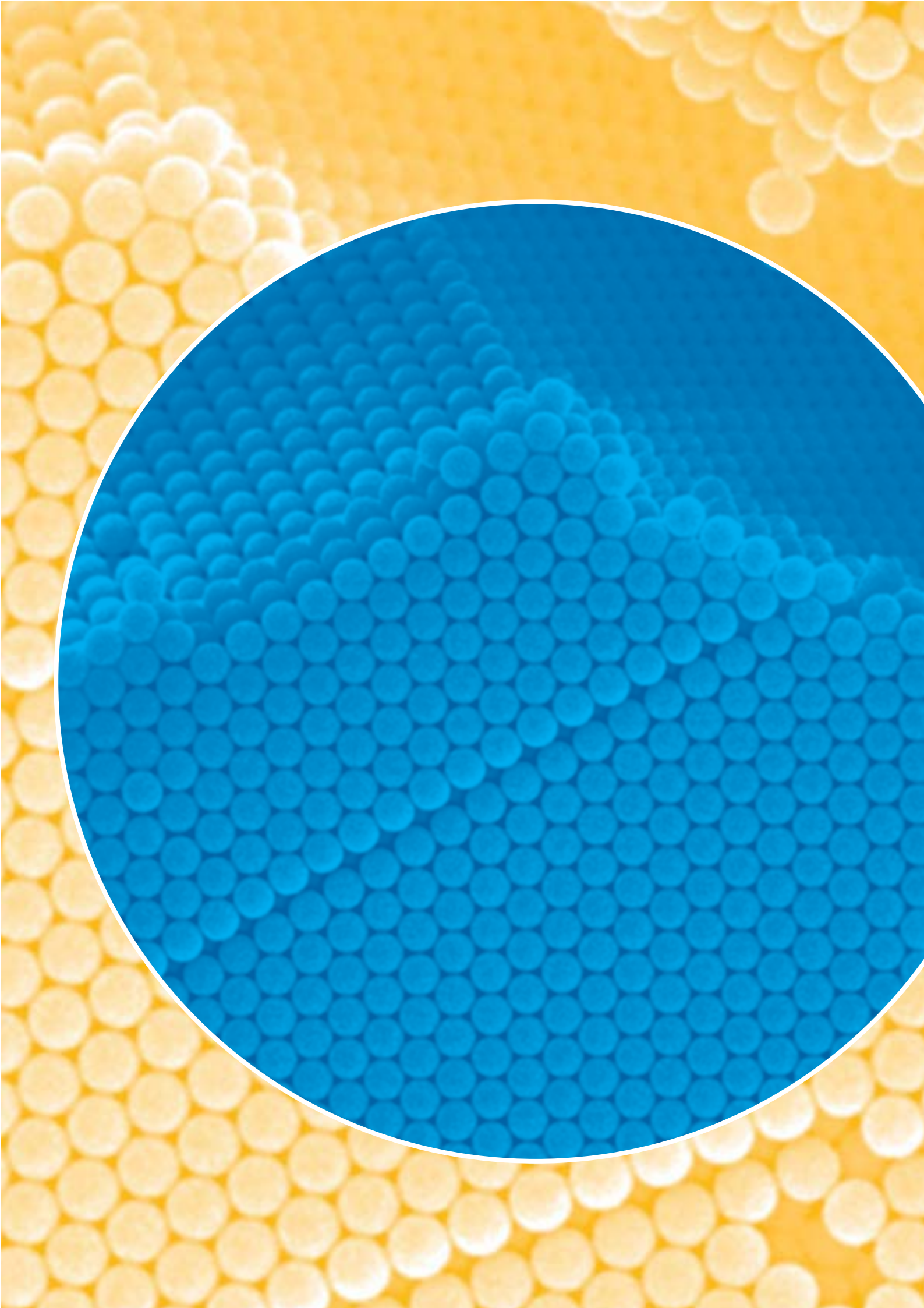




COLLOID CHEMISTRY

COLLOID CHEMISTRY



# Research in the Department of Colloid Chemistry

## Scientific Profile

The activities of the Colloid Chemistry Department are a mixture of "old" strongholds found in the former Institute, activities brought by the director, and new topics developed by young researchers. The overall size of the department is 60 people, covering a wide range of research topics.

The effective constituting elements of the group are "projects", a structure headed by senior scientists involving 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 reevaluate 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 of the institute.

Incentives for the choice of a new research direction are usually scientific curiosity and promise, but research is 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 came from the outside. In detail, the following topics are treated by 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.

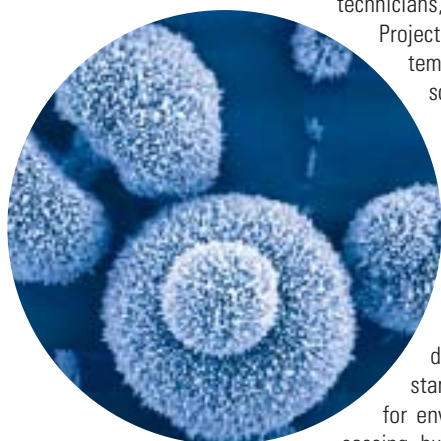
Central points of interest of the project teams working on heterophase polymerization are:

- to gain a better understanding of the nucleation period and particle formation. For this purpose, new experimental on-line multidetection techniques are developed and supplemented by theoretical approaches (Dr. Klaus Tauer).
- to simplify the synthesis of complex polymer molecules (e.g. block & graft copolymers) and colloids (e.g. core-shell latices, reinforced materials) by emulsion polymerization and rational use of the particle interfaces (Dr. Klaus Tauer).
- Inisurfs, Transsurfs, and Surfmers, and new stabilizers for better polymer dispersions (Dr. Klaus Tauer).

## Self-organizing Polymers

Amphiphilic polymers consist of components with 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 "extreme" 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).
- 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. Helmut Schlaad).
- 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 copolymers 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 synthetic block. We also expect that such polymers help to address the interface between the biological and technical world (Dr. Hans Börner).





### Mesoporous Materials & Nanoparticles

Template routes have recently been extended to surfactant assemblies. Our contribution in this field is the use of more robust and adjustable polymer and colloidal templates which allows a real "nanocasting", i.e.

a 1:1 replication of the original soft matter template into an inorganic nanostructured replica. Current activities in this field include:

- the employment of membranes and beads as supports for designer catalysts where nanoparticle formation is an integral part of the nanostructure set-up and profitably controlled by either the porogens or the pore geometry (Dr. Markus Niederberger, the "Zeit-Project" together with the Fritz Haber Institute).
- the synthesis of new well defined nanoparticles with function by solvent and ligand assisted synthetic pathways and their self-assembly into organized 3D superstructures by ligand encoding (Dr. Markus Niederberger)
- the use of nanocasting as an analytical tool, i.e. to characterize fragile soft matter superstructures, such as the worm-like assemblies of cyclodextrines or other supramolecular entities (Markus Antonietti)
- 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 (Markus Antonietti)
- the generation of crystalline thin mesoporous layers by evaporation induced self-assembly (EISA) for catalysis, electrochemistry and sensing (Dr. Bernd Smarsly)



### Modern Techniques of Colloid Analysis

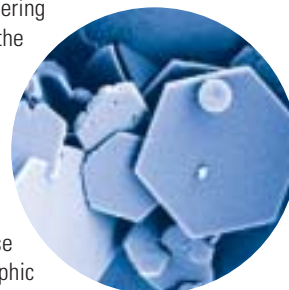
All the work described above is necessarily accompanied by a considerable amount of colloid analysis. This includes fully commercial techniques, but also implies the development of new techniques or methods of data handling, as:

- 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 (Dr. Helmut Cölfen).
- special techniques of transmission and scanning electron microscopy on soft, structured matter (Dr. Jürgen Hartmann).
- the improvement of diverse techniques of hydrodynamic chromatography such as thermal field flow fractionation and asymmetric flow field flow fractionation (Dr. Helmut Cölfen)
- computational analysis of high precision static light scattering experiments (Dr. Gudrun Rother)
- development of new techniques of dynamic light scattering to colloidal systems, e.g. using optical near fields or the "ellipsometric light scattering" (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 ultracentrifugation, 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.



Markus Antonietti,  
Director of the  
Department  
of Colloid  
Chemistry

## Heterophase Polymerizations – Polymer Dispersions



### Controlled Radical Polymerization in Aqueous Heterophase Polymerization (S. Nozari)

The field of controlled radical polymerization has been, and continues to be, one that carries strong interest from both the academic and industrial polymer communities. Among the various techniques to tame free radical polymerizations the reversible addition fragmentation chain transfer (RAFT) process is one of the most recent developments, since only 6-7 years, but one of the more efficient methods in this field regarding versatility and robustness. In a comprehensive experimental study the possibilities of controlling *ab-initio* aqueous heterophase polymerizations via the RAFT process with hydrophobic dithioester transfer agents were investigated. Special emphasis was placed on the interplay between the hydrophilicity/hydrophobicity of both the RAFT agents and the primary initiator radicals.

Fig. 1

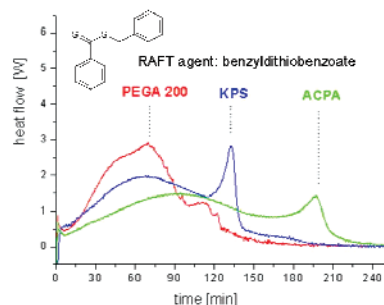
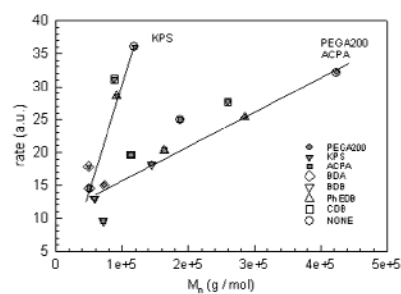


Fig. 2



Conditions

Recipe:

80 g of water, 4 g of 5% aqueous SDS solution, 20 g of Styrene,  $4.26 \cdot 10^{-4}$  mole of RAFT agent,  $3.41 \cdot 10^{-4}$  mole of initiator,  $T = 80^\circ\text{C}$ , reaction calorimeter CPA200, in all runs complete conversion

The selected data in **Figs. 1** and **2** confirm that in RAFT aqueous heterophase polymerizations the achievable average molecular weight and the average rate of polymerization can be tailored by the proper choice of both the initiator and the RAFT agent [1]. Among the RAFT agents investigated benzyl dithioacetate leads to the highest degree of control as expressed by the lowest polydispersity index of the molecular weight distribution with 1.5 compared with 4 for the uncontrolled polymerization.

### Interfacial Energy Promotes Aqueous Heterophase Polymerization (N. Öz, DD. He, S. Nozari)

It was found [2] that aqueous heterophase polymerization can be carried out at room temperature without redox-systems if the surfactant concentration is above the critical micelle concentration and the initiator concentration is greater than 6 mM (**Fig. 3**). This effect was observed for different initiators regardless they are water- or oil-soluble and various types of surfactants (anionic, cationic, nonionic, monomeric, and polymeric).

Fig. 3

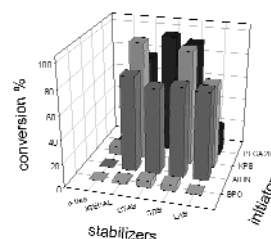
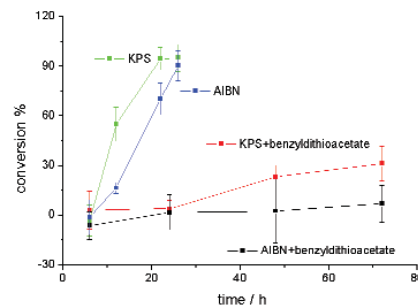


Fig. 4



Conditions

Recipes:

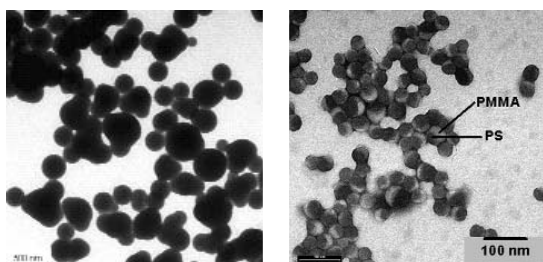
Fig. 3:  $25^\circ\text{C}$ , 36 hours, rotation thermostat, 10 g of water, 0.1 g of stabilizer, 0.67 ml of styrene, 60 mg of initiator, (e-free : stabilizer-free)

Fig. 4: as for Fig. 3 but 0.02 g of AIBN, 0.033 g of KPS, 0.028 g of benzyl dithioacetate RAFT agent

Compared with elevated temperatures the rate of polymerization is drastically reduced. Hence, it was possible to detect differences between oil- and water-soluble initiators especially during the initial period which have not been seen hitherto [2]. In the presence of RAFT agents (**Fig. 4**) the polymerization is even more slowed down thus proving the maintained activity of the RAFT agent.

