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Polymer and Colloids **PO 1**

The coiled-coil connection; from self-assembly to membrane fusion

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Biological self-assembly is very complex and results in highly functional materials. In effect, it takes a bottom-up approach using biomolecular building blocks of precisely defined shape, size, hydrophobicity, and spatial distribution of functionality.[1] Inspired by, and drawing lessons from self-assembly processes of the natural occurring SNARE protein complex,[2] which is involved in membrane fusion, we used a small heterodimeric coiled-coil motif to control the supramolecular assembly of block copolymers and lipids. Depending on the type of polymer attached to the coiled-coil peptides we are able to develop responsive micelles, stable polypeptide-peptide based vesicles and disk-like micelles.[3] In another example we show that the fusion of large and giant unilamellar vesicles can be controlled by these amphiphilic peptides.[4] The model system impart all of the key characteristics to membrane fusion that are observed in SNARE mediated fusion. The mechanism of the fusion process will be discussed as well as recent advances in the fusion of vesicles (LUVs with GUVs). Possible applications as microreactors are discussed.

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[3] H. Robson-Marsden, J.W. Handgraaf, N.A.J.M. Sommerdijk, **A. Kros**. *J. Am. Chem. Soc.* **2010**, *132*, 2370–2377.
[4] H. Robson Marsden, N.A. Elbers, P.H.H. Bomans, N.A.J.M. Sommerdijk, and **A. Kros**. *Angewandte Chemie Int. Ed.* **2009**, *48*, 2330–2333.

Polymer and Colloids **PO 2**

One-step synthesis of Janus Nanoparticles by self-assembly monolayers.

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Janus Nanoparticles (JNPs) are nanoparticles with two different sides. They can be synthesized with a lot of different methods and strategies, however most of these methods are not suitable to produce small Janus Nanoparticles (<10nm), they produce low quantities, and are complex approaches that involve several steps.

Here we report the synthesis of gold nanoparticles covered with self-assembled monolayers (SAMs) of two ligands of different lengths (1-hexanethiol and 1-dodecanethiol) that phase-separate in two patches producing JNPs. The synthesis is a one-step, one-phase synthesis that can be scaled-up to high quantities.

A scanning tunneling microscopy (STM) study together with a mesoscale simulation have been done on series of these mixed ligand NPs with different ligand ratios to shed light on the mechanism of phase-separation on SAMs of metallic nanoparticles.

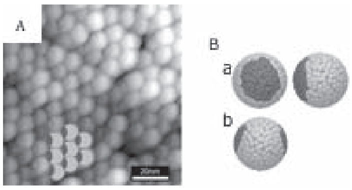

Figure: A) STM image of a monolayer of nanoparticles 1:2 HT:DDT Janus NPs (The cartoon has been drawn to help the reader to identify the Janus NPs). B) Mesoscale simulation of the same particles showing a phase-separation in equilibrium with distributions in 2 or 3 domains (a and b respectively).

Polymer and Colloids **PO 3**

pH-Responsive Lyotropic Liquid Crystals for Controlled Drug Delivery

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We present a food-grade lyotropic liquid crystal system, capable to respond to pH-variations with a reversible switch in both the structure and physical properties. The system, which is composed by monolinolein and linoleic acid (97:3 wt% ratio) in presence of excess water at 37°C and 150mM ionic strength, is specifically designed to reversibly change from a reverse Im3m bicontinuous cubic phase to a H_{II} reverse columnar hexagonal phase, when changing the pH from neutral (pH=7) to acidic (pH=2) conditions, to simulate intestine and stomach conditions, respectively. The pH-responsiveness is provided by the linoleic acid, which being a weak acid ($pKa \approx 5$), is essentially in the de-protonated charged state at pH 7 and mainly protonated and neutral at pH 2, imposing changes in the critical packing parameter (CPP) of the lyotropic liquid crystal. The use of this system as an efficient controlled-release delivery vehicle is demonstrated on the hydrophilic drug phloroglucinol, by both release and diffusion studies at different pH, as followed by UV-Vis spectroscopy. The Im3m cubic phase at pH 7 is shown to release four times faster than the H_{II} phase at pH 2, making this system an ideal candidate for oral administration of drugs for targeted delivery in intestine or colon tracts.

Polymer and Colloids **PO 4**

Design of Water Soluble Initiators for the Modification of Alumina Surfaces by SI-ATRP

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Protocols for the functionalization of aluminum oxide with polymer brushes generally involve the use of organosilane based initiators [1]. These initiators have been developed for the modification of silicon oxide surfaces and are not specifically adapted to alumina surface chemistry. As aromatic acids are water soluble and have the ability to strongly bind to aluminum oxide, four new organic acid based initiators were designed and synthesized. Phthalic and benzoic acid initiators were found to graft in very low concentration on alumina surfaces whereas catechol and salicylic acid produced high density polymer brushes. As catechol chemisorption is pH-dependent, the grafting density of polymer brushes could be controlled by elevating the pH during the initiation. The surface deposition of salicylate initiators show a different pH sensitivity as it strongly binds to the surface at low pH. Stability studies showed that polymer brushes tethered on alumina using salicylate initiator were more stable as compared to the trimethoxysilane initiator. Salicylate based initiators represent an improved procedure to graft polymer brushes from alumina surfaces, which is of potential interest for biomedical applications.

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Polymer and Colloids **PO 5**

Transition from repulsive double layer forces to attractive van der Waals forces observed between model latex paticles using colloidal probe technique

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Using a novel multiparticle colloidal probe technique based on the atomic force microscope (AFM), we measure interaction forces between two amidine latex particles (diameter 3.3 µm) immersed in KCl electrolyte solution across a range of ionic strengths. Repulsive double layer forces could be fitted with solutions to the Poisson-Boltzmann equation using constant regulation boundary condition. In each case, appropriate van der Waals component is taken into account and is interpreted in terms of the Hamaker parameter. Purely attractive forces, on the other hand, are found to be consistent with van der Waals forces represented solely in terms of the Hamaker parameter.

At pH 4.0, where these particles are positively charged, we could clearly observe the transition from repulsive to attractive interactions, with increasing ionic strength. The extracted potentials are well described by the Gouy-Chapman fit using surface charge density as a fit parameter.

At pH 5.6, where these particles are neutral, increase of ionic strength screens the van der Waals forces. Ab initio theoretical calculations for salt dependence of van der Waals forces evaluated from the dielectric permittivity functions are compared with experimental results. Particle surface roughness, measured through Tapping Mode AFM images, are incorporated in the theoretical model and plays a crucial role in the weakening of van der Waals forces.

We further show that such experiments are equally possible with amidine latex particles of diameter 1 µm thereby opening up a size regime where both colloidal probe technique and simultaneous static and dynamic light scattering can operate. This allows us to study aggregation behavior of the very same latex particles exposed to the same conditions using two different techniques.

Polymer and Colloids **PO 6**

Shear Stress Sensitive Nanocontainers for Targeted Drug Delivery

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The lack of biomarkers in critically stenosed arteries demands the development of alternative methods for targeted drug delivery during heart attack. We propose using the body's own changes in shear stress as a purely physical trigger for the release of a vesicle payload. Formulations of 100 nm large uni-lamellar vesicles for such applications have been investigated.

Formulations containing only the artificial phospholipid Pad-PC-Pad were found to release an additional 51% of their payload after one pass through a critically constricted artery model (shear stress approx. 10 Pa), whereas in a common artery model (shear stress approx. 2 Pa), only 27% additional release was observed. In contrast, vesicles formulated from mixtures of the natural phospholipid Egg-PC and 0-1 mol% of the surfactant Polyoxyethylene (10) Stearyl Ether (Brij S10) were found to release a total of only an additional 14% of their payload after 40 passes through a critically stenosed artery model, and 3% after 40 passes through a common artery model. In both cases, background release was around 20%. Mixtures of Pad-PC-Pad and Egg-PC become unstable, or leaky, with an increase in Pad-PC-Pad, and although a higher background release was observed, they did not significantly increase their susceptibility to shear-induced release.

The release from pure Pad-PC-Pad vesicles is an order of magnitude higher than formulations including Egg-PC. Investigations are ongoing for the suitability of these and similar non-natural lipid formulations for specificity in drug delivery at elevated shear stresses, for example for cardiac, neurologic or angiologic applications.

Polymer and Colloids **PO 7**

Relaxation and Flow of Soft Colloids

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Suspensions of soft, deformable and compressible particles exhibit dynamics and flow behavior that is qualitatively different from that observed for hard particles. A wide range of materials including foods, creams and biological systems contain such soft particles. Nevertheless, their behavior remains poorly understood.

As a basis for understanding this behavior, it is important to first quantify the properties of the particles themselves. I will give a short overview of methods used to experimentally access the elastic properties of single soft particles, focusing on a new method, Capillary Micromechanics [1], that we have recently introduced. It enables us to access both the elastic shear modulus as well as the elastic compressive modulus of a single soft particle.

I will further illustrate the importance of particle softness by discussing the use of soft particle suspensions as model glass formers. Colloidal particles have been widely employed as models for understanding glass formation; their behavior is surprisingly similar to that found for molecular glass formers. However, for different molecular glass-forming liquids, the dynamic behavior upon approach to the glass transition shows broad variations. These variations can be described by the so-called fragility, which describes the sensitivity of their viscosity or structural relaxation time on temperature as the glassy state is approached. In hard-sphere colloids only highly fragile behavior has been observed.

By using soft, deformable particles we have extend the concept of fragility to colloidal soft materials and captured the entire range of dynamic behaviors merely by varying the softness of the individual mesoscopic particles. Hard particles make "fragile" glasses and soft particles make non-fragile, or "strong", glasses [2].

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Polymer and Colloids **PO 8**

Heterogeneous dynamics in dense monodisperse emulsions

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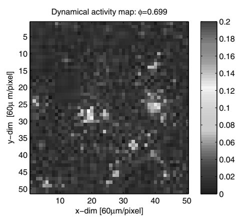
We present our work on the dynamical properties of dense monodisperse oil in water emulsions [1,2]. We use an experimental approach that allows spatially revolved dynamic light scattering in highly turbid media [3,4]. An example of the results for a compressed emulsion at $\phi = 0.699$ is shown in the Figure. Here we constructed a dynamical activity map using the intensity structure function $d_2(\tau, \mathbf{r})$, where each pixel contains the dynamical contribution of a small volume of linear dimension of approximatively 30 droplet diameters. Domains of high and low dynamical activity are color-coded by warm and cold colors, respectively. At these length scales, we observe a dynamics that is extremely heterogeneous. Our experiments allow to characterize the size and spatial distribution of dynamical heterogeneities. We aim at connecting our observations to a dynamical transition from thermally driven regime below random close packing[2], to a stress-relaxation regime as the system gets jammed and droplets starts to be in a compressed state [1].



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Polymer and Colloids **PO 9**

Protein Based Catalysts for Atom Transfer Radical Polymerization

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Atom transfer radical polymerization (ATRP) is one of the most powerful and dynamically developing techniques to produce polymers with precise chain length, low polydispersity and known composition. However, there are some disadvantages of this method. The copper based catalysts used for ATRP are difficult to remove from the polymer product. Since copper ions are mildly toxic, the products become non environmental friendly and often do not comply with standards for medical and food grade plastics.

To get greener ATRP, we started to use protein based, copper containing catalysts to produce polymers in aqueous solutions. We investigated some commercially available and in house synthesized ligands, conjugated to bovine serum albumin (BSA) and enhanced yellow fluorescent protein (eYFP), as ATRP catalysts. Polymerization of N-isopropylacrylamide carried out with these catalysts yielded polymers of low polydispersity. The reaction kinetics was found to be first order, which indicates that this polymerization is indeed a controlled radical polymerization. In order to remove the catalyst from solution, we have used organic solvents such as THF and salts, to precipitate the protein conjugate, thus removing the toxic metal compound to levels in the parts per billion range. Work is currently underway to track the copper removal by the fluorescence of the eYFP.

Polymer and Colloids **PO 10**

Interrelationship between Structure, Hydration and Lubricity of the Biomimetic Graft Copolymer Poly(L-lysine)-*graft*-Dextran

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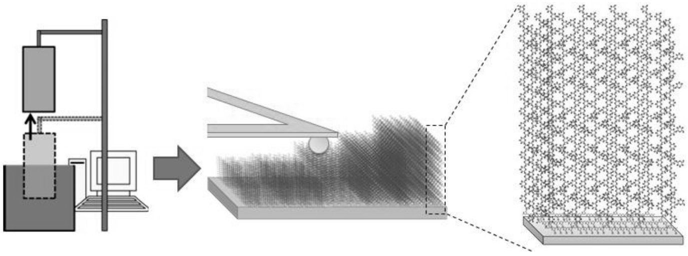
Surface density gradients of the graft copolymer poly(L-lysine)-graft-dextran (PLL-g-dex) were produced on silicon oxide substrates. The poly(L-lysine) backbone spontaneously adsorbs from aqueous solutions to sufficient surface density to cause the dextran side chains to extend into solution, forming a lubricious brush. The influence of the variation of dextran chain density, and therefore brush structure, along the gradient on the hydration and lubricity of the film were investigated via colloidal-probe lateral force microscopy, quartz crystal microbalance (QCM) and transmission interference adsorption sensor (TInAS). Characterization of the complex interdependence of these film properties can shed light on the behavior of comparable bottlebrush biomolecules in natural lubricating systems.



Polymer and Colloids **PO 11**

Tubular helices based on substituted oligo(*p*-benzamide)s

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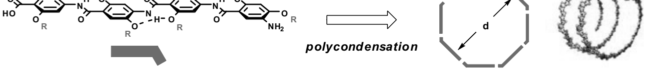
We present the synthesis of large tubular helices via polycondensation of substituted oligo(*p*-benzamide)s, which are highly interesting tools for the construction of nanoscopic objects due to their chain stiffness, shape persistence and ability of intramolecular hydrogen bond formation. Automated solid supported synthesis of these oligomeric precursors has already been established in our group allowing for sequence control.[1] In addition, we developed new routes to organo-soluble, non-aggregating rigid rods.[2, 3]



Prominent examples for self-organization are proteins which assemble into functional supramolecular structures through storage of information on molecular level. In this project, formation of the helix will be ensured by three-center hydrogen bonds resulting from disubstituted 4-amino-2,5-dihydroxybenzoic acid and 5-amino-2,4-dihydroxybenzoic acid monomers. Altering the number of these linear and angled segments enables us to tune the size of the oligomers and therefore the diameter of the helix.

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Polymer and Colloids **PO 12**

A Wet Chemical Approach towards Functional Carbon Nanostructures

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Carbonaceous materials with a feature size on the nanometer scale offer considerable prospects for emerging technologies such as lithium batteries or hydrogen storage. Currently, the methods most widely employed to prepare carbon nanostructures rely on harsh reaction conditions that limit a functionalization to post-synthetic steps. Our strategy for the preparation of nanostructured carbonaceous materials is based on the synthesis of amphiphilic oligo(ethynylene)s.[1, 2] For this purpose, glycosylated hexa(ethynylene) was synthesized on the multi-gram scale. The self-assembly behavior of these molecules in aqueous solution was investigated by UV/Vis spectroscopy and cryo-TEM. We found that the molecules formed vesicles with a controllable size in water. The conversion of the vesicles into carbon nanocapsules upon UV irradiation or thermal annealing was investigated.

[1] T. N. Hoheisel, S. Schrettl, R. Szilluweit, H. Frauenrath *Angew. Chem. Int. Ed.* **2010**, 49, 6496.

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Polymer and Colloids **PO 13**

Novel PEG-hexPLA micellar drug carriers with a covalently labeled Nile Red fluorescence marker

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For the characterization of polymeric micelles typically Nile Red (NR) as a fluorescence marker is used, which has the unique property to be fluorescent only in hydrophobic environments as it is present in the micelle core. However, simply incorporated Nile Red can diffuse out of the micelles that is of disadvantage for using them e.g. for pathway tracing *in vitro* and *in vivo*. In order to inhibit an uncontrolled diffusion the NR derivative 2-((9-(diethylamino)-5-oxo-5H-benzo[a]phenoxazin-2-yl)oxy)acetic acid [1, 2] was synthesized and covalently attached to a novel PEG-hexPLA block-copolymer [3] via a mild Mitsunobu reaction to yield the desired labeled PEG-hexPLA-NR. Composite micelles made of 0.5% (w/w NR) PEG-hexPLA-NR and pure PEG-hexPLA copolymers were prepared and fully characterized. For a proof of concept of controlling "non-diffusion" of NR labeled micelles the deriving micelle solutions were compared with classically NR incorporated micelles. Various experiments following the fluorescence intensity of the NR in the solutions were carried out at different temperatures and different pH-values over a period of 8 weeks. Indeed, the solutions of classically NR incorporated micelles showed a loss of fluorescence intensity in dependence of the storage conditions. In contrast, the novel labeled micelle solutions showed a 100% retention of the starting fluorescence intensity under all tested conditions. The novel labeled micelles were successfully tested as a model drug carrier system in a promising topical ophthalmic application *in vivo*.

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Polymer and Colloids **PO 14**

Development of light responsive membranes for controlled drug release

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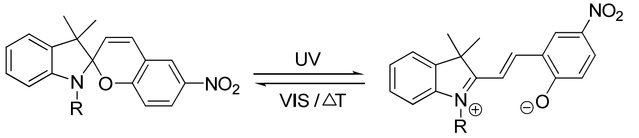
Plasma treatment of a polymeric porous membrane creates radicals on its surface. [1] Starting from those radicals, polymerization of hydroxyethyl acrylate (HEA) provides a free alcohol containing membrane surface.
Spiropyrans are photochromic molecules which can be switched from its nonpolar spiro-state (**1**) to a highly polar, coloured merocyanine-state (**2**). [2]



1 **2**

Spirobenzopyran can be either reacted with the free alcohol group of pHEA or an acrylate derivative can be co-polymerized with HEA from the plasma treated membrane surface.
Illuminating such a modified membrane by UV-light (366nm) caused ring opening of the spirobenzopyrane. This is accompanied by a decrease of the membrane resistance and an increase of the flux of different molecules across the membrane. Illuminating the membrane with visible light (470nm) returned the spirobenzopyran to its closed state (**1**). The original membrane resistance could be achieved again.[1]
By choosing an appropriate matrix material, specific pore size, the right surface modification conditions and the optimal photochromic molecule, the system can be fine-tuned for the diffusion of different specific molecules.

[1] D. J. Chung, *J. Appl. Polym. Sci.*, **1994**, *51*, 2027-2033
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Polymer and Colloids **PO 15**

Tuning *in-meso*-Crystallized Lysozyme Polymorphism by Lyotropic Liquid Crystal Symmetry

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Lipid-based lyotropic liquid crystals (LLCs) show great potential for applications in fields as diverse as food technology, cosmetics, pharmaceutics or structural biology. Recently, these systems have provided a viable alternative to the difficult process of membrane protein crystallization, owing to their similarities with cell membranes. Nonetheless, the process of *in-meso* crystallization of proteins still remains poorly understood.
In this study, we demonstrate that *in-meso* crystal morphologies of lsozyme (LSZ) -a model hydrophilic protein-, can be controlled by both the composition and symmetry of the mesophase, inferring a possible general influence of the LLC space group on the protein crystal polymorphism.
Lysozyme was crystallized *in-meso* from three common LLC phases (lamellar, inverse hexagonal and inverse bicontinuous cubic) composed of monolinolein and water. Different mixing ratios of mesophase to crystallization buffer were used in order to tune crystallization both in the bulk mesophase and in excess water conditions.
Two distinct mechanisms of crystallization were shown to take place depending on available water in the mesophases. In the bulk mesophases, protein nuclei form and grow within structural defects of the mesophase and partially dehydrate the system inducing order-to-order transitions of the liquid crystalline phase towards stable symmetries in conditions of lower hydration. The formed protein crystals eventually macrophase separate from the mesophase allowing the system to reach its final symmetry. On the other hand, when excess water is available, protein molecules diffuse from the water channels into the excess water, where the crystallization process can take place freely, and with little to no effect on the structure and symmetry of the lyotropic liquid crystals.

Polymer and Colloids **PO 16**

Formation of Metastable Bilayers by an Artificial Phospholipid

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A simple and robust synthesis of an artificial amide-bearing phospholipid featuring a phosphormidate as a protecting unit was designed and performed [1,2]. Experimental data revealed that intrinsic stability of the vesicles made of Pad-PC-Pad is comparable to that of the natural phospholipids DPPC and *N*-palmitoylsphingomyelin. Under increased shearing, Pad-PC-Pad vesicles showed an unprecedented behavior and released their cargo [2].
To understand this release pattern, monolayers and vesicles were studied. The form of the pressure-area isotherm hinted at the presence of a beginning crystallization in the monolayer and Brewster angle micrographs of the monolayers revealed the rapid growth of the new solid phase within seconds. The crystalline features were also detected by microscopic studies of LUVs and GUVs and new, non spherical vesicle geometries were detected.
Our ongoing research is directed towards the elucidation of the role of H-bonds in the metastability of Pad-PC-Pad bilayers.

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Polymer and Colloids **PO 17**

New polyether ether ketone (PEEK) with silver for implants

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PEEK is a very resistant and robust polymer, which was discovered in the 80's. It is used in many different applications like aeronautics, chemical processes and medical implants. One of the major problems of implants is the infection rate after *in vivo* implantation. In order to prevent infection, antimicrobial coatings containing silver ions were developed[1]. This type of coating could easily attach to the implant's surface by surface modification[2] for metallic implants (e.g. gold, titanium). For polymeric surfaces, this is much more difficult. The simplest way is to modify the polymer itself. In our case we have modified the monomer of PEEK in order to have a binding site for silver ions: a pyridine group was attached to the 4,4'-difluorobenzophenone. The polymerization was done by condensation polymerization with different hydroquinone derivatives with polar aprotic solvent. We had also studied the binding of silver with the monomer.

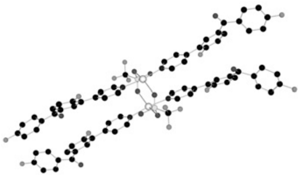

Figure 1: Crystal structure of PEEK monomer with silver trifluoromethanesulfonate.

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Polymer and Colloids **PO 18**

Humidity controlled production of different silicon nano and microstructures

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Polysiloxane nanofibers with high aspect ratio have been recently developed and they are receiving a lot of attention due to wide range of possible applications. The current research presents an extensive study of the influence of water content during the reaction on formation of different nano- and microstructures from different polysiloxane precursors. Methyltrichlorosilane (MTCS) and Ethyltrichlorosilane (ETCS) were used like precursors and it is shown that even such a slight difference in chemical composition of starting compounds under same reaction conditions can lead to different topography and hydrophobic properties of coating. Superhydrophobic properties of coating produced from ETCS appear to be less sensitive on water content during reaction than coating produced from MTCS. ETCS precursor formed exceptionally large fibers with lengths in excess of 50 µm at high humidity levels. Using double coating procedure - which consists of coating substrate at high humidity level and subsequent coating with middle humidity level ideal for dense nanofilament formation – "ideally superhydrophobic" surface with contact angle of 170° and sliding angle below 4° were produced.

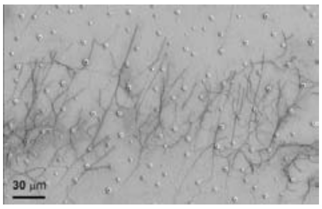

Figure: SEM image of microfilaments produced at high humidity content

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Polymer and Colloids **PO 19**

General Self-Assembly Mechanism Converting Hydrolyzed Globular Proteins Into Giant Multistranded Amyloid Ribbons

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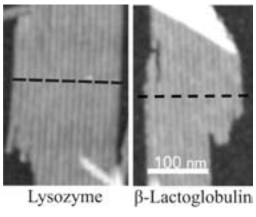
We report a rationale for the formation of amyloid fibrils from globular proteins and we infer about its possible generality by showing the formation of giant multi-stranded twisted and helical ribbons from both lysozyme and β-lactoglobulin. We follow the kinetics of the fibrillation in the same conditions of temperature (90°C) and incubation time (0-30 hours) for both proteins and we assess the structural changes during fibrillation by single-molecule atomic force microscopy (AFM), circular dichroism (CD) and SDS-PAGE. With incubation time, the width of a multi-stranded fibril increases up to an unprecedented size, with a lateral assembly of as many as 17 protofilaments (173 nm width). In both cases, a progressive unfolding and hydrolysis of the proteins into very short peptide sequences occurs. The molecular weights of peptide fragments, the secondary structure evolution and the morphology of the final fibrils present striking similarities between lysozyme and β-lactoglobulin. Due to additional analogies with synthetic peptide fibrils, these findings support a universal common fibrillation mechanism in which hydrolyzed fragments play the central role.



Lysozyme β-Lactoglobulin

Polymer and Colloids **PO 20**

Adsorption characteristics of polyelectrolytes on latex particles

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Control of stability of colloidal suspensions containing charged particles by polyelectrolytes comes into renewed focus due to the growing importance of polyelectrolytes in several applications, such as waste-water treatment, papermaking, as well as formulation of foods, paints, cosmetics or pharmaceutical products. To improve the effectiveness of these processes, polyelectrolyte adsorption on surfaces has to be well understood. In the present study, a comprehensive investigation including charging, stability and surface properties of charged nanoparticles in the presence of polyelectrolytes has been performed.

Electrophoretic measurements revealed that polyelectrolytes strongly adsorb on the surface of oppositely charged nanoparticles leading to charge neutralization at the isoelectric point and also charge reversal upon further addition of polyelectrolytes. The suspensions were unstable near the isoelectric point and more stable away from it where the particles possess charge as observed by time-resolved dynamic light scattering experiments. Both surface charge properties and suspension stabilities showed significant ionic strength dependence indicating an electrostatic origin of the predominant repulsive forces in the case of dispersions of bare and polyelectrolyte coated latex particles. The adsorbed amount increases with increasing salt level and decreases with increasing molecular mass. The structure of the adsorbed polyelectrolyte layer has been investigated by dynamic light scattering and a significant increase was observed in the layer thicknesses by increasing the ionic strength indicating that the polyelectrolytes adsorb in a flat configuration at low salt level and in a more extended configuration at higher ionic strengths. Moreover, the hydrodynamic layer thickness is independent of the molecular mass at low salt levels, but increases with the molecular mass at higher salt concentrations.

Polymer and Colloids **PO 21**

Biomimetic Block Copolymer Membranes for Functionalized Surfaces

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The functionalization of surfaces through biomimetic block copolymer membranes aims at developing smart surfaces for biotechnological applications such as biosensing. Amphiphilic block copolymer membranes were chosen instead of lipid membranes as mimics of biological membranes because of their properties, such as thickness, chemical and mechanical stability, lower permeability, fluidity, mobility, etc. ATRP was successfully applied to the grafting of ABA-triblock copolymer membranes from gold supports. The length of each individual block was controlled by varying the polymerization time. The amphiphilic character of the triblock copolymer brushes provided a responsive surface that showed a solvent-dependent arrangement of the block copolymer chains, which was also reflected in the morphologies of the dried films [1]. Polymer brushes such as these, exhibiting a hydrophilic-hydrophobic-hydrophilic sequence, could be regarded as the first example of solid supported, biomimetic block copolymer membranes prepared by a "grafting-from" approach. Upon insertion of membrane proteins, these systems could allow for the preparation of mechanically and chemically robust and air-stable biosensor devices.

[1] E.Rakhmatullina, et al., *J. Polym. Sci. A*, **2009**, *47*:1-13.

Polymer and Colloids **PO 22**

Interactions between sulfate latex particles with adsorbed linear poly(ethylene imine) studied using colloidal probe technique

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Interaction forces between negatively charged sulfate latex particles with adsorbed cationic linear poly(ethylene imine) (LPEI) are studied using colloidal probe technique based on the atomic force microscope (AFM). Tuning the polymer dose, the interaction forces are observed to switch from repulsive to attractive and back to repulsive again. The repulsive ones are given by the overlap of the diffuse part of the electrical double layer around the charged surfaces of two particles. Their strength decreases as one approaches the isoelectric point (IEP) and increases away from it. Close to the IEP, the surface of the particle is neutralized by the polymer and the electrical double layer does not exist any longer. This situation is described by short range van der Waals interactions. At very high adsorbed amount, the surface saturates and the strength of the interactions remains constant.

Polymer and Colloids **PO 23**

AFM study of mechanical properties of single dendronized polymers

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Dendronized polymers have attracted considerable scientific interest in recent years. They consist on a central linear polymeric core with appendent dendrons and attain a rod-like, cylindrical shape. In contrast to the conventional polymers, the diameter of the dendronized polymers is on the order of a few nanometers rather than a few angstroms [1].

Polymethacrylate-based dendronized polymers of different generations (PGn) adsorbed on a mica substrate were imagined with atomic force microscopy (AFM) in solution. The pH dependence investigation of PG5 revealed that with increasing pH the persistence length of polymer chain decreases.

Mechanical properties of individual dendronized polymers adsorbed on a mica substrate were investigated using single-molecule force spectroscopy (SMFS). SMFS was used for the mechanical manipulation of single polymer chains in solution. The force measurement was performed directly after imaging on the precise position on the molecule. The measured force-distance curves using AFM-based SMFS revealed a detailed insight into material properties at the molecular level.

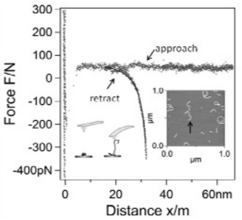

Figure 1: AFM height image and force curve of PG3 adsorbed on mica in solution at pH4.

[1] Schlüter, A. D., Rabe, J. P., Angew. Chem. Int. Ed. **2000**, 39, 864-883.

Polymer and Colloids **PO 24**

Silicone Nanofilaments as Carrier for Titania

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High surface area materials are highly desirable as carriers for nanosized catalysts. Many nanoporous materials have been developed to meet this demand, but low diffusion rates due to the pore size can limit applications involving larger molecules. Better accessibility of the catalytic sites can be provided by fibrous materials like silicone nanofilaments (SNFs) [1, 2]. For the first time, we prove the suitability of SNFs as a substrate for the immobilization of nanoparticles. Titania (TiO_2) is one of the most promising photocatalytic materials. We have thus deposited titania nanoparticles on the filaments via facile coating with TiF_4 as precursor. Reaction time screens were performed in various ethanol/water ratios: Particle morphology and distribution of the nanoparticles along the filaments can be adjusted by temperature, reaction time and polarity of the solvent.

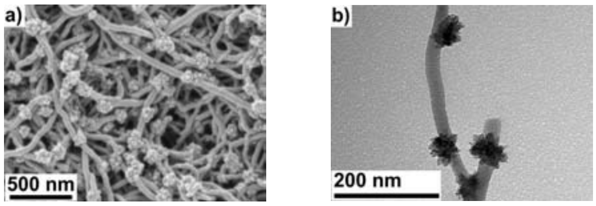

Figure SEM (a) and TEM (b) micrographs of SNF-TiO_2 hybrids.

[1] G. R. J. Artus, S. Jung, J. Zimmermann, H.-P. Gautschi, K. Marquardt, S. Seeger *Adv. Mater.* **2006**, *18*, 2758.

[2] J. Zimmermann, M. Rabe, D. Verdes, S. Seeger *Langmuir* **2008**, *24*, 1053.

Polymer and Colloids **PO 25**

Synthesis and Characterization of Poly(isobutylene)-Oligopeptide Conjugates

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Biomaterials such as silk exhibit extraordinary properties, in particular, spider dragline silk, which shows outstanding physical properties and has received considerable attention in recent decades.[1] Similar to synthetic thermoplastic elastomers, it contains repetitive sequences of glycine-rich soft segments as well as well-defined L-alanine-rich hard segments.[2] In order to mimic certain aspects of its molecular and nanoscopic structure, we prepared several poly(isobutylene)-oligopeptide conjugates with the structures $\text{R-Ala}_n\text{-PIB}$ and $\text{R-Ala}_n\text{-PIB-Ala}_n\text{-R}$, which consist of poly(isobutylene) (PIB) as the soft segment and one or two monodisperse, chiral, and β-sheet-forming terminal oligopeptides Ala_n, with up to five alanine residues, as well as acetyl end group R. The properties of these two series of materials, such as their secondary structure formation in the solid state and in organic solvent, as well as their thermal properties, including decomposition, glass transition temperature, and crystallization behavior were investigated and compared. The acetylated PIB-oligopeptide conjugates showed defined secondary structures both in the solid state and in organic solvents. They exhibited a low solubility in organic solvent, high decomposition temperatures, and a high degree of crystallinity as well.

[1] F. Vollrath, D. P. Knight, *Nature* **2001**, *410*, 541-548
[2] R. V. Lewis, *Chem. Rev.* **2006**, *106*, 3762-74

Polymer and Colloids **PO 26**

Tailoring the solubility properties of aryltriazene photopolymer films for LIFT applications

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In a conventional laser-induced forward transfer (LIFT) process the material to transfer is directly exposed to a laser pulse, which can alter the properties of the functional material[1]. This technique of transfer, has been improved by adding an absorbing sacrificial dynamic release layer (DRL)[2]. This is where the aryltriazene photopolymers play an important role. The irradiation of the laser decomposes the absorbing photopolymer in easily volatile fragments, which generate the pressure to transfer the overlaying layers towards a receiver substrate. For a layer-by-layer deposition of different materials mainly solution-based thin-film coating methods are used. To avoid a redissolution of the precoated DRL, orthogonality of the solvents of the different substances is a crucial requirement. As it isn't trivial to change the solubility of complex transfer materials to transfer without altering their properties, the alternative remedy is to adapt the solubility of the triazene polymers. While the photolabile chromophore in the core of the polymer determines the absorption, the introduction of more polar moieties along the photopolymer backbone and in its side chains can allow a modulation of the solubility. Thus new triazene photopolymers, which show different solubility (e.g. soluble in water), but similar ablation properties compared to the original ones have been synthesized.

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[2] Shaw-Stewart J., Lippert T., Nagel M., Nuesch F., Wokaun A.; *ACS Appl. Mater. Interfaces* **2011**, *3*; 2

Polymer and Colloids **PO 27**

Synthesis and Postpolymerization Modification of Poly(pentafluorophenyl methacrylate) (PPFMA) brushes

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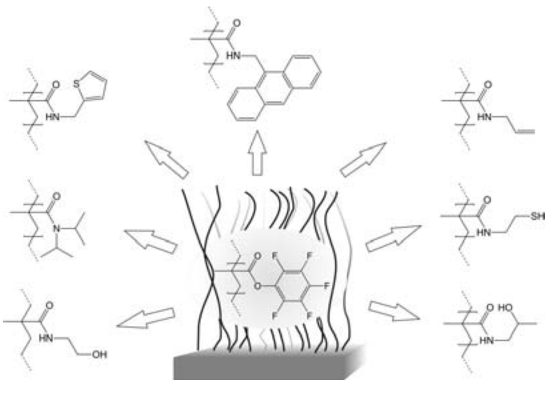
EPFL, STI/IMX/MXD/LP, Station 12, CH-1015, Lausanne, Switzerland

Surface-initiated reversible addition fragmentation transfer (SI-RAFT) polymerization was employed to synthesize poly(pentafluorophenyl methacrylate) (PPFMA) brushes grafted from silica substrates. The kinetics of the polymerization was investigated with or without the presence of free chain transfer agent (CTA). The thickness of the brushes increased linearly with the polymerization time up to 32 nm in 4 hours for both polymerization conditions. Secondly, postpolymerization modification of PPFMA brushes was investigated. While the aliphatic amines reacted quickly and quantitatively with PPFMA; we observed that the aromatic amines were not able to postmodify the active ester. We also demonstrated that PPFMA films are highly stable toward base-mediated hydrolysis.



Polymer and Colloids **PO 28**

Polylysine Analogues for Gene Transfer in Mammalian Cells: Structure-Activity Relationship

Zuzana Kadlecova[1], Laurence Abrami[2], Lucia Baldi[3], F. Gisou van der Goot[2], Florian M. Wurm[3], Harm-Anton Klok[1*]

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Polymeric cations are widely used as nonviral transfection agents. A fundamental understanding of the relationship between their structure, internalization properties and biological activity is still lacking and is mostly based on empirical observations. We investigated the role of the structural parameters of the polycations, for which a library of the transfection agents based on L-lysine monomer unit was constructed, covering a broad range of molecular weight and degrees of branching. Based on this a new class of cationic polymers, prepared by polycondensation of L-lysine, was developed to explore the impact of very high molecular weights. The internalization kinetics of the polycation and pDNA complex was measured at a macroscopic scale by fluorescence methods. The microscopic distribution and the trafficking kinetics were studied by subcellular fractionation and confocal scanning laser microscopy with subsequent image analysis. The localization of the polycation and polyplex at defined time points post gene transfer was followed by indirect immunocytochemistry. We found that the molecular weight is an important parameter for the quantity of internalized pDNA. High molecular weight polycations appear to bind instantaneously and persistently to the plasma membrane and the polyplex remain partially localized at the plasma membrane. Moreover high molecular weight polycations appears to possess a unique capacity to prevent the degradation of pDNA by endonucleases. Degradation of plasmid DNA and its resulting inactivation, suspected to be one of the limiting factors of efficient gene delivery, can be thus potentially circumvented. In summary the data show the close correlation between the physico-chemical parameters of the polycations and their transfection activity. The appropriate design of the polycations as gene delivery vectors leads to high transfection efficiency and high yield of recombinant protein.

Polymer and Colloids **PO 29**

QCM and reflectometry study of stimuli responsive polyelectrolyte monolayers

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In the present work, the swelling properties of polyelectrolytes (PE) adsorbed on a flat surface were studied using quartz crystal microbalance (QCM) and reflectometry. It was proven that, at high salt concentrations, the PE chains adsorb in “loop and tail” conformation with significant amount of trapped water. Swelling behavior of PE layers physisorbed on silica surface was demonstrated with QCM. Influence of the initial conditions of polymer physisorption on the surface such as the length of the polymer chain, pH and ionic strength of the solution on swelling was studied. Our results show that the swelling is more pronounced for weak PE.

Polymer and Colloids **PO 30**

Generation of Silver Nanoparticles in the Presence of Oligoproline Derivatives

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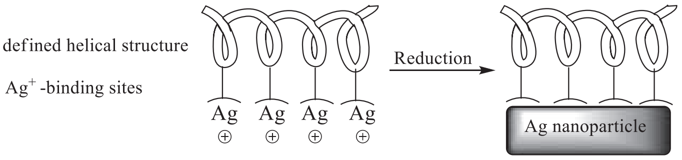
Silver nanoparticles offer great opportunities for applications in for example electronics, catalysis, imaging and for antimicrobial coatings [1]. The properties depend on their shape and size [1]. The generation of silver nanoparticles in defined sizes is therefore important and still remains a challenge.
We envision to address this goal by utilizing oligoproline peptides that form a defined and rigid helical secondary structure (PPII) [2]. By decorating this template with functional groups that bind to silver ions, they could be involved as scaffolds in the generation process and therefore allow the formation of defined nanoparticles. We will report the results of the generation process with various oligoprolines and discuss the differences in the resulting silver nanoparticles which were analyzed by TEM and UV-Vis studies.



[1] C-L. Chen, N. L. Rosi, *Angew. Chem. Int. Ed.* **2010**, *49*, 1924.
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Polymer and Colloids **PO 31**

Shear thickening fluids for damping applications

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Highly concentrated suspensions of silica particles in polyethylene glycol (PEG) present shear thickening properties. Their viscosity increases instantly and reversibly, when submitted to a critical shear rate along with strain. This sharp rise in viscosity is associated with a large energy absorption that can be exploited for damping. A potential application is to damp large amplitude vibrations in space launchers.

Damping properties of shear thickening fluids (STF) are strongly related to their rheological properties. The energy dissipated per cycle (E_d) is an absolute measure of damping for a material. It is obtained through dynamic oscillatory shear tests between parallel plates, and corresponds to the area of the hysteresis curve in a Lissajous plot of stress vs. strain signals.

In this work, we measure E_d for a monodisperse STF as a function of strain, and evaluate the influence of particle concentration and size. Below the transition from a low to high viscosity, the behavior is typical of a viscoelastic fluid, and the dissipated energy per cycle then strongly increases during the transition. E_d was found to increase with a rise in particles concentration or a decrease in particle size. E_d also increased with test frequency. The damping properties of STF were also compared to those of current damping materials such as SMACTANE and the silicone RTV-3318. The investigated STF was shown to potentially overtake these materials for high frequency, high strain applications.

Polymer and Colloids **PO 32**

Nanostructured Materials Containing Organic Semiconductors

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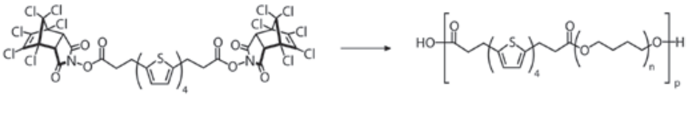
Due to the specific energy conversion mechanisms taking place in organic photovoltaics, the active part of organic solar cells, an interface between n- and p-type semiconductors, has to be shaped at the nanometer scale.[1] In this context, the synthesis and self-assembly of block copolymers comprising π-conjugated rod (opto-electronically active part) and flexible coil segments (structuring part) is expected to provide well-ordered and electronically active thin films.[2] For this reason, we investigated the preparation of multiblock copolymers containing semiconducting rods and flexible poly(tetrahydrofurane) (PTHF) coils, their characterization and their processing into nanostructured materials. The PTHF coils can be selectively removed and then replaced by another type of semiconductor, required for suitable photovoltaic properties.



Representative example of the multiblock copolymers investigated.

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Polymer and Colloids **PO 33**

Paramagnetic Ag(0) and Cu(0) containing polymeric nanocomposites

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The developments upon the nanocomposites materials containing metal particles and possessing complex properties relevant for of up-to-date catalysts, drugs, etc. have been widely spread especially in the recent years. This trend is closely connected with the problem of nanoparticles' stabilization within the matrix [1].

Nanocomposites on the basis of poly-1-vinyl-1,2,4-triazole-acrylonitrile copolymer (VT-AN) containing zero-valence silver and copper have been obtained by the thermal reduction of $AgNO_3$ and $CuCl_2$ in the presence of (co)polymer in solid phase. According to X-ray data silver and copper nanoparticles have sizes 17-20 nm and 25-26 nm in the composites, respectively. Nanocomposites materials on the basis of VT-AN matrix possess of electroconductivity (10^{-6}-10^{-10} S/cm) and paramagnetism (10^{19}-10^{20} spin/g). In their EPR spectra at room temperature narrow singlets with *g*-factor of 2.005 were recorded and identified as zero-valence silver and copper signals [2, 3].

The temperature dependences of EPR signals intensity, *g*-factor and lines width is in accordance with the X-ray data and confirmed that main size of nanoclusters do not exceed 30 nm. Silver and copper containing nanocomposites studied are quite stable and do not change their paramagnetic properties during at the least year.

[1] C.N.R. Rao, A. Müller, A.K. Cheetman, *The Chemistry of Nanomaterials*. Wiley-VCH, Weinheim, **2004**.
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[3] M. Eichelman, K. Rademann, A. Hoell, D.M. Tatchev, W. Weigel, R. Stößer, G. Pacchioni, *Nanotechnology*. **2008**, 19, 1-9.

Polymer and Colloids **PO 34**

Synthesis of silver nanoparticles and their polydimethylsiloxane composites

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[2] Ecole Polytechnique Fédérale de Lausanne (EPFL),
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A challenge in the field of dielectric elastomer actuators is to prepare an elastomeric material with a high dielectric constant which can be operated at low electric field and yet providing large strains. It is well known that the dielectric constant of a polymer matrix can significantly be increased by blending with conducting fillers, however the breakdown field as well as the elastic properties decreases due to the inhomogeneous dispersion of the particles. We propose a method to create new dielectric polydimethylsiloxane (PDMS) based materials with high dielectric constant (ε), low dielectric loss, and low conductivity. The intrinsically low ε of PDMS ($\varepsilon = 2.3$) is increased by dispersing highly polarizable silver nanoparticles (AgNPs). PVP stabilized AgNPs were prepared starting from $AgNO_3$ by the polyol route [1]. To avoid problems with the percolation and subsequent electrical short circuits, AgNPs were coated by insulating shells (organic and inorganic) prior to their dispersion into the matrix.

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Polymer and Colloids **PO 35**

Universal End-capping Reagents for Living Olefin Metathesis Polymerisation

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One of the fundamental requirements in polymer chemistry today is the control of functionality and functionality placement. Our research deals with the development of methods for introducing end-groups to living olefin metathesis polymers. One major drawback of this living polymerization technique compared to most others is, that it doesn´t offer a straightforward synthetic method for introducing functional end-groups. Therefore we investigate reaction pathways that transform the propagating living chain end into a functional group. Using different synthetic approaches we aim at end-functionalization reactions that give high degrees of end-group functionality while offering precise control over molecular weight and polydispersity. Functionally substituted vinyl lactones, vinyl esters and vinyl halides form metal carbenes that energetically disfavor further productive metathesis with residual olefinic monomers. Moreover, in a second reaction step they form a ruthenium species, which does not undergo further olefin metathesis [1]. In short, they terminate the polymerization reaction by transforming the living chain end into a functional group without the need for further derivatization reactions. One of our goals is to create universal end-capping reagents. These are terminating reagents that carry a pre-functionalizable group that allows the attachment of desired functional groups or molecules prior to the end-capping reaction. Such end-capping reagents will be particularly useful for grafting-to surfaces or functional solid supports.

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Polymer and Colloids **PO 36**

Amine End-Functionalized Polymers by Living Ring Opening Metathesis Polymerization and Sacrificial Synthesis

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There are several methods for chain end-functionalization of polymers synthesized by ring opening metathesis polymerization, one of which is the 'Sacrificial Synthesis' strategy developed by our group. In this strategy, a sacrificial block is polymerized onto the main polymer and then cleaved to yield the desired functionality at the chain end of the polymer.

Our group has successfully synthesized alcohol and thiol monotelechelic polymers by this method. Here, we present amino end-functionalized polymers using sacrificial synthesis.

Amines are useful nucleophiles that can readily be further functionalized. More complex polymeric architectures or polymer conjugates with functional molecules, oligomers or biomolecules are thus readily accessible.

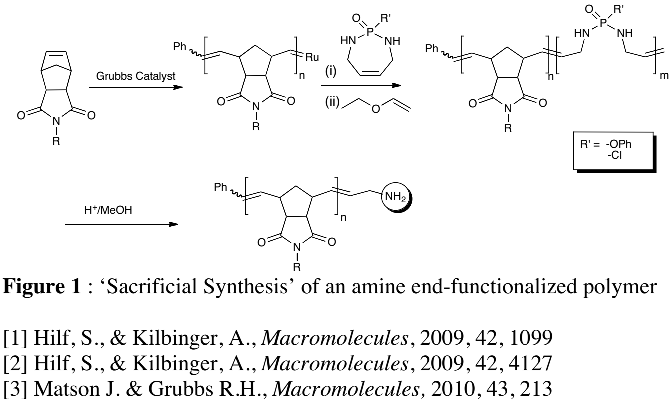

Figure 1 : 'Sacrificial Synthesis' of an amine end-functionalized polymer

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[3] Matson J. & Grubbs R.H., *Macromolecules,* 2010, 43, 213

Polymer and Colloids **PO 37**

Chemical and kinetic description of metal oxide nanoparticle formation in benzyl alcohol by combined on line spectroscopic monitoring and kinetic modeling

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The study of nanoparticle formation and growth under real synthesis conditions remains a fascinating and challenging objective. In the case of non-aqueous syntheses an exhaustive monitoring has to include, in addition to the inorganic reaction, the organic chemical transformations as well as the evolution of the organic-inorganic interface [1-2]. Moreover, the time resolved analysis of a multiphase system requires orthogonal instrumental technology as well as powerful methods capable of rapidly and efficiently extracting the chemical information.

In this contribution, ATR UV-vis, ATR FTIR and Raman dip probe spectroscopic techniques are shown to be tools of choice for the on line monitoring of metal oxide nanoparticle formation in organic solvents. Combined techniques allow the description of the precursor dissolution, precursor-solvent reaction, nucleation and aging. Multivariate curve resolution methods are proposed to overcome the difficulties of complex systems involving, for example, distinct phases, complex baseline or uncolored species [3].

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Polymer and Colloids **PO 38**

Molecular Dynamic simulation strategy for the lipophilic drug incorporation prediction in polymeric micelles

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Many newly developed drugs possess low water solubility, making them difficult to formulate for pharmaceutical products. To overcome this problem nanosized drug delivery systems can be used, e.g polymeric micelles, that have a hydrophilic corona and a lipophilic core, wherein lipophilic drugs can be incorporated and overall solubilized in aq. solutions. For micelle cores with a high lipophilicity and an improved affinity to such drugs, we developed novel poly(hexyl-substituted PLA) (hexPLA) based micelles [1,2]. To obtain formulations with sufficient drug loadings, it is desirable to predict the incorporation of lipophilic drugs into these micelles. The use of simulation methods could reduce the number of experimental trials and thus reduce material and time expenses. We developed a new prediction strategy on the base of Molecular Dynamic (MD) simulations, wherein the Flory-Huggins interaction parameter appears as the characteristic of the incorporation possibility. The MD simulation of two copolymers PEG-hexPLA and PEG-PLA and four hydrophobic drugs with different solubilities in water were carried out to test this MD strategy and its reliability. The results show that the Flory-Huggins interaction parameters, as a result of these calculations, are in good agreement with the experimental data.

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Polymer and Colloids **PO 39**

Towards model bioactive polymer self-assembly

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Nowadays, there is a major interest in the design of bioactive polymeric materials. Some of the prominent examples are the developments of platforms for tissue engineering and the design of medical devices as well as carriers for drug or gene therapy. In this context, soft templates based on self-assembled nucleotide-based amphiphilic copolymers present a new class of very promising biologically active materials.

Bioactive self-assemblies were prepared by the polymer modification of short nucleotide sequences with a hydrophobic poly(isobutylene) segment through solid phase synthesis[1]. Self-assembly into vesicular structures in dilute aqueous solution enabled the design of nanoreactors. The permeability of the resulting nanocontainers was allowed by the functional incorporation of naturally occurring pore-forming proteins in the polymeric membrane. The self-assembled structures were further immobilized on surfaces via base pairing between the nucleotide sequences composing the self-assembled copolymers and the surface-tethered complementary sequences.
Using E.coli K12 wild and mutant strains, we observed the influence of the modified surfaces on the dynamic of bacterial attachment as well as on the number and the motility of adherent bacteria through real-time observations via confocal laser scanning microscopy.

Authors want to acknowledge the SNSF (PPOOP2-128380) for providing financial support to this project.

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Polymer and Colloids **PO 40**

Non-ideal polymerization of cationic monomers and solution behavior of the resulting polyelectrolytes

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Water-soluble synthetic polyelectrolytes (PEL) are increasingly interesting due to their widespread already established or potential application fields, which usually rely on strong electrostatic interaction in solution or at interfaces. Electrostatic effects cause deviation of the polymerization kinetics from the ideal case. However, also other than electrostatic interactions cannot be neglected. Despite practical importance, appropriate kinetic-mechanistic studies are rare.
Two double-charged cationic monomers 1,3-bis(*N,N,N*-trimethylammonium)-2-propylmethacrylate dichloride (di-M) and 1,3-bis(*N,N,N*-trimethylammonium)-2-propylacrylate dichloride (di-A) allowed for studying the free radical solution polymerization under strong electrostatic influences in detail and quantifying this impact comparing the kinetic results with those of the mono-charged analogue *N,N,N*-trimethylammonium-2-propylacrylate chloride.
It was confirmed that both the charge density and the chemical structure of the polymer backbone govern the solution behavior of the resulting PEL and the complex formation characteristics with oppositely charged PEL. The properties of polycation - polyanion complexes (PECs) in solution, their size, stoichiometry and stability have been studied for various model polyanions.
Acknowledgement: The research is supported by the SNSF, grants 200021-107737/1, 200020_119818/1, and 200020_135162/1

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Polymer and Colloids **PO 41**

Synthesis and study of physico-chemical properties of PVAc-b-PCL block copolymers: Effect of using click chemistry on the crystalline properties of the copolymers

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The synthesis of new PVAc-b-PCL block copolymers was studied using a combination of click chemistry, reversible addition-fragmentation chain transfer (RAFT) and ROP polymerizations. Two approaches have been studied; "coupling reaction" based on 1, 3 cyclo addition reaction " click chemistry " and “macroinitiator".

The comparisons of thermal properties of PVAc-b-PCL obtained with these two approaches are studied with differential scanning calorimetry (DSC). The results indicate a decrease of the crystallinity of the PCL block in copolymers obtained by the “coupling” method, compared to PCL homopolymers, contrary to copolymers obtained through the “macroinitiator” approach for which the crystallinity of the PCL was much less affected. This influence of the method of synthesis was explained by the presence, in copolymers synthesized by click reaction, of a rigid triazol cycle (cycle binding the two blocks of polymer). This triazol cycle will limit the relative mobility of the two blocks and thus will decrease the possibility of organization and crystal formation. The presence of this cycle is able to decrease of more than 50% the crystallinity of copolymers.

The Study of growth of PVAc-b-PCL block copolymers crystals in Langmuir films at the air/water interface is realized. This study provides a detailed examination of the nucleation and the growth of these block copolymers in Langmuir monolayers at the interface at the A/Winterface.

The effect of using click chemistry on the crystalline properties of the copolymers was shown.

Polymer and Colloids **PO 42**

New Polymeric Materials for light upconversion *via* triplet-triplet annihilation

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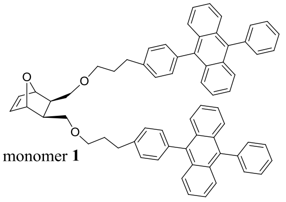
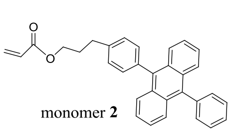
One interesting approach to generate blue-shifted light with respect to an incident beam is upconversion by triplet-triplet annihilation, as this mechanism can be exploited with very low power densities (< 100 mW•cm^{-2}). Mostly studied in solution, this phenomenon has been transposed in rubbery polymers by blending strategies of anthracene derivatives and porphyrin complexes [1]. In this work, we focused on the synthesis of novel monomers (**1** and **2**) allowing to increase the content of light-emitter within the material by covalently tethering diphenylanthracene (DPA) to a polymerizable unit. In conjunction with palladium octaethylporphyrin, the DPA-unit led to upconverted light and prevented crystallization and phase separation of the emitter. Monomer 1 was obtained from reduction of oxanorbornene anhydride and subsequent Williamson ether synthesis and used for polymerization by ring-opening metathesis polymerization. Monomer 2 was obtained by reacting acryloyl chloride with a hydroxyl-derivatized DPA and used for atom transfer radical polymerization. We are currently investigating the photochemical properties of the resulting materials and the influence of physical properties of the polymer on the upconversion efficiency.


monomer **1**


monomer **2**

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Polymer and Colloids **PO 43**

Vesicle-Assisted Enzymatic Synthesis of Conductive Polyaniline

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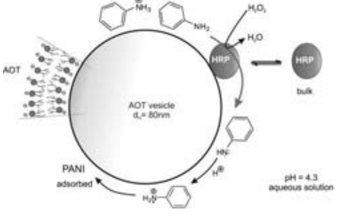
The conductive emeraldine salt form of polyaniline (PANI) can be obtained from aniline at pH 4.3 in presence of vesicles and horseradish peroxidase (HRP)/H_2O_2 to trigger the polymerization reaction.[1] The vesicles act as templates, thereby (i) increasing the local concentration of the reacting aniline monomers, (ii) promoting mainly the *para*-addition of the aniline, (iii) acting as dopant, and (iv) increasing the processability of the polyaniline obtained. The use of vesicles formed from AOT (= bis-(2-ethylhexyl) sulfosuccinate) was found to be particularly promising.[2] Compared with previously used templates, the use of vesicles offers the unique possibility of preparing hollow capsules which are coated with *in situ* formed PANI.



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Polymer and Colloids **PO 44**

Multifunctional Dendronized Polymer-Enzyme Hybrids

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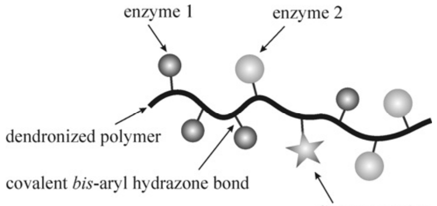
A bio-hybrid between a water-soluble, amine-decorated dendronized polymer[1] and two different kinds of enzymes and a fluorescent dye was prepared by covalent attachment. The resulting conjugate contained multiple copies of the two enzymes and the fluorescent dye. For the covalent attachment, a stable, UV/Vis quantifiable *bis*-aryl hydrazone bond was formed.[3]



The enzymes were coupled stepwise to the fluorescently-labeled dendronized polymer. The thereby formed *bis*-aryl hydrazone bond allowed measuring the amount of bound enzymes and fluorescent dye easily *via* UV/Vis spectroscopy. The conjugate formation was not only fast and highly efficient but also occurred under mild conditions and under retention of the enzymatic activities.

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Polymer and Colloids **PO 45**

Study of Polymer Clay Nanocomposites with Pulse EPR Spectroscopy

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In recent years polymer clay nanocomposites have gathered considerable interest in polymer science as well as in industry because of the improvements of their properties compared to unmodified polymers [1]. In spite of the considerable amount of published work on these nanocomposites, knowledge about their nanoscale structure is still poor, so that the basis of the improved material characteristics is not well understood.

EPR techniques can be useful to study weakly ordered materials like polymers on the nanoscale by probing the environment of stable nitroxide molecule radicals inserted into the material [2,3]. The availability of highly diverse spin probes makes it possible to selectively adress regions of different polarity in weakly ordered materials like nanocomposites.

On this poster we present results of pulse EPR experiments with nanocomposites consisting of PMMA-co-Bu and Laponite B. The nanocomposites were produced from an aqueous SDS-stabilized polymer dispersion and exfoliated clay. By adding the polar spin probe 4-trimethylammonium-2,2,6,6-tetra-methylpiperidine-1-oxyl (CAT-1) or the amphoteric spin-probe sodium-5-DOXYL-stearate (S5D) we could adress different regions of the resulting polymer clay nanocomposite.

We used pulse EPR methods to study the hyperfine interaction in the presence of nuclei. This provides information in the environment of the spin probes and on the distance of closed approach to such nuclei.

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Polymer and Colloids **PO 46**

Proton Conductivity Studies on Radiation-Grafted Membranes

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Due to the attractive conductivity and chemical stability, Nafion is widely used as membrane electrolyte in the polymer electrolyte fuel cell (PEFC) [1]. However, to obtain tailor-made and cost-effective membranes, we are looking at utilizing radiation grafted polymer membranes instead of Nafion. ETFE and FEP are two qualified candidates of base polymers because of their chemical and thermal stability and mechanical robustness [2]. As functional monomers, styrene or α-methylstyrene (AMS) are co-grafted with methacrylonitrile (MAN) into pre-irradiated base polymers (25 µm film) followed by sulfonation, by which we are able to introduce proton exchange sites and thus conductivity of the membrane [2,3].

In view of the desire to operate PEFCs at reduced relative humidity (RH) to simplify fuel cell systems design, the proton conductivity of various radiation grafted membranes as a function of relative humidity at a temperature of 80°C was investigated. The crosslinked styrene based membranes showed conductivities comparable to those of Nafion 212 at high RH, but slightly higher loss in conductivity towards low RH. In addition, we investigated the effect of the MAN content in uncrosslinked styrene / MAN cografted membranes with fixed ion exchange capacity of 1.5 mmol/g. At RH above 90%, membranes with different MAN content displayed similar conductivities of around 0.15 S/cm. However, at decreasing RH, the membranes with increasing MAN content showed a more pronounced loss in conductivity. This phenomenon is not understood so far. On the other hand, the incorporation of MAN improves the chemical stability of the membranes in the fuel cell.

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Polymer and Colloids **PO 47**

Polymers from Artificial Phospholipids

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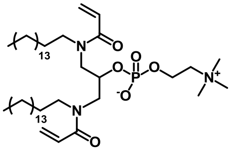
Phospholipids are the main constituents of our biomembranes. They help protecting the cell and its information against a hostile environment. It was only logical that phospholipids were used to produce Nature-mimicking vesicles for the encapsulation of drugs or cosmetics. To assure an increased stability of these vesicles, polymerization of the self-assembled phospholipids was investigated. However, thus far the structure of the involved phospholipids was mostly composed fatty acids or fatty ethers linked to a glycerol-type polar head group. This allowed the introduction of polymerizable functions in the head group or the tail regions but never in the biophysically more forgiving interface region between the two. By replacing the ester or the ether moieties by an amine, we now have the possibility to attach a polymerizable group to the phospholipid backbone.



The synthesis of the amine-bearing phospholipid (see figure) was achieved using BODP, a phosphorous (III) reagent we have rediscovered recently [1]. 100 nm-diameter vesicles formulated from these phospholipids were polymerized by UV irradiation. Instead of forming individual polymeric nanocontainers, the vesicles aggregated into a large agglomerate of hundreds of polymeric vesicles. Here we give further insights into the architectures of these 350 µm-diameter-particles and discuss possible uses for this fresh type of polymer.

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Polymer and Colloids **PO 48**

Modification of protein with comb-shaped polymers

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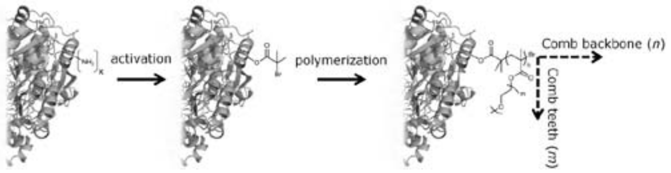
For over 30 years, the grafting of poly (ethylene glycol) to therapeutic proteins, a process referred to as PEGylation, has been exploited to prevent their renal clearance, their recognition by the immune system, or proteolytic digestion. However, polymers cannot and should not be considered as inert entities within protein–polymer conjugates, as they can strongly positively or negatively influence bioactivity [1].

In this contribution, we explore the possibility of tuning conjugate bioactivity by adjusting polymer architecture. Numerous protein–polymer conjugates were prepared within a tridimensional parameter space describing conjugate structure (*vide infra*). The bioactivity of these conjugates was evaluated using several complementary tests in order to probe the properties of the grafted polymer coatings.



[1] MA Gauthier and H-A Klok, *Polym. Chem.*, **2010**, *30*, 1341–1520.

Polymer and Colloids **PO 49**

Solubility and aggregation behavior of dendronized poly(*p*-benzamide)s[1]

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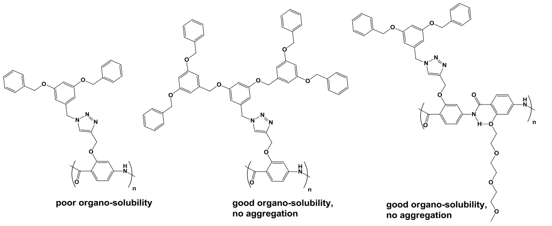
There has been a great interest in molecular rods that can be assembled in precise constitution from individual building blocks. Aromatic amides such as poly(*p*-benzamide)s have a great potential to built shape persistent molecular rods due to their rigid backbone. The main challenge to work with these materials is to improve their solubility and prevent aggregation.

Here, we present a new and highly modular synthetic approach to sterically demanding *p*-aminosalicylic acid monomers using Fréchet dendrons as side groups. Polymerization of these bulky monomers yielded to increase solubility and to prevent aggregation via π-interactions. The aggregation behavior was investigated by dynamic light scattering.



These investigations are an important step toward the synthesis of non-aggregating sequence controlled molecular rods. The modular approach to functional aromatic amino acid monomers will be most useful for the rapid evaluation of monomer libraries carrying substituents of different functionality. Polymerization of these precursors will yield segmented polymers consisting of linear arrays of sequence controlled monomer units.

[1] C.Storz, M. Schulze, A.F.M. Kilbinger, *Macromol. Rapid. Commun.* **2011**, 32, 238.

Polymer and Colloids **PO 50**

Tuning Microphase Separation in Diblock Copolymers via Post-Polymerization Volume Fraction Modification

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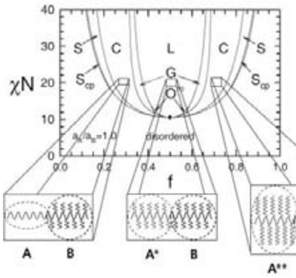
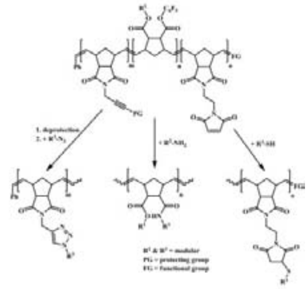
Our research aims at the development of a robust synthetic technique that will allow a post-polymerization volume fraction modification of highly functionalized living ROMP block copolymers. Due to the immiscibility and the covalent linkage of the respective blocks (figure on the right), these polymers microphase segregate into nanostructures that have been well investigated and theoretically described, what renders this method an extremely versatile bottom-up approach to high aspect ratio patterning on the nanometer scale. Our approach enables us to shift the position of e.g. a diblock copolymer within the phase diagram, as depicted in the figure on the left, via increasing the volume fraction of block **A** after the polymerization.





The gyroid represents a bicontinuous phase, in which both polymer blocks interpenetrate each other, enabling the accessibility of each block from either side of a thin film. This significant advantage, is envisaged to be a powerful tool e.g. for charge separation and transport in optoelectronic applications (photovoltaic devices, OLEDs, etc.).

Polymer and Colloids **PO 51**

Population Balance Breakage Kernel through Stokesian Dynamics Simulations

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Population balance equations (PBE), implementing aggregation and breakage kinetics, are commonly used to investigate and predict the evolution of aggregate formation under different conditions. However, PBE require lumped parameters, called kernels for both aggregation and breakage processes, to include all the physical information about the process. In the literature, the aggregation kernels are well established, whereas the breakage kernels hold a great degree of uncertainty as the aggregate breakup process is relatively more complex to study.

We have formulated a model to study the breakup of colloidal aggregates made of identical spherical particles in shear flow under laminar flow conditions, using Stokesian dynamics [1] to estimate the hydrodynamic interactions among the particles, DLVO theory to describe the normal inter-particle interactions, and discrete element method to account for the tangential contact interactions [2]. Simulations were performed to study different characteristics of the breakage process of fractal aggregates, composed of a number of uniform sized spheres and characterized by fractal dimensions, at different flow magnitudes in simple shear flow. The developed model was first used to investigate the dependence of the breakage rate on the cluster geometry and flow conditions. In addition, the dependence of the fragment mass distribution at the instance of first breakage on the cluster mass and morphology has been studied. The study was used to develop a breakage kernel which can be directly used in PBE.

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Polymer and Colloids **PO 52**

Novel porous materials via magnetic assisted self-assembly

Furlan Marco and Lattuada Marco

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There is a growing interest in the production of porous materials via the self-assembly of nano- and microparticles. Applications for such materials can be found in chromatography, membrane separation, catalyst support, bio-inspired materials, and scaffolds for tissue engineering. These materials, which can be prepared from colloidal suspension of polymers or ceramics, have usually a random porous structure. The preparation of these materials with better organized pores is of paramount interest for many applications. In this work we introduce a new technique for the preparation of porous materials with anisotropic structure. This new method takes advantage of the alignment in the presence of a magnetic field of non-magnetic colloidal nanoparticles, either polymeric or ceramic (e.g. silica, alumina), dispersed in an aqueous highly stable ferrofluid. Once the magnetic field is applied, the non-magnetic nanoparticles act as magnetic holes, i.e., they acquire a magnetic moment in the opposite direction to that of the external field. These moments generate dipolar interactions capable of aligning non-magnetic particles in the direction of the applied field. The obtained structures can be frozen by adding a water-soluble monomer, a crosslinker and an initiator to the aqueous solution, so that once the structure is formed a free radical polymerization process can be utilized to produces a hydrogel that locks it. Once the obtained anisotropic structure is blocked inside the hydrogel, the ferrofluid can be removed by immersing the hydrogel in a concentrated hydrochