochemical reduction/oxidation between W(VI) and W(V) and insertion/desertion of Li^+ or H^+ ions, respectively. These color changes can be easily detected and quantified in terms of the coloration efficiency, the switching time, etc., and related to the porosity and crystallinity of the material. Since current devices based on dense, non-porous WO_3 -coatings (e.g. WO_3 -covered rear-back mirrors) suffer from relatively slow (de)coloration times, a highly mesoporous, crystalline WO_3 film should theoretically show improved performance owing to the facilitated diffusion of the electrolyte in and out the WO_3 film through the pores. The well-defined mesostructure is well seen by microscopic techniques (Fig. 1), revealing arrays of almost monodisperse spherical mesopores, which

are slightly deformed. The films have a thickness between ca. 100 and 1000 nm. However, microscopic techniques inevitably present only local information about the structural order. To test the overall quality of the mesostructure over larger areas, we have developed special small-angle x-ray scattering (SAXS) techniques to study the mesostructure in such thin film. In essence, the films are prepared on ultrathin Si wafers, which can be penetrated by x-ray beams. Using our in-house rotating anode setup, equipped with a specially designed sample-holder and a 2D area detector, even thin films of only 100 nm in thickness can be investigated. Fig. 2 shows typical 2D SAXS patterns of mesoporous WO_3 films. SAXS analyses reveal that these patterns are attributable to a body-centered cubic (BCC) packing of 14 nm spherical pores with a pore-to-pore distance of ca. 22 nm.

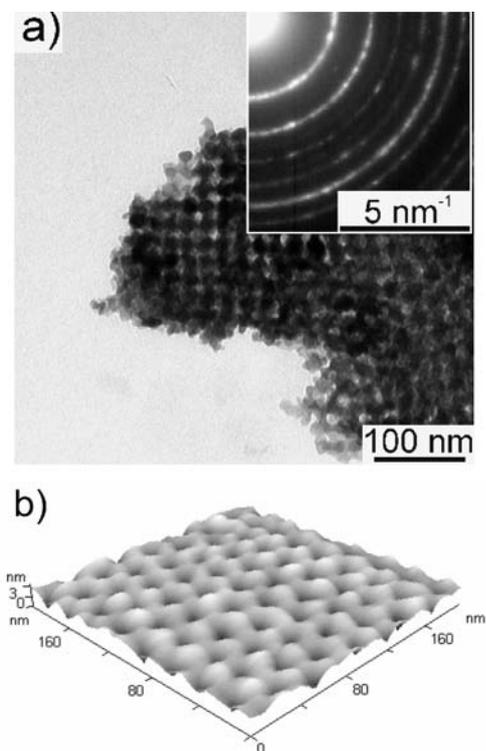


Fig. 1: Microscopic characterization of WO_3 films.

a) Transmission Electron Microscopy and electron diffraction (inset) of.
b) Atomic Force microscopy (tapping mode).

Since the X-ray beam can be scanned over the specimen, such experiments allow to study the macroscopic homogeneity of thin mesostructured coatings. Also, only 2D SAXS measurements allowed to determine the orientation of the mesostructure. In contrast to powder materials, mesostructured films often exhibit a preferred orientation of the mesostructure relative to the substrate, in this case a [110] orientation of the BCC mesopore arrangement

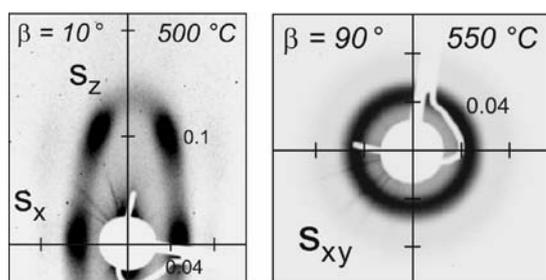


Fig. 2: 2D-SAXS patterns of WO_3 films treated at high temperature (to induce crystallization) as a function of the angle of incidence, between the x-ray beam and the film surface. The scattering vector s is given in units of nm^{-1} .

In order to understand, if such mesoporous, crystalline films indeed show improved physico-chemical performance, the coloration behaviour of WO_3 films was studied during the electrochemical oxidation/reduction process. As a suitable criterion, we used the "coloration efficiency" η , which basically describes a measure for the color depth (blue) per applied charge. η was determined as a function of the porosity and degree of crystallinity. Since usually windows may be exposed to varying temperatures (sun-light), also the operation temperature was varied. Such experiments (Fig. 3) reveal interesting trends regarding the influence of the structural parameters (porosity, crystallinity). First, mesoporous WO_3 films show a significantly faster coloration switching response between blue and transparent state on the order of several seconds only (not shown), owing to the better accessibility of the WO_3 nanocrystals, which is ca. 3 times faster than non-porous films. Second, the coloration behaviour itself is substantially influenced by the state of WO_3 . We found that only mesoporous WO_3 films with a high degree of crystallinity showed good electrochemical stability and coloration efficiency, while mesoporous films with an amorphous or only partially crystalline matrix lack sufficient stability upon long-term treatment and exposure to higher temperatures, i.e. harsh environmental conditions. Furthermore, also the absolute values of the coloration efficiency were good taking into account the relatively low film thickness. In conclusion, these experiments demonstrated that mesoporous films of metal oxides indeed show improved electrochemical properties. Similar results were obtained for other mesoporous metal oxide films (TiO_2 , ITO) [3].

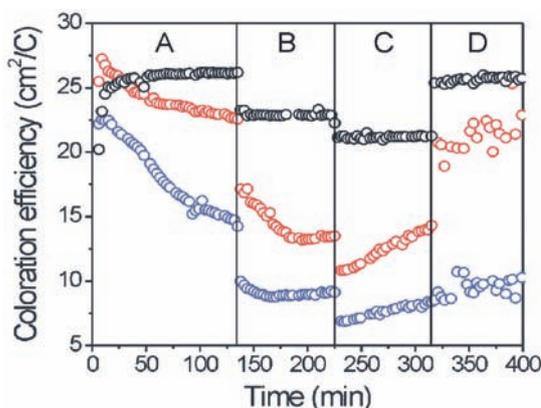


Fig. 3: Coloration efficiency of mesoporous WO_3 thin films with varying degrees of crystallinity (tuned by different heat-treatment temperatures) as a function of the operating temperature. The notation of films is as follows: amorphous (blue circuits), partially crystalline (red circuits), and fully crystalline (black circuits). A, B, C and D correspond to the following operating temperatures: 20 °C, 50 °C, 70 °C and 20 °C (after cooling from 70 °C).

B. Smarsly, M. Antonietti, Philipp Adelhelm, Torsten Brezesinski, Laemthong Chuenchom, Helena Kaper, Regina Rothe, Sébastien Sallard, Özlem Sel, Wu Jin-Ming, Wang Yude
bernd.smarsly@mpikg.mpg.de

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Fractionating Colloid Analytcs



Analytical Ultracentrifugation (AUC) and Field-Flow fractionation (FFF) are powerful fractionating analysis methods for colloids and polymers. AUC is available as an active service unit for a large variety of colloid and polymer analysis problems from the institute and external cooperation partners [1-4]. We have three main working directions in this project: a) detector development b) method development

c) colloid and polymer characterization. For the latter, special emphasis was laid on complex polymer and supramolecular systems as well as polymer-inorganic hybrid particles, which are very difficult to characterize by other analytical methods. One example is Zn metallosupramolecular architectures, where AUC could prove the molecular integrity of the defined and monodisperse metallosupramolecular complex in solution [1].

A second generation dendronized polymer resulting from free radical polymerization of the macromonomer could also successfully be characterized in terms of molar mass and polydispersity as an example for polydisperse polymers with a very high molar mass $> 10^6$ g/mol [2]. The results were found in good agreement with those from other analytical techniques but AUC could yield a distribution instead of average values from other techniques like light scattering.

AUC is a versatile analytical technique, which can be applied to many more analytical questions than the traditional molar mass or sedimentation coefficient distribution. For the example of microgels containing partially uncrosslinked material, the amount of each component can be quantitatively determined [3]. However, the sedimentation coefficients depend on friction and a sedimenting swollen microgel has a higher friction and thus lower sedimentation coefficient compared to the unswollen microgel. Therefore, the swelling degree can be calculated from the sedimentation coefficients of swollen and non-swollen samples. Determining the sedimentation coefficient distribution of swollen and deswollen microgels for the first time enabled the determination of a swelling degree distribution as shown in Fig. 1. Despite some instability of the evaluation at the highest swelling degree of the weakly cross-linked microgel, the swelling degree distributions allow for a detailed analysis of the homogeneity of cross-linking, which is expressed in a narrow swelling degree distribution.

