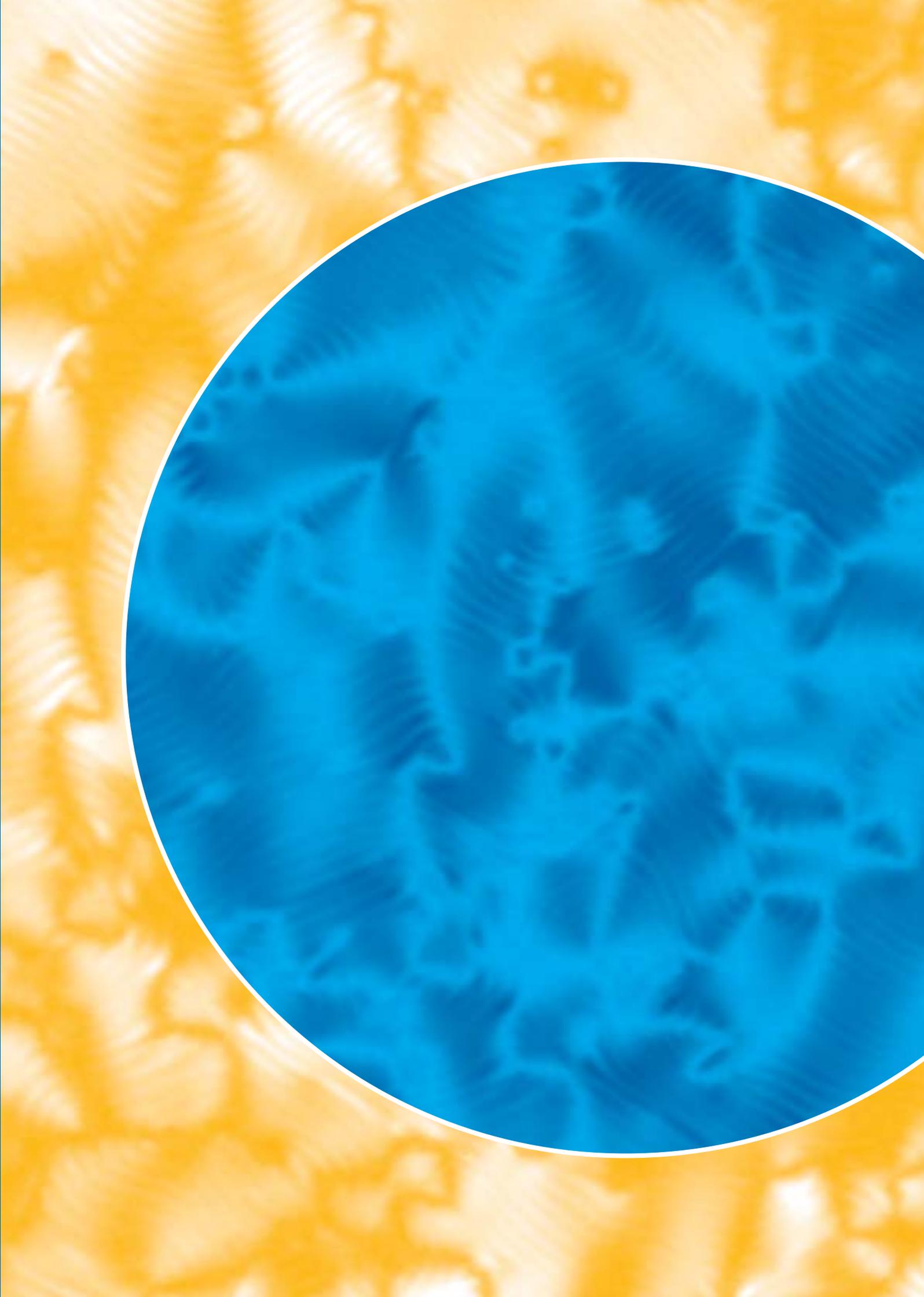




COLLOID  
CHEMISTRY

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 element of the group are "projects", a structure headed by senior scientists involving technicians, graduate students and postdocs (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.

In the time of this report, Karl-Heinz Goebel, Herbert Dautzenberg (retirement), Rachel Caruso (Melbourne) and Hans-Peter Hentze (Newark) left the department, while three new groups, headed by Hans-Börner, Charl Faul and Markus Niederberger, have been established. This turnover is rather typical and keeps the department dynamic.

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
- Polyelectrolytes and their Complexes
- Amphiphilic Polymers
- Mesoporous Materials
- 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 online 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 lattices, reinforced materials) by emulsion polymerization and rational use of the particle interfaces (Dr. Klaus Tauer).
- Inisurfs and Surfmers, and new stabilizers for better polymer dispersions (Dr. Klaus Tauer).
- Miniemulsion polymerization allows the formulation of very small polymer lattices by high shear treatment of dispersions. Since one polymerizes preformed oil droplets under preservation of droplet number, composition, and inner structure, miniemulsion polymerization significantly extends the possibilities of emulsion polymerization. (Dr. Katharina Landfester).
- Synthesis of organic/inorganic hybrids by encapsulation of inorganic colloids or magnetic particles using miniemulsions. Those particles have strong impact in diagnostics and magnetotherapy (Dr. Katharina Landfester, within a DFG-Schwerpunkt).
- Single Molecule Chemistry on Polymers and confined crystallization in miniemulsion droplets Physical or chemical procedures are performed in a molecule-per-molecule fashion. Examples for this are complex reactions or folding/crystallization of polymers or proteins in the absence of any intermolecularity. (K. Landfester, Markus Antonietti)

## Polyelectrolytes and their Complexes

Polyelectrolytes are water soluble and combine sustainability with a broad spectrum of properties. Polyelectrolytes can be found in many aspects of daily life, such as thickeners, diapers or in waste water treatment. Our research is focused on the basic understanding of diverse polyelectrolyte properties and modern derivatives of polyelectrolytes:

- Polyelectrolyte/polyelectrolyte complexes and polyelectrolyte/surfactant complexes offer a wide range of structured materials, the diversity of which is far from being fully explored. Our work is focused on the construction of nanostructures with astonishing complexity. Due to their simple synthesis (common precipitation from water) and the commercial starting materials, they represent the cheapest polymer liquid crystals. Such complexes can exhibit selective gas permeation or ultra-low surface energies. Current work extends this Ionic Self Assembly (ISA) towards inorganic polymers, dyes, and biological tectons (Dr. Charl Faul).

## Amphiphilic Polymers

Amphiphilic polymers consist of components which different solubility, e.g. a hydrophilic and a hydrophobic part. Both components can be sensitively adjusted to the dispersion medium as well as the dispersant, and "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 by Nanocasting and Nanocoating

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 use of polymer gels, fiber, membranes and beads to create structures and shaped objects made from nanoparticles by nanocasting and nanocoating (Dr. Markus Niederberger)
- the employment of these structures as supports for designer catalysts where nanoparticle formation is a integer 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 supra-molecular entities (Markus Antonietti)

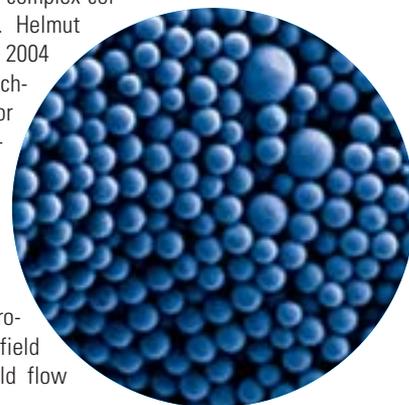
- implementation of experiments within the pore system for "nanochemistry", i.e. the analysis of specific effects of a nanoconfinement on a physical properties and chemical reactions (Markus Antonietti)



### 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 would allow an in-situ chemical analysis within a separating complex colloidal mixture and revitalize the AUC. (Dr. Helmut Cölfen, Project Analytical Ultracentrifugation 2004 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)
- exploratory research for the application 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, wide and small angle X-ray scattering, various chromatographic facilities, reaction calorimetry with online multidetection, analytical and preparative ultracentrifugation, thermal analysis, DSC, porosimetry, and FT-ATR for liquid analysis.

Two of the labs, the electron microscopy and the X-ray lab, are so-called "central service labs", i.e. they belong and are operated by the department, but are designated to perform scientific routine measurements for the whole institute.

Prof. Markus Antonietti  
Director of the Department of Colloid Chemistry

## Miniemulsions



### What Are Miniemulsions?

Miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobe. Polymerizations in such miniemulsions, when carefully prepared, result in latex particles which have about the same size as the initial droplets. This means that the appropriate

formulation of a miniemulsion suppresses coalescence of droplets or Ostwald ripening. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials or with respect to the stability of the formed latexes.

### Polyurethane Dispersions

Polyurethane latexes can be made by direct miniemulsification of a monomer mixture of diisocyanate and diol in an aqueous surfactant solution followed by heating (Fig. 1). This is somewhat special since one might expect a suppression of the polyaddition by side reactions between the very reactive diisocyanates and the continuous phase water. However, polymer dispersions with high molecular weight polymer were obtained after optimizing the reaction parameters.

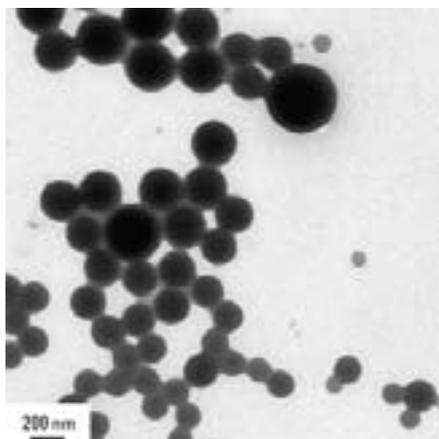


Fig. 1: Polyurethane latex obtained by polyaddition in miniemulsion

### Polyester Dispersions

Hydrophobic polyesters have been synthesized in miniemulsion in the presence of large amounts of water. The yield of the esterification and the molecular weight of the polyester have been determined for different reaction conditions. Important parameters are the water concentration inside the particles and the structure of the alcohol monomer. Alcohol compounds bearing electron-donating groups allow displacing the equilibrium toward ester formation. It was also shown that polyester/polystyrene hybrid particles can be synthesized in a very simple way using a one pot procedure.

### Amphiphilic Copolymers

The polymerization process of two monomers with different polarities was carried out in direct or inverse miniemulsions using the monomer systems of different hydrophilicity. The monomer, which is insoluble in the continuous phase, was miniemulsified in the continuous phase in order to form stable and small droplets. The monomer with the opposite hydrophilicity dissolves in the continuous phase. Starting from those two dispersion situations, the locus of initiation (in one of the two phases or at the interface) was found to have a great influence on the reaction products and the quality of the obtained copolymers (Fig. 2).

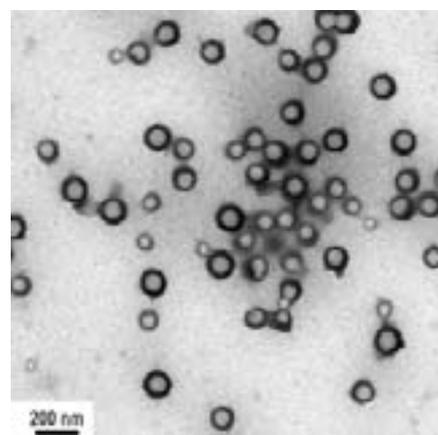


Fig. 2: Acrylamide/methyl methacrylate copolymer particles obtained in a direct miniemulsion polymerization with interfacial initiation

### Chitosan Stabilized Polymer Dispersions, Capsules and Chitosan Grafting Products

The potential of chitosan as an emulsion stabilizer was combined with the miniemulsion technique to generate oil droplets, hollow capsules, and latex particles in the diameter range of 100 nm to 300 nm carrying a functional biopolymer surface. The addition of biocompatible costabilizers with higher flexibility either to the oil phase or the water phase, allowed making very small nanocapsules of biopolymer hybrids (Fig. 3).

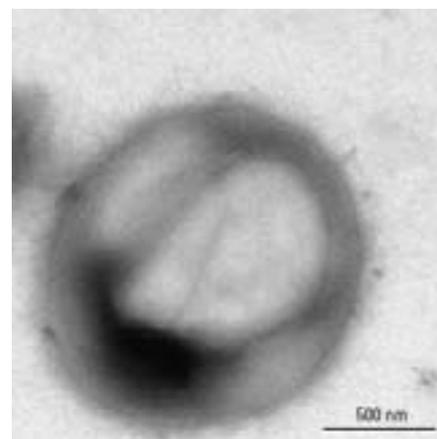


Fig. 3: Capsule preparation using chitosan as biocompatible stabilizer

**Katharina Landfester** 11.06.1969  
**1993:** Diploma, Chemistry  
(Technical University Darmstadt)  
Thesis: Synthesis and characterization of impact modifying core-shell latexes  
**1995:** PhD, Chemistry  
(Max Planck Institute for Polymer Science/University of Mainz)  
Thesis: Synthesis and characterization of core-shell latexes by transmission electron microscopy and solid-state NMR  
**1996-97:** Postdoc  
(Lehigh University, Bethlehem, USA)  
**Since 1998:** Group Leader  
(Max Planck Institute of Colloids and Interfaces, Golm)  
**2002:** Habilitation, Chemistry  
(Max Planck Institute of Colloids and Interfaces, Golm/University of Potsdam)  
Thesis: Reactions in Miniemulsion

### Fluorinated Latexes

Fluorinated latexes in the size range of 100 to 250 nm were made by the polymerization of miniemulsions of fluoroalkyl acrylates as fluorinated monomers under employment of rather low doses of protonated surfactants. In addition, it was shown that miniemulsification of mixed monomer species allows efficient copolymerization reactions to be performed with standard hydrophobic and hydrophilic monomers in a joint heterophase situation, resulting either in core-shell latexes or in statistical copolymers (Fig. 4). Contrary to the pure fluorinated polymers, those copolymers dissolve in organic solvents but still show the profitable interface properties of the fluorinated species.

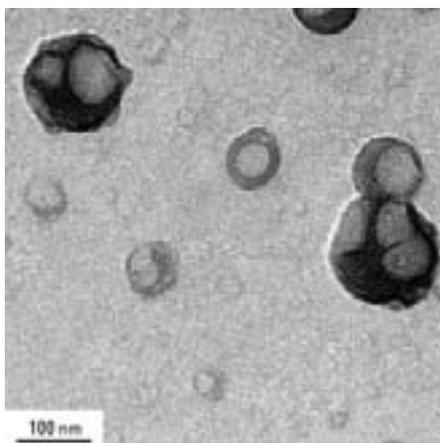


Fig. 4: Copolymer particles consisting of fluorinated and protonated acrylates

### Encapsulation of Magnetite Particles

The encapsulation of high amounts of magnetite into polystyrene particles could efficiently be achieved by a new three-step preparation route including two miniemulsion processes. Characterization by thermogravimetry, preparative ultracentrifugation, and transmission electron microscopy showed that up to 40 % magnetite could be encapsulated resulting in particles with a high homogeneity of the magnetite content (Fig. 5). Magnetometry measurements revealed that the included iron oxide aggregates still consisted of separated superparamagnetic magnetite particles.

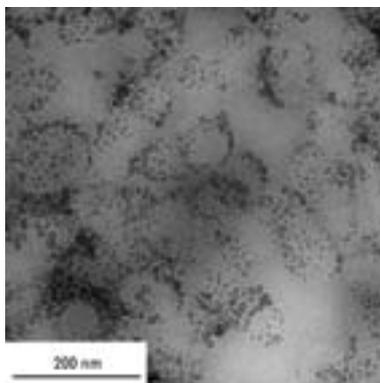


Fig. 5: Encapsulation of magnetite in polystyrene

### Semiconducting Polymer Spheres

Layers of conjugated semiconducting polymers could be deposited from aqueous dispersion prepared by the miniemulsion process (Fig. 6). Dispersions of particles of different conjugated semiconducting polymers could be prepared with well controllable particle sizes ranging between 70 to 250 nm by using a miniemulsion process. The concept of semiconducting polymer nanoparticles also allowed to form multilayer structures by e.g. depositing a first layer from a solution of a polymer and overcoated it by semiconducting polymer nanospheres of the second polymer from an aqueous phase, followed by annealing and film formation.

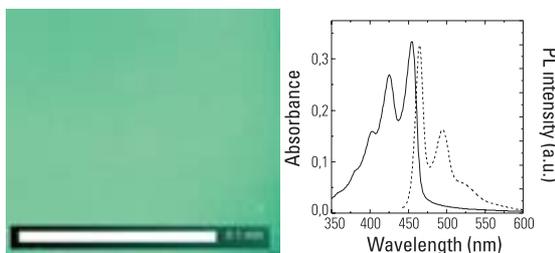


Fig. 6: a) Photoluminescence micrograph of a layer deposited from a semiconducting nanoparticle dispersion. b) Absorption and photoluminescence spectrum of the layer in a).

### Crystallization in Miniemulsion Droplets

Crystallization in miniemulsion droplets was shown to be strongly influenced due to the infinite size of the droplets. It was shown that the temperature of crystallization in miniemulsion droplets is significantly decreased as compared to the bulk material. This could be attributed to a very effective suppression of heterogeneous nucleation. In some case, the confinement in small droplets changed, e.g. in even alkanes the crystal structure changed from a triclinic (in bulk) to an orthorhombic structure.

K. Landfester, M. Barrère, C. Holtze, E. Marie, R. Montenegro, L. Ramirez, R. Rothe, A. Taden, O. Tongcher, U. Yildiz  
katharina.landfester@mpikg-golm.mpg.de

### References:

- [1] Landfester, K.: Polyreactions in miniemulsions. *Macromol. Rapid Comm.* 22, 896-936 (2001).
- [2] Tiarks, F., Landfester, K. and Antonietti, M.: One-step preparation of polyurethane dispersions by miniemulsion polyaddition. *J. Polym. Sci., Polym. Chem. Ed.* 39, 2520-2524 (2001).
- [3] Willert, M. and Landfester, K.: Amphiphilic copolymers from miniemulsified systems. *Macromol. Chem. Phys.* 203, 825-836 (2002).
- [4] Marie, E., Landfester, K. and Antonietti, M.: Synthesis of Chitosan Stabilized Polymer Dispersions, Capsules and Chitosan Grafting Products via Miniemulsion. *Biomacromolecules* 3, 475-481 (2002).
- [5] Landfester, K., Rothe, R. and Antonietti, M.: The convenient synthesis of fluorinated latexes and core-shell structures by miniemulsion polymerisation. *Macromolecules* 35, 1658-1662 (2002).
- [6] Hoffmann, D., Landfester, K. and Antonietti, M.: Encapsulation of magnetite in polymer particles via the miniemulsion polymerization process. *Magneto hydrodynamics* 37, 217-221 (2001).
- [7] Landfester, K., Montenegro, R., Scherf, U., Güntner, R., Asawapirom, U., Patil, S., Kietzke, T. and Neher, D.: Semiconducting polymer nanospheres in aqueous dispersion prepared by miniemulsion process. *Adv. Mater.* 14, 651-655 (2002).

## Heterophase Polymerization



Heterophase polymerization techniques are a fascinating and attractive example of applied polymer colloid chemistry. Our main research topics of the last two years were (a) exploration of new ways to prepare block copolymers by radical heterophase polymerization, (b) mechanistic investigation of controlled radical polymerization with 1,1-diphenylethylene (DPE) based precursor polymers, (c) further evaluation of poly(ethylene glycol)-azo-initiators, and (d) development of procedures to prepare  $\mu\text{m}$ -sized, monodisperse particles with surface poly(ethylene glycol) groups.

**Klaus Tauer** 27.09.1951

**1974:** Diploma, Polymer Chemistry (Friedrich-Schiller University, Jena)

Thesis: On the photoconductivity of polyarylene-vinylene polymers

**1978:** PhD, Polymer Chemistry (Friedrich-Schiller University Jena)

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

**1977-1991:** Scientific Coworker (Institute for Polymer Chemistry, Academy of Sciences, Teltow)

**1987:** Habilitation, Chemistry (Academy of Sciences, Teltow)

Thesis: Modelling emulsion polymerization of vinyl chloride

**Since 1992:** Group Leader (Max Planck Institute of Colloids and Interfaces, Golm)

### Preparation of Block Copolymers

The strategy employed consists of a multi-stage radical heterophase polymerization by utilizing the ceric ion redox initiation mechanism to generate radicals at preferably hydroxyl group substituted polymer chain ends that subsequently form polymeric micelles or particles during an aqueous heterophase polymerization as isolated reaction loci where the further block copolymer formation takes place after addition of another batch of monomer. This strategy allows the preparation of very unique block copolymers, which are not accessible by any other route. Examples are poly(ethylene glycol)-*b*-poly(*N*-isopropyl acrylamide)-*b*-poly(acrylamidopropane sulfonate), polystyrene-*b*-poly(*N*-isopropyl acrylamide)-*b*-poly(styrene sulfonate), or poly(styrene sulfonate)-*b*-poly(methacrylic acid) [1]. Besides the chemical distribution the block copolymer nanoparticles possess at least under wet conditions (in the dispersed state) also a characteristic density distribution which changes upon electrolyte addition and/or temperature changes. Moreover, particles of this kind exhibit interesting features which are not yet completely understood. For example, transmission electron microscopy (TEM) images of poly(ethylene glycol)-*b*-poly(*N*-isopropyl acrylamide)-*b*-poly(methyl methacrylate) (PEG-PNIPAM-PMMA) triblock copolymer particles show a hairy morphology whereas atomic force microscopy (AFM) images reveal a rather tubular morphology (Fig. 1). This polymerization strategy can also be used to prepare block copolymer particles with special core morphology such as PEG-*b*-PNIPAM-*b*-poly(styrene sulfonate) particles where the core consists of cross-linked poly(styrene sulfonate). These hydrophilic gel particles have been used to prepare redispersible polyelectrolyte surfactant complexes that are colloidal particles with anisotropic, crystalline cores. Fig. 2 shows a TEM picture of cross sections of such colloidal complexes with tetradecyltrimethyl ammonium counterions [2].

### Control of Radical Polymerizations with DPE Precursor Polymers

Recently it was found that the use of (DPE) in conventional free radical polymerization allows a high degree of structural control [3]. The principle of this new method consists of a two-step polymerization. In the first step a DPE-containing precursor polymer is prepared, which in a second polymerization

leads to the formation of block copolymers. The two steps can be carried out either sequentially and spatially separated or conducted like a one pot synthesis with consecutive addition of monomers. In contrast with all other methods of controlled radical polymerization, the DPE-based technique can be applied for all types of acrylate, methacrylate, vinyl and styrene monomers. Moreover, it can be applied in bulk, solution as well as heterophase polymerizations and the DPE-precursor polymer can be either hydrophilic or hydrophobic. In collaboration with the BASF Coatings AG the mechanism of this reaction was investigated. It turned out that the active species in the precursor polymer is the  $\alpha$ ,  $\beta$ -dimer unit which is formed by combination termination of two DPE-ended radicals (Formula 1) [4, 5]. The results of comprehensive studies reveal that the semiquinoid structure of the precursor polymer is activated by the attack of free radicals and thus, in a second stage polymerization with a second monomer, block copolymers are formed. The block copolymer yield can be well above 90 % but depends strongly on the ratio between the amount of DPE-containing precursor polymer and the initiator and monomer concentration used in the second stage (Fig. 3). The mechanism proposed is able to explain at least qualitatively all experimental results including the restriction of this mode of control of radical polymerization to the formation of diblock copolymers only.

### Poly(Ethylene Glycol)-Azo-Initiators in Heterophase Polymerizations

The use of nonionic poly(ethylene glycol)-azo-initiators (cf. Formula 2) instead of ionic initiators in emulsion polymerizations offers interesting possibilities to modify colloidal and polymeric properties of polymer dispersions. Experimental results have been obtained for various kinds of anionic, cationic, and nonionic stabilizers. For example, in a styrene emulsion polymerization with monomer to water mass ratio of 1:4 at a given concentration of 1 % with respect to monomer mass of either an anionic or a cationic surfactant the replacement of either peroxydisulfate or 2,2'-azobis(2-amidinopropane)-dihydrochloride, respectively, by PEGA200 leads to particles with considerably smaller size, polymers with higher molecular weight, and latexes with higher viscosity. These results indicate on the one hand a special interaction between the PEG-radicals and ionic surfactant and on the other hand the influence of the ionic strength on aqueous heterophase polymerization [6].

### Large, Monodisperse Poly(Ethylene Glycol) – Coated Latex Particles

Polymer particles with polar functional groups such as poly(ethylene glycol) on the surface are widely utilized in biomedical applications particularly for protein immobilization and cell adhesion studies. Depending on the size and morphology, the particles prepared are also considered to be useful for use as size-exclusion and HPLC packings. The objective of this project was to develop synthetic routes to prepare large monodisperse particles with a PEG shell. For

this the following synthesis strategy was developed which is illustrated in **Fig. 4** by means of scanning electron microscopy (SEM) and light microscopy (LM) images. First, polystyrene seed particles have been prepared by dispersion polymerization in ethanol – water mixtures with poly(vinyl pyrrolidone) as stabilizer and 2,2'-azobisisobutyronitrile as initiator. These particles have been swollen with a large excess of styrene by activated swelling procedures (step A in **Fig. 4**) and subsequently polymerized (step B in **Fig. 4**). Finally, these particles were used as seed in a second seed copolymerization with styrene/PEG-mono methyl methacrylate with average molecular weights of PEG chains of 1000 g mol<sup>-1</sup> and 4000 g mol<sup>-1</sup> as monomer mixture and PEGA200 (**Formula 2**) as initiator (step C in **Fig. 4**). The developed strategy allows the preparation of monodisperse polystyrene particles with PEG shells in the size range between 1 and 10 μm [7-9].

K. Tauer, H. Ahmad, V. A. Khrenov, U. Lubahn, S. Pirok, R. Rafler, S. Viala  
klaus.tauer@mpikg-golm.mpg.de

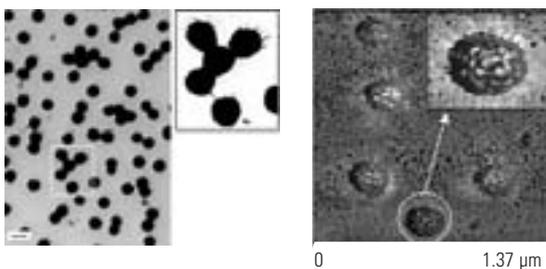


Fig. 1: TEM (left) and AFM image (right) of PEG-PNIPAM-PMMA triblock copolymer particles; the bar indicates 200 nm

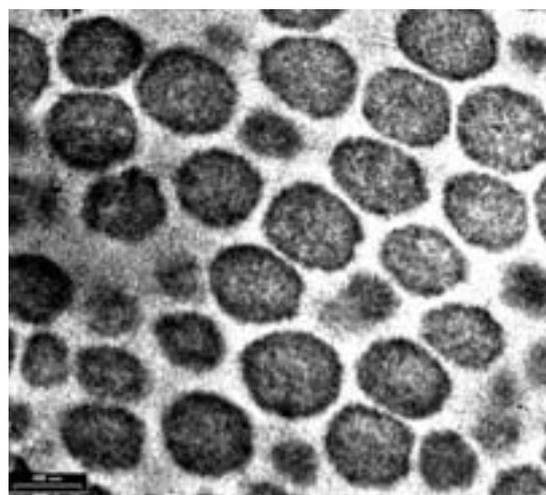
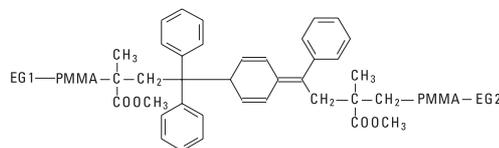


Fig. 2: TEM picture of cross section of polyelectrolyte surfactant complex particles; the bar indicates 300 nm



Formula 1: Active semiquinoid structural unit ( $\alpha, p$ -dimer) in DPE – PMMA precursor polymers; EG1 and EG<sup>2</sup> denote different end groups arising from initiating radicals

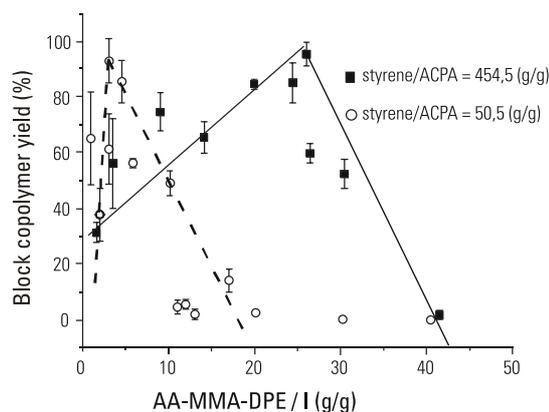
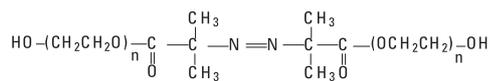


Fig. 3: Block copolymer yield between a hydrophilic precursor polymer made of acrylic acid, methyl methacrylate and DPE (AA-MMA-DPE) and styrene during an aqueous heterophase polymerization with 4,4'-azobis(4-cyanopentanoic acid) (ACPA) as initiator (I) in dependence on the precursor polymer to initiator ratio for two different monomer to initiator ratios (each experiment was repeated four times; lines are just for guiding the eyes)



Formula 2: Poly(ethylene glycol)-azo initiators (PEGA) (PEGA200 n=4-5)

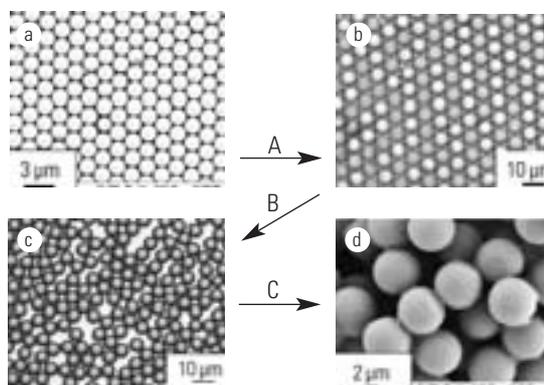


Fig. 4: Images of monodisperse polymer particles: a – SEM of seed particles (polystyrene), b – LM of swollen seed particles (styrene + polystyrene), c – LM of polymerized swollen particles (polystyrene), d – SEM of composite particles PS/P(S-PEGMMA)

## References:

- [1] Tauer, K. and Khrenov, V.: Polymer Dispersions as Intermediate State during the Synthesis of Specialty Polymers. *Macromol. Symp.* 179, 27-52 (2002).
- [2] Hentze, H.-P., Khrenov, V. and Tauer, K.: A New Approach towards Redispersible Polyelectrolyte-Surfactant Complex Nanoparticles. *Coll. Polym. Sci.* 280, 1021-1026 (2002).
- [3] German Patent WO 00/37507, 2000. German Patent DE19909803 A1, 2000. German Patent WO 00/39169, 2000 all to BASF Coatings AG
- [4] Viala, S., Tauer, K., Antonietti, M., Krüger, R.-P. and Bremser, W.: Structural control in radical polymerization with 1,1-Diphenylethylene: 1. Copolymerization of 1,1-Diphenylethylene with Methyl Methacrylate. *Polymer* 43(26), 7231-7241 (2002).
- [5] Viala, S., Antonietti, M., Tauer, K. and Bremser, W.: Structural control in radical polymerization with 1,1-Diphenylethylene: 2. Behavior of MMA-DPE copolymer in radical polymerization. *Polymer* 44(5), 1339-1351 (2003).
- [6] Tauer, K. and Müller, H.: On the role of initiator in emulsion polymerization. *Coll. Polym. Sci.* 281, 52-65 (2003).
- [7] Ahmad, H. and Tauer, K.: Production of micron-sized polystyrene particles containing PEG near the particles surface. *Coll. Polym. Sci.* in press, online published 11 December 2002,
- [8] Ahmad, H. and Tauer, K.: Poly(ethylene glycol) Coated Monodisperse Micronized Composite Polymer Particles. *Macromolecules* 36(3), 648-653 (2003).
- [9] Ahmad, H. and Tauer, K.: Study of the Preparation Monodisperse Micron-Sized PEG-Coated Polymer Particles Utilizing Different Methods. *Progr. Coll. Polym. Sci.* (in press).

# POLYELECTROLYTES AND THEIR COMPLEXES

## Ionic Self-Assembly: Facile Route for the Production of Functional Nanostructured Materials



In the field of supramolecular chemistry a variety of noncovalent synthesis strategies or approaches e.g. hydrogen bonding, charge-transfer interactions, electrostatic interactions, have been established over the last few years to organize matter on a molecular level. Recently, we introduced a new, facile synthesis strategy, so-called ionic self-assembly (ISA).

ISA makes use of electrostatic interactions between charged surfactants and oppositely charged oligoelectrolytic species to direct the molecular assembly of these tectonic units into highly organized arrays (**Fig. 1**).

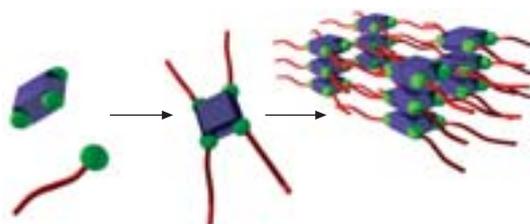


Fig. 1: Schematic representation of the ISA process

In initial investigations into the ISA process [1] supramolecular complexes were synthesized from commercially available azobenzene dyes and a series of alkylammonium surfactants. In order to ascertain the binding behavior of such complexes, binding isotherms were calculated from titration data obtained with a surfactant-selective electrode. This showed that the binding process was indeed cooperative and exhibited, similar to polyelectrolyte-surfactant complexes, a critical aggregation concentration.

The resulting complexes produced materials that exhibited either gel-like or crystalline needle-like morphologies. The crystalline materials show a very high degree of pleochroism, with dichroic ratios over 40, i.e. the single azo-dye tectons are perfectly aligned over larger distances.

Detailed investigations [2] of the structures of such complexes showed that the morphology of these nanostructured complexes could be tuned through careful choice of the starting materials. Through variation of the charge substitution pattern on the azodyes, as well as changing the length and number of the alkyl tails of the amphiphile, highly ordered crystalline or thermotropic liquid-crystalline materials were accessible (**Fig. 2**).

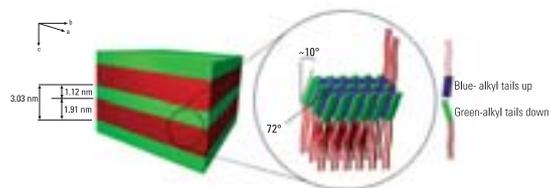
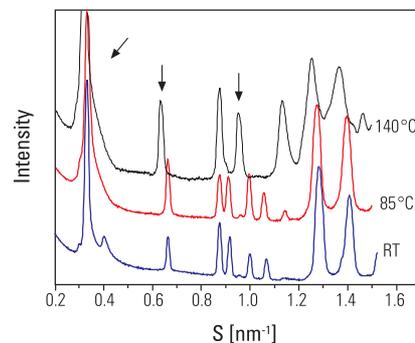


Fig. 2: Small-Angle X-ray Scattering Diffractogram and structure proposal for a highly ordered crystalline dye-surfactant complex

In an effort to extend and generalise the ISA concept [3] a variety of other oligoelectrolytic materials were also employed as tectonic units. This provides the opportunity to include not only shape-rigid organic tectons into the 'molecular toolbox' available for construction of nanostructured materials, but also shape-rigid inorganic tectons, as well as more complicated functional organic tectons. These will be discussed briefly below.

### Functional Organic Tectons: Perylenediimide-surfactant complexes [4]

The ionic self-assembly strategy is applied to a cationic derivative of the technologically important perylenediimide with its exceptional optical and conducting properties, in conjunction with double tail surfactants of varying length. This yields highly organized thermotropic liquid-crystalline materials.

In order to prove the potential of these novel liquid-crystalline materials for application in devices and as optical components, initial optical investigations were performed. Optical anisotropy was observed by shearing the complexes to a thin film of less than 5  $\mu\text{m}$  thickness onto a clean glass slide. Aligned films of quite good quality were prepared in this way and used to determine the dichroic ratio and to calculate the order parameter. Dichroic ratios higher than 5 and order parameters in the range of 0.6-0.7 were determined.

Charl F. J. Faul 06.10.1971

1996: M.Sc., Physical Chemistry  
(University of Stellenbosch,  
South Africa)

Thesis: The evaluation of a reductive  
pyrolysis reactor for the destruction  
of CFC-12, production of HCN.

2000: PhD, Polymer Chemistry  
(University of Stellenbosch,  
South Africa)

Thesis: Directed Synthesis of  
Polymer Mesostructures

2001: Postdoctoral Fellow  
(Max Planck Institute of  
Colloids and Interfaces, Golm)

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

### PAMAM Dendrimer–Fluorosurfactant complexes [5]

Complexes were synthesized making use of amine-functionalised dendrimeric tectons (chemically defined, flexible shape definition) and fluorinated carboxylic acid surfactants. The resulting ordered materials were used as nanoreactors for the preparation of CdS nanoparticles.

### Functional Inorganic Tectons

#### Switchable Cluster-Surfactant Complexes [6]

Facile organization of the inorganic crown-shaped  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anion into room temperature liquid-crystalline materials by complexation with double tail ammonium surfactants via the Ionic Self-Assembly (ISA) route is presented. It is shown by small angle X-ray diffraction, UV-Visible spectroscopy and  $^{31}\text{P}$  NMR analyses that these complexes show an interesting solid-state structure transition. Due to the heating, the inorganic crown species polymerises to the inorganic polyelectrolyte  $^{1\infty}[\text{NiPS}_4]$ . This structural transition is nevertheless reversible, involving a dissolution cycle (Fig. 3).

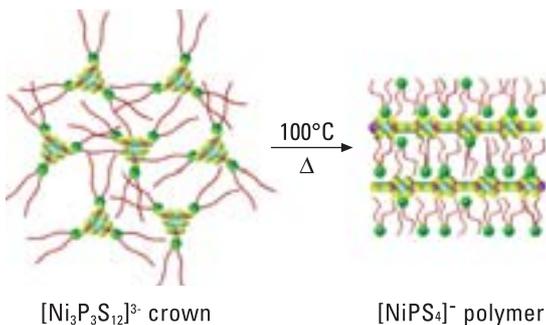


Fig. 3: Inorganic Crown-to-Polymer Switchable System

#### Switchable copper-metallomesogens via ISA: [7]

In a stepwise noncovalent multiple-interaction strategy, copper(II) salts were complexed with the sodium salts of bathophenanthrolinedisulfonic acid ( $\text{C}_{24}$ ) and bathocuproinedisulfonic acid ( $\text{C}_{26}$ ), and organized into nanostructured materials by the addition of ammonium surfactants via the Ionic Self-Assembly (ISA) route. In the case of the methyl-substituted  $\text{C}_{26}$  complexes, a slow color change from green to brick red was observed. UV and EPR investigations showed that the color change was due to a change in oxidation state, yielding brick-red complexes typical for  $\text{Cu(I)}$  species. It is concluded that steric interaction and mechanical packing drive this electronic transition in the metal center into a supramolecular structure (Fig. 4).

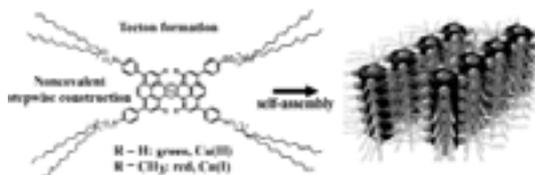


Fig. 4: Multiple interactions for functional nanostructured materials

#### Ongoing Project: Reactions within Confined Molecular Environments (with D. Ganeva): [8]

Polyaddition reactions performed within a highly ordered polyelectrolyte-surfactant monomer complex of polydiallyldimethylammonium chloride and di(undecenyl) phosphate give a 1:1 copy of the original lamellar host structure. No phase disruption or disordering occurs during the reaction. The phase morphology of the host before and after swelling and after polymerization is investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The polymer simplex has improved thermal and mechanical stability.

C. F. J. Faul, F. Camerel, D. Franke, Y. Guan, B. H. Ozer, C. Remde; Visitor: D. Ganeva, University of Stellenbosch, South Africa  
charl.faul@mpikg-golm.mpg.de

### References:

- [1] Faul, C. F. J. and Antonietti, M.: Facile Synthesis of Optically Functional, Highly Organized Nanostructures: Dye-Surfactant Complexes. *Chem. Eur. J.* 8, 2764-2768 (2002).
- [2] Guan, Y., Antonietti, M. and Faul, C.F.J.: Ionic Self-Assembly of Dye-Surfactant Complexes: Influence of Tail Lengths and Dye Architecture on the Phase Morphology. *Langmuir* 18, 5939-5945 (2002).
- [3] Faul, C. F. J. and Antonietti, M.: Ionic Self-Assembly: Facile synthesis of supramolecular materials. *Adv. Mater.* 15, in press (2003).
- [4] Guan, Y., Sakrevskiy, Y., Stumpe, J., Antonietti, M. and Faul, C.F.J.: Peryleneimide-surfactant complexes: Thermotropic LC Materials via Ionic Self-Assembly. *Chem. Commun.*, 894-895 (2003).
- [5] Faul, C. F. J., Antonietti, M., Hentze, H.-P. and Smarsly, B.: Solid-state nanostructure of PAMAM dendrimer fluoro-surfactant complexes and nanoparticles synthesis within the ionic subphase. *Colloids and Surfaces A* 212, 115-121 (2003).
- [6] Camerel, F., Antonietti, M. and Faul, C.F.J.: Organized nanostructured complexes of inorganic clusters and surfactants exhibiting thermal solid-state transformations. *Chem. Eur. J.* 9, 2160-2166 (2003).
- [7] Camerel, F., Strauch, P., Antonietti, M. and Faul, C.F.J.: Copper-metallomesogen structures obtained by Ionic Self-Assembly (ISA): molecular electro-mechanical switching driven by cooperativity. *Chem. Eur. J.* 9, in press (2003)
- [8] Ganeva, D., Faul, C. F. J. Götz, C. and Sanderson, R. D.: Directed reactions within confined reaction environments: Polyadditions in polyelectrolyte-surfactant complexes. *Macromolecules* 36, 2862-2866 (2003).

# AMPHIPHILIC POLYMERS

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



### Abstract

The integration of bioorganic or biomimetic polymers with specific aggregation behavior into synthetic polymer molecules is an approach toward inducing organization in polymeric materials. The structure of the resulting materials and their properties will be analyzed and compared to the ones of unorganized materials. Following this approach "smart materials" with good mechanical properties and responsive to external stimuli are expected.

**Hans G. Börner** 15.09.70

1996: Diploma, Chemistry

(Philipps-Universität Marburg)

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

1997-2000: Ph.D, Macromolecular

Chemistry (Philipps-Universität

Marburg) Thesis: Synthesis of Novel

Phosphine Substituted Block

Copolymers and Application as

Building Blocks for Nano Reactors

2000-2001: Postdoctoral Fellow

(Carnegie Mellon University,

Pittsburgh, USA)

Since 2001: Group Leader

(Max Planck Institute of Colloids

and Interfaces, Golm)

2002: Visiting Researcher

(Department of Biochemistry,

Stellenbosch University, South Africa)

### Introduction

This project focuses on the development of routes to program structure in polymeric materials. The utilized supramolecular approach is based on the stoichiometric integration of "directing groups" into polymer molecules and the spontaneous or induced self-organization of these groups exploiting molecular recognition mechanisms.

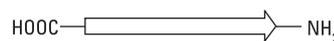
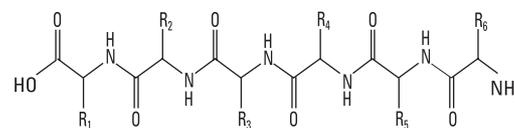
As a result of the organization of the "directing groups", the so-called ordinator\*-groups, structure formation is expected to be induced in the polymer compound on a molecular level.

### Project Description

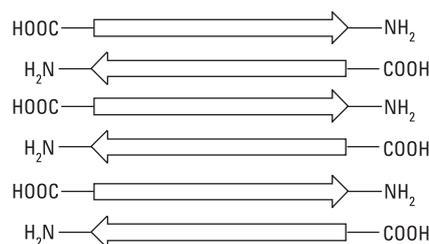
The ordinator-groups will be chosen from the class of bioorganic and biomimetic polymers such as polypeptides, polynucleotides and their artificial derivatives. By using solid phase supported synthesis and successive monomer assemble as polymerization technique, the monomer sequence can be controlled. Thus the ordinator-groups can be achieved in a homodisperse way exhibiting molecular and chemical uniformity.

Due to the defined character of the bioorganic or biomimetic ordinator-groups a multitude of specific aggregation motifs and highly selective aggregation mechanisms can be exploited [e.g. assembling of oligopeptide into anti parallel  $\beta$ -sheet rich quaternary structures (Fig. 1)].

In contrast to the project "Molecular Chimeras" from Dr. H. Schlaad, aggregation behavior is controlled by molecular recognition mechanisms encoded into ordinator-groups by a specific monomer sequence.



a



b

Fig. 1a)  $\beta$ -sheet secondary structure of linear oligopeptide; 1b) anti parallel  $\beta$ -sheet rich quaternary structures.

The synthetic polymer component is expected to be the primary contributor to the mechanical properties of the resulting materials. Therefore, classical synthetic polymers like polystyrene, poly(meth)acrylates, polyamides and polyesters will be utilized. In contrast to the literature where poly(ethylene oxide) [1] is widely used due to its commercial availability or biocompatibility the synthetic polymer should exhibit good mechanical properties.

To realize defined hybrid systems controlled synthesis of the synthetic polymers is required. Furthermore end functionalities like amine, alcohol and carboxylate have to be introduced. Therefore living or "controlled/living" polymerization techniques will be adopted. Depending on the end functionality of the synthetic polymer introduction to the bioorganic compound can be done at complementary functionality either at terminal or at side chain functionalities of the bioorganic oligomer [e.g. oligopeptide (Fig. 2)].

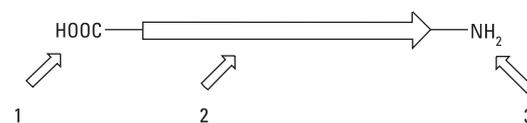
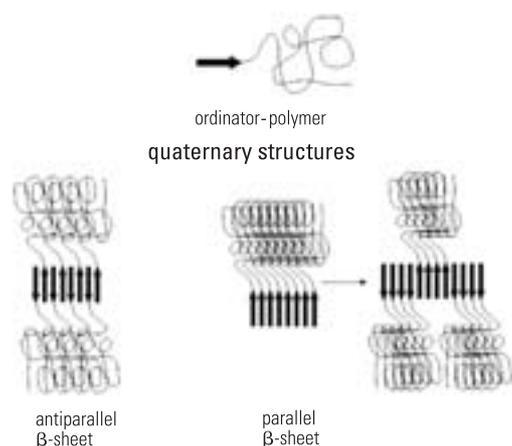


Fig. 2: Introduction of the synthetic polymer, 1, 3) terminal functionalities, 2) Side chain functionality (e.g. Tyrosine, Serine)

\*Ordinator (Latin): guider, disposer, person responsible for arranging the troops in battle formation.

Under proper conditions, the assembly of the ordinator-groups will induce organization of the synthetic polymer. As an example **Fig. 3** shows the aggregation of a hybrid system composed out of an oligopeptide and a synthetic polymer in parallel or anti parallel  $\beta$ -sheet rich quaternary structures.

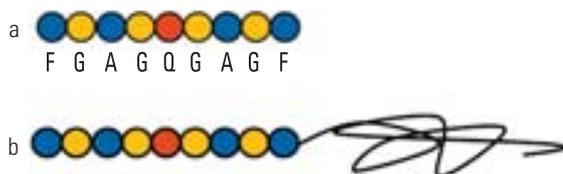


*Fig. 3: Ordinator-polymer hybrid system and targeted aggregation behavior*

During a visit in Stellenbosch University, South Africa in the research group of Dr. Rautenbach (Biochemistry Department) the synthesis of a first model hybrid system via solid phase supported synthesis was investigated.

Inspired by spider silk proteins [2] an amino acid sequence has been extracted. In the native form of the silk protein the function of this segment is to form  $\beta$ -sheet rich quaternary structures. This "crystalline" domains physically cross link amorphous segments to achieve a molecular level structure that is responsible for the excellent mechanical properties of dragline silk high performance fibers.

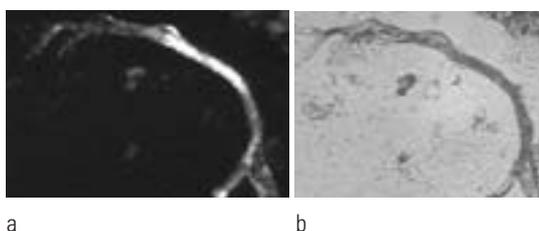
The chosen primary structure (FGAGQ) exhibits a typical polarity sequence (unpolar-nonpolar-unpolar-polar). By artificial extension of this sequence towards a symmetric one (FGAG-Q-GAGF) an oligopeptide with very high tendency to form either parallel or anti parallel  $\beta$ -sheet rich quaternary structures was designed (**Fig. 4a**). The oligopeptide synthesis was done using solid phase supported synthesis following standard Fmoc chemistry protocols. The successful synthesis was confirmed by mass spectrometry (ESI-MS  $M=811$  D). As synthetic polymer part carboxylate end functionalized polystyrene ( $M_n=1400$ ,  $M_w/M_n=1.07$ ) was introduced at the amino terminus of the supported oligopeptide (**Fig. 4b**).



*Fig. 4: Linear hybrid system: a) oligopeptide; b) oligopeptide-polystyrene.*

In preliminary analysis of the aggregation behavior of the oligopeptide the high tendency to form ordered structures like filaments and super structures like fibrils is confirmed (**Fig. 5**). After 3 days at 25°C the pure oligopeptide forms fibril type of supramolecular structures in acetonitrile/water (50/50 v%) which can be observed with light microscopy. The structure exhibits birefringent indicating high molecular order.

Further analysis of the molecular and the supra molecular order of the pure oligopeptide and the hybrid system are in progress.



*Fig. 5: Polarization microscopy micrograph of fibril structures formed by the oligo-peptide: a) polarizer 90°; b) polarizer 0°*

## Outlook

The assembled structured materials should be analyzed in solution and in bulk. Potentially functional materials can be achieved having the probability to response to an external stimuli e.g. change in pH-value, temperature, ionic strength or light irradiation. These responsive materials will have applications in areas of tissue repair, bioadhesive or -compatible materials or pH-sensitive drug release systems.

H. G. Börner, D. Eckhardt, H. Rettig, H. Runge, I. Shekova  
hans.boerner@mpikg-golm.mpg.de

## References:

- [1] Burkoth, T. S., Benzinger, T. L. S., Urban, V., Lynn, D. G.; Meredith, S. C., Thiyagarajan, P. J. *Am. Chem. Soc.* 121, 7429-7430 (1999).
- [2] Kaplan, D.: *Silk Polymers: Materials Science and Biotechnology*. American Chemical Society: Washington, DC, (1994).

## 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, Golm)

**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

- [1] Cölfen, H.: Double-hydrophilic block copolymers: Synthesis and application as novel surfactants and crystal growth modifiers. *Macromol. Rapid Commun.* 22, 219-252 (2001).
- [2] Sedlak, M. and Cölfen, H.: Synthesis of double-hydrophilic block copolymers with hydrophobic moieties for the controlled crystallization of minerals. *Macromol. Chem. Phys.* 202, 587-597 (2001).
- [3] Rudloff, J., Antonietti, M., Cölfen, H., Pretula, J., Kaluzynski, K., and Penczek, S.: Double-hydrophilic block copolymers with monophosphate ester moieties as crystal growth modifiers of  $\text{CaCO}_3$ . *Macromol. Chem. Phys.* 203, 627-635 (2002).
- [4] Rudloff, J.: Doppelt hydrophile Blockcopolymer: Synthese und Einsatz in der biomimetischen Morphosynthese von  $\text{CaCO}_3$ . PhD Thesis, Potsdam (2001).
- [5] Kasparova, P.: Doppelhydrophile Blockcopolymer als Mineralisations-template. PhD Thesis, Potsdam (2002).

We have continued our efforts to explore the potential of biomimetic mineralization processes using simple model polymers for proteins which are active in biomineralization processes, the so called Double Hydrophilic Block Copolymers (DHBC's) [1]. These polymers consist of two water soluble blocks where one block can interact with a crystal surface and the other one just provides water solubility [e.g. Poly(ethylene oxide)] so that these polymers serve as a tool to provide nm sized building blocks for further self assembly into complex structures. We were successful in expanding our set of block copolymers to functional poly(ethylene imine) blocks modified by carboxylate, sulfonate, phosphonate and thiol groups as well as hydrophobic moieties [2], monophosphate ester [3], polyoxazoline [4], and various polypeptide blocks [5]. Polypeptides are sometimes already itself active in crystal morphogenesis in a limited experimental range [6]. These DHBC's could serve numerous purposes. In the simplest case, they could be used for nanoparticle stabilization in water. For the stabilization of high quality CdS using poly(ethylene imine) block copolymers with different architectures of the PEI block, it could be shown that branched functional blocks have the highest activity compared to linear or dendritic blocks [7]. In addition, the nanoparticle size could be simply controlled by the block copolymer concentration and the electron donating functional amine groups protected the semiconductor against photocorrosion. This indicates that tailor made DHBC's can fulfill multiple tasks.

Such stabilized nanoparticles can be used for the self-assembly of complex structures, if the stabilizing PEO block is short enough to allow only for a temporary stabilization. If  $\text{CaCO}_3$  nanoparticles are temporarily stabilized by DHBC's with monophosphate functional moieties, and the crystallization is carried out via a  $\text{CO}_2$  evaporation technique,  $\text{CaCO}_3$  is formed at the air water interface and emerging  $\text{CO}_2$  gas bubbles can be used as a template for complex  $\text{CaCO}_3$  structures according to Fig. 1 [4]. Here, the water surface tension determines how big the aggregate structures can grow before they sink to the bottom. This shows that already a very simple template like a gas bubble can be used for the production of complex morphologies and indicates the potential of using DHBC stabilized nanoparticles for hierarchical self-assembly.

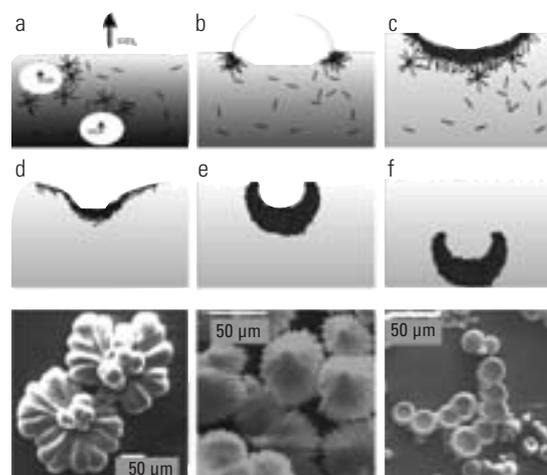


Fig. 1: Upper scheme: Aggregation mechanism of temporarily DHBC stabilized  $\text{CaCO}_3$  nanoparticles with a  $\text{CO}_2$  gas bubble as template. The lower figures represent the obtained structures with from left to right decreasing water surface tension.

However, it is also possible to form complex higher order assemblies without templates. This was demonstrated for  $\text{CaCO}_3$ , and it could be shown that beside the choice of the block copolymer, experimental parameters like the pH or the  $\text{CaCO}_3$ /polymer concentration ratio are also important for the morphogenesis [8]. It is remarkable that a rod-dumbbell sphere transition was observed in a kinetic study, which was speculatively explained by the action of intrinsic electric fields [9] and that the initially observed nanoparticles are amorphous. If a slow gas diffusion precipitation technique is used under otherwise unchanged conditions, these particles grow to a much bigger size of up to 100  $\mu\text{m}$  and are finally overgrown by calcite rhomboeders which make them a promising chromatography column filling material due to the exposition of multiple calcite faces [10].

Another interesting morphogenesis scenario, also starting from amorphous precursor aggregates was observed for  $\text{BaSO}_4$  in presence of a partially phosphonated poly(ethylene oxide)-block-poly(methacrylic acid) block copolymer, which resulted in the formation of fiber bundles consisting of defect free single crystalline fiber bundles [11]. The mechanism as outlined in Fig. 2 was also speculatively explained with the action of intrinsic electric fields, although a literature reported oriented attachment mechanism for the removal of high energy surfaces could explain the results equally well.

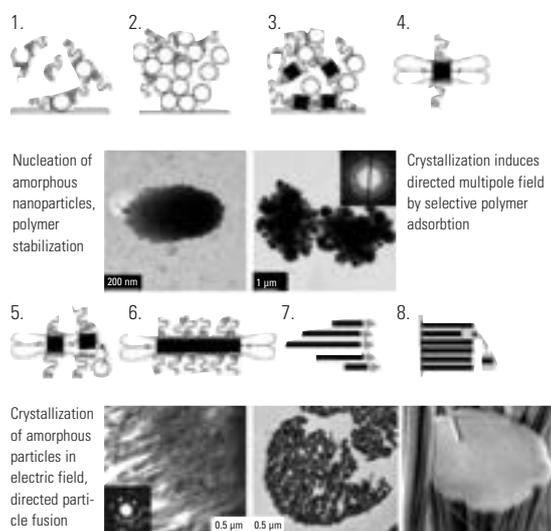


Fig. 2: Mechanism of the polymer mediated formation of single crystalline  $\text{BaSO}_4$  fibers [11]

Similar results were obtained with the structurally identical  $\text{BaCrO}_4$  and the role of various block copolymer functional patterns as well as experimental conditions was explored in detail [12]. DHBC's can also modify crystal morphologies by face selective adsorption. An example is the forbidden 10-fold symmetry of a single flower-like  $\text{BaSO}_4$  crystal, which could be obtained by face-selective polymer adsorption and the resulting modification of the growth [13]. The formation of this unusual morphology could be explained by a multi-step growth mechanism and shows that the polymer influences the crystal growth on different hierarchies.

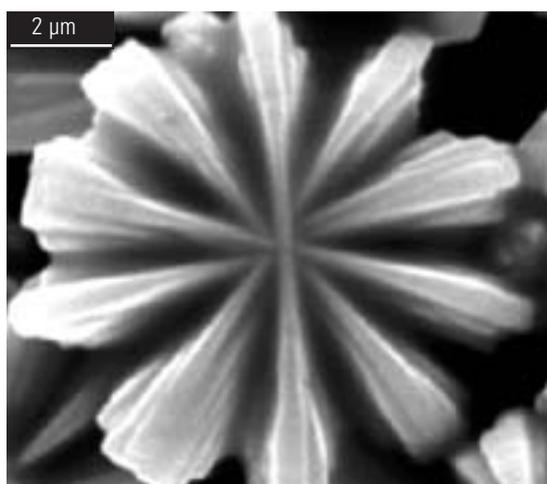


Fig. 3: Single-crystalline  $\text{BaSO}_4$  flower-like morphology obtained in the presence of a sulfonated Poly(ethylene oxide)-block-poly(ethylene imine) DHBC [13]

In addition to these fundamental studies, we explored the DHBC modified crystallization also for functional materials. For  $\text{CdWO}_4$ , we were able to synthesize very thin nanoparticles, which showed an improved fluorescence behavior compared to the default material. This was attributed to the modified crystal morphology with perfect crystal structure as well as to a quenching of surface defects [14].

Beside the crystallization modification of inorganic materials, DHBC's were also found to be active with other materials. It could be shown that the structure of liquid water and ice can be modified by poly(ethylene oxide)-block-poly(hydroxyethyl ethylene) and its partially phosphorylated derivative, resulting even in changes/distortions of the ice unit cell [15]. This indicates that the role of DHBC's as additives for crystallization control may be more complicated than so far assumed, as all crystallizations are performed in water. When chiral functions are added to a DHBC, it appears possible that the fundamentally and industrially important separation of a racemic mixture into the enantiomers can be achieved by selective DHBC interaction with one enantiomer upon crystallization. We were able to show that beside the morphology modification of calcium tartrate tetrahydrate, an enantiomeric excess of about 40 % could be achieved, when the racemic mixture was crystallized in presence of a chiral DHBC, although the racemic crystal is thermodynamically stable [16]. With time, the enantiomeric excess decreased due to reformation of the racemic crystal indicating that a successful racemate separation by crystallization modification can only be achieved by kinetic control.

H. Cölfen, P. Kasparova, Y. Mastai, L. Qi, J. Rudloff, S. Wohrab, S. H. Yu  
Coelfen@mpikg-golm.mpg.de

- [6] Peytcheva, A., Cölfen, H., Schnabl-egger, H., and Antonietti, M.: Calcium phosphate colloids with hierarchical structure controlled by polyaspartates. *Colloid Polym. Sci.* 280, 218-227 (2002).
- [7] Qi, L. M., Cölfen, H., and Antonietti, M.: Synthesis and characterization of CdS nanoparticles stabilized by double-hydrophilic block copolymers. *Nano Lett.* 1, 61-65 (2001).
- [8] Cölfen, H. and Qi, L. M.: A systematic examination of the morphogenesis of calcium carbonate in the presence of a double-hydrophilic block copolymer. *Chem. Eur. J.* 7, 106-116 (2001).
- [9] Cölfen, H. and Qi, L. M.: The mechanism of the morphogenesis of  $\text{CaCO}_3$  in the presence of poly(ethylene glycol)-b-poly(methacrylic acid). *Progr. Colloid Polym. Sci.* 117, 200 – 203 (2001).
- [10] Yu, S. H., Cölfen, H., Hartmann, J., and Antonietti, M.: Biomimetic crystallization of calcium carbonate spherules with controlled surface structures and sizes by double-hydrophilic block copolymers. *Adv.Funct. Mater.* 12, 541-545 (2002)
- [11] Qi, L. M., Cölfen, H., Antonietti, M., Li, M., Hopwood, J. D., Ashley, A. J., and Mann, S.: Formation of  $\text{BaSO}_4$  fibres with morphological complexity in aqueous polymer solutions. *Chem. Eur. J.* 7, 3526-3532 (2001).
- [12] Yu, S. H., Cölfen, H., and Antonietti, M.: Control of the morphogenesis of barium chromate by using double-hydrophilic block copolymers (DHBCs) as crystal growth modifiers. *Chem. Eur. J.* 8, 2937-2945 (2002).
- [13] Cölfen, H., Qi, L. M., Mastai, Y. and Börger, L.: Formation of unusual 10-petal  $\text{BaSO}_4$  structures in the presence of a polymeric additive. *Crystal Growth & Design* 2, 191-196 (2002).
- [14] Yu, S. H., Antonietti, M., Cölfen, H., and Giersig, M.: Synthesis of very thin 1D and 2D  $\text{CdWO}_4$  nanoparticles with improved fluorescence behavior by polymer-controlled crystallization. *Angew. Chem. Internat. Ed.* 41, 2356-2360 (2002).
- [15] Mastai, Y., Rudloff, J., Cölfen, H., and Antonietti, M.: Control over the structure of ice and water by block copolymer additives. *Chem. Phys. Chem.* 3, 119-123 (2002).
- [16] Mastai, Y., Sedlak, M., Cölfen, H., and Antonietti, M.: The separation of racemic crystals into enantiomers by chiral block copolymers. *Chem. Eur. J.* 8, 2430-2437 (2002).

## Amphiphilic Block Copolymers



The research of the work group is devoted to the following topics: (i) development of new controlled polymerization techniques, (ii) characterization of polymers with fractionation methods, and (iii) study of the phase behavior of amphiphilic diblock copolymers.

Regarding the latter, it is the main focus to examine the effects of  $\beta$ -structures and specific interactions on structure formation on the nanometer length scale. It is expected (or rather known) that additional contributions to the mixing free energy lead to other, more complex superstructures than the classical BCC, HEX, or LAM. The systems we are particularly interested in are "molecular chimeras" of synthetic polymers and  $\alpha$ -helical polypeptides, diblock copolymers with metal-binding sites, and polyion complexes of oppositely charged block ionomers.

**Helmut Schlaad** 04.08.1967

**1993:** Diploma, Chemistry (Johannes Gutenberg-Universität Mainz)  
Thesis: Studies of the anionic polymerization of methyl methacrylate in toluene in the presence of aluminium alkyls.

**1997:** PhD, Chemistry (Johannes Gutenberg-Universität Mainz)  
Thesis: Studies of the mechanism of the anionic polymerization of methacrylates in the presence of aluminium alkyls in toluene.

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

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

### Publications:

**[1]** Kukula, H., Schlaad, H., Falkenhagen, J., Krüger, R.-P.: Improved synthesis and characterization of  $\omega$ -primary amino-functional polystyrenes and polydienes. *Macromolecules* 35, 7157-7160 (2002).

**[2]** Schlaad, H., Kukula, H., Rudloff, J., Below, I.: Synthesis of  $\alpha$ ,  $\omega$ -hetero-bifunctional poly(ethylene glycol)s by metal-free anionic ring-opening polymerization. *Macromolecules* 34, 4302-4304 (2001).

**[3]** Schlaad, H., Kitz, P.: Determination of molecular weight distributions of diblock copolymers with conventional size exclusion chromatography. *Anal. Chem.* 75, 1548-1551 (2003).

**[4]** Völkel, A., Cölfen, H., Schlaad, H.: Characterization of synthetic polystyrene-poly(Z-L-lysine) block copolymers with Analytical Ultracentrifugation. (Manuscript in preparation).

### "Molecular Chimeras" of Synthetic Polymers and Polypeptides

Linear and star-shaped block copolymers were synthesized via the ring-opening polymerization of  $\alpha$ -amino acid N-carboxyanhydrides (N<sup>ε</sup>-Z-L-lysine and  $\gamma$ -benzyl-L-glutamic acid) initiated by  $\omega$ -amino-functional polymers (polystyrene, polybutadiene, **[1]** and poly(ethylene glycol) **[2]**). Block copolymers were analyzed by means of NMR, size exclusion chromatography, and analytical ultracentrifugation. Samples usually exhibit a monomodal distribution with a polydispersity index in the range of 1.2-1.8 **[3, 4]**. However, branched samples could not yet be analyzed with respect to number and distribution of polypeptide grafts.

Linear polystyrene-block-poly(Z-L-lysine)s adopt a hexagonal-in-lamellar structure in the solid state, irrespective of composition. Analysis of structural details revealed that the interfaces between layers are not planar but undulated. Samples with a star-shaped architecture also arrange in lamellar structures, but the intersheet distance is always  $\sim 20$  nm. It is evident that polypeptide brushes stabilize a larger surface area than linear chains, thus enhancing the generation of undulations. Depending on the conformation of the polypeptide chains, either planar, superundulated, or corrugated lamellar phases can be formed (see the generalized phase diagram in **Fig. 1**,  $\iota$  = averaged normalized interface area;  $\kappa$  = normalized scattering-average of curvature).

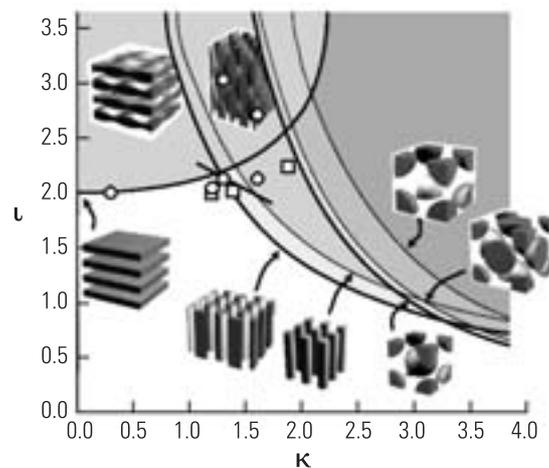


Fig. 1

In dilute aqueous solution, polybutadiene-block-poly(L-glutamate)s can aggregate into spherical micelles or large vesicles/"peptosomes" ( $R_h \sim 70$  nm), depending on the chemical composition of the copolymer. The polypeptide corona can undergo a pH-induced coil-helix transition without seriously altering the size and morphology of aggregates (**Fig. 2**) **[6]**.

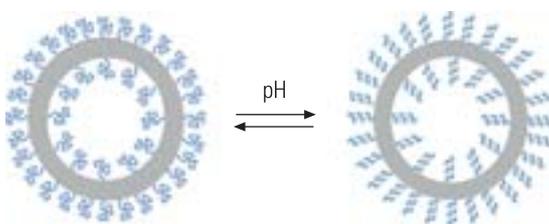


Fig. 2

Linear and star-shaped polystyrene-block-poly(D,L-glutamate)s were used in emulsion polymerization to produce electrosterically stabilized polystyrene latexes with a polypeptide corona **[7]**. The main latex properties, namely the average particle size, distribution, electrolyte stability, and electrophoretic mobility, were strongly affected by the architecture of the stabilizer. Star-shaped stabilizers exhibit a higher stabilizing efficiency than linear ones and are able to stabilize a second generation of particles, producing bimodal dispersions.

### Diblock Copolymers with Metal-Binding Sites

Well-defined block copolymers with  $\beta$ -dicarbonyl chelating segments (**Fig. 3**) were synthesized (for the first time) via two different routes: (i) synthesis of copolymers with a poly-alcohol segment by living anionic or group transfer polymerization and subsequent azeotropic acetoacetylation of hydroxyl units **[8]** and (ii) reversible addition-fragmentation chain transfer (RAFT) radical polymerization of 2-(acetoacetoxy)ethyl methacrylate **[9]**. The obtained polymers usually exhibit monomodal and narrow molecular weight distributions (polydispersity index < 1.2).

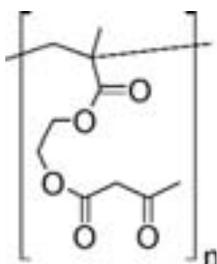


Fig. 3

In cyclohexane, poly(*n*-butyl methacrylate)-block-poly(2-(acetoacetoxy)ethyl methacrylate)s form spherical or cylindrical micelles ( $R_h=10-50$  nm). Aggregation numbers were found to be much higher than what is reported for other micellar systems. The higher density of chains at the core-corona interface is presumably due to attractive interactions between acetoacetoxy units via hydrogen bonding **[10]**.

These micellar aggregates were used to solubilize various metal ion salts in media, in which otherwise they were totally insoluble (e.g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in cyclohexane). Poly( $\beta$ -dicarbonyl) block copolymers were also used as additives for biomimetic mineralization processes and for the nano-casting of inorganic materials.

### Polyion Complexes of Block Ionomers

By mixing dilute solutions of oppositely charged block ionomers with strongly segregating solvating segments ( $\chi_N \sim 40$ ), namely polybutadiene-block-poly(cesium methacrylate) and polystyrene-block-poly(1-methyl-4-vinyl-pyridinium iodide), polyion complexes are formed which self-assemble into vesicular aggregates ( $R_h \sim 65$  nm). These vesicles exhibit a phase-separated microstructure (**Fig. 4**) and are thus amphiphilic in nature. Which of the segments is forming the outer and inner layer of the vesicle membrane can be controlled by the selectivity of the solvent, i.e., these vesicles are able to respond to an external stimulus **[11]**.

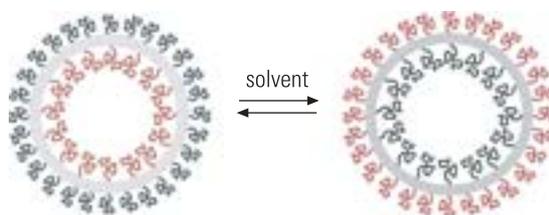


Fig. 4

This modular approach shall be used to generate a library of complex superstructures with reduced or even broken symmetry ("Janus micelles").

H. Schlaad, I. Below, I. Dimitrov, T. Krasia, H. Kukula, M. Losik, S. Schrage, R. Soula  
helmut.schlaad@mpikg-golm.mpg.de

**[5]** Schlaad, H., Kukula, H., Smarsly, B., Antonietti, M., Pakula, T.: Solid-state morphologies of linear and bottlebrush-shaped polystyrene-poly(Z-L-lysine) block copolymers. *Polymer* 43, 5321-5328 (2002).

**[6]** Kukula, H., Schlaad, H., Antonietti, M., Förster, S.: The formation of polymer vesicles or 'peptosomes' by polybutadiene-block-poly(L-glutamate)s in dilute aqueous solution. *J. Am. Chem. Soc.* 124, 1658-1663 (2002).

**[7]** Kukula, H., Schlaad, H., Tauer, K.: Linear and star-shaped polystyrene-block-poly(sodium glutamate)s as emulsifiers in the heterophase polymerization of styrene. *Macromolecules* 35, 2538-2544 (2002).

**[8]** Schlaad, H., Krasia, T., Patrickios, C. S.: Controlled synthesis of coordination block copolymers with  $\beta$ -dicarbonyl ligating segments. *Macromolecules* 34, 7585-7588 (2001).

**[9]** Krasia, T., Soula, R., Börner, H. G., Schlaad, H.: Controlled synthesis of homopolymers and block copolymers based on 2-(acetoacetoxy)-ethyl methacrylate via RAFT radical polymerisation. *Chem. Commun.* 2003, 538-539 (2003).

**[10]** Krasia, T., Schlaad, H., Antonietti, M.: Micellization behavior of coordinating block copolymers based on 2-(acetoacetoxy)ethyl methacrylate in dilute solution. (Manuscript in preparation).

**[11]** Schrage, S., Sigel, R., Schlaad, H.: Formation of amphiphilic polyion complex vesicles from mixtures of oppositely charged block ionomers. *Macromolecules* 36, 1417-1420 (2003).

## Porous Materials via Nanocasting Procedures: Innovative Materials and Learning about Softmatter Organization



**Markus Antonietti** 06.02.1960

**1983:** Diploma, Chemistry  
(University of Mainz)

Thesis: Bestimmung der Diffusion von photomarkiertem Polystyrol: spezielle Systeme, chemische und physikalisch-chemische Aspekte

**1985:** Doctorate for natural science (summa cum laude, University of Mainz)  
Thesis: Diffusion in topological constraint polymer melts with Prof. Dr. H. Sillescu

**1990:** Habilitation, Physical Chemistry (University of Mainz) Thesis: Microgels – Polymers with a special architecture

**02/1991:** Associate Professor (University of Mainz)

**09/1991:** Full Professor

(Philipps University Marburg)

**Since 1993:** Director

(Max Planck Institute of Colloids and Interfaces, Golm),

Full Professor (University of Potsdam)

### References:

**[1]** Polarz, S., Antonietti, M.: Porous materials via nanocasting procedures: innovative materials and learning about soft-matter organization. Chem. Commun., 2593-2604 (2002).

**[2]** Han, B. H. and Antonietti, M.: Cyclodextrin-based pseudopolyrotaxanes as templates for the generation of porous silica materials. Chem Mater. 14, 3477-3485 (2002).

**[3]** Antonietti, M., Hentze, H. P., Smarsly, B., et al.: Structure characterization of surfactant assisted polymer thickeners by silica nano-casting. Macromol. Mater. Eng. 287, 195-202 (2002).

**[4]** Caruso, R. A. and Antonietti, M.: Silica films with bimodal pore structure prepared by using membranes as templates and amphiphiles as porogens. Adv. Funct. Mater. 12, 307-312 (2002).

Nanocasting, the 3D-transformation of self-assembled organic nanostructures into hollow inorganic replicas under preservation of fine structural details has recently turned out to be a versatile tool in colloidal material science. In nanocasting or the “true lyotropic liquid crystal approach”, as introduced by Attard and Göltner, one starts from a high concentration ordered template phase, and the liquid continuous phase is just solidified by chemical gelation reactions [1]. Already in previous work, it was shown that this technique offers the possibility to make a 1:1 imprint or negative copy of the organic mesophases. X-ray measurements performed throughout the process showed that the solidified hybrid preserves all structural features throughout solidification of the matrix, and even the calcined or hollowed replica possesses the same structure, and only slightly shrinks. To enable nanocasting, the casted structure must be compatible with both the liquid precursor phase as well as the final solidified replica. If this is not the case, the enormous interfaces involved (up to 1000 m<sup>2</sup>/g) will add unfavorable energies, and replication breaks down.

In the report period, we have tried to learn about the mechanistic aspects of this procedure. Major work was attributed to the quantitative SAXS and SANS characterization of those samples [6, 14, 15].

It was shown that a so-called “three-phase” model described the whereabouts of the template in the matrix, and that micropores are an inevitable side-product on the concept, as solvating moieties stay mixed with the silica phase.

Beside diverse amphiphilic block copolymers (Fig. 1), the base of possible templates was significantly extended. Mixtures of different non-ionic surfactants allowed the adjustment of pore size with Angstrom precision and also gave a cohesive picture about the general process of mixed micelles formation [9].

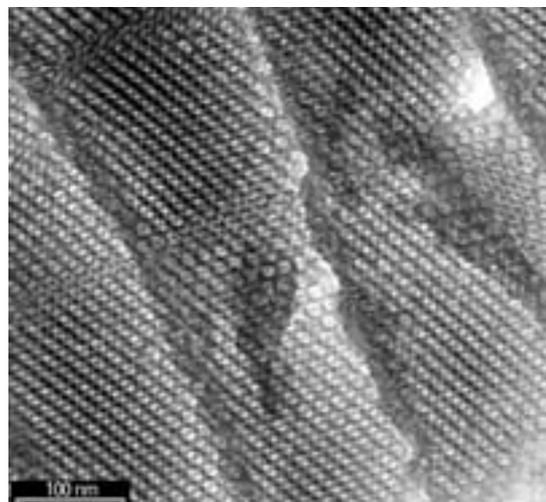


Fig. 1: Porous silica made by nanocasting of the FCC micellar phase of an amphiphilic block copolymers

Fig. 2 depicts the experimental and fitted dependence of pore radius on both the hydrophilic and hydrophobic length of the surfactants, as established by about 20 different samples.

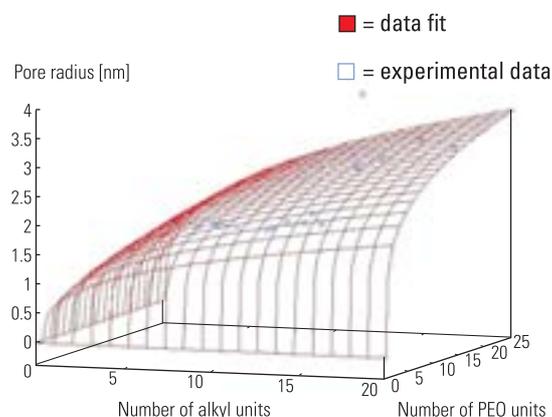


Fig. 2: Angstrom-control of worm-like pores by appropriate choice of commercial surfactants and their mixtures

Cyclodextrines (CDs) as templates not only allowed to depict the natural self-organization of CDs [7] and their supramolecular complexes with polymers, the pseudorotaxanes [2], they also were the base for a simple one-step synthesis of nanoparticle@porous silica systems [8], promising candidates for the rational synthesis of heterogeneous catalysts. In another set of experiments, the same system was used as a conceptual new solar energy absorber, where efficient IR-emission was spectroscopically excluded [5].

Another case where the analytical potential of nanocasting was favourably used is found in the characterization of the interaction of polyelectrolyte thickeners with surfactant formulations [3], an admittedly industrial driven question.

The actual work on new templates is exploring the potential of new systems, such as room temperature ionic liquids (RTILs), which have the potential advantage to work also in the absence of water, thus allowing a much broader chemistry for the generation of the porous host.

First work in this direction where the RTIL is used as solvent and template simultaneously indicates the extraordinary potential of this class of substances, such as the generation of crystalline lamellar materials (Fig. 3).

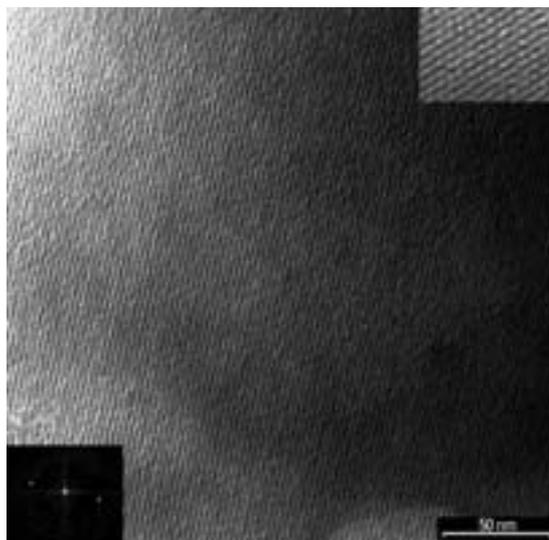


Fig. 3: Nanostructured hybrid material with a lamellar structure with 2.7 nm repeat period. Inlet 1: electron diffraction; inlet 2: magnification of the structure

Other current work is dealing with chiral templates and corresponding chiral pore systems, such as cellulose derivatives or ionic surfactant assemblies with chiral counterions. A chiral pore system would have the advantage to overlay chiral properties in an otherwise non-chiral system, e.g. by filling dye solutions into the chiral silica. In addition, we can examine the question of chiral recognition in chromatography, i.e. is it just the imprinted molecule which is bound or is there a general chiral polarization force.

The broad accessible variety of pore sizes and surface structures is also used to exert control of chemistry through confinement in space ("nano-chemistry"). In cooperation with the University of Potsdam, the altered thermodynamics of excimer formation in confined space is examined. Together with colleagues from Marburg, we examine the possibility to make new objects out of engineering plastics and carbon, using the diverse well-defined pores again as moulds for reaction.

M. Antonietti, M. Groenewolt, B.-H. Han, S. Polarz, B. Smarsly, A. Thomas, Y. Zhou

Visitor: Lyudmila Bronstein (Moscow State University)  
Markus.Antonietti@mpikg-golm.mpg.de

[5] Mastai, Y., Polarz, S. and Antonietti, M.: Silica-carbon nanocomposites: A new concept for the design of solar absorbers. *Adv. Funct. Mater.* 12, 197-202 (2002).

[6] Smarsly, B., Antonietti, M. and Wolff, T.: Evaluation of the small-angle x-ray scattering of carbons using parametrization methods. *J. Chem. Phys.* 116, 2618-2627 (2002).

[7] Polarz, S., Smarsly, B., Bronstein, L., et al.: From cyclodextrin assemblies to porous materials by silica templating. *Angew. Chem. Int. Edit.* 40, 4417-4419 (2001).

[8] Han, B. H., Polarz, S. and Antonietti, M.: Cyclodextrin-based porous silica materials as in situ chemical "nanoreactors" for the preparation of variable metal-silica hybrids. *Chem. Mater.* 13, 3915-3919 (2001).

[9] Smarsly, B., Polarz, S. and Antonietti, M.: Preparation of porous silica materials via sol-gel nanocasting of nonionic surfactants: A mechanistic study on the self-aggregation of amphiphiles for the precise prediction of the mesopore size. *J. Phys. Chem. B* 105, 10473-10483 (2001).

[10] Caruso, R. A. and Antonietti, M.: Sol-gel nanocoating: An approach to the preparation of structured materials. *Chem. Mater.* 13, 3272-3282 (2001).

[11] Hentze, H. P. and Antonietti, M.: Template synthesis of porous organic polymers. *Curr. Op. Solid State Mater. Sci.* 5, 343-353 (2001).

[12] Bronstein, L. M., Polarz, S., Smarsly, B., et al.: Sub-nanometer noble-metal particle host synthesis in porous silica monoliths. *Adv. Mater.* 13, 1333-1336 (2001).

[13] Polarz, S., Smarsly, B. and Antonietti, M.: Colloidal organization and clusters: Self-assembly of polyoxometalate-surfactant complexes towards three-dimensional organized structures. *Chemphyschem.* 2, 457-461 (2001).

[14] Göltner, C. G., Smarsly, B., Berton, B. and Antonietti, M.: On the microporous nature of mesoporous molecular sieves. *Chem. Mater.* 13, 1617-1624 (2001).

[15] Smarsly, B., Göltner, C., Antonietti, M., et al.: SANS investigation of nitrogen sorption in porous silica. *J. Phys. Chem. B* 105, 831-840 (2001).

## Templating Strategies to Fabricate Controlled Morphology Networks



Nanocoating, the covering of materials with a layer on the nanometer scale, or covering of a nanoscale entity, using the sol-gel process is a powerful tool for the preparation of nanocomposites and structured materials [1]. Spherical nanoparticles, porous membranes [2], polymer fibers [3] and gels [4], or porous polymeric beads [5] can be used as templates. A combination of porous membrane templates

with amphiphilic supramolecular aggregates makes possible the synthesis of materials with bimodal pore structure [6]. The inorganic framework usually consists of metal oxides which have numerous applications in catalysis and photovoltaics. The main research goal is the production of novel inorganic networks that have high surface areas as well as high porosity. These properties increase the number of accessible catalytically active sites and provide enhanced flow rates.

### Titanium Dioxide Tubes:

A sol-gel procedure has been applied for the metal oxide coating of polymer fibers. For coating, the poly(L-lactide) fibers were soaked in a titanium alkoxide precursor solution and subsequently hydrolysed in a water/isopropanol mixture. Thermal treatment at 500 °C removed the polymer leaving a hollow titanium dioxide structure of interwoven fibers [3]. Fig. 1a shows an SEM image of the final titanium dioxide tubes. The diameter of the inorganic material is dependent on the initial polymer fiber, with some shrinkage occurring during the heating process. The tube wall thickness is below 200 nm. According to TEM images indentations in the poly(L-lactide) fibers are filled with the metal oxide leading to secondary structures within the tubes (Fig. 1b).



Fig. 1a: SEM image of the hollow titania fibers, b: TEM image of the tubes showing the mimicking nature of the sol-gel coating technique (scale bar is 5  $\mu\text{m}$ )

### Porous Silica and Titania Spheres:

The sphere with its simple morphology allows for improved flow properties and is ideal for adsorption or chromatographic packing. Spherical beads that are porous throughout can be used to improve the properties of a material, due to increased accessible surface plus the added benefits of smaller pore characteristics. The use of polymeric beads as templates has been examined for the formation of silica and titania spheres with porous inner structuring [5]. This approach allows direct control of the final sphere size, which is dependent on the initial bead diameter. The porous organic beads were composed of polystyrene cross-linked with divinyl benzene. Both titania and silica spheres were obtained by applying the sol-gel, where the alkoxide precursor underwent hydrolysis and condensation reactions to form the metal oxide within the organic structure. On calcination of the hybrid spheres, the organic material is removed, leaving the inorganic, porous spheres. Fig. 2a shows the titania spheres. They are monodisperse, and the porous surface structure is visible.

The TEM image in Fig. 2b shows that the inner structure of the titania spheres is porous and that the spheres consist of nanoparticles with diameters between 20 and 70 nm. The surface area of the porous inorganic spheres varies substantially for the titania and silica spheres. The crystalline titania exhibits BET specific surface areas in the range of 30 to 35  $\text{m}^2/\text{g}$ , whereas the amorphous silica has surface areas between 550 and 700  $\text{m}^2/\text{g}$ .

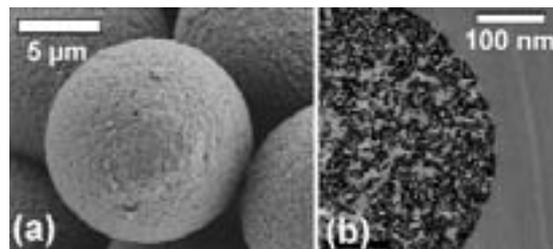


Fig. 2a: SEM image of titania spheres, b: TEM cross-section of a titania sphere consisting of individual nanoparticles

### Macroporous Titania and Titania/Zirconia:

A variety of polymer gels with different chemical composition, architecture, porosity, and surface area have been used as templating materials for the fabrication of porous titania and titania/zirconia networks [4, 7]. The homogeneously porous polymer gel with a globular structure (Fig. 3a) is placed into alkoxide solutions of the corresponding metal(s). After hydrolysis and condensation the metal oxide/polymer hybrid was heated to 500 °C to remove the organic template and to induce crystallization of the amorphous inorganic gel. An SEM image of the resulting titania material is shown in Fig. 3b. The structures prove that a coating of the initial polymer was obtained, yielding a hollow globular material on removal of the template.

An overall shrinkage of about 20 % can be observed when comparing the initial gel and the final inorganic structures. The samples produced using a mixture of titanium and zirconium alkoxides gave similar SEM images.

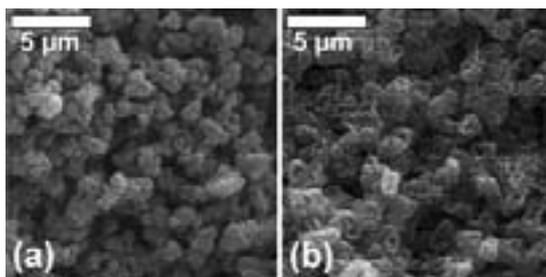


Fig. 3a: SEM image of the initial polymer gel template, b: SEM image of the final titania network

According to X-ray analysis the titania samples mainly consist of anatase nanocrystals with traces of the rutile modification. The addition of 10 mol% zirconia stabilizes the anatase form, whereas a further increase of the zirconia content inhibits crystallization. Samples containing zirconia as the major component can be assigned to either the monoclinic or tetragonal modification of zirconia.

The surface areas vary from 30 to 40 m<sup>2</sup>/g for titania and from 26 to 126 m<sup>2</sup>/g for the mixed titania/zirconia networks. The crystalline systems have lower surface areas than the amorphous ones.

### Bimodal Silica Films:

Using simultaneously tetramethyl orthosilicate as silica precursor, porous membrane templates and amphiphilic supramolecular aggregates as porogens, extended porous silica films with thicknesses in the range of 60 to 130 µm and pores on both the meso- and macro-scale have been prepared [6]. The macropore size is determined by the cellulose acetate or polyamide membrane structure and the mesopores by the chosen block copolymer or non-ionic surfactants. Both the template and the porogen are removed during an annealing step leaving the amorphous silica material with a porous structure which results from sol-gel chemistry occurring in the aqueous domains of the amphiphilic liquid-crystalline phases and casting of the initial template membrane. SEM (Fig. 4a) and TEM images (Fig. 4b) show the macro- and mesoporous morphology of the silica materials, respectively. The surface area and total pore volume of the inorganic films vary from 470 to 850 m<sup>2</sup>/g, and 0.50 to 0.73 cm<sup>3</sup>/g, respectively, depending on the choice of template and porogen.

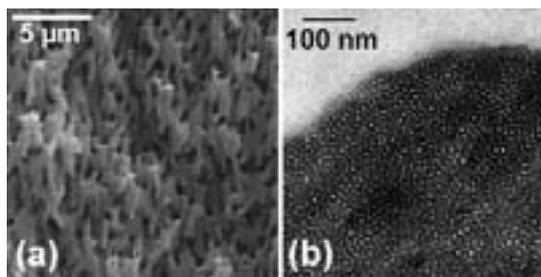


Fig. 4. a) SEM and b) TEM images of the silica material giving evidence for the bimodal porous structure.

### Photocatalytic Properties of Porous Metal Oxides:

Investigations of the photocatalytic activities of different porous materials such as titania, titania/zirconia, and titania/indium oxide obtained from a polymer gel templating technique have been performed in comparison with Degussa P25 [7, 8]. In the photodecomposition of salicylic acid and 2-chlorophenol, the titania-containing structures showed excellent photocatalytic activity, with efficiencies better than the Degussa P25 standard. The presence of the second metal oxide in the titania structure even leads to an increase in photocatalytic activity.

R. A. Caruso, A. S. Deshpande, M. Niederberger, H. Runge, J. H. Schattka, D. G. Shchukin  
rcaruso@unimelb.edu.au

### References:

- [1] Caruso, R. A. and Antonietti, M.: Sol-Gel Nanocoating: An Approach to the Preparation of Structured Materials. *Chem. Mater.* 13, 3272-3282 (2001).
- [2] Caruso, R. A. and Schattka, J. H.: Cellulose Acetate Templates for Porous Inorganic Network Fabrication. *Adv. Mater.* 12, 1921-1923 (2000).
- [3] Caruso, R. A., Schattka, J. H. and Greiner: Titanium Dioxide Tubes from Sol-Gel Coating of Electrospun Polymer Fibers. *A., Adv. Mater.* 13, 1577-1579 (2001).
- [4] Caruso, R. A., Antonietti, A., Giersig, M., Hentze, H.-P. and Jia, J.: Structural Control of TiO<sub>2</sub> Networks Using Polymer Gel Templates. *Chem. Mater.* 13, 1114-1123 (2001).
- [5] Meyer, U., Larsson, A., Hentze, H.-P. and Caruso, R. A.: Templating of Porous Polymeric Beads to Form Porous Silica and Titania Spheres. *Adv. Mater.* 14, 1768-1772 (2002).
- [6] Caruso, R. A. and Antonietti, M.: Silica Films with Bimodal Pore Structure Prepared by Using Membranes as Templates and Amphiphiles as Porogens. *Adv. Funct. Mater.* 12, 307-312 (2002).
- [7] Schattka, J. H., Shchukin, D. G., Jia, J., Antonietti, M. and Caruso, R. A.: Photocatalytic Activities of Porous Titania and Titania/Zirconia Structures Formed by Using a Polymer Gel Templating Technique. *Chem. Mater.* 14, 5103-5108 (2002).
- [8] Shchukin, D. G., Schattka, J. H., Antonietti, M. and Caruso, R. A.: Photocatalytic Properties of Porous Metal Oxide Networks Formed by Nanoparticle Infiltration in a Polymer Gel Template. *J. Phys. Chem. B.* 107, 952-957 (2003).

## Fractionating Colloid Analysis



This project is focused on the analysis of complex mixtures by fractionating techniques namely Analytical Ultracentrifugation (AUC) and Field-Flow-Fractionation (FFF). The main advantage of these techniques is that they operate without stationary phases so that an undesired sample-column interaction can be excluded. In the past, our AUC work was focused on the determination of particle size distributions of

smallest nanoparticles down to sizes even below 1 nm. These efforts are continued both, on the service basis for the institute as well as on a research basis [1] with the goal of the latter to explore the possibilities for the determination of critical crystal nuclei or subcritical complexes in solution to allow conclusions about particle growth mechanisms. An example for the high resolution of such particle size distributions is given in Fig. 1 for  $ZrO_2$  which was quenched during particle growth.

**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, Golm)

**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

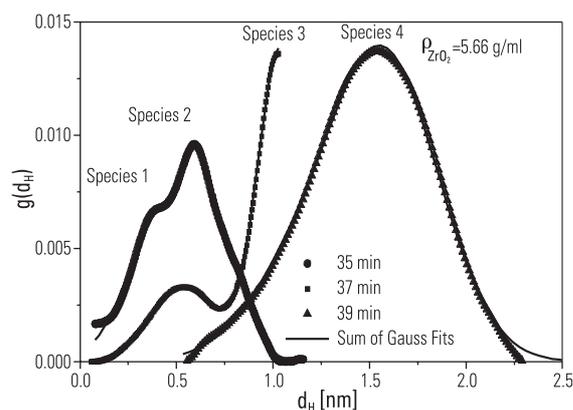


Fig. 1: Apparent particle size distributions of growing  $ZrO_2$  prepared by acid hydrolysis of  $Zr(SO_4)_2 \cdot 4 H_2O$  at  $70^\circ C$  and quenched in liquid  $N_2$  after different reaction times [2]

It can be clearly seen that the small species are subcritical complexes with Angström size. However, a serious drawback is that the determined particle size distributions depend on the density of the particles which is unknown in most cases for very small species at the transition from molecules to solid bodies. The workaround of determining the particle size distributions for two extremes of densities to give a particle size range is not satisfying. A further problem exists for the assignment of the detected species as their size is only given as a hydrodynamic equivalent diameter. Therefore, we tried to develop an equilibrium method for the detection and preparative isolation of critical crystal nuclei. To achieve this, a dynamic equilibrium between crystallization and dissolution of a crystal has to be established which is potentially possible using a pH gradient in the ultracentrifuge cell according to Fig. 2.

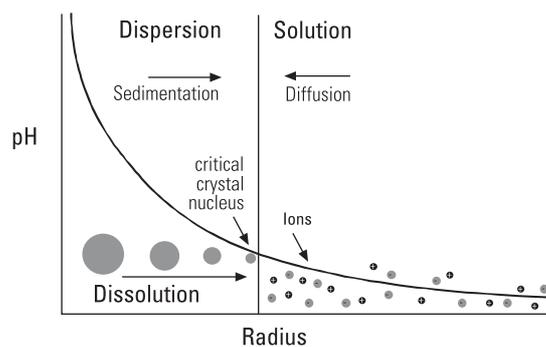


Fig. 2: Dissolution of a crystal in a pH gradient [3].

Here, a crystal can gradually dissolve upon sedimentation as the pH is steadily decreasing towards the bottom of the centrifuge cell. At a certain position, the crystal will dissolve completely into ions which have a higher diffusion coefficient and thus diffuse back into regions of higher pH which should lead to a supersaturation and thus crystallization, so that it should be possible to generate a narrow band where crystallization and dissolution are in a dynamic equilibrium which is the critical crystal nucleus per definition. Although it was possible to generate such pH gradients by sedimentation of a polyacid and equilibrium conditions could be proven, it was not yet possible to isolate critical crystal nuclei, although some indications for their presence were found by AUC [3]. Solubility gradients in the ultracentrifuge can also be generated using ionic strength gradients or via solvent mixtures and their potential is under exploration for the isolation of critical crystal nuclei as well as for other applications which can take advantage of a continuous gradient of a physicochemical property like complex dissociation, protein unfolding, electron gradients etc.

Chemically reacting or organic-inorganic hybrid systems are important but notoriously difficult systems for the characterization of their particle size distribution. In that respect, we could show for the synthesis of iron oxide nanoparticles inside lumazine synthase capsids, that already sedimentation coefficient distributions can yield remarkable insight into the system reflecting structural or compositional changes of the sample [4]. Also, chemically reacting systems can be characterized with high statistical accuracy if it is possible to completely quench the chemical reaction. This was shown for nanoparticle-enhanced turbidimetric immunoassays where an antibody coated latex mixture with different sizes and antibody reactivities reacted with the antigen CRP [5]. The mixture was designed in a way that at low antigen concentrations, only the bigger latices aggregate whereas at higher antigen concentrations, the smaller latices aggregate as well and this mechanism could be proven (Fig. 3).

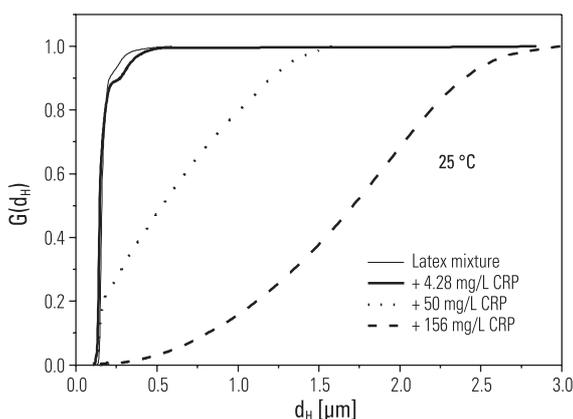


Fig. 3: Mass weighted integral AUC particle size distributions of an agglutinated latex mixture at different CRP concentrations after 10 min at 25 °C. [ $d_H$  = Diameter of the particles,  $G(d_H)$  = Integral particle size distribution].

Beside the important application of AUC for particle size analysis, the technique was also applied for the more classical solution analysis of macromolecules, both as service for the institute and as research. Here, especially chitosans were of interest due to their biocompatibility and polycationic properties. In combination with light scattering, the hydrodynamic solution structure could be determined beside molar mass and other standard parameters [6, 7] and it could be shown that chitosan is not as extended, as it was described in the previous literature indicating the potential of combining AUC with other techniques like light scattering. Such combination is currently also investigated for AUC & FFF coupling which shows special promise for the analysis of complex hybrid colloid mixtures. Beside the soluble systems, biopolymer gels were also investigated with respect to their demixing in an ultracentrifugal field [8].

Although AUC has proven its versatility and fractionation power for many colloidal systems a present limitation are the optical detection systems which can only detect light absorbance or refractive index changes. In addition, the adsorption optics is slow and of bad quality. We therefore started a joint project with a partner from chemical industry concerning the development of improved or new detectors for AUC. We have started the development of a fiber optics based UV-Vis detector which is able to acquire a whole spectrum in as little as 2ms and have currently finished the hardware set-up. Such spectrometer should even allow the observation of chemically reacting systems in the future.

H. Cölfen, G. Lucas, P. Maciejewska, A. Völkel  
Coelfen@mpikg-golm.mpg.de

- [1] Pang, G. S., Sominska, E., Cölfen, H., Mastai, Y., Avivi, S., Kolytyn, Y., and Gedanken, A.: Preparing a stable colloidal solution of hydrous YSZ by sonication. *Langmuir* 17, 3223-3226 (2001).
- [2] Cölfen, H., Schnablegger, H., Fischer, A., Jentoft, F. C., Weinberg, G., and Schlögl, R.: Particle growth kinetics in zirconium sulfate aqueous solutions followed by dynamic light scattering and analytical ultracentrifugation: Implications for thin film deposition. *Langmuir* 18, 3500-3509 (2002).
- [3] Lucas, G., Börger, L., and Cölfen, H.: Solubility equilibrium gradients in the analytical ultracentrifuge: An approach towards the isolation of critical crystal nuclei in solution. *Progr. Colloid Polym. Sci.* 119, 11-18 (2002).
- [4] Shenton, W., Mann, S., Cölfen, H., Bacher, A., and Fischer, M.: Synthesis of nanophase iron oxide in lumazine synthase capsids. *Angew. Chem.-Intl. Ed.* 40, 442-445 (2001).
- [5] Cölfen, H., Völkel, A., Eda, S., Kobold, U., Kaufmann, J., Puhlmann, A., Göltner C., Wachernig, H.: Mechanism of nanoparticle-enhanced turbidimetric assays applying nanoparticles of different size and immunoreactivity. *Langmuir* 18, 7623-7628 (2002).
- [6] Cölfen, H., Berth, G., and Dautzenberg, H.: Hydrodynamic studies on chitosans in aqueous solution. *Carbohydr. Polym.* 45, 373-383 (2001).
- [7] Berth, G., Cölfen, H., and Dautzenberg, H.: Physicochemical and chemical characterisation of chitosan in dilute aqueous solution. *Progr. Colloid Polym. Sci.* 119, 50-57 (2002).
- [8] Borchard, W., Cölfen, H., Kisters, D., and Straatmann, A.: Evidence for phase transitions of aqueous gelatin gels in a centrifugal field. *Progr. Colloid Polym. Sci.* 119, 101-112 (2002).

## Electron Microscopic Studies of Colloidal Systems



**Jürgen Hartmann** 18.10.1953

**1977:** Diploma, Physics (Humboldt-Universität zu Berlin; Institute of Low-Temperature Solid State Physics)

Thesis: Application of square-wave polarography and a density method for the analysis of bismuth-antimony alloys

**1977–1991:** Research Scientist (Institute for Polymer Chemistry, Teltow)

**1987:** PhD, Polymer Physics (Institute of Polymer Chemistry, Teltow)

Thesis: Contribution to the formation mechanism of coagulation structures of polymers using electron microscopy

**1992–1995:** Research Scientist (Max Planck Institute of Colloids and Interfaces, Golm)

**Since 1995:** Group Leader

(Max Planck Institute of Colloids and Interfaces, Golm)

The chemical and physical properties of colloidal nanostructured materials depend sensitively on their chemical composition, the size of the structural elements and their spatial arrangement in the system and the media in which the components are dispersed. The dimensions of dispersed particles, pores or the mesh size of polymer networks, are in the range of 1 nm to 1  $\mu\text{m}$ . Transmission and scanning electron microscopy have proved to be powerful analytical methods to investigate the relationship between the synthesis conditions and morphological structure. So, we are working closely together a number of groups of the colloid chemistry and interface departments.

In the last two years, we have focused our research activities on the investigation of the morphological structure of polymer micelles, inorganic crystals, metal colloids, microporous silica and polymer particles produced by heterophase polymerization techniques.

These studies are important to analyze, e.g., the complex structure formation processes in miniemulsions in the presence of colloidal silica particles. Under alkaline conditions well-covered polymer particles can be formed (Fig. 1). A mixture of styrene and 4-vinylpyridine is used as the monomers. The diameter and morphology of latex particles can be varied as functions of the composition of the system, the pH, and the adsorption of cationic components.

There is a continued scientific interest in the formation of inorganic solids with well-defined properties such as size, shape, and surface roughness. Calcium carbonate ( $\text{CaCO}_3$ ) has been used as a model system for studying the biomimetic synthesis of  $\text{CaCO}_3$  crystals in the presence of organic templates and/or additives.

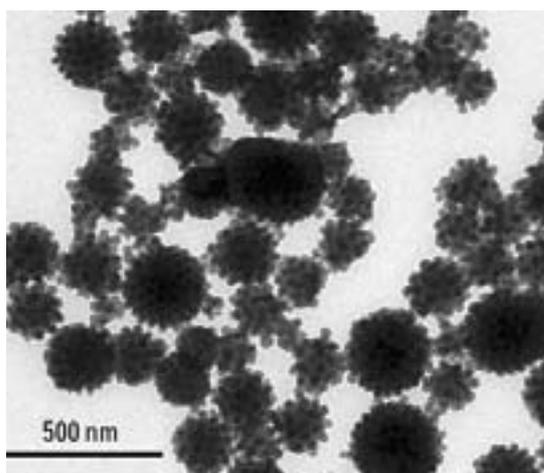


Fig. 1: Latex particles with a monomer to silica ratio of 1:0.64

To modify the morphology of the crystals, special double-hydrophilic block copolymers are used.

The biomimetic crystallization of  $\text{CaCO}_3$  was realized by a slow gas-liquid diffusion reaction of  $\text{CO}_2$  in the presence of poly(ethylene glycol)-block-poly(ethyleneimine)-poly(acetic acid) (PEG-b-PEIPA). The slow precipitation process leads to the formation of uniform spherical crystals. After few days the system contains a variety of intermediates (Fig. 2) with different shapes such as elongated rods (a), peanuts (b), dumbbells (c), and overgrown spherical particles (d). After two weeks of ripening, and on reaching equilibrium, all particles have a spherical superstructure with a nearly uniform diameter of around 80  $\mu\text{m}$ . Their surface is composed of smaller truncated and randomly oriented calcite crystallites with an average size of about 2-5  $\mu\text{m}$ . The biomimetic crystallization of  $\text{BaCrO}_4$  and  $\text{BaSO}_4$  in the presence of sodium polyacrylate yields highly-ordered funnel-like  $\text{BaCrO}_4$  superstructures with a complex form and a remarkable self-similar growth pattern as well as long  $\text{BaSO}_4$  fibre bundles (Fig. 3). The crystallization can be affected by variation of temperature, pH, and concentration.

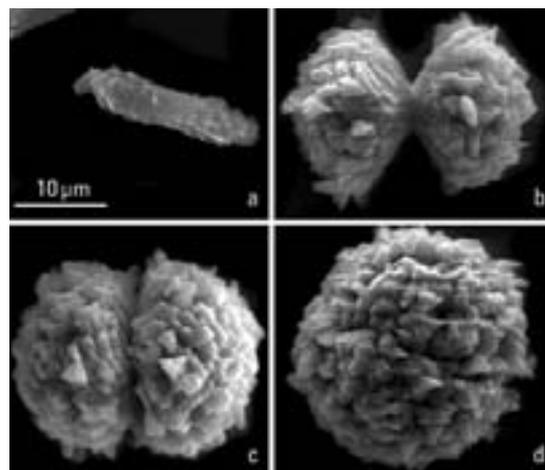


Fig. 2: Different  $\text{CaCO}_3$  crystals showing the morphological evolution process

In the field of crystal engineering, there are special strategies which allow one to control the parameters of the crystallization process. Some of these concepts use restricted reaction environments. The morphology of a range of inorganic crystals, growing inside micrometer-sized polyelectrolyte-complex capsules was studied. The diameter of the selectively permeable capsule walls depends on the size of the templates and can be varied in the range of 0.2  $\mu\text{m}$  to 10  $\mu\text{m}$ .

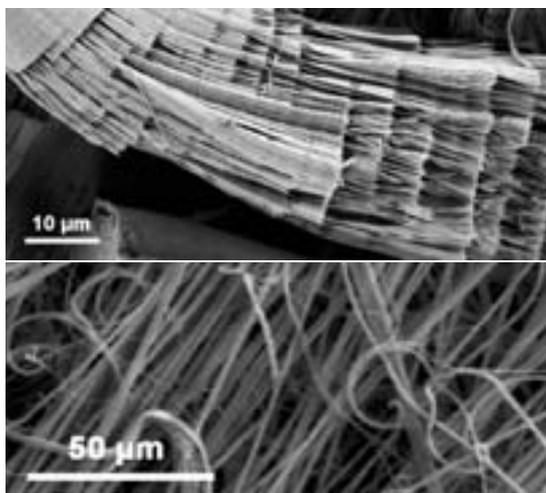


Fig. 3: Highly-ordered funnel-like superstructure (top) and nanofibers of  $BaSO_4$

In Fig. 4a are shown  $BaCO_3$  crystals which are grown within the polyelectrolyte capsules. With additional energy-dispersive X-ray analysis (EDS) we have determined the chemical composition of the inorganic nanoparticles (Fig. 4). The gold peaks result from the soft gold sputtering process used to avoid charge effects during the measurement.

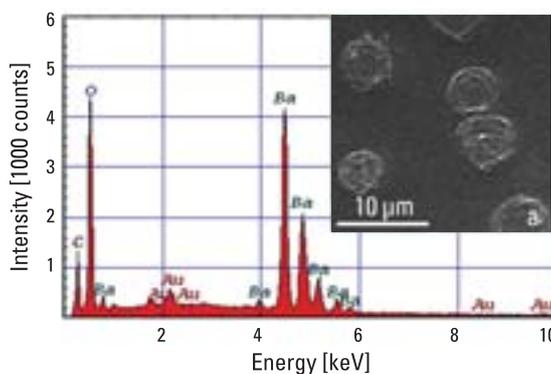


Fig. 4:  $BaCO_3$  nanoparticles within polymer shells (a) and the characteristic EDS spectrum

Another interesting field in colloid science we are studying is the formation of polymer capsules containing metal colloids that are useful for catalytic applications. To characterize, e.g., silver colloids inside the polymer shell, we studied the morphology of the empty capsules with TEM. The structure of the shells containing silver nanoparticles can be varied. Two systems of polymer shells containing different sized silver particles are shown in Fig. 5a and Fig. 5b.

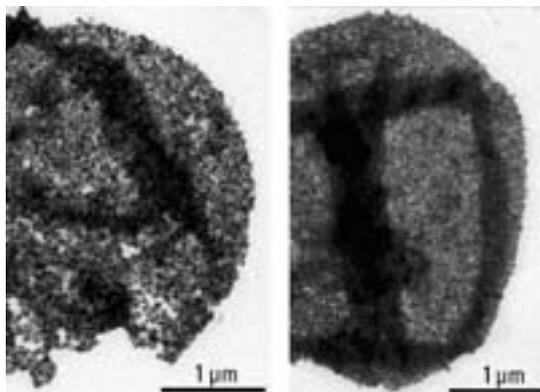


Fig. 5: Empty PSS-Ag capsules. Reduction before dissolution of the core (left) and after that (right)

In cooperation with the Department of Physical Chemistry of the University of Hamburg, interesting phase morphologies of poly(butadiene-*b*-ethylene oxide) (PB-PEO) block copolymer hydrogels are studied using critical-point drying and cryo-ultramicrotomy. In Fig. 6 the structure of a self-assembled PB-PEO block copolymer hydrogel at a polymer weight fraction of 0.8 is shown. The lamellar spacing depends on the molecular parameters and the composition of the polymer/water mixtures, and can be precisely depicted using transmission electron microscopy.

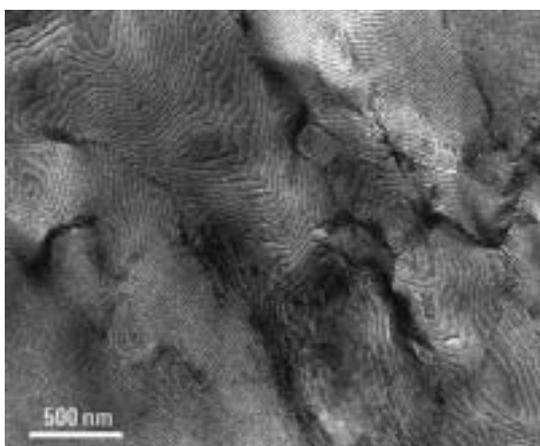


Fig. 6: Lamellar structure of PB-PEO block copolymer hydrogel

J. Hartmann, H. Cölfen, K. Landfester, S. H. Yu, G. Sukhorukov  
juergen.hartmann@mpikg-golm.mpg.de

#### References:

- [1] Antipov, A. A., G. B. Sukhorukov, Y. A. Fedutik, J. Hartmann, M. Giersig and H. Möhwald: Fabrication of a novel type of metallized colloids and hollow capsules. *Langmuir* 18, 6687-6693 (2002).
- [2] Sukhorukov, G. B., A. S. Sussha, S. Davis, S. Leporatti, E. Donath, J. Hartmann and H. Möhwald: Precipitation of inorganic salts inside hollow micrometer-sized polyelectrolyte shells. *Journal of Colloid and Interface Science* 247, 251-254 (2002).
- [3] Yu, S. H., H. Cölfen, J. Hartmann and M. Antonietti: Biomimetic crystallization of calcium carbonate spherules with controlled surface structures and sizes by double-hydrophilic block copolymers. *Advanced Functional Materials* 12, 541-545 (2002).
- [4] Yu, S. H., M. Antonietti, H. Cölfen and J. Hartmann: Growth and self-assembly of  $BaCrO_4$  and  $BaSO_4$  nanofibers towards hierarchical and repetitive superstructures by polymer controlled mineralization reactions. *Chem.Comm.*, 1-3 (2002).

# Gel Permeation Chromatography (GPC), Static Light Scattering (SLS)



**GPC:**

We focus on methods and equipment allowing simultaneous RI (refraction index), UV (ultraviolet spectrophotometric) and MALLS (multi-angle laser light scattering) detection. The research is influenced by actual characterization problems in cooperation with projects from the colloid chemistry and interfaces departments of the institute.

**Gudrun Rother**

**1963:** Diploma, Physics  
(Friedrich-Schiller-Universität Jena)  
Thesis: Relativistische Theorie der Mechanik der Kontinua  
**1979:** PhD, Geophysics  
(Academy of Sciences, Central Institute Physic of the Earth, Potsdam)  
Thesis: Untersuchung der Wechselbeziehungen zwischen Feld- und Quellencharakteristika des anomalen geomagnetischen Feldes hinsichtlich Möglichkeiten zur Bestimmung der Tiefenlage der magnetischen Krustenbasis  
**1963-1982:** Research Scientist, (Academy of Sciences, Geomagnetic Institute, Central Institute Physic of the Earth, Potsdam)  
**1982 – 1991:** Research Scientist (Academy of Sciences, Institute for Polymer Chemistry, Teltow)  
**Since 1992:** Senior Scientist (Max Planck Institute of Colloids and Interfaces, Teltow – Golm)

**MALLS (Multi Angle Laser Light Scattering):**

The highly sophisticated MALLS instrument DAWN EOS of Wyatt (USA) is normally equipped with a flow cell for use in chromatographic studies. The scattering intensity is simultaneously registered at 18 scattering angles and can be recorded along time for a huge number of slices. The time interval can be selected from 0.125 seconds upwards. In principle, this instrument could also be used for batch measurements. However, an index-matching bath is not provided. Moreover, test studies with the recommended simple vial revealed that a lot of reflected light falsifies the measured scattering intensities. The scattering cell cannot be positioned in a reproducible way eliminating the strange light. We (cooperation with Herbert Dautzenberg) solve the problem using a special model of an index-matching bath, normal quartz glass light scattering cuvettes and a cover plate with bore to position the cuvette. The special bath was manufactured by Hellma according to our instructions. An attenuation filter to lessen the laser beam offers an additional extension of the measuring range. Calibration and normalization of the detection diodes can be carried out with high precision.

**Capabilities:**

**Fig. 1** demonstrates the general capabilities of our equipment enabling the investigation of time dependent structure formation processes. The graphs show the reactions of a PEL (polyelectrolyte complex) solution to addition of salt.

The 3D-plot (**Fig. 1d**) and the plot of the scattering intensity for one angle (**Fig. 1a**) qualitatively show the kinetics of the process. After interpretation of the scattering curves for single slices /single time points, plots of the molecular parameters vs. time can be produced immediately. As an example **Fig. 1b, c** are given, using traditional interpretation procedures.

For particle sizes around or above 100 nm, more sophisticated algorithms of data interpretation are required. Respectively, special software was developed allowing to import the MALLS-data into our SLS-interpretation application.

This system offers additional procedures, especially a model interpretation using the entire angle range of the scattering curves [1]. Such a scaled interpretation yields results about the molecular parameters, polydispersities and structure densities. Moreover, the system offers the consideration of bimodal systems.

In this way, a large variety of time-dependent structural changes can be investigated. The advantage of the very high registration frequency of MALLS allows studying fast processes too.

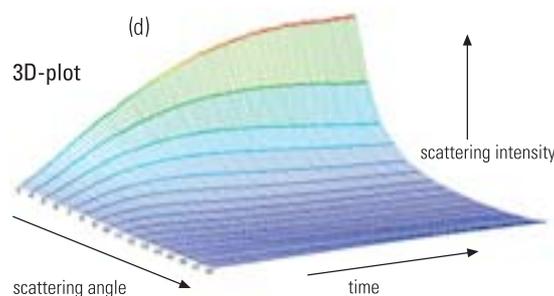
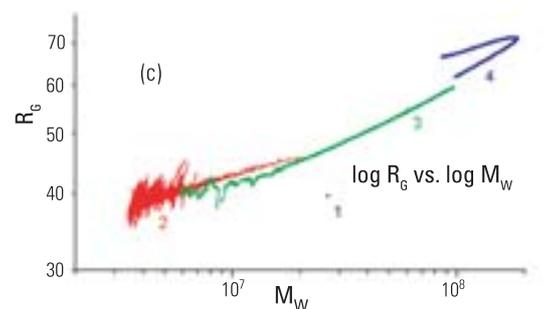
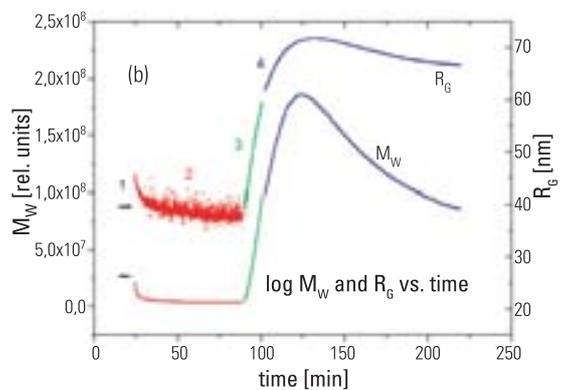
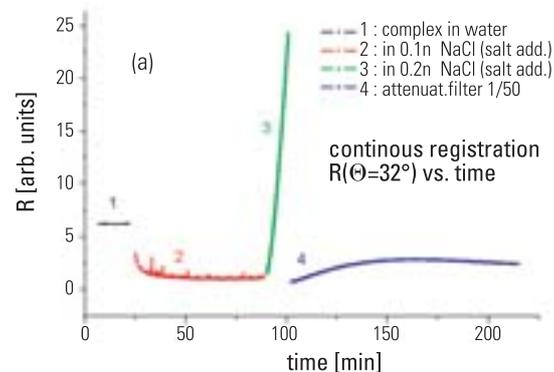


Fig. 1: MALLS of a PEL-complex, a: scattering intensity of one angle vs. time, b: molecular mass and radius of gyration vs. time, c: double logarithmic plot  $R_g$  vs.  $M_w$ , d: 3D-plot

**Example:**

We studied the dissolution of highly aggregated PEL particles formed in water after addition of salt [2]. The complex formation in pure water results in large highly aggregated complex micelles with an aggregation number of several thousand macromolecules. Mixing two polyelectrolyte components, a bimodal system is obtained. The first component is given by the complex micelles with a charge stoichiometry near 1:1, the second component consists of the excess free polyelectrolyte. The addition of salt allows a polyelectrolyte exchange reaction between the free polyelectrolyte chains in the solution and the aggregated particles. This leads to a redistribution between the short (deficient) and the long (excess) chain components resulting together with structural rearrangements in the decrease of the aggregation level and eventually in a monomodal system of "soluble" complex particles.

In order to investigate such a transition of a PEL structure from highly aggregated particles to "soluble" complexes of the molecular level, MALLS studies were performed. The time series of scattering for one angle (90°) was used for the study of the process kinetics.

The redistribution rate increases with increasing salt concentration in the solution. It decreases with an increasing mixing ratio (the ratio between the charges in deficiency and in excess in the mixture of two polyelectrolytes) and increases with a higher concentration of polyelectrolytes in solution. An interesting fact is that the dependence of the rate on the polymer concentration weakens with increasing salt concentration in the solution (Fig. 2).

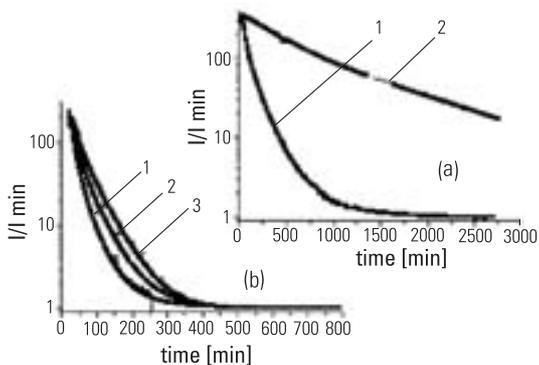


Fig. 2: Relative scattering intensity ( $\Theta=90^\circ$ ) as a time function for different polymer concentrations 1-3 (10, 5, 2)  $10^4$  M, in 0.01N (a), 0.02N (b) NaCl

To explain this fact structural changes were studied. Scattering curves of the system corresponding to different times after the process start have been analyzed by scaled interpretation. Fig. 3 shows that in the small angle range the curvature of the scattering curves increases only slightly indicating a slight increase of the dimensions of the aggregate particles. In the wide angle range, the difference between the experimental curves and theoretical ones increases. This indicates an increase of the fraction of small particles of soluble complexes. The changes in the intensity correspond mostly to the changes of the fraction of the aggregates in the solution and not to the changes in their mass. DLS (dynamic light scattering) studies confirm these results. The experimental data allows explaining the mechanism of aggregate transformation as a two step process. In a first step, the free polyelectrolyte chains in excess remove the short chain component from the particle via a polyelectrolyte exchange reaction. In the second step, the aggregated particle is destroyed by the osmotic pressure which increases with the increasing stoichiometry of the aggregate particle.

**References:**

- [1] Rother, G.: Model interpretation in Static Light Scattering. *Macromol. Symp.* 162, 45-61 (2000).
- [2] Zintchenko, A., Rother, G., Dautzenberg, H.: Transition Highly Aggregated Complexes – Soluble Complexes in Context with Polyelectrolyte Exchange Reactions: Kinetics, Structural Changes, Mechanism. *Langmuir* 19(6), 2507-2513 (2003).

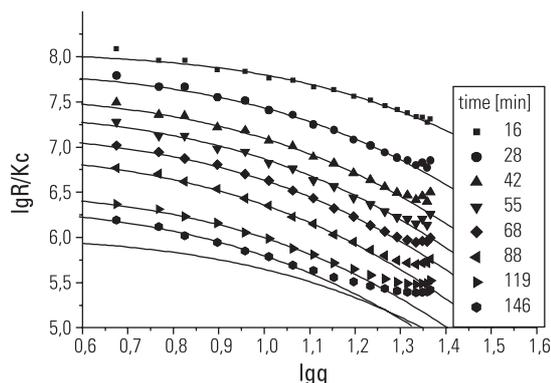


Fig. 3: Experimental and theoretical scattering curves for a PEL in 0.2N NaCl for different times

G. Rother

gudrun.rother@mpikg-golm.mpg.de

## Modern Methods of Light Scattering



Static and dynamic light scattering are important methods for the characterization of macromolecular materials. The target of the research is to extend and apply these methods to problems specific to colloids and interfaces.

**Reinhard Sigel** 14.03.1965

**1990:** Baccalaureus, Mathematics  
(Albert-Ludwigs-Universität Freiburg)

**1992:** Diploma, Physics  
(Albert-Ludwigs-Universität Freiburg)  
Thesis: Stress Optical Behaviour of Liquid Crystalline Elastomers

**1997:** PhD, Physics  
(Albert-Ludwigs-Universität Freiburg)

Thesis: Investigation of the Nematic Wetting Layer in an Isotropic Liquid Crystal by Evanescent Light Scattering

**1997-1998:** Postdoc  
(Albert-Ludwigs-Universität Freiburg)

**1998-2000:** Postdoc  
(Institute of Electronic Structure and Laser, Heraklion, Crete, Greece)

**Since 2000:** Group Leader  
(Max Planck Institute of Colloids and Interfaces, Gölml)

### Ellipsometric Scattering

A special feature of colloidal materials is their large surface due to the fine dispersion of matter. Combining light scattering with polarization optics common to ellipsometry results in a new experimental technique capable to access this characteristic surface.

The high resolution of classical ellipsometry is achieved by measuring the amplitude ratio  $\tan(\psi)$  and especially the relative phase shift  $\Delta$  of two polarization modes  $E_p$  parallel and  $E_s$  perpendicular to the plane of reflection (Fig. 1a). Here, the phase shift arises from the reflection at a planar interface with a refractive index profile, e.g. a two-step profile with indices  $n_1$ ,  $n_2$  and  $n_3$ . Similarly, in a scattering experiment (Fig. 1b), the amplitude ratio and relative phase shift of two polarization modes  $E_p$  parallel and  $E_s$  perpendicular to the scattering plane is determined by the refractive index profile of the scattering particle.

The availability of a correlator for dynamic light scattering immediately gives access to the dynamics of the refractive index profile, i.e. breathing modes of the particle. Another important aspect is the effect of sample polydispersity, where ellipsometric scattering allows distinguishing the scattering of an average particle (coherent scattering) from scattering caused by deviations from the average size (incoherent scattering).

As an example, Fig. 2 shows experimental data and corresponding fits for the characterization of coated colloid particles.

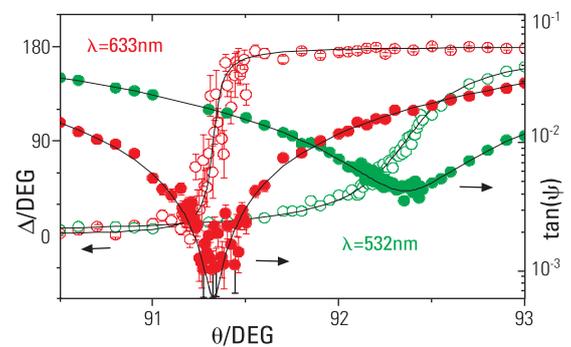


Fig. 2: Ellipsometric scattering data from PMMA particles with PNIPAM coating in water with 190 nm core diameter and 20nm surface layer at the temperature 32 °C

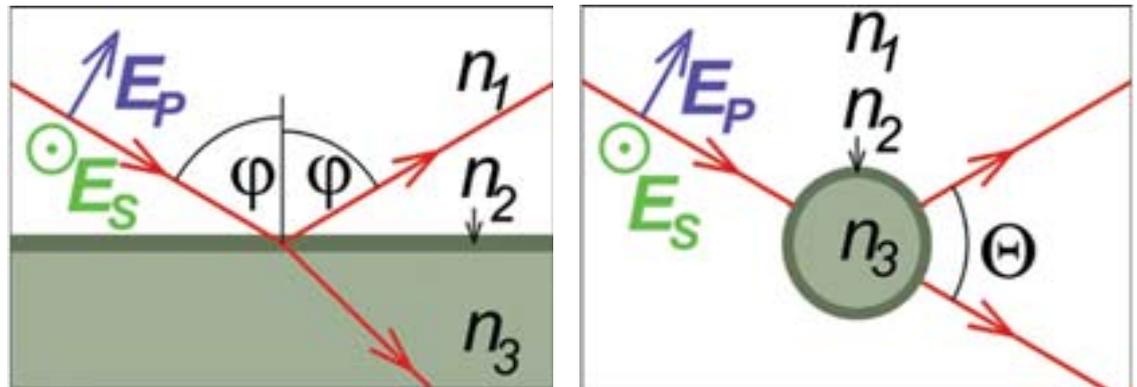


Fig. 1: Comparison of reflection ellipsometry (a) and Scattering ellipsometry (b).

### Procedures of Interface Light Scattering (PILS-Project)

A liquid-liquid interface is a soft system with many possible fluctuations. It is possible to monitor these fluctuations by reflecting a light beam at the interface, as displayed in **Fig. 3**. The polarization analysis of the reflected beam (E) yields the interface thickness (ellipsometry), while small angle scattering (C) is sensitive to capillary waves. For total internal reflection, the evanescent wave with exponentially decaying field profile (depicted in blue in **Fig. 3**) defines a scattering volume with a thickness comparable to the wavelength of light,  $\lambda$ . Scattering of the evanescent wave (S) reflects structure and dynamics close to the interface.

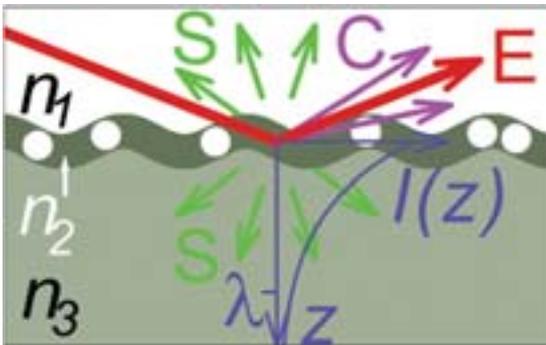


Fig. 3: Characterization of an interface with light (see text).

A new setup combining ellipsometry, evanescent light scattering and capillary wave detection is under construction. Planned experiments deal with 2D-diffusion of colloids in the interface under the effect of capillary waves and dynamics of exchange processes through the interface.

R. Sigel, A. Erbe, B. Schonert, I. Zenke  
sigel@mpikg-golm.mpg.de

## Adsorption Properties of Surfactants at Fluid and Solid Interfaces



### Aims:

Investigations on the true adsorption properties of surfactants, including lung surfactant and solvosurfactants. Elucidating surfactant functionality in terms of surfactant structure, charge and counterion size. Development of a generally applicable method for swift foam characterization and of a method for surfactant adsorption at solid/liquid interfaces.

### Results:

Systematic investigations on basic and applied adsorption properties of amphiphiles at air/water and solid/liquid interfaces have been continued by strictly keeping the requirements of "surface-chemical purity" (scp) to avoid artefacts due to surface-active trace impurities [1]. The surfactants investigated include simple and more complicated structures.

### 1. Basic Research

#### 1.1 Novel Surfactants

Novel surface-active di-*n*-alkylaldonamide derivatives (sugar surfactants) were synthesized from biologically available materials. Their adsorption behavior is quite unusual. Unlike ordinary *n*-alkyl surfactants the amphiphiles cross-sectional area and the surface interaction parameter show a strong increase with rising alkyl chain length, but abruptly decrease after having reached a certain medium chain length. These thermodynamic results suggest that for the longer chain homologues an abrupt deviation from that surface conformation occurs which is met for the lower numbered homologues: one alkyl chain is protruded upright from the boundary while the second one remains flat [2]. This hypothesis is supported by HyperChem Computer Simulations.

#### 1.2 Phase Transition

Investigations of surface potential and surface tension of the homologous series of the sugar surfactants *n*-alkyl-β-D-glucopyranosides revealed a first order phase transition so far unknown at air/water interfaces. Unlike known phase transitions, it occurs at negligible surface interaction [3]. It seems to be induced by changes in the water structure of the interfacial layer.

#### 1.3 Counterion Effect

Equilibrium surface tension of anionic *n*-decylsulfates for various monovalent alkali counterions revealed that the surface activity of the scp decylsulfates significantly decreases with decreasing hydrated size of the counterion. By the assumption that the counterions penetrate the Stern layer where the surfactant head groups are adsorbed an adsorption model was developed taking into account that head group and counter ion have a finite size ("surface exclusion effect"). Good correlation between the relative counter ion size in the Stern layer, the effective radius and the area excluded by the adsorbed counter ion was obtained [4]. The resulting cross-sectional areas of the adsorbed decylsulfates for the various counterions Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> are in good agreement with those measured by neutron scattering.

#### 1.4 Solvo-Surfactant

Investigations on solvosurfactants using Dowanol DPnB (dipropylene glycol *n*-butyl ether) were performed to learn why solvosurfactants have solvent and surfactant properties as well. First results with scp-solutions suggest that this effect is obviously brought about by trace impurity components the adsorption properties (molecular structure) of which are rather different from that of the main component [5].

#### 1.5 Lung Surfactant

The high-performance purification apparatus developed by us previously was applied to bronchoalveolar lavage (BAL) to isolate the native surface film of the lung surfactant system. By this technique the surface-active material is aspirated from the solution surface. The aspirated solutions, the original BAL fluid pool as well as the residual bulk phase were analyzed for the total protein, total phospholipids and phospholipid subclasses. Generally, the protein and the phospholipid concentrations in the aspirated solutions were two to three times higher than in the BAL fluid. These results prove that proteins and different phospholipids are an integral part of the surface film of the BAL fluid. Moreover, this technique provides a new advantageous possibility for the isolation of lung surfactant.

Measuring surface pressure and applying quantitative Brewster Angle Microscopy (BAM) the inhomogeneous nature of the surfactant film with three distinct different morphological phases was observed. On the basis of these results a mechanism of the lung stabilizing mechanism has been proposed that is in line with surfactant behavior at interfaces and the morphological structure of the lung surfactant (Fig. 1) [6].

**Klaus Lunkenheimer** 03.04.1939

**1963:** Diploma, Inorganic Chemistry (Ernst-Moritz-Arndt-Universität Greifswald)

Thesis: Zur Darstellung von Lithium-phthalocyanato-chromat(0)

**1970:** PhD, Physical Chemistry

Thesis: Untersuchungen zur Bestimmung der Elastizität von

Adsorptionsschichten löslicher grenzflächenaktiver Stoffe

(Humboldt-Universität Berlin)

**1972:** Group Leader (Zentralinstitut für Organische Chemie of the

Academy of Sciences of the GDR)

**1980-1982:** Teaching Assignment

(Technical University of Dresden)

**1984:** Dr. sc. nat. (Academy of

Sciences of the GDR, Berlin)

Thesis: Über einige thermodynamische

und kinetische Eigenschaften der

Adsorptionsschichten löslicher

grenzflächenaktiver Stoffe

**1992:** *Facultas docendi* (Martin-Luther-

Universität Halle-Wittenberg)

**1992:** Dr. rer. nat. habil. (Martin-Luther

Universität Halle-Wittenberg)

**1992:** Speaker of a Scientific Research

Group (Max Planck Institute of Colloids

and Interfaces, Berlin-Adlershof)

**Since 1999:** Head of the Independent

Research Group Surfactant Adsorption

Layers (Max Planck Institute of Colloids

and Interfaces, Golm)

**1999:** Guest Lecturer

(University of Karlstad, Sweden)

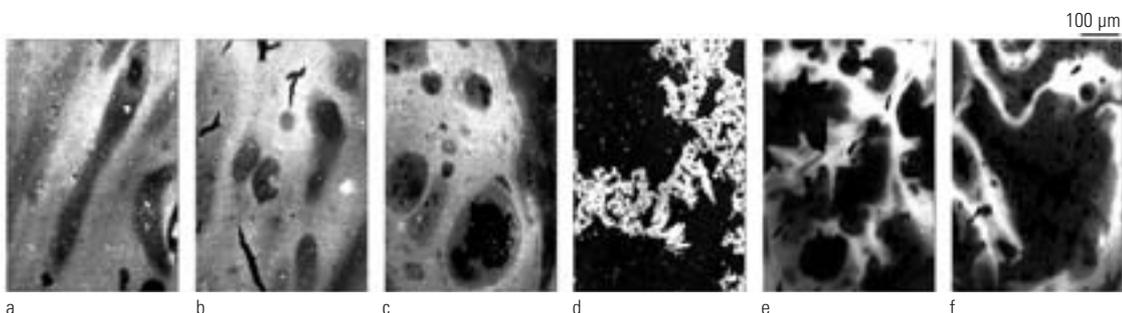


Fig. 1 BAM images of different stages of lung surfactant during spontaneous adsorption

### 1.6 Adsorption Isotherms of Surfactants on Solid Phases

The determination of surfactant adsorption on solid surfaces by the old batch-technique is very complicated and requires a great time exposure. In order to improve this method a new technique based on dynamic frontal high performance liquid chromatography using ELS- and/or MS-detection was developed. The limit of detection is 5 and/or 1  $\mu\text{g/ml}$  of surfactant, also in the presence of partially soluble substances and contaminations. Additionally, the MSD can discriminate between soluble substances and surfactant that increases the specification of the method considerably. The method is applicable for insoluble and partially soluble substances.

## 2. Applied Research

The development of a new, generally applicable method for swift characterization of foam stability was continued. The advantage of this pneumatic method is that the foam parameters by means of which stability is characterized are related to well-defined boundary conditions of the system [7]. A patent about this method has been submitted [8]. Investigations are now in progress to describe the dynamic foam behavior and the new foam parameters concentration dependence quantitatively. To get further insight into the foam stabilizing mechanism the relevant foam parameters are compared with the structure of the surfactants, their adsorption and bulk properties. In cooperation with our partner in Poland we look for a correlation between the behavior of a single foam bubble during its rise through a surfactant solution and its foam properties. Analysis of the high-speed camera pictures revealed an unknown periodically bouncing of the bubble when it meets the air/solution interface [9].

### Cooperations

- Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Cracow, Poland
- Institute of Organic and Polymer Technology, Technical University of Wroclaw, Poland
- Royal Institute of Technology, Department of Surface Chemistry, Stockholm, Sweden
- Bundesanstalt für Materialforschung, Berlin, Germany
- Institute of Physical and Theoretical Chemistry, University of Regensburg, Germany
- Institute of Inorganic Chemistry, University of Würzburg, Germany
- Fraunhofer-Institut für Angewandte Polymerforschung, Golm, Germany
- Technische Fachhochschule Wildau

### External Funding

- BAYER-Project
- German Academic Exchange Service (DAAD)

Dr. habil. K. Lunkenheimer, Dipl.-Chem. K. Geggel, Dipl.-Ing. G. Wienskol, Dr. sc. K. Winsel  
 Klaus.Lunkenheimer@mpikg-golm.mpg.de

Cooperation Partners: Dr. W. Barzyk [Cracow], Prof. R. Hirte, Prof. W. Kunz [Regensburg], Prof. K. Malysa, Prof. A. Piasecki [Wroclaw]; M.Sc. D. Pilakowska-Pietras, Doc. Dr. P. Warszynski

### References:

- [1] Lunkenheimer, K.: Purity of Surfactants and Interfacial Research. Review-Article, Encyclopedia of Surface and Colloid Science, pp. 3739-3772 Marcel Dekker Inc., New York (2002).
- [2] Pilakowska-Pietras, D., Lunkenheimer, K., Piasecki, A.: Synthesis of new N,N-di-n-alkylaldonamides and properties of their surface-chemically pure adsorption layers at the air/water interface. J. Colloid Interface Sci. (submitted).
- [3] Lunkenheimer, K., Barzyk, W., Hirte, R.: Lecture entitled: Unusual phase transition in surfactant adsorption layers. presented at the XVIth Conference of the European Colloid and Interface Society, ECIS 2002, Paris.
- [4] Warszynski, P., Lunkenheimer, K., Czichocki, G.: Effect of Counterions on the Adsorption of Ionic Surfactants at Fluid-Fluid Interfaces (Alkali-decylsulfates). Langmuir 18, 2506-2514 (2002).
- [5] Lunkenheimer, K. and Kunz, W.: DOWANOL DPNB in water as an example of a solvosurfactant system: adsorption and foam properties. Poster at XVIth ECIS 2002, Paris, Progr. Colloid & Polymer Sci. (submitted).
- [6] Winsel, K., Hönig, D., Lunkenheimer, K., Geggel, K., Witt, C.: Quantitative Brewster Angle Microscopy of the Surface Film of Human Bronchoalveolar Lavage Fluid. European Biophysics Journal, DOI 10.1007/s00249-003-0288-9 online (in press).
- [7] Lunkenheimer, K., Malysa, K.: Simple and Generally Applicable Method of Determination and Evaluation of Foam Properties. J. Surfactant and Detergents 6, 69 (2003).
- [8] Lunkenheimer, K., Malysa, K., Wienskol, G., Baranska, B.: Method and Procedure for Swift Characterization of Foamability and Foam Stability. (submitted).
- [9] Krzan, M., Lunkenheimer, K., Malysa, K.: Pulsating and Bouncing Bubble at a Free Surface. Langmuir (submitted).