### Synthesis of Model Colloids (A. M. I. Ali, N. Shirshova, M. Mukhamedjanova)

This project focuses on the preparation of various types of model colloids such as special double hydrophilic block copolymer particles as exemplary poly(diethylaminoethyl methacrylate)-b-poly(N-isopropylacrylamide)-b-poly(methacrylic acid cross-linked) (PDEAEMA-PNIPAM-PMAA) [3], monodisperse latexes in the size range between 100 and 2000 nm, and the exploration of possibilities to get composite particles with diameters much less than 100 nm preferentially below 50 nm. Exemplary, the double hydrophilic particles can be used as stabilizers in aqueous hetero-phase polymerizations leading to a special particle shape due to limited flocculation (TEM image **Fig. 5**).



Conditions

Recipes:

Fig. 5: 50 g of water; 5 g of styrene; 0.025 g AIBN; 0.04 g of PDEAEMA-PNIPAM-PMAA stabilizer particles; 50 °C

Fig. 6: seed: 15g of styrene, 0.785g of DPE, 1g of surfactant E30, 2.1g of KPS, 250g of water, composite: seed swollen with MMA and AIBN for 24 h; 70 °C; stained with CsOH/RuO<sub>4</sub>

The attempts to synthesize composite particles as small as possible is illustrated by the TEM picture of polystyrene-*b*-poly(methyl methacrylate) particles (Fig. 6) made from polystyrene-1,1-diphenylethylene (DPE) precursor particles by the so-called DPE method [4]. The block copolymer yield is almost 100 % as no homo-poly(methyl methacrylate) has been detected.

**Particle Nucleation in Aqueous Heterophase Polymerizations (S. Kozempel)**

The investigations were concentrated on the elucidation of the so-called “Jumbo effect” meaning an increase in the transmission during the particle nucleation period as described in [5]. Results of multi angle laser light scattering investigations as described in [6] questioned the generally accepted assumption that a styrene in water solution (without macroscopic phase separation) consists of only molecularly dissolved molecules. Contrary, these measurements revealed that a saturated styrene solution in water contains also droplets with average diameters of about 300 nm. During the equilibration period both the size and the number of drops increases. This saturation of styrene with water lasts up to several hours depending on temperature and stirrer speed. Basically, the MALLS data have been confirmed by UV spectroscopy (red squares in Fig. 7) and gas chromatography (not shown here).

The black squares in Fig. 7 prove the enormous influence of the degree of saturation of the continuous water phase with the styrene monomer on the duration of the pre-nucleation period. Its duration varies almost by a factor of ten i.e. between 40 and 4 min at the lowest and highest degree of saturation, respectively. Moreover, the intensity and the duration of the Jumbo effect are influenced by the monomer concentration in the aqueous phase before starting the polymerization. The greater this concentration is the less pronounced the increase of the transmission during the nucleation period.

Fig. 7

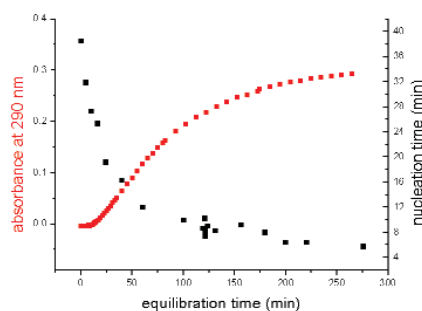
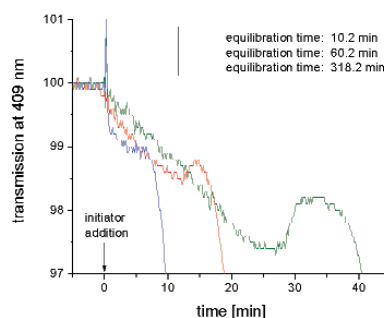


Fig. 8



Conditions

Recipe:

Figs. 7, 8: 390 ml of degassed water, 3.3 g of styrene, 10m of 20 mM KPS solution, 70 °C

UV data in Figs. 7 and 8 monitored with Uvikon 931 at 290 nm and Spekol 11 at 409 nm, respectively

Hence, the Jumbo effect might be caused by an increased monomer flux from the droplets through the water phase into the particles leading to a decrease in the index of refraction between the continuous phase and the scattering objects as, compared with pure water, the index of refraction of the continuous phase and of the particles is increased and decreased, respectively, due to the higher styrene concentration.

**Co-operation**

The MALLS-investigations during the particle nucleation period of aqueous heterophase polymerization were carried out in collaboration with G. Rother from the “Colloid Chemistry” department. Special double hydrophilic triblock copolymer particles and diblock copolymers were applied in crystallization processes in collaboration with the “Biomineralization” group (H. Coelfen). Thermo-sensitive block copolymers and colloidal particles with N-isopropylacrylamide blocks were prepared for investigations in the “Thin Liquid Films” group of the “Interface” department (R. von Klitzing). Monodisperse polymer particles in the size range between 300 nm and 1.2 µm were prepared and supplied for various investigations in the Heyrovsky Institute Prague (Marketa Zúkalova), the ETH Zurich (Vahid Sandoghar), and the University Leipzig (Friedrich Kremer).

K. Tauer, A. M. Imroz Ali, D.D. He, S. Kozempel, U. Lubahn, M. Mukhamedjanova, S. Nozari, N. Öz, S. Pirok, N. Shrishowa klaus.tauer@mpikg.mpg.de

**References:**

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## Biomimetic Mineralization



**Helmut Cölfen** 24.07.1965

**1991:** Diploma, Chemistry  
(University of Duisburg)

Thesis: Investigation of Thermoreversible Gelatin and  $\kappa$ -Carrageenan Gels by Analytical Ultracentrifugation

**1993:** PhD, Chemistry  
(University of Duisburg)

Thesis: Analytical Ultracentrifugation of Gels

**1993-1995:** Postdoc (National Centre 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

## References:

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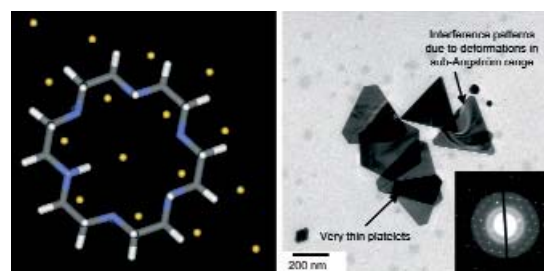
**[4]** Cölfen, H., Mann, S.: Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures. *Angew. Chem. - Int. Edit.* **42**, 2350-2365 (2003).

In this project, the polymer controlled crystallization of inorganic and organic compounds is investigated as a mimic of natural biomineralization processes **[1]**, **[2]**, **[3]**. The goal is to apply model systems in order to understand the basic processes and self assembly mechanisms to complex hierarchically structured materials **[4]**. Whereas we have initially focused on the preparation of complex crystal morphologies by polymer controlled crystallization, we have started to analyze selected systems in detail in the report period to elucidate the structure formation mechanisms supported by computer modeling using the Cerius<sup>2</sup> software. Synchrotron small angle X-ray scattering (SAXS) with high time resolution for the system CaCO<sub>3</sub> revealed that the applied double hydrophilic block copolymers (DHBC's) act as initially proposed: One part interacts with the crystal surface of a nanoparticle directly after its formation and sticks to it, whereas the other part provides an at least temporary stabilization, so that aggregation of amorphous primary nanoparticles is delayed but not suppressed **[5]**. These nanoparticle building units aggregate and crystallize and later on form spherical vaterite superstructures.

Small angle neutron scattering (SANS) was also applied to understand the formation of spherical CaCO<sub>3</sub> superstructures via rod and dumbbell precursor morphologies under control of a Poly(ethylene oxide)-block-Poly(methacrylic acid) DHBC **[6]**, **[7]**, **[8]**. Time resolved contrast variation experiments revealed that the polymer concentration is low but homogeneous inside the crystalline superstructures throughout the rod-dumbbell-sphere morphogenesis process, whereas the inorganic structure continuously densifies from a loose aggregate to a compact structure as evidenced from the power law behaviour. In addition, the block copolymer yields smaller primary particles, which initially are amorphous and surprisingly, the majority of the polymer remains in solution and does not participate in the crystallization process.

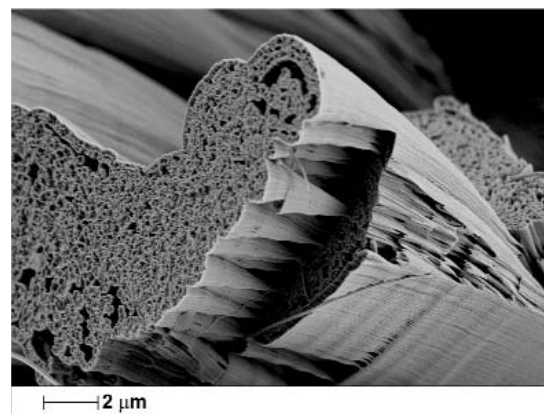
Parallel to these mechanistic investigations, we continued our synthetic efforts to understand the formation of complex crystal morphologies by self assembly of nanocrystal precursor particles. For example, a template as simple as a CO<sub>2</sub> gas bubble can be used to generate complex flower-like, shuttlecock and hollow half sphere self-assembled CaCO<sub>3</sub> morphologies from polymer stabilized nanoparticle precursors via variation of the solution surface tension **[9]**. Another open question in polymer controlled crystallization is if the secondary polymer structure of dissolved macromolecules plays an important role as suggested from the two dimensional templates in nacre biomineralization. We therefore synthesized peptide DHBC's, where the secondary structure could be reversibly switched from random coil to  $\alpha$ -helix via pH or temperature changes and applied these additives for CaCO<sub>3</sub> crystallization **[10]**. Against the expectation, the highest level of control over the crystallization process could be achieved with the random coil conformation. This speaks against the epitaxial match between mineral and polymer, as suggested in biomineralization. Instead, a high density of functional groups on the mineral surface seems to be of more importance than an unflexible polymer template.

However, if a stiff molecule is applied, which selectively matches a crystal surface, a highly selective adsorption to this face can be achieved resulting in complete inhibition of this face from further growth. This is demonstrated for the (111) face of gold, which can be stabilized by a hexacyclic DHBC resulting in very thin crystalline gold platelets, which are transparent in the electron beam and show interference patterns upon bending (see **Fig. 1**) **[11]**.



**Fig. 1:** Left: 1,4,7,10,13,16-Hexaazacyclooctadecan (Hexacyclen) macrocycle adsorbed on gold (111) Right: TEM micrograph of gold platelets with exposed (111)

A mineral system, which forms very complex self-repetitive hierarchical structures by polyacrylate triggered oriented attachment of BaSO<sub>4</sub> or BaCrO<sub>4</sub> nanoparticles to fiber bundles or cones is shown in the figure below **[12]**. These structures are very similar to those, previously obtained in presence of phosphonated block copolymers but have more defects in the bundle structure as a result of the worse nanoparticle stabilization capability of polyacrylate.



**Fig. 2:** Hierarchical BaSO<sub>4</sub> superstructures by oriented attachment and self assembly of BaSO<sub>4</sub> nanoparticles triggered by polyacrylate.

It was possible to generate single fibers by attachment of particles to the fiber surface as steric blockers upon fiber growth resulting in very high aspect ratio single crystalline BaCrO<sub>4</sub> nanofibers **[13]**. Simultaneous application of a DHBC, which generates BaSO<sub>4</sub> fibers and one, which generates BaSO<sub>4</sub> spheres resulted in a cumulative growth mechanism at low polymer concentrations e.g. fibers growing on spheres (see **Fig. 3**) **[14]**.



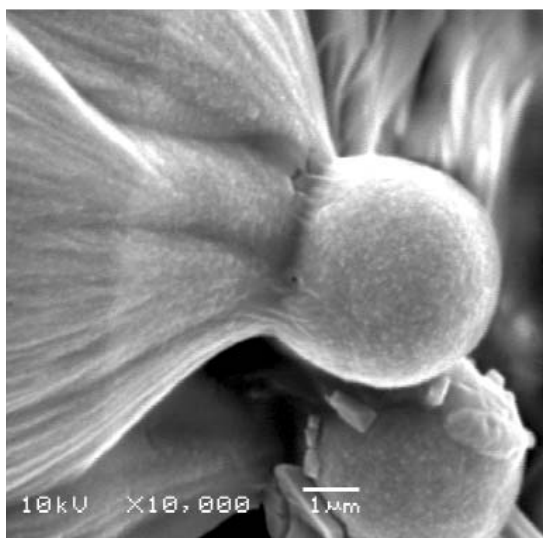


Fig. 3: BaSO<sub>4</sub> fibers growing on first formed spheres demonstrating additive effects of the structure directing DHBC's in a mixture.

However, at higher polymer concentrations, the action of the DHBCs is cooperative resulting in new morphologies, which are no derivatives of the underlying spheres or fibers anymore.

Reduction of silver salts in presence of starch under hydrothermal conditions yielded silver fibers coated with carbon, which were very uniform in diameter indicating that a polymer can fulfill multiple roles in a controlled crystallization process [15].

Other investigated polymer controlled crystallizing systems were self assembled BaCO<sub>3</sub> spheres and dumbbells [16] and CaCO<sub>3</sub> hollow sphere formation via a sacrificial spherical template of metastable vaterite [2]. Also, we have explored the stabilization capability of DHBC's for the generation of high quality CeO<sub>2</sub> nanocrystals [17], ways to control morphologies of various cerium compounds via solvent variations [18] and a procedure to generate ternary interpolymer complexes with silica [19].

Our approach enabling selective adsorption of block copolymers to code defined crystal surfaces and to trigger the self assembly to complex morphologies could even be applied to generate chiral helical nanocrystal superstructures from a racemic phosphonated polymer and achiral BaCO<sub>3</sub> (see Fig. 4) [20].

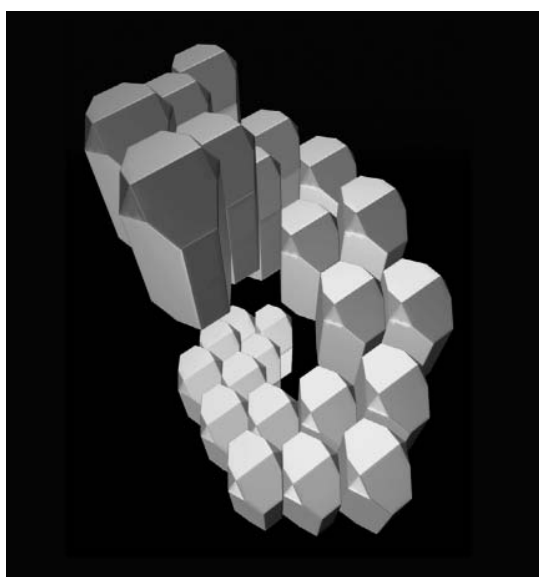
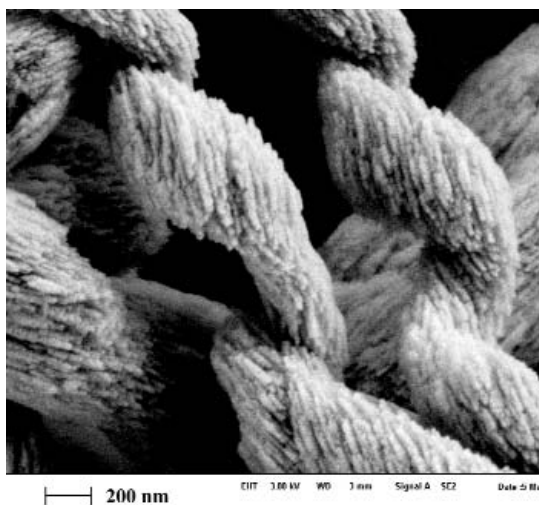


Fig. 4: Upper: Self assembled BaCO<sub>3</sub> helices generated by selective coding of orthorhombic nanoparticle faces with a phosphonated stiff polymer. Lower: Schematic representation of the nanoparticle self assembly to a helix

Here, the steric demand of a block copolymer leads to a staggered arrangement resp. axial growth with a direction defined by the first three aggregated nanoparticles. On the other hand, a clockwise or counterclockwise turn is preferred by the requirement of epitaxial matching of a further attaching nanoparticle to the existing aggregate. Overlay of these two processes leads to the observed helix formation. These processes show the level of control, which can be achieved by polymeric additives.

H. Cölfen, H. Endo, N. Gehrke, P. Kasparova, Y. Luo, N. Nassif, M. Page, M. Riedl, J. Rudloff, T. X. Wang, S. Wohlrab, A. W. Xu, S. H. Yu  
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## Functional Mesostructured Inorganic-Organic Materials – Advanced X-ray Scattering Methods



Materials composed of self-assembled nano-scaled domains, such as mesoporous structures, are of crucial importance for various future technologies such as catalysis, photovoltaics and smart devices. Our research is directed towards the fabrication of nanostructures of classical materials like carbon and also metal oxide species with functionality such as electrochromism, etc., for instance in the form of

thin coatings. Mesostructured metal oxides (e.g.  $\text{TiO}_2$ ) can be obtained through sol-gel templating using suitable templates as structure-directing agents: the metal oxide is formed by sol-gel reactions within the hydrophilic domains of a lyotropic mesophase, obtained from the self-assembly of amphiphiles in water or other polar solvents. The underlying strategy is to develop and use suitable templates, possessing optimum self-assembly properties, because structural perfection of these materials is not accessible through standard templates. The self-assembly and the solidification of these mesoscopic systems are studied by novel experimental and theoretical concepts of x-ray scattering, which are also applied to a profound characterization of mesostructured materials.

### Ionic Liquids as Templating Reagents

In the past years, growing interest emerged in ionic liquids (ILs) as reaction media and solvents in chemical processes. In addition, we observed that certain ionic liquids can also serve as excellent templates for the generation of mesostructured materials such as mesoporous oxides and nanoparticles. In this project, the special templating properties of ILs are explored in detail and used for the fabrication of previously inaccessible materials. For instance, a hierarchical porous material could be made using colloidal particles, a block copolymer ("KLE",  $(\text{H}(\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH})\text{CH}_2\text{CH}_2)_{69}(\text{OCH}_2\text{CH}_2)_{79}\text{OH})$ ) and an IL as templates, leading to porous silica with the small pores being organized with the walls of the corresponding larger pores [1] on three length-scales. While the block copolymer produces spherical mesopores of ca. 14 nm, the IL gives rise to 3 nm mesopores, both pore types located in the walls of macropores (350 nm) of tuneable size. The hierarchical pore arrangement is clearly seen in Transmission Electron microscopy (TEM) and small-angle x-ray scattering (SAXS) data, revealing a dense mutual packing of the KLE mesopores and the IL mesopores between them, providing an extremely high porosity. Surprisingly, the ordering of the KLE mesopores is not disturbed by the presence of the IL. These results suggest different, superior templating behaviour of ILs compared to standard surfactants [2].

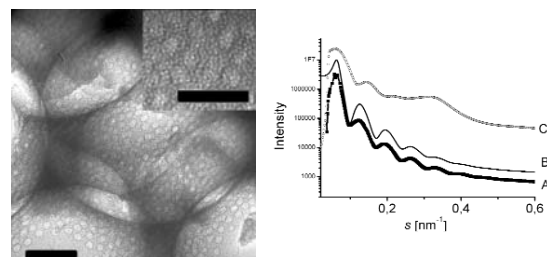


Fig. 1: TEM images (left) of a trimodal porous silica. The scale bars correspond to 100 nm and 50 nm. Right: SAXS patterns. A: Mesoporous silica (KLE). B: Simulation of A. C: Trimodal porous silica.

### Fabrication and Characterization of Thin Films of Mesoporous Metal Oxides with Crystalline Pore Walls

Sol-gel chemistry in combination with a suitable structure-directing amphiphile is a versatile strategy for the fabrication of mesoporous films of crystalline metal oxides. Typically, after dip-coating of a solution containing a metal precursor (alkoxides, etc.) and a template, a suitable temperature program is necessary to generate the crystalline mesoporous oxide nanocrystals in the pore walls. However, the fabrication of such materials usually involves difficulties due to mesostructural collapse, and several oxides had not been reported at all in this form. The KLE templates significantly facilitated the fabrication of crystalline mesoporous binary and ternary oxide films [1-3]. For the first time chemically pure, highly crystalline mesoporous  $\text{CeO}_2$ ,  $\text{HfO}_2$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Ta}_2\text{O}_5$  and perovskites were obtained, allowing for a detailed understanding of the particularity of these templates compared to standard amphiphiles. The main research objective is the elucidation of the self-assembly and crystallization mechanism, and also the study of physico-chemical properties, such as electrochromism for  $\text{WO}_3$ , as a function of the porosity and pore size. The crystallisation and mesostructural changes upon temperature (T) treatment were studied by T-dependent SAXS and WAXS, High-Resolution TEM, Atomic Force Microscopy (AFM) and physisorption, as exemplified for  $\text{CeO}_2$  mesoporous films (Fig. 2, 3). Together with AFM and TEM (Fig. 2), from a novel quantitative SAXS analysis (Fig. 3b) the size and aspect ratio of the deformed spherical pores could be determined for the first time with high precision, e.g. 6 nm normal and 14 nm parallel to the substrate in this case. The walls consist of cerium oxide nanoparticles, which grow upon temperature treatment (Fig. 3a), but not exceeding the wall thickness imposed by the block copolymer.

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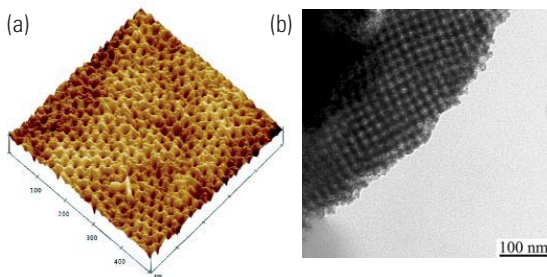


Fig. 2: AFM (a) and TEM (b) images of a mesoporous  $\text{CeO}_2$  film with crystalline pore walls.

Our studies revealed that key features of these polymers are an enhanced thermal stability and hydrophilic-hydrophobic contrast [1-3].

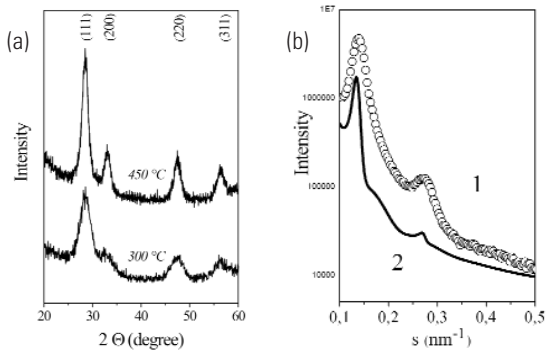


Fig. 3:  $\text{CeO}_2$  mesoporous films: WAXS as a function of temperature (a) and SAXS (b) 1: experimental 1D SAXS data, 2: fitting based on ref. [5].

Also, the block lengths are designed to be long enough to allow for sufficiently thick walls, being compatible with the growth of nanoparticles without destroying the mesostructure.

### Structural Characterization of Carbons by X-ray Scattering Methods

Porous carbons have been used for hundreds of years and represent an important class of porous materials. In spite of their widespread application

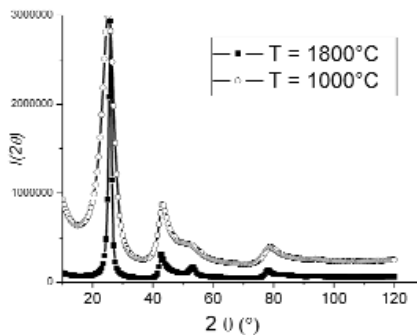


Fig. 4: WAXS analysis [6] of two carbons, treated at different temperatures.

(e.g. in filtering etc.) the details of their microstructure are still unclear, in particular the relationship with macroscopic properties (sorption). In this project mesostructures of carbons are produced and studied by the combination of novel WAXS/SAXS evaluation techniques which are developed and compared with Raman spectroscopy and physisorption. Fig. 4 shows the successful fitting of entire WAXS curves of carbons for the first time by a novel approach [6], providing various structural parameters.

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# POLYELECTROLYTES AND THEIR COMPLEXES

## Nanostructured Materials by Ionic Self-Assembly: Function and Switchability



The use of the ionic self-assembly strategy and a basic understanding of the property-structure-function relationship [1] has been established for the production of nanostructured materials. Building on the initial work with azobenzene dye-surfactant complexes, the use of single-crystal X-ray analysis has provided further insights into unexpected packing motives found for such complexes (see Fig. 1 below). [2]

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- [1] Faul, C. F. J.: Structure-Function Relationship in Optically and Electronically Active ISA Materials. *Synthetic Metals* **147**, 63-65 (2004).  
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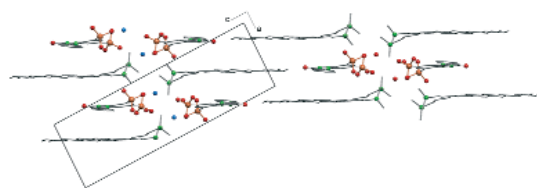


Fig. 1: The triclinic unit cell of a dye-surfactant complex. Note that no  $\pi$  stacking is found.

However, to investigate and expand the possibilities to incorporate further functionalities and interaction motives into such nanostructured materials, several approaches were used. These included the following, which will be briefly discussed below:

### Complexes with Perylenediimide Dyes:

The orientation of liquid-crystalline materials into large monodomain structures are of importance for applications in display devices and as optical components.

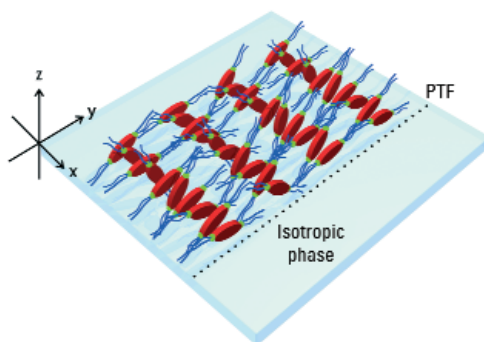


Fig. 2: Orientation of the perylenediimide tectons at the phase transition front (PTF).

We have found that, by making use of branched double-tail surfactants, it is possible to produce lyotropic perylenediimide-surfactant complexes. [3] Although all conventional methods for orientation of such lyotropic phases (in DMSO) failed, it was found that a phase-transition front (PTF) developed during an isotropic-lyotropic phase transition. This led to the formation of highly oriented large monodomains of the perylene dyes with a dichroic ratio of close to 20. Null-ellipsometry confirmed the 3D orientation of the perylenediimide tectons, as depicted in Fig. 2.

In a bid to exploit the use of this versatile tecton, a cationic perylenediimide derivative and an oppositely charged phthalocyanine dye were combined in a 1:1 charge ratio. [4] Combination of the two tectons leads to the formation of highly viscous organogels. These gels were investigated by a number of techniques, indicating that very long polymeric fibers of stacked dye molecules were formed.

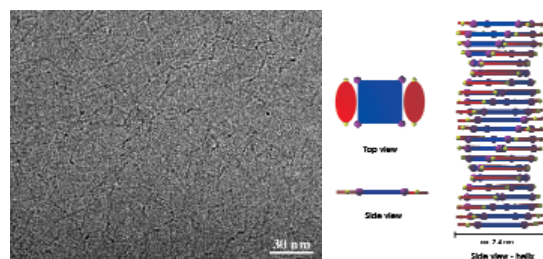


Fig. 3: Cryo-TEM micrograph showing the presence of infinitely long fibers (left). Schematic representation of the helical stacking motive found (right).

Digital analyses, in conjunction with AFM, TEM and X-ray analyses, indicated that the dyes interact to form side-by-side stacked helical polymeric aggregates.

### Liquid-Crystalline Material from Discotic Precursors

The use of discotic precursors for the formation of columnar LC phases is well known. The use of further intermolecular hydrogen bonding has been used to stabilise such phases, and even cause gelation behaviour at low concentration.

The combination of hydrogen bonding and the ISA synthesis route was used to investigate the possibilities to mimic the covalent routes presented before. Synthesis of a charged tricarboxyimide derivative and subsequent complexation with surfactants led to the formation of columnar LC phases. [5] In one specific case gelation behaviour was observed at very low concentrations in DMSO and DMF.

Continuing investigations into the use of hetero-atom-containing discotic precursors led to the use of tricycloquinazoline (TCQ) core as tecton. [6] Hydrolysis of a hexaalkoxy precursor led to the in-situ formation of a hexa-anionic tecton. Complexation of this potential discotic core with double tail surfactants yielded, surprisingly, a lamellar LC phase (Fig. 4).

Further investigations [7] using small multicharged discotic tectons, such as benzene hexacarboxylic acid (BHC), led to similar results as found for the TCQ core. After complexation with double tail surfactants, X-ray analyses (both transmission and reflection mode), null-ellipsometry and temperature-dependent UV and IR analyses proved the existence of very large monodomains of spontaneously aligning Smectic A phases, with the layers aligned parallel to the substrate surface.

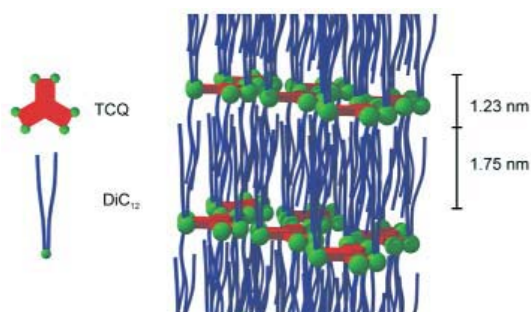


Fig. 4: Schematic representation of the packing of the TCQ tectons into a lamellar phase structure.

### Functional ISA Complexes – Towards Devices

In a bid to explore a variety of different materials for use in ISA complexes, a new class of highly luminescent polyoxometalates were synthesized and complexed with both normal alkyl as well as ferrocene-derived surfactants. [8] The influence of the phase and packing behaviour and the presence of electron-accepting moieties were investigated by a variety of techniques, including determinations of lifetimes and absolute quantum yields. A lyotropic LC phase was described for the first time for polyoxometalate complexes (Fig. 5).

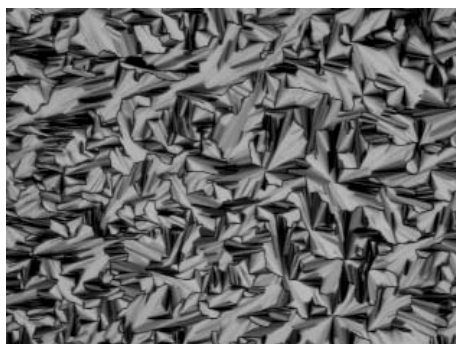


Fig. 5: Lyotropic POM-surfactant phase in chloroform.

In a continuation of the project investigating reactions within confined environments, a ternary co-polyaddition of an unsaturated surfactant, dithiol and diene was employed. [9] This led to the incorporation of varying amounts of polymerised materials into lamellar phase structures.

However, the incorporation of a polymerisable surfactant does not ensure the presence of functionality within an ISA complex. Investigations have therefore turned toward the production of pyrrole-containing surfactant systems for the production of conducting nanostructured materials. These surfactants were synthesized, and their thermotropic and lyotropic phase behaviour studied in detail. [10]

In a separate investigation into the use of conducting tectons, well-defined phenyl-capped tetra- and octaaniline materials were synthesized. [11] These materials were then used for the formation of soft, nanostructured ISA complexes. Temperature-dependent investigations indicated the existence of reversible structural transitions at higher temperatures. This was confirmed by conductivity measurements, which showed highly reversible 3 orders of magnitude changes in the conductivity of the tetraaniline complexes.

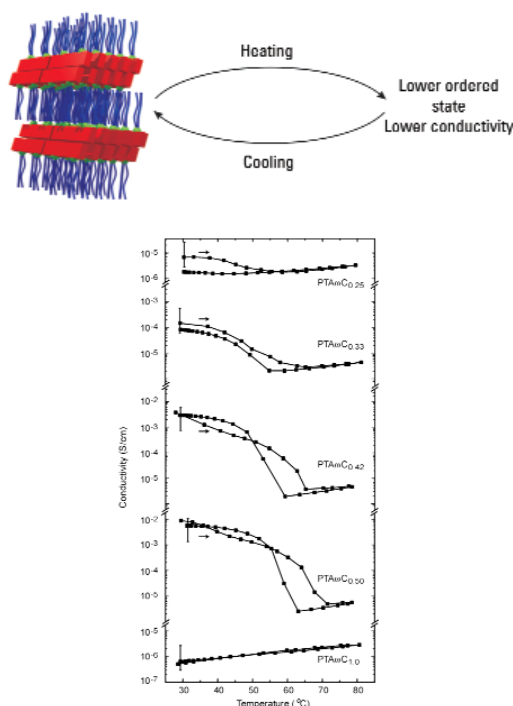


Fig. 6: Switchable conductivity in TANI-surfactant complexes.

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# AMPHIPHILIC POLYMERS

## Bioorganic - Synthetic Hybrid Polymers as Molecular LEGO<sup>®</sup> - Bricks



### Introduction

Controlled processes of structure formation, yielding defined, hierarchical structures, are one of the most important tools in biological systems to realize well-adapted, high-performance materials (e.g. bone, mussel shells, hair and wool etc.).

Particularly polypeptides and proteins provide beautiful examples of highly controlled structure formation processes. Precisely defined structures are essentially needed for the complex function of such molecules (e.g. mussel byssus thread, spider silk, aqua- or ion-porins, enzymes, etc.).

We have contributed our efforts to transfer native structure formation principles observed in polypeptide systems towards the organization of synthetic polymers. This biomimetic approach might advent new possibilities in the design of structured polymeric materials (Fig. 1).

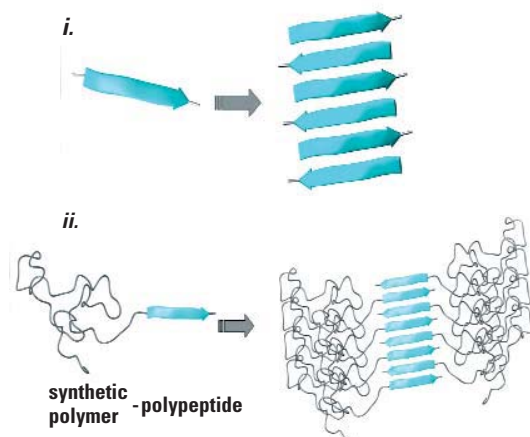


Fig. 1: Schematic presentation of the organization of synthetic polymers induced by oligopeptides;

(i) Organization of beta strands into a  $\beta$ -sheet motif;

(ii) Induction of structure in hybrid building blocks via self-assembly of oligopeptide-based organizer units.

### Aims and Strategy

- Design of building blocks by conjugation of oligopeptide-based organizer units to synthetic polymers (e.g. poly(ethylene oxide), poly(meth)acrylates, polystyrene, etc.)
- Investigation of structure formation via spontaneous or induced self-assembly of the building blocks.
- Understanding of the relationship between chemical structure of the organizer unit and resulting organization of the building blocks.
- Rational design of defined structures in polymeric materials by tailor-made organizer units.

### Synthetic Approaches

To access polymer-organizer building blocks (e.g. AB-block copolymers, Fig. 1, ii) routes have to be developed allowing the defined conjugation of synthetic polymers to oligopeptides. Difficulties during conjugation often originate from the multifunctional character of the oligopeptides as well as from different solubilities of oligopeptide and polymer.

Two major synthetic strategies were investigated:

i. *Polymerization approaches* include the sequence specific introduction of an initiator functionality to an oligopeptide. The resulting macroinitiator is applied in a controlled radical polymerization process to initiate the polymerization of synthetic monomers (e.g. *n*-butylacrylate). Defined polymer-oligopeptide conjugates could be obtained exhibiting controllable molecular weight and low polydispersity (Fig. 2). [1]

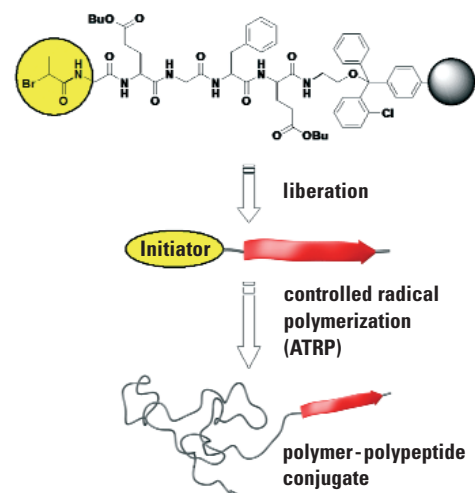


Fig. 2: Schematic presentation of the oligopeptide macroinitiator approach.

ii. *Coupling approaches* that include the coupling of a synthetic polymer exhibiting a defined end-group functionality with a complementary, selectively addressable functionality of an oligopeptide. Contributions were made by developing routes to defined chain-end functionalities of synthetic polymers e.g. polyacrylates or polystyrene. Therefore controlled radical polymerization techniques were combined with either orthogonal protected functional initiators or highly specific chain-end-group transformation reactions. [2]

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### Pre-organized Oligopeptides as Organizer Units [3]

The attachment of oligopeptides to a suitable template results in the pre-organization of oligopeptide strands. The restriction in conformational freedom as well as optimization of the geometry of the strands increases mainly driven by entropy, the tendency to form aggregates. [4] Therefore pre-organized oligopeptides are potentially applicable as highly effective organizer units.

Derived from literature-known systems, a template was tailor-made to pre-organize two oligopeptide strands for the formation of an anti parallel  $\beta$ -sheet motif. The template design includes an additional functionality that can be selectively addressed to conjugate the synthetic polymer chain (Fig. 3). As a proof of concept, poly(ethylene oxide) was conjugated as a first model polymer yielding water-soluble polymer-organizer building blocks. These allow the analysis of structure formation with established analytical tools in determination of protein structure e.g. UV-circular dichroism spectroscopy (UV-CD).

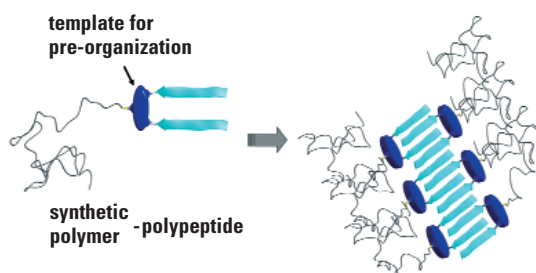


Fig. 3: Schematic presentation of the organization of synthetic polymers by template preorganized oligopeptides.

Consistent with the model in Fig. 3, strongly anisometric aggregates could be observed exhibiting a persistent stiff behavior (Fig. 4). UV-CD spectroscopy verifies the presence of  $\beta$ -sheet secondary structures by exhibiting the typical Cotton effects (maximum at 195 nm and minimum at 218 nm) (Fig. 4 inset).

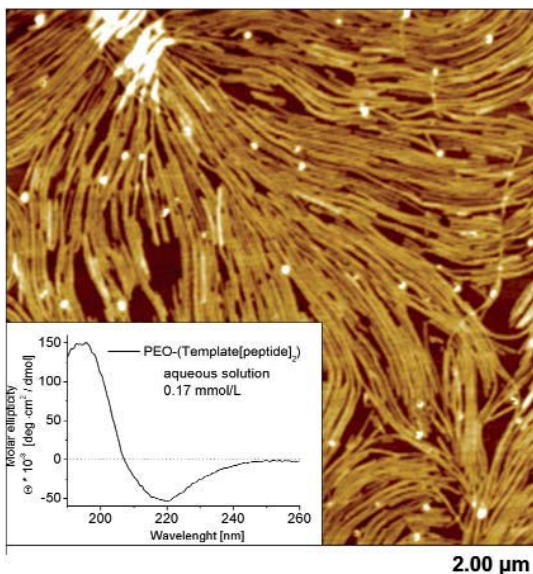


Fig. 4: AFM micrograph of anisometric aggregates of PEO-(Template-[Oligopeptide]<sub>2</sub>); CD spectrum of the aqueous solution before spin coating (inset).

### Biomedical Applications

The development of defined conjugates of synthetic polymers and oligo- or polypeptides allows the addressing of biomedical or pharmacological applications. Conjugates consisting of poly(ethylene oxide) and monodisperse polypeptides have been successfully applied as carriers for cytostatica in anticancer therapy. Contributions in this field were made by an improvement of the degree of definition of the applied carrier systems in comparison to existing carriers, by the development of a new application method of carrier drug conjugates as well as by the incorporation of "smart" features into the polymeric carriers e.g. predefined degradability.

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## Amphiphilic Block Copolymers



The research of the group is devoted to (i) the development of new controlled polymerization techniques and modular synthetic pathways, (ii) characterization of functional polymers, and (iii) study of the phase behavior of amphiphilic diblock copolymers. Particularly interesting are effects of secondary structures and specific interactions (electrostatic, dipole-dipole, hydrogen bridging interactions, etc.), which should add complexity to block copolymer mesostructures (biomimetics). The systems under study are "molecular chimeras" of synthetic polymers and  $\alpha$ -helical polypeptides, polymers with chelating acetoacetoxy units, and complexes of copolymers with complementary recognition sites.

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### References:

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### Block Copolymer Synthesis

Linear polypeptide-based block copolymers were synthesized via the ring-opening polymerization of  $\alpha$ -amino acid *N*-carboxyanhydrides (NCA) initiated by  $\omega$ -primary amino-functional polymers. Screening of the free amine initiating/propagating species as hydrochloride promoted a controlled polymerization of NCA (**Fig. 1**), producing block copolymers with nearly monodisperse molecular weight distribution (MWD) (polydispersity index, PDI < 1.03) [9, 14]. Earlier reported recipes yielded polymers with PDI > 1.3.

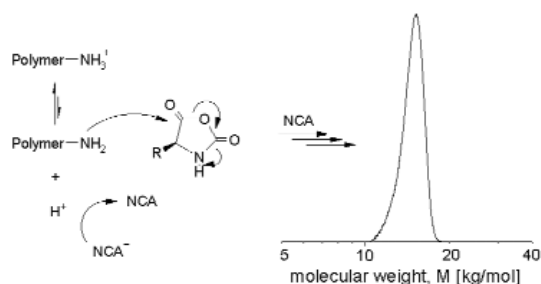


Fig. 1: Synthesis of polypeptide block copolymers by „ammonium-mediated“ polymerization of NCA.

The radical addition of  $\omega$ -functional mercaptanes to the vinyl double bonds of 1,2-polybutadiene-*block*-poly(ethylene oxide) was used for a modular synthesis of well-defined functional block copolymers (**Fig. 2**). The modification reaction proceeds smoothly and yields quantitatively functionalized copolymer samples without altering the MWD of the parent polymer (PDI < 1.09) [12].

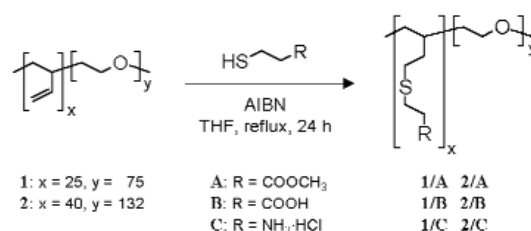


Fig. 2: Modular synthesis of functional block copolymers.

### Block Copolymer Characterization

Absolute MWDs of diblock copolymers can be determined with conventional size exclusion chromatography (SEC) without referring to any kind of calibration curve and/or molar mass-sensitive detecting device. Evaluation of two independent detector signals provides the chemical composition, which together with the molecular weight of the first block segment (determined independently) yields the absolute molecular weight of every copolymer fraction. From this set of data, the MWD of the sample can be calculated. Results obtained by this method are in good agreement with the ones determined by NMR and SEC with on-line viscosity or multi-angle light scattering detection [3].

### Block Copolymer Mesostructures

Thick polymer films made from poly(Z-L-lysine)-polystyrene rod-coil block copolymers (PDI = 1.01-1.64) exhibit a hexagonal-in-zigzag lamellar morphology (Fig. 3a). The zigzag superstructure results from the hexagonal packing of polypeptide helices being fractionated according to length. Thus, there is a correlation between the MWD of the polypeptide segment and the interface-curvature properties of the morphology (Fig. 3b) [10].

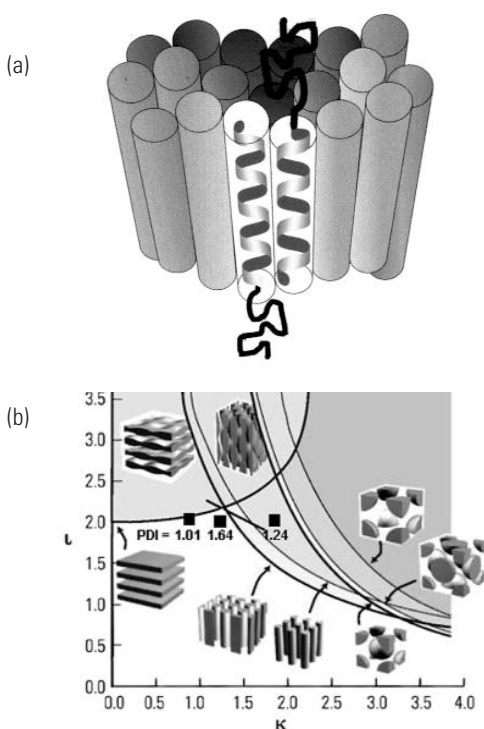


Fig. 3: a) Illustration of the undulated or zigzag lamellar structure of polypeptide block copolymers. b) Interface-curvature ( $\nu$ - $\kappa$ ) properties of lamellar structures of polypeptide block copolymer with different PDI.

Poly[2-(acetoacetoxy)ethyl methacrylate]s can self-assemble into hierarchical superstructures, i.e. double-stranded helical tubes of either screw sense. Both diameter and pitch of the superhelices are  $\sim 12$  nm and their length is 200-500 nm (Fig. 4a). It is proposed that the polymer chains first organize into ribbons, the width of which determines the pitch of the helix, and then coil up into the helical superstructure (Fig. 4b). Formation of these structures is driven by the establishment of hydrogen bridging interactions between adjacent acetoacetoxy groups and compensation of dipole moments [13].

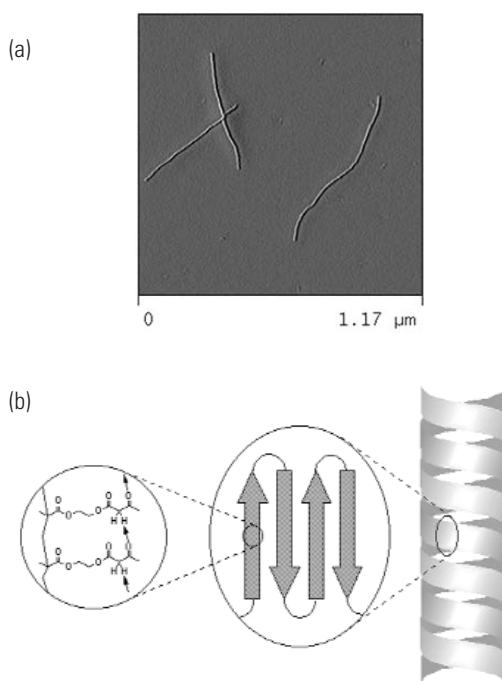


Fig. 4: a) Scanning force micrograph of poly[2-(acetoacetoxy)ethyl methacrylate] superhelices. b) Illustration of the hierarchical structure of superhelices.

Mixing of block copolymers with complementary recognition sites is used for the generation of a library of complex mesostructures [2].

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## SYNTHESIS AND ASSEMBLY OF NANOPARTICLES

# Synthesis, Functionalization, Assembly and Application of Metal Oxide Nanoparticles



Transition metal oxides constitute one of the most important classes of materials with properties covering almost all aspects of materials science and solid state physics such as semiconductivity, superconductivity, ferroelectricity, magnetism, and catalytic activity. Accordingly, they play an outstanding role in many emerging technologies such as sensing, pigmentation, catalysis, electroceramics, energy

storage and conversion, and the trend towards further miniaturization of functional devices demands the production of nanoparticulate transition metal oxides with the highest possible purities, small crystallite sizes, well-defined particle morphologies, and small particle size distributions. It is expected that particle sizes in the nano-regime and specific crystal shapes enhance the performance, lower sintering temperatures, and allow a fine-tuning of the chemical and physical properties. However, the synthesis of nanoparticles is just the beginning towards their use in nanotechnology. In a next step, these nanoparticle building blocks have to be arranged into well-defined ensembles and superstructures leading to novel and unique properties that are not found in the individual components. One of the most promising strategies for the fabrication of such hierarchical structures is the use of self-assembly processes. The organisation is determined by the interactions among the primary building blocks, and there is no doubt that adequately tailored surface properties are the fundamental parameter in the design of novel nanobuilding blocks.

Our research goal is to develop general concepts for the fabrication of complex architectures, made up of nanocrystalline metal oxide components that are hierarchically ordered by specific interactions between the nanoparticle building blocks. We are focussing on three main objectives: i) synthesis of crystalline metal oxide nanoparticles with appropriate surface functionality, ii) assembly of these nanoscale building blocks into hierarchically organized superstructures, and iii) implementation of the gained expertise to fabricate nanodevices.

### Nanoparticle Synthesis

In spite of the high scientific and technological interest in transition metal oxides, their synthesis at the nanoscale is still a big challenge and many complex metal oxides remain to be explored. In order to circumvent some drawbacks of aqueous sol-gel chemistry such as poor crystallinity, fast hydrolysis rate of transition metal alkoxides and presence of counterions, we developed a variety of nonaqueous synthesis routes to transition metal oxide nanoparticles. The reaction of metal acetylacetonates, metal halides, or metal alkoxides with either alcohols, ketones, aldehydes or amines allows the preparation of a large collection of binary and ternary metal oxide nanoparticles such as  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{HfO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $(\text{Ba,Sr})\text{TiO}_3$ ,  $\text{BaZrO}_3$ ,  $\text{LiNbO}_3$ , and  $\text{BaSnO}_3$  [1]-[7]. TEM images of selected nanopar-

ticles are given in Fig. 1, along with HRTEM images as insets proving the high crystallinity of the nanoparticles. In the case of yttrium oxide, a lamellar nanohybrid was obtained, consisting of crystalline yttrium oxide layers with intercalated benzoate molecules (Fig. 1d) [8].

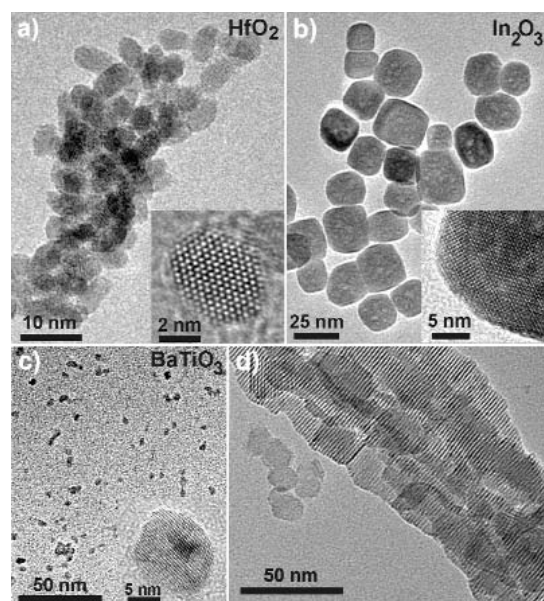


Fig 1: TEM images of a)-c) selected metal oxide nanoparticles and d) yttrium oxide nanohybrid.

### Formation Mechanism

The formation mechanism of metal oxide nanoparticles in nonaqueous reaction media is not yet well understood. Therefore, we carefully analyzed the organic species in the final reaction mixtures after removal of the inorganic precipitate to gain some information about possible reaction pathways. The results were surprising and depending on the reaction system, we found several novel reaction mechanisms. For example, in the case of  $\text{HfO}_2$  prepared from hafnium alkoxide in benzyl alcohol, nanoparticle formation occurs via ether elimination as shown in Fig. 2a [4]. In the case of  $\text{BaTiO}_3$ , which was prepared by dissolution of metallic barium in benzyl alcohol and addition of titanium alkoxide, hardly any ether was found. Instead, the presence of 4-phenyl-2-butanol in stoichiometric amounts gave evidence that the formation mechanism proceeded mainly via a novel pathway involving a C-C bond formation between benzyl alcohol and the isopropanolate ligand (Fig. 2b) [5].

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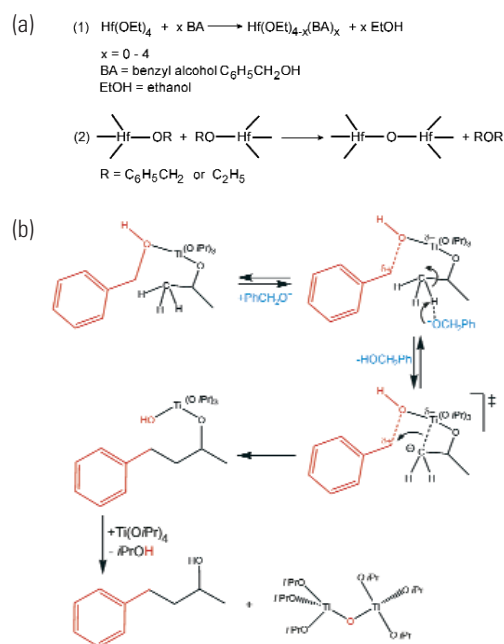


Fig. 2: a) Formation of  $\text{HfO}_2$  via ether elimination; b) Formation of  $\text{BaTiO}_3$  involving coordination of benzyl alcohol, activation of the benzylic carbon atom via weakening of the C-O bond, deprotonation of the  $\beta$ -carbon atom of the isopropoxy ligand, nucleophilic attack leading to 4-phenyl-2-butoxide formation and OH, finally condensation and elimination of 4-phenyl-2-butanol.

### Nanoparticle Assembly

The controlled organization of the metal oxide nanoparticles into well-defined nanostructures was achieved by two different approaches, either via specific surface functionalization of the nanoparticles or via polymer-directed assembly.

Following the first strategy, we synthesized titania nanoparticles in the presence of a small amount of 2-amino-2-(hydroxymethyl)-1,3-propanediol ( $[\text{HOCH}_2)_2\text{CNH}_2$ , Trizma]. Upon redispersion of the Trizma-functionalized titania nanopowder in water, the nanocrystals start to assemble into highly anisotropic arrangements (Fig. 3a, inset) [9] [10]. HRTEM shows that these pearl-necklace structures consist of perfectly oriented nanoparticles forming a pseudo-single crystal along the [001] direction (Fig. 3a). The polymer-directed assembly of crystalline cerium oxide nanoparticle sols [11] resulted in the formation of highly ordered, 3D mesoporous materials (Fig. 3b) [12]. Similar results were obtained with  $\text{SnO}_2$  nanocrystals (Fig. 3c).

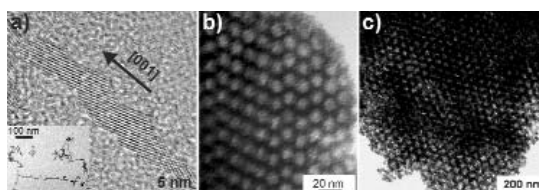


Fig. 3: TEM images of nanoparticle assemblies. a)  $\text{TiO}_2$  nanowires, b) mesoporous  $\text{CeO}_2$ , and c) mesoporous  $\text{SnO}_2$  (after calcination).

### Applications

Some of the prepared metal oxide nanoparticles such as  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$  are promising candidates for gas sensing devices. In order to test the sensing properties of these nanopowders, sensor devices were fabricated by deposition of thin films of the respective nanopowders dispersed in water onto alumina substrates (details are given in Fig. 4). The front side of the substrate is equipped with gold contacts and on the backside is a platinum heater. The measurement of the electrical current in dependence of gas flow showed that the nanopowders exhibited high sensitivity and good recovery time. Especially the indium oxide nanoparticles were highly sensitive towards  $\text{NO}_2$  with a detection limit of 1 ppb at low temperature [6].

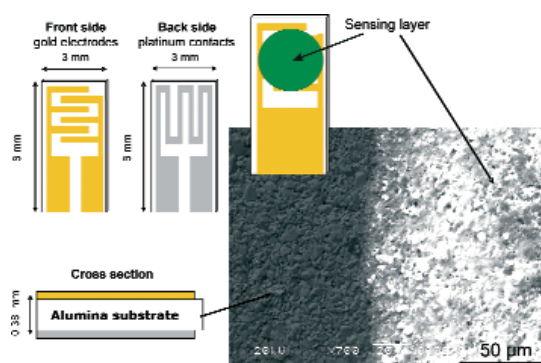


Fig. 4: Design of a gas sensing device.

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## Fractionating Colloid Analysis



As in the years before, Analytical Ultracentrifugation (AUC) and Field-Flow Fractionation (FFF) were available as an active and versatile service unit for a large variety of colloid and polymer analysis problems from the institute and external cooperation partners [1-5]. Special emphasis was laid upon the investigation of new particle properties by AUC.

We could reveal that AUC is very sensitive to the nanoparticle surface structure in terms of charges by clearly distinguishing between TiO<sub>2</sub> particles of very similar size and shape but different exposed crystal faces [6]. This implies that AUC should be capable to determine particle charge distributions in addition to particle size distributions in the future, but the basic theory for the treatment of such experiments is still missing.

Also, we were able to show that the complete dependence of the spectral properties of quantum size nanoparticles can be determined in a single AUC run on a polydisperse sample [7] (Fig. 1). Up to now, such dependencies had to be elucidated via the tedious synthesis of monodisperse nanoparticles of various sizes with subsequent spectral characterization.

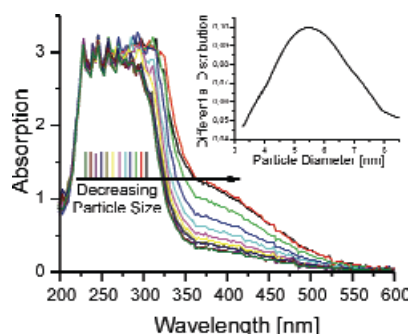


Fig. 1: AUC measurements showing UV-Vis absorption spectra of dopamine-functionalized titania nanoparticles dependent on the particle size fractions. Inset: particle size distribution curve of dopamine functionalized titania nanoparticles.

For very complex systems, one fractionating technique alone cannot yield the full information about the system. One example of such system is ferritin, which is consisting of different oligomers, each of which is filled with varying amounts of iron oxide. Thus, ferritin has a particle size distribution superimposed with a density distribution. Flow-Field-Flow Fractionation (FI-FFF) can yield the particle size distribution as this technique is independent of the particle density (Fig. 2).

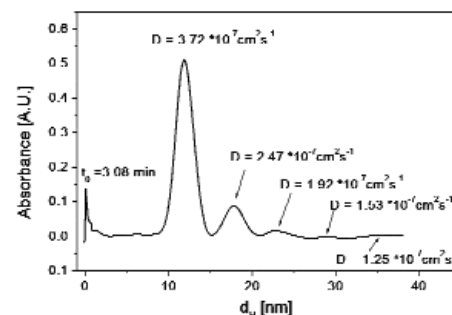


Fig. 2: FI-FFF elugram of ferritin after conversion to particle size distribution.

Analytical ultracentrifugation on the other hand is dependent on particle size and density so that the corresponding distribution is more smeared as compared to that from FI-FFF (Fig. 3).

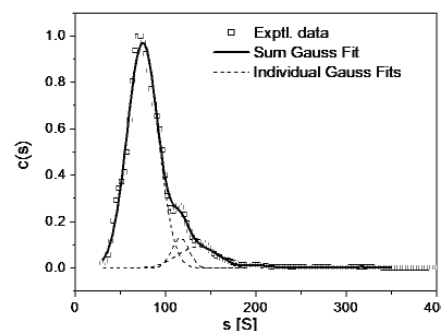


Fig. 3: Diffusion-corrected *s* distribution of ferritin from AUC.

However, the combination of the sedimentation and diffusion coefficient data from both techniques yields additional information like the buoyant molar mass and the solution shape of the different oligomers [8]. Although this analysis was only performed for the peak maxima, combination of the whole distributions could in principle yield distributions like molar mass and density distributions in such global analysis approach for experiments performed in different solvents.

Improved detectors are important for a sophisticated analysis of the increasingly complex colloidal systems. In cooperation with BASF AG, we have developed a fast fiber based UV/Vis detector for the Analytical Ultracentrifuge. This detector has several advantages: 1) Very fast detection down to 2 ms compared to several minutes for the current commercial design, 2) Simultaneous detection of the whole UV/Vis wavelength range (200 – 1000 nm) opening up a further dimension with the associated analytical information 3) Modular design adaptable to every preparative ultracentrifuge. The increased information of the three dimensional data space as compared to the two dimensional detection with commercial instruments is visualized for one scan in Fig. 4.

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and pathways towards their analysis

in solution



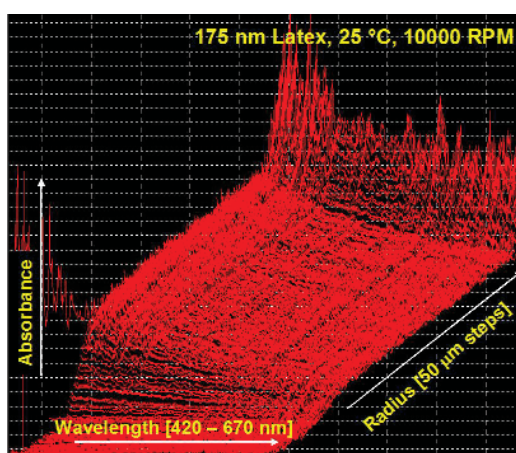
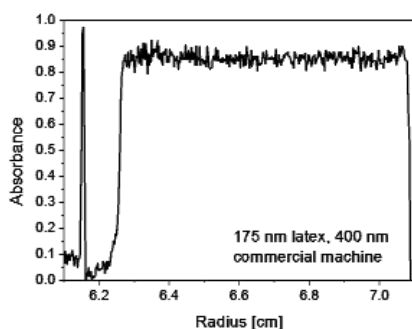


Fig. 4: Single Scan for a sedimenting latex with the commercial instrument (upper) and the developed fibre optics detector (lower)

In the example shown in **Fig. 4**, the wavelength dependence of the detected turbidity contains information about the particle size so that in the future, colloid density distributions may become available simultaneously to particle size distributions. The multiwavelength detector should also prove valuable for interaction studies of compounds with dissimilar chromophores. The first prototype was developed and installed and is currently tested for sophisticated applications. Also the hard- & software is further improved.

These developments indicate a new trend in fractionating colloid analysis: Multidetector application and global analysis of experiments with various physicochemical techniques like AUC combined with FFF.

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## Electron Microscopic Studies of Colloidal Systems and Biomaterials

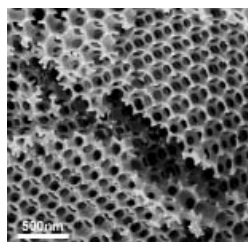


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Transmission and scanning electron microscopy are powerful analytical tools to investigate the relationship between the morphological structure and the physical properties of colloidal systems and biomaterials on the one hand and the relationship between their synthesis conditions and morphological structure on the other hand. Because of the structure of the institute, we are working together with a number of groups in the colloid chemistry, interface and the biomaterials departments. Our research activities are focussed on the electron microscopic exploration of the morphological structure of polymer micelles and particles, inorganic crystals, biominerals, polyelectrolyte complex shells and biomaterials. Some interesting results are presented here.

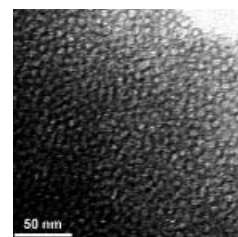
Templating techniques are used for the controlled formation of highly porous materials with a defined structure and desired properties, which are interesting for analytical applications, photonics and catalysis. Colloidal crystals, polymer gels, porous inorganic microspheres and polymer particles are suitable templates for the synthesis of new inorganic (e.g. silicon dioxide) or specific organic networks (e.g. molecularly imprinted polymers). The empty space of a colloidal crystal of polystyrene particles can be filled, e.g. with a mixture of an amphiphilic ionic liquid and tetramethylorthosilicate, used as the sol-gel precursor. To control the synthesis processes of the three-dimensional structural hierarchies both the structures of ordered latex spheres and the final pore structure of silica skeleton after calcination the materials are characterized by electron microscopy. **Fig. 1** reveals that the removal of both templates did not destroy the original ordered structure replicated into the inorganic matrix. The interconnected network of the spherical voids left in the silica was still arranged in wellordered close-packed structures. The average size of the voids and thickness of the walls are about 175 nm and 25 nm, respectively, the void size is slightly smaller than that of the PS sphere, due to shrinkage during calcination. Further TEM investigations shows that the wall architecture is made up of larger domains of an ordered nanoporous lamellar phase surrounding the macropore. The interlayer periodicity of the lamellae is about 2.7 nm, with ca. 1.3 nm thick slit pores and 1.4 nm thick walls, respectively.



*Fig. 1 : Tailored bimodal three-dimensional order of porous silica after calcination*

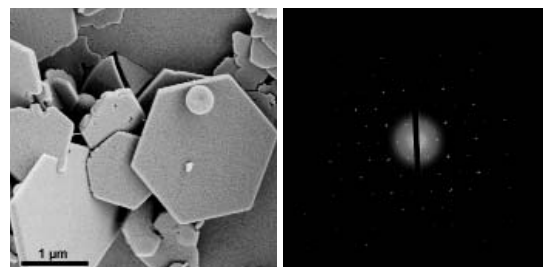
Mesoporous silica materials are suitable materials for the examination of nanoreactor effects. For their synthesis the so-called nanocasting process was used where different template phases are transferred to the pores in a 1:1 imprint-

ing process. Depending on the templates, different pore sizes can be achieved. Cyclodextrins lead to pores between 1.5 nm and 2 nm, nonionic surfactants or mixtures of them lead to pores between 2 nm and 4 nm, and poly(styrene)-poly-(ethyleneoxide) block copolymers (SE) result in pore diameters between 4.5 nm and 10 nm (**Fig. 2**).



*Fig. 2: Mesoporous structure of SE-based silica material*

One of the main projects is the electron microscopic investigation of biomimetic synthesized inorganic minerals with complex forms. Organic additives and/or templates with complex functionalization patterns are used to control the nucleation, growth, and alignment of inorganic crystals. It is possible to stabilize the  $\text{PbCO}_3$  platelet-like intermediates permanently by increasing the binding strength of double hydrophilic block copolymers.



*Fig. 3a:  $\text{PbCO}_3$  nanoplates with a quasi-hexagonal crystal morphology  
 Fig. 3b: Electron diffraction pattern of the  $\text{PbCO}_3$  plates*

Thin platelet-like particles with a smooth surface and a thickness of about 90 nm are growing, if the strong binder PEG-*b*-[[2-[4-dihydroxy phosphoryl]-2-oxabutyl]acrylate ethylester] ( $1 \text{ g L}^{-1}$ ) is used. **Fig. 3a** reveals the morphology of  $\text{PbCO}_3$  particles, formed after two weeks at room temperature and  $\text{pH} = 5$ . The electron diffraction pattern (**Fig. 3b**) taken along  $\langle 001 \rangle$  shows its single crystalline nature, corresponding to uniaxially elongated quasi-hexagonal thin plates.

Low molecular weight polyelectrolytes can be used for the self-assembly of complex spherical  $\text{BaCO}_3$  superstructures through a facile mineralization process under ambient conditions. Without adding polymer additives and through either rapid mixing or slow gas diffusion dendritic growth of  $\text{BaCO}_3$  occurs. In **Fig. 4a** the morphology of  $\text{BaCO}_3$  particles are shown synthesized by a mineralization reaction for two weeks at room temperature ( $\text{pH} = 5$ ,  $[\text{BaCl}_2] = 10 \text{ mM}$ ). Energy-dispersive X-ray analysis confirms the stoichiometric molar ratio for  $\text{BaCO}_3$ . However, mineralization in the presence of  $1 \text{ g L}^{-1}$  poly(styrenesulfonate) (PSS) produced well-

defined  $\text{BaCO}_3$  microspheres with a diameter in the range of 2-3.5  $\mu\text{m}$  (**Fig. 4b**). They were built from smaller, elongated rodlike building blocks with a typical diameter of 50 nm and length of 200 nm, which apparently adopted the more equilibrated isostructural aragonite appearance.

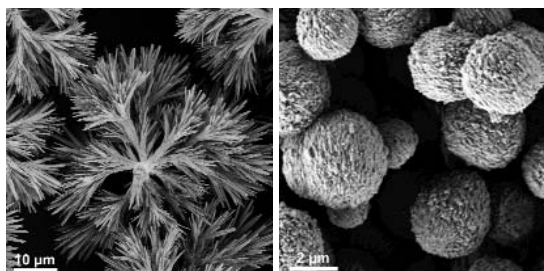


Fig. 4a: Dendritic  $\text{BaCO}_3$  crystals without additives

Fig. 4b:  $\text{BaCO}_3$  microspheres in the presence of PSS

Colloidal crystals have been extensively explored as model systems of condensed matter physics. The actual research is devoted to the design and controlled fabrication of non-close packed 2D colloidal crystals on silica wafers via dip-coating. Different from the routine colloidal crystallization procedures swollen polymer hydrogel spheres are used as building blocks. As basic colloids poly(N-isopropylacrylamide) (PNIPAM) latex particles with a hydrodynamic diameter of 670 nm are employed. In addition to the original PNIPAM dispersion the in situ mineralization of  $\text{CaCO}_3$  in the hydrogel particles was used for the fabrication of a  $\text{CaCO}_3$ /PNIPAM composite spheres. If the reduction of the inter-sphere distance is smaller than the shrinkage of the individual spheres, the non-close packing arrays on solid surfaces can be formed. **Fig. 5** reveals a typical 2D colloidal crystal produced by dip-coating of a 0.1 wt-%  $\text{CaCO}_3$ /PNIPAM composite dispersion at a withdrawing speed of 5  $\mu\text{m/s}$ . The non-close packing array consist of disc-like particles of around 550 nm in diameter and the center-to-center distance between particles is about 1040 nm, corresponding to a 490 nm interparticle gap, which is similar to that derived from the pure PNIPAM spheres.

This may likely be due to the fact that the loading amount of  $\text{CaCO}_3$  is quite low. If the withdrawing speed is reduced to 1  $\mu\text{m/s}$ , the center-to-center distance between particles decreases to 730 nm, corresponding to a 180 nm gap between the particles. The exploration of the mechanisms behind the formation of 2D non-close packing arrays based on hydrogel spheres is an ongoing project in the interface department.

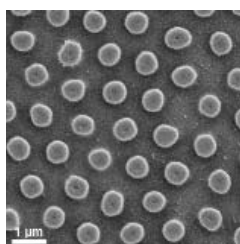


Fig. 5: Typical 2D colloidal crystal structure of  $\text{CaCO}_3$ /PNIPAM composite

Hierarchically structured biomaterials, e.g. grasses, bamboo, and bones, with a high mechanical performance may serve as models for the development of biomimetic materials.

In cooperation with the biomaterials department we are interested in the silica distribution in horstail *Equisetum hyemale*, which can be used as model plant for biomineralization and biosilicification. To determine the location of the accumulated silicon we examine cross sections of various significant horstail structures using scanning electron microscopy for structural and analytical investigations (**Fig. 6a**). Energy-dispersive X-ray spectroscopy and elemental mapping of silica was done to identify positions where silica is concentrated.

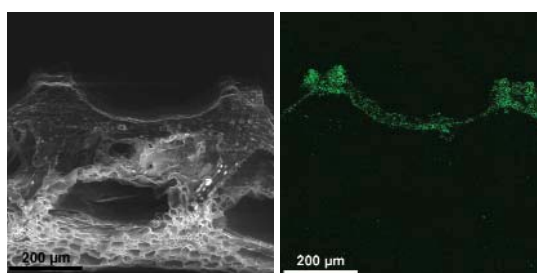


Fig. 6a: Cross-section of the stem of the horstail

Fig. 6b: Silica distribution in the region of Fig. 6a

In general the silica is localized as a thin layer on the outer surface. It seems that the silica can not enter the cell membranes and remains concentrated on the surface (**Fig. 6b**). The thickness of the silica layer varies in the range of 3  $\mu\text{m}$  to 15  $\mu\text{m}$ .

Another project is the investigation of the mineral-collagen composite structure of cattle femur at the nano-structural level to determine the degree of mineralization. A special embedding technique for the oriented fixation of the biomaterial structure was developed. The ultra-thin cross-section **Fig. 7** reveals that the mineral is embedded in the fibrillar collagen structure. In certain localized areas circular oriented mineral pattern are observed. The crystals have a platelet-like shape with irregular edges and the crystal size range in length from 15 nm to 150 nm, in width from 10 nm to 80 nm, and in thickness from 2 nm to 6 nm.

In the future more detailed investigations the crystal shape, size, order and the location of the minerals in dependence on the degree of mineralization are of special interest.

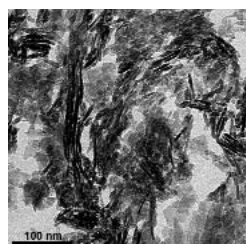


Fig. 7: Ultra-thin cross-section of a mineralized cattle femur

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## Multi Angle Laser Light Scattering in Dependence on Time



Aggregation and disaggregation processes of supermolecular structures often take place in time intervals, which interfere with the time needed for a measurement of the angular dependence scattering curve by goniometer type LS instruments. This results in inconsistent scattering curves as measurements for different angles are taken at different times.

MALLS may solve this problem by simultaneous measurement of the intensity for the entire angle range. This way complete scattering curves vs. time can be produced.

The MALLS instrument DAWN EOS (Wyatt, USA), designed and mainly used as detector for online measurements with a flow cell after fractionation methods (GPC or FFF) has been modified in our lab. The combination of the advantages of the DAWN instrument, the introduction of an index-matching bath and additional equipment to improve the accuracy of measurements and further development of our software package LISA yields an effective tool.

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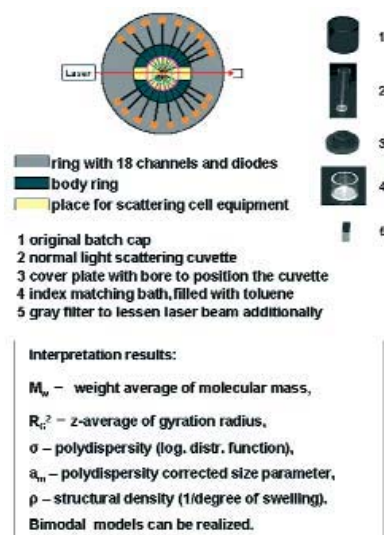


Fig. 1: Scheme of the sample room, additional equipment, general results

### Polyelectrolyte Complexes – Subsequent Addition of Salt

Polyelectrolyte complexes (PECs) are of high practical relevance, ranging from large-scale industrial use up to special purposes in biotechnology and medicine. An important feature in all applications is their sensitivity to environmental changes, especially alteration of salt conditions. During the addition of sodium chloride, PECs with carboxylic groups containing polyanions show swelling, aggregation and finally dissolution at a critical salt concentration. Such processes were studied in detail by MALLS.

Materials: PEC Cop47/NaPMA, polyanion: NaPMA, polycation: Cop47 (a copolymer of diallyldimethylammonium chloride and acrylamide with 47 mol-% of cationic groups), PEC prepared in pure water, mixing ratio X=0.6

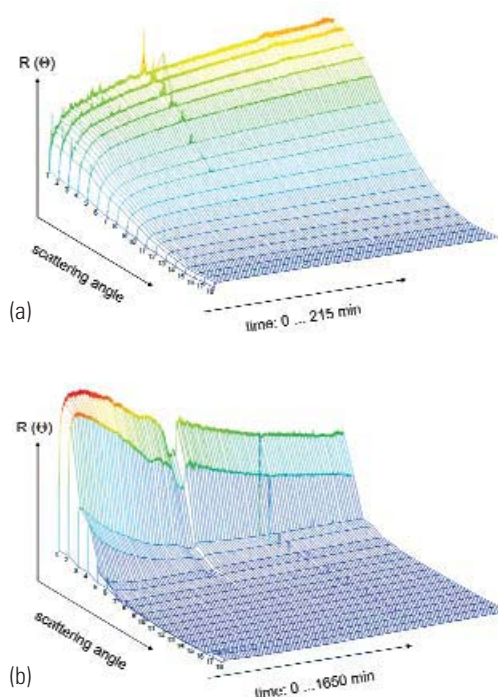


Fig. 2: Scattering curves recorded after adjustment to an ionic strength of 0.4 (a) and 0.475 N NaCl

Steps: (1) start with PEC in light scattering cuvette – characterization in pure water, (2) addition (very fast under vigorous stirring) of a 2N NaCl solution, immediately inserting the cuvette into the DAWN instrument (delay time about 10 sec), (3) light scattering studies in dependence on time.



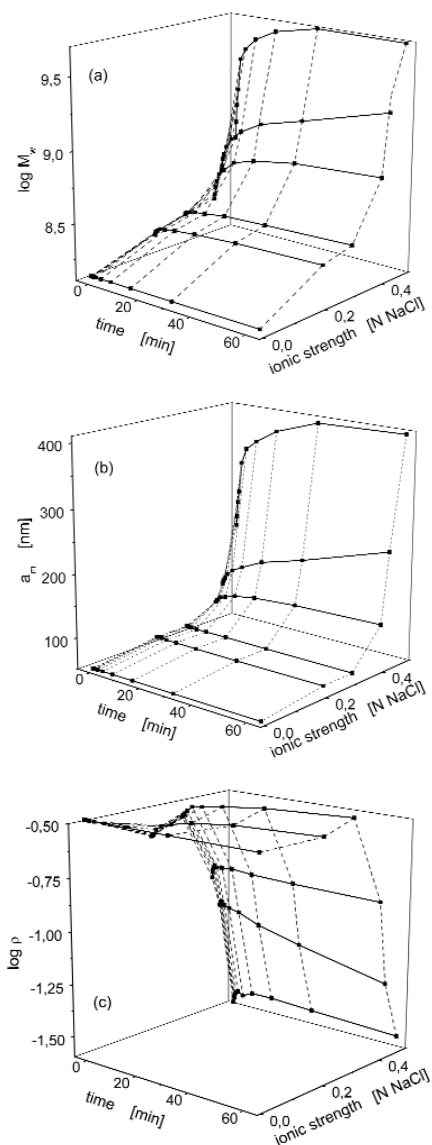


Fig. 3: Time dependence (64 min) of (a) particle mass  $M_w$ , (b) polydispersity corrected radius  $a_m$ , (c) structure density  $\rho$  at different ionic strength (0, 0.2, 0.3, 0.4, 0.425, 0.475 N NaCl)

### Aqueous Heterophase Polymerization of Styrene

Online MALLS experiment, addition of initiator to a styrene solution in water.

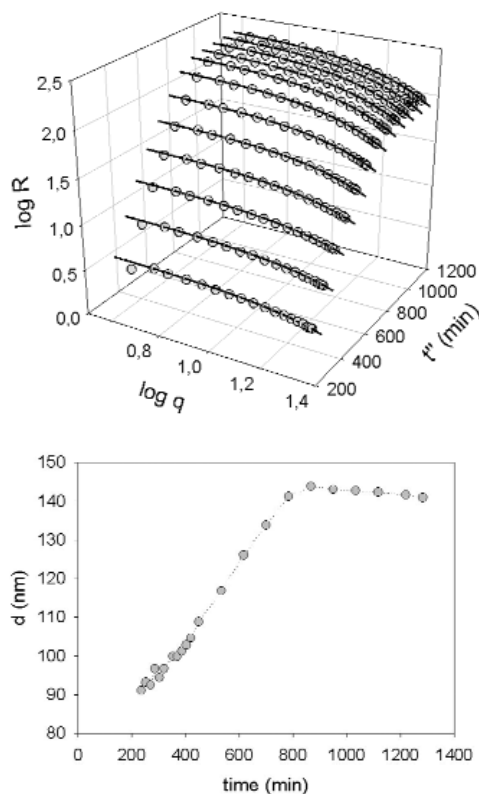


Fig. 4: (a) Scattering curves during predominant particle growth, symbols – experimental points, solid lines – adequate interpretation models; time after the addition of initiator, (b) average size (spheres, diameter) of the colloidal particles

### Conclusion

A detailed analysis of the scattering curves provided the structural parameters particle mass, radius and structure density and offers the chance to distinguish between the time dependence of the processes of swelling, secondary aggregation and complete dissolution of the PEC particles.

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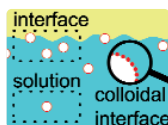
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## Modern Methods of Light Scattering



Light scattering measurements are versatile and well-established tools for the investigation of colloids and polymers in solution. With special polarization dependent experiments or total internal reflection geometry, the scattering experiments become sensitive to interfacial properties. The target of the



research is to develop new methods and apply them to questions concerning the physics of colloidal particles and polymer aggregates.

### Ellipsometric Light Scattering

By combining a light scattering experiment with polarization optics of an ellipsometer, a new technique has been established for the investigation of the interface of colloidal particles to the surrounding solvent. While classical reflection ellipsometry detects a thin layer on a flat interface, ellipsometric light scattering characterizes thin layers on spherical colloidal particles. Experiments on different colloidal systems have been performed in collaboration with the group of Klaus Tauer.



As an example, **Fig. 1a** displays data for colloids with a corona composed of poly-electrolyte chains (sodium polystyrene sulfonate). Here,  $\Theta$  is the scattering angle and  $\tan(\Psi)$  and  $\Delta$  are the measured ellipsometric parameters (amplitude ratio and relative phase difference of the scattering amplitudes for two polarization modes). Similar to reflection ellipsometry, the information about the refractive index profile at the interface is encoded in the shape of  $\tan(\Psi)$  and  $\Delta$  and has to be determined in a fitting procedure. For the poly-electrolyte corona, the profile of the refractive index difference to the solvent follows a power law with the exponent  $\alpha$ . Data for  $\alpha$  obtained from simultaneous fit of measurements at the available two wavelengths of light (532nm and 633nm) are

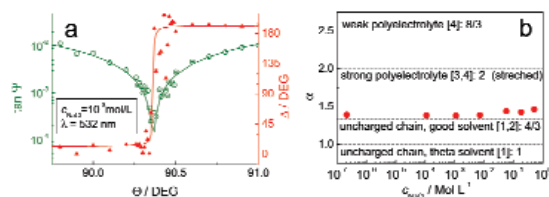


Fig. 1: Ellipsometric light scattering on colloidal particles with a poly-electrolyte corona. (a) Raw data. (b) Exponent  $\alpha$  of the power law describing the refractive index profile.

displayed in **Fig. 1b**. The comparison to different theories shows, that  $\alpha$  corresponds to the value for uncharged chains, independent of the concentration  $c_{\text{NaCl}}$  of the added sodium chloride salt. The stretching of the poly-electrolyte chains by electrostatic interactions or osmotic pressure of the low molecular weight counterions (not shown here) does not affect the exponent of the refractive index profile.

Another experiment with an unexpected result is the behaviour of charged colloidal particles at different concentrations  $c_{\text{NaCl}}$  of added salt. Raw data for  $\tan(\Psi)$  are displayed in **Fig. 2a**. There are two regimes at low and high  $c_{\text{NaCl}}$ . Experimental data for different  $c_{\text{NaCl}}$  overlap within the regimes, respectively, but there is a transition between the two regimes at around the  $c_{\text{NaCl}}=10^{-4}$  mol/L. While the  $\tan(\Psi)$  and  $\Delta$  data for two wavelengths of light are well described by a model of a homogenous sphere at low  $c_{\text{NaCl}}$ , a reasonable fit in the high  $c_{\text{NaCl}}$  regime requires the introduction of an additional layer at the interface of the colloid. The nature of the layer is not clear yet.

Since ellipsometric scattering is affected by birefringence within a particle shell, it was possible to determine the order of lipid vesicles. Experiments on colloidal particles with a corona of polymers with thermo-responsive solubility

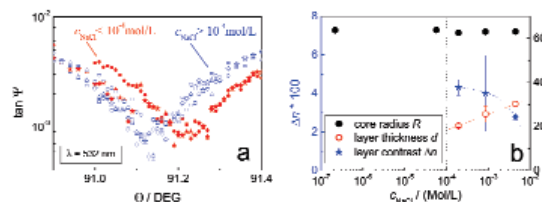


Fig. 2: Ellipsometric light scattering on charged colloids. (a) Data for  $\tan(\Psi)$  at several salt concentrations  $c_{\text{NaCl}}$ . (b) Core radius  $R$ , shell thickness  $d$  and contrast factor  $\Delta n$  obtained from the fitting procedure.

(Poly-[N-isopropylacrylamide, PNIPAM]) indicate that the thickness resolution of ellipsometric light scattering with two wavelength of light is better than 20nm. For improved accuracy, a new multi wavelength apparatus is under construction. Other future plans concern – beside the application of the technique to different samples – the experimental and theoretical investigation of effects of particle interaction, multiple scattering, and non-spherical particle shape.

### Procedures of Interface Light Scattering

Although a liquid-liquid interface is of special interest for exchange processes and interface fluctuations, it is much less investigated than other types of interfaces. For transparent solvents (e.g. oil and water), various properties of the interface can be determined by non-perturbing optical methods. Reflection ellipsometry gives the average surface concentration of dissolved colloids or polymers, while capillary wave spectroscopy yields the interface tension. In a total-internal-reflection geometry, the solvent of lower refractive index is illuminated only by the evanescent wave, which penetrates just a fraction of the wavelength. The scattering of this light contains information about amplitude and dynamics of fluctuations close to the interface. A home-built apparatus for all three experiments is shown in Fig. 3.

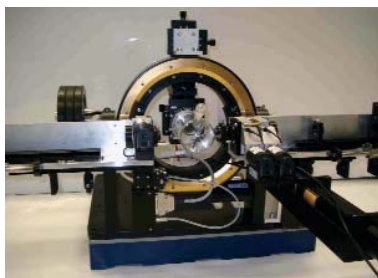
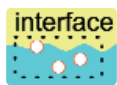


Fig. 3: Home-built apparatus for ellipsometry, evanescent wave scattering and capillary wave spectroscopy at the liquid-liquid interface.

A first project is the investigation of the interface behaviour of colloidal particles with pH-dependent amphiphilicity, in collaboration with the group of Steve P. Armes (University of Sussex, UK). Ellipsometry yields the height of the particles within the interface and the interface concentration. While at the water-air interface the colloids form a sub-monolayer with decreasing interface concentration at higher temperature, the water-oil interface is covered with a double layer where the interface concentration increases with temperature (see Fig. 4). The pH-dependent height reflects the change of contact angle.

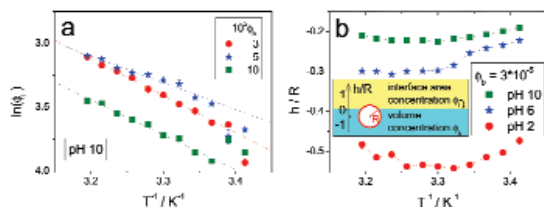
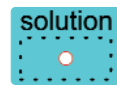


Fig. 4: Colloids with pH-dependent amphiphilicity at the water-dodecane interface. (a) Interface concentration  $\phi$ . (b) Height in the interface.

### Results Obtained by Classic Static and Dynamic Light Scattering



The aggregation behaviour of simple block copolymer samples in a selective solvent is well understood in terms of geometrical packing arguments. The incorporation of specific interactions like H-bridges of polypeptides or electrostatic attraction of opposite charges into block copolymer samples changes the structure of the aggregates significantly. In collaboration with the group of Helmut Schlaad, their synthetic activity was complemented by structure analysis of aggregates in solution by combined static and dynamic light scattering.

As an example, Fig. 5 displays experimental data for a block copolymer including a poly peptide block (1,2-polybutadiene-*block*-poly[L-lysine]). In water, the polymer forms wormlike aggregates. The switching of the peptide conformation from a gaussian coil (pH 7) to a helix (pH 10) induces a change in the linear packing density: the value of the dotted line at low values of the scattering vector  $q$  indicates the number of polymers per nanometer.

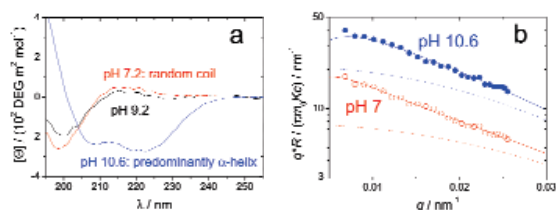


Fig. 5: Wormlike aggregates of block copolymers with a polypeptide block. (a) pH-dependent conformation of the poly peptide determined by circular dichroism. (b) Holtzer plot of the specific scattering intensity  $R_w/Kc$  normalized with the molecular mass  $m_0$  of a single polymer. The dotted line indicates the asymptotic behaviour due to the finite worm thickness, calculated from the fit parameters.

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