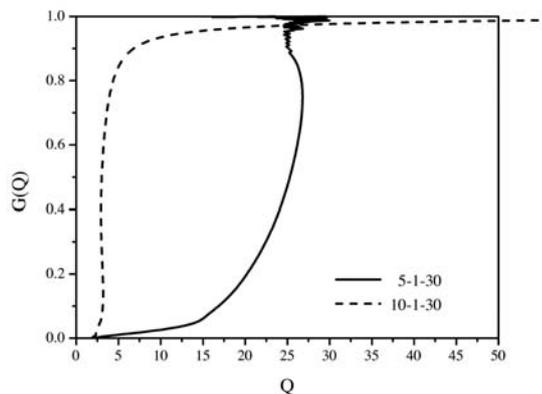


Fig. 1: Integral volume degree of swelling distributions evaluated from sedimentation coefficient distributions in the collapsed and swollen state for a highly crosslinked (10-1-30) and weakly crosslinked (5-1-30) microgel of poly(N-isopropylacrylamide) (NIPAAm).

However, in the present example, it can be seen that the highly cross-linked microgel (10-1-30) has a tailing towards higher swelling degrees meaning that ca. 5% of the microgels are more weakly crosslinked. In turn, the weakly cross-linked microgel has a similar fraction of more cross-linked microgels.

The integrity of organic-inorganic hybrid particles can also advantageously be investigated by AUC. In case of DNA coated hydroxyapatite, which was synthesized in several layers for gene transfection applications, the formation of DNA resp. hydroxyapatite shells could be shown directly in solution and the integrity of the nanoparticles was demonstrated [4]. This is another application taking advantage of the fractionating capability of an AUC to detect all components present in a complex mixture.

Another focus of our work was the development of new experimental methods for AUC. By sedimentation of a polyacid like poly(styrene sulfonate) under salt free conditions, a pH gradient spanning a few units of pH can be built up in the AUC cell. If charged particles are sedimented in such gradient, information about their charge or aggregation behaviour can be deduced as was demonstrated for gold colloids with different charge [5].

Helmut Cölfen 24.07.1965

1991: Diploma, Physical Chemistry

(University of Duisburg)

Thesis: Analytical

Ultracentrifugation of Gels

1993: PhD, Physical Chemistry

(University of Duisburg)

Thesis: Analytical Ultracentri-

fugation of Gels

1993-1995: Postdoc (National Center

for Macromolecular Hydrodynamics,

University of Nottingham)

Since 1995: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Potsdam)

2001: Habilitation, Chemistry

(University of Potsdam)

Thesis: Biomimetic Mineralisation

Using Hydrophilic Copolymers:

Synthesis of Hybrid Colloids with

Complex Form and Pathways towards

their Analysis in Solution

Since 2004: Private Docent;

University of Potsdam

If hybrid colloids or very small colloids are investigated by AUC, the determination of the particle density is often problematic, as the samples can exhibit a density distribution. This could in principle be accessed by density gradient ultracentrifugation for densities up to 2 g/ml. However, particle stability issues hinder the application of salts and organic solvent mixtures endanger preferential solvation problems. Application of the density variation method running experiments in H₂O and D₂O combining the respective sedimentation coefficient distributions can circumvent this problem and can yield density distributions with a quite robust determination of the particle density [6]. This method appears promising for the analysis of hybrid organic-inorganic as well as nanoparticles with higher density by AUC.

The improvement of the AUC detection systems is of great importance for colloid analysis by AUC to derive more information on the fractionated samples. We have therefore continued our development of a UV-Vis multiwavelength detector as well as Raman and small angle laser light scattering detector in cooperation with the BASF AG.

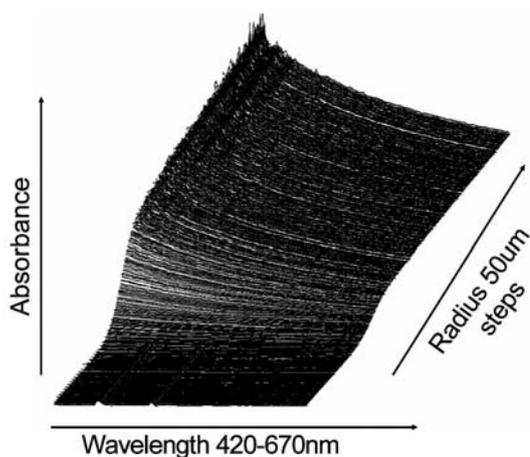


Fig. 2: Radial Scan for a 175 nm polystyrene latex sample (10000rpm, 25°C).

The UV-Vis multiwavelength detector could be advanced to a prototype stadium including hard- and software development and the quality of the experimental results be improved [7]. The detector has two main advantages: Speed and simultaneous detection of a whole UV-Vis spectrum instead of a single wavelength as in all previous analytical ultracentrifuges. This is shown in Fig. 2. The additional spectral information allows for example for multiple sensitivity in the investigation of colloid particle size distributions as the turbidity is wavelength dependent. Therefore, small colloids can advantageously be investigated at smaller wavelengths, bigger colloids at a higher wavelength, which is advantageous if particles with very broad particle size distributions or multi-component mixtures are to be investigated. Multiple wavelength detection is also useful to average information over several wavelengths to improve the signal to noise ratio or to investigate complex mixtures with multiple chromophores. Generally, the increase in the data space by a further dimension increases the information content of an experimental scan very much.

The detector also allows for the application of a speed profile with a fixed detector position, where all particles pass the detector at a defined speed. This is useful if unknown samples or samples with very broad sedimentation coefficient distributions are to be investigated.

Another detection system which is improved is the Rayleigh interference optics, which is currently installed on the commercial instrument. Application of a larger camera as detector as well as of a new laser mount should significantly improve the data quality of this optical system as more data are captured and the light source is mechanically decoupled. We hope that improvement of this detector together with the multiwavelength detector will enable faster measurements with much more information content than present to date on a routine basis. This is important to enable the investigations of increasingly complex colloidal systems.

H. Cölfen, A. Völkel, S.K. Bhattacharyya, A.M. Gülsün,
H.B. Cicek, M. Strickhausen, H. Strauss
Coelfen@mpikg.mpg.de

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Electron Microscopic Studies of Colloidal Systems and Biomaterials



Jürgen Hartmann 18.10.1953

1977: Diploma, Physics

(Humboldt University Berlin; Institute of Low-Temperature Solid State Physics)

Thesis: Application of Square-Wave Polarography and a Density Method for the Analysis of Bismuth-Antimony Alloys

1977–1991: Research Scientist

(Institute for Polymer Chemistry, Teltow)

1987: PhD, Polymer Physics

(Institute of Polymer Chemistry, Teltow)

Thesis: Contribution to the Formation Mechanism of Coagulation Structures of Polymers Using Electron Microscopy

1992–1995: Research Scientist

(Max Planck Institute of Colloids and Interfaces, Potsdam)

Since 1995: Group Leader

(Max Planck Institute of Colloids and Interfaces, Potsdam)

Transmission, high-resolution scanning and environmental electron microscopy are suitable tools to investigate the morphological structure of polymer micelles and particles, organic and inorganic crystals and nanoparticles, aggregates of biopolymers, poly-electrolyte complex shells, composite materials and naturally-grown biomaterials. The determination of structural parameters like the size and size distribution of colloidal particle systems, the pore size of polymeric and inorganic networks, the spatial arrangement of crystallites and the determination of crystal structures are the main aspects of our electron microscopic research. Because of the organization of the institute, there is a close cooperation with a number of research groups of the colloid chemistry, interface and biomaterials departments. Some of the interesting results are presented here.

An especially fascinating class of crystals are colloidal crystals with non-spherical and perfectly-aligned building blocks. The crystallization of organic molecules, e.g. amino acids, controlled by double hydrophilic block copolymers (DHBC's) such as poly(ethylene glycol)₃₀₀₀-((L-Glutamic Acid)-(L-Glutamic Acid)-(L-Serine))₁₁₀₀ (PEG-EES) are suitable for studying the nanoparticle formation of DL-alanine and their self-assembly and subsequent mesoscopic transformation to core-shell and hollow alanine rods.

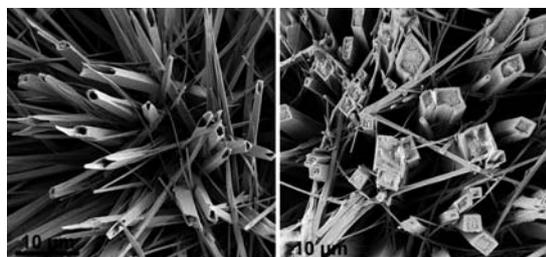


Fig. 1: DL-alanine tubes formed under supersaturated conditions in the presence of 3.3 gL⁻¹ of PEG-EES (left) and of 0.67 gL⁻¹ PEG-EES (right) at room temperature.

Whereas the normal crystallization of DL-alanine from a supersaturated solution in the absence of additives results in compact needle-like crystals, the use of PEG-peptide conjugate as a crystal growth modifier generates elongated DL-alanine crystals with tubular characteristics (**Fig.1**). The main axis is longer than 50 μm , the tubes have diameters of about 1-2 μm and the wall thickness is in the range of 80-120 nm. Some of the crystals have square cross-sections. At lower PEG-EES concentrations, the rate of crystallization of DL-alanine and the number of crystals are decreased and the diameters of the aggregated nanoparticles are about 200 nm and they are located inside the tubes (**Fig. 1**). The edge lengths of the core-shell structure are in the range of 2-4 μm and the maximum length of the tubes is longer than 100 μm . The tube-like crystals illustrates the morphology control provided by the DHBC.

A different type of solidification is the crystallization of microdroplets consisting of amino acids and oppositely charged polyelectrolytes in ethanol/water mixtures. For the basic amino acids L-lysine and L-histidine, polyacrylic acid ($M_w = 2000 \text{ g mol}^{-1}$) is used as a cationic polyelectrolyte. To promote the crystallization, the amino acid concentration has to be increased up to 10 wt%. The diameters of the grown spherical crystalline superstructures are in the range of 10-100 μm . The more or less radially-aligned smaller platelet-like crystals with a diameter of few microns and a thickness of around 30 nm are forming spheres of high inner surfaces (**Fig. 2**). L-lysine usually forms compact, irregular, elongated crystals with a size of 50 to 400 μm . The thin platelet-like crystal growth indicates the morphology control provided by the cationic polyelectrolyte.

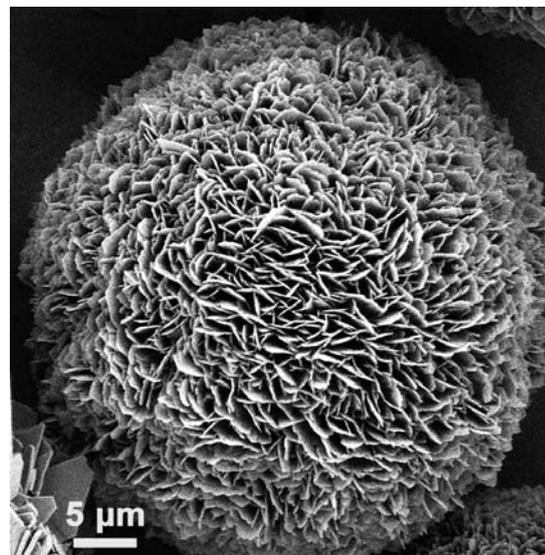


Fig. 2: L-lysine crystal superstructures.

One of the main projects is the electron microscopic investigation of gold-patterned, spherical, colloidal, particles. Using the upper single or double layers of colloidal crystals as masks during gold vapour deposition, various gold patterns were successfully produced on the surfaces of the spheres in lower regions (**Fig. 3**). The gold atoms reach the spheres in the second layer only through interstices between the top layer spheres. The dimension and geometry of the generated gold patterns depends on the particle size, the structure of the colloidal crystal templates, the number of upper layers, and the time of plasma etching.

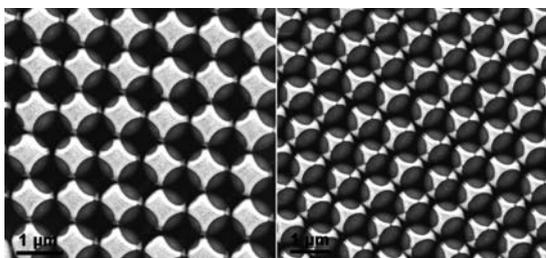


Fig. 3: Gold-patterned polystyrene (PS) particle sur-faces generated by templating the top monolayers of colloidal crystals with preferential crystal orientation of (100) (left) and gold-coated PS colloidal crystals, etched by O_2 - plasma for 10 min. The preferential orientation of the crystal is (111) parallel to the sub-strate (right).

An interesting example for the combination of electron microscopy and elemental analysis is the control of the preparation of hierarchical molecular imprinting of polymer (MIP) materials. After immobilisation of target molecules on the surface of a mesoporous inorganic substrate, followed by a complete pore filling appropriate monomer mixture, subsequent polymerisation and removal of the inorganic support the final MIP material is produced. To investigate the internal structures an effective embedding technique for ultra-thin sectioning of the composite materials was developed. The structure of the mesoporous silica precursor and imprinted polymer composite and the pure imprinted polymer material is shown in Fig. 4.

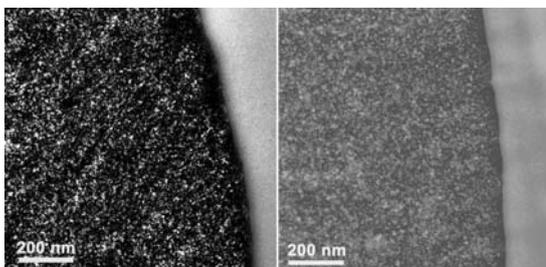


Fig. 4: Ultra-thin section of the porous silica template (left) in the presence of the hierarchical imprinted polymer of the dipeptide sequence *H*-phenylalanine-glycin-Si and the pure imprinted polymer material after removal of the silica matrix (right).

The electron microscopic investigations indicate that the porosity of the replicated polymeric material is of the same order of magnitude as in the silica template.

The success of the imprinting process is also checked by measuring the carbon content of the silica precursor/imprinted polymer composite and the determination of the silica content of the imprinted polymers after removal of the silica template by treatment with aqueous solution of NH_4HF_2 by EDX spectroscopy (Fig. 5).

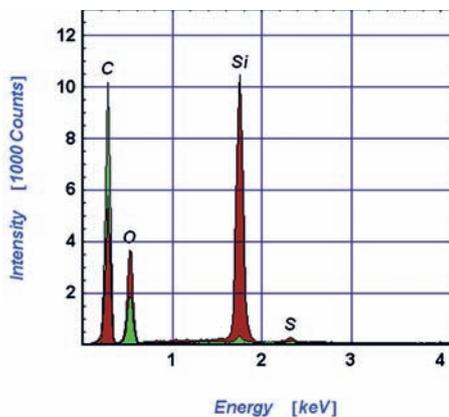


Fig. 5: EDX spectra of the silica/polymer composite (brown curve) and of the imprinted polymer material (green curve).

Another example of the formation of hierarchical structured materials is the inorganic nanoparticle casting of wood, which is well suited as a template. The cell-wall layers consist of parallel arrays of cellulose fibrils embedded in a matrix of hemicelluloses and lignin. To obtain cellulose/nanoparticle composites $Ce_{0.5}Zr_{0.5}O_2$, nanoparticle sols (particle diameter ≈ 1.5 nm) were incorporated into the native tissue. After drying and slow calcination at $500^\circ C$, mechanically stable, pure, inorganic materials were formed. It is shown in Fig. 6 that the templating occurs at the level of the cellulose microfibrils and not at the level of the fibrillar aggregates.

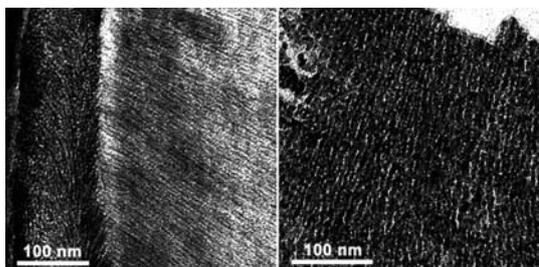


Fig. 6: Ultra-thin cross section of impregnated and dried compression wood tissue (left) and after calcination (right)

The spacing between the dark filaments representing the inorganic nanoparticles for the impregnated sample is around 2-4 nm which is consistent with the diameter of cellulose fibrils, and is about double sized in the calcined sample. After calcination the nanoparticles are partly coalesced and sintered together, but they represent the typical fibrillar structure of the cellulose.

In the future, more detailed electron microscopic investigations of the spatial distribution of inorganic compounds in hierarchically structured biomaterials are of special interest.

J. Hartmann, H. Cölfen, H.G. Börner, S. Wohlrab, M.M. Titirici, D. Wang, O. Paris, H.S. Gupta, I. Burgert, A. Deshpande
juergen.hartmann@mpikg.mpg.de

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Light Scattering at Interfaces



Soft interfacial structures are of high interest because of their ability to react on an external excitation. Abundant examples are found in biological interfaces. Life relies on function of the constituting structures, and this function is induced by a suitable stimulus. Target of research are such soft structures at interfaces, especially the spherical interfaces of dispersed colloidal particles and planar liquid-air or liquid-liquid interfaces. Intrinsically tied to soft degrees of freedom are fluctuations. They can be used for the detection of softness and, correspondingly, of function. For bulk samples, light scattering is a well established tool to detect fluctuations. The team focuses on the development and the application of interface sensitive light scattering techniques for the characterization of soft, functional interfaces.

Reinhard Sigel 14.03.1965
1992: Diploma, Physics
 (Albert-Ludwigs-Universität Freiburg)
 Thesis: Stress Optical Behaviour of Liquid Crystalline Elastomers
1997: PhD, Physics
 (Albert-Ludwig University of Freiburg)
 Thesis: Investigation of the Nematic Wetting Layer in an Isotropic Liquid Crystal by Evanescent Wave Light Scattering
1997-1998: Postdoc
 (Albert-Ludwig University of Freiburg)
1998-2000: Postdoc
 (Institute of Electronic Structure and Laser, Heraklion, Crete, Greece)
Since 2000: Group Leader
 (Max Planck Institute of Colloids and Interfaces, Potsdam)

Colloidal Interfaces

Ellipsometric light scattering is a technique developed in our group for the characterization of thin interfacial layers on dispersed colloidal particles [1]. Its working principle is similar to classical reflection ellipsometry, where the reflection at the planar interface is replaced by a scattering process. Data evaluation is based on Mie scattering theory.

As an application, the salt concentration around charged stabilized colloids was investigated [2]. Unexpectedly, there is a transition from a low salt concentration compatible with a Poisson-Boltzmann description to a rather high concentration within a layer around the colloidal particles. This sudden transition at a defined average salt concentration has been identified as a first order pre-wetting transition at the colloidal particles interface.

Vesicles composed of DPPC (1,2-Dipalmitoyl-sn-glycero-3-phosphocholine) are anisotropic spherical shells. The two parameters of ellipsometric light scattering, $\tan(\Psi)$ and Δ , show a high sensitivity on this anisotropy, as displayed in Fig. 1. While for isotropic shells the minimum of $\tan(\Psi)$ and the step in Δ is expected at a scattering angle Θ larger than 90° , they are found below 90° for the anisotropic vesicles. The quantitative evaluation of these data yields an order parameter $S=0.71$ within the vesicle shell [3], corresponding to an average tilt angle β larger than 29° . This lower limit fits well to the value $\beta=32^\circ$ found in planar DPPC-layers. Packing arguments confirm, that the effect of the layer bending in the vesicles is negligible for this rather low curvature.

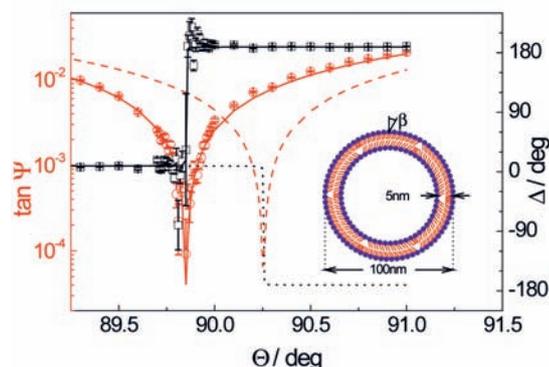


Fig. 1: Ellipsometric data $\tan(\Psi)$ (red) and Δ (black) versus the scattering angle Θ for DPPC vesicles. The broken lines mark the expected behaviour of a vesicle with an isotropic shell. The inset shows a sketch of a vesicle with an anisotropic shell.

As an experimental improvement, a new apparatus for spectroscopic ellipsometric light scattering was built up. Measurements at several wavelengths of light are expected to yield a substantial increase in resolution. The usage of a camera as a two dimensional detector drastically speeds up the measurements, so multi wavelength measurements are feasible in a reasonable amount of time. First data on charge stabilized colloidal of 100nm radius are shown in Fig. 2. There is a characteristic evolution of the position and the depth of the minimum of $\tan(\Psi)$. In parallel, the position and the slope of the step in Δ change. While at large wavelength the step goes from $\Delta=0^\circ$ to $\Delta=-180^\circ$, it is reversed to a step $\Delta=0^\circ$ to $\Delta=180^\circ$ at short wavelengths. The wavelength where the transition of the step direction occurs is highly sensitive on the thickness of a layer on the colloidal particles. Its detection is the basis of the improvement in resolution.

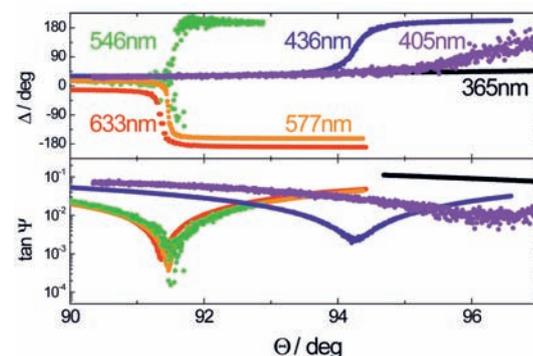


Fig. 2: Ellipsometric parameters Δ and $\tan(\Psi)$ versus the scattering angle Θ for several wavelengths of light (as indicated in the plot).

Fluctuations at Planar Liquid-Fluid Interfaces

Fluctuations close to a planar interface can be accessed by light scattering with an evanescent wave illumination. This interface wave with a penetration depth comparable to the light wavelength is created in a total internal reflection geometry. While such experiments were so far restricted to solid-liquid interfaces, we built up a new apparatus for an investigation of the water-air or the water-oil interface. As an essential step, the procedure of optical adjustment and clean sample preparation were optimized to meet the high experimental demands. The scattering contribution of capillary waves depends strongly on the angle of incidence. It can be distinguished from other scattering contributions, e.g. concentration fluctuations close to the interface.

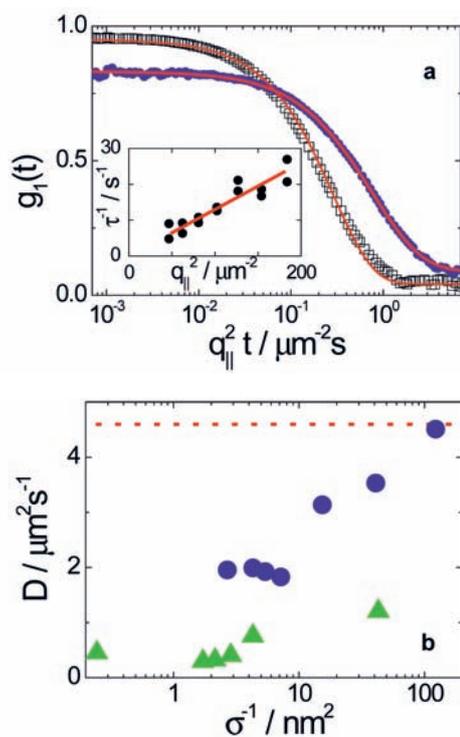


Fig. 3: Dynamic light scattering data of a polyisoprene-polystyrene block copolymer at the water-air and the water-dodecane interface. (a) Comparison of the field correlation function $g_1(t)$ for the water-air interface (\bullet , $\sigma^{-1}=7\text{nm}^2$) and for bulk scattering (\square) versus a reduced time scale. The inset shows the inverse relaxation time τ^{-1} versus the squared scattering vector component tangential to the interface, q_{\parallel} . The slope yields the diffusion constant D . (b) D versus the nominal interface area σ^{-1} per molecule for the water-air (\bullet) and the water-dodecane (\blacktriangle) interfaces. The dotted red line indicates the bulk diffusion of the polymer below the critical micelle concentration.

Target of the investigations was a comparison of the dynamics of a polyisoprene-polyethyleneoxide block copolymer sample at the water-air and the water-dodecane interface.

Fig. 3a shows field auto-correlation functions for scattering at the water-air interface and in bulk water (concentration below the critical micelle concentration). The quadratic dependency of the inverse relaxation time τ^{-1} on the tangential component q_{\parallel} of the scattering vector, as shown in the inset, hints to a two dimensional diffusion within the interface. The evolution of the diffusion constant D for varying nominal interface area per molecule, σ^{-1} , is depicted in Fig. 3b. D decreases with decreasing σ^{-1} . Also included in Fig. 3b is the diffusion of the same polymer at the water-dodecane interface. The lowering of D compared to the air-water interface exceeds the effect expected from the additional friction of the dodecane part. Analogous to data evaluation in bulk light scattering, this can be interpreted as an enhanced two dimensional hydrodynamic radius. For the water-dodecane interface, the diffusing entities consist of several block copolymer molecules.

Colloid Characterization by Bulk Light Scattering

Classical bulk light scattering was applied for the characterization of several colloidal systems. A first example is an investigation of emulsified liquid crystals [4]. In addition to a size measurement by dynamic light scattering, temperature dependent depolarized light scattering yields the phase behaviour of the liquid crystal within the droplets. There is a decrease over 20K of the phase transition temperature compared to the bulk value, which, however, probably rather reflects the presence of impurities than effects of finite size or curvature. It was shown, that at finite values of the scattering vector the internal director fluctuations within the droplets affect the dynamic light scattering data.

In cooperation with the biomaterials department, the temperature dependent aggregation of amelogenin nanospheres was investigated [5]. Amelogenin is a biopolymer which plays an essential role in the tooth formation. While small angle X-ray scattering shows that the nanospheres remain intact as individual entities, dynamic light scattering detects an irreversible aggregation of those nanospheres above a temperature of 40°C.

R. Sigel, A. Stark, A. Stocco, B. Schonert
sigel@mpikg.mpg.de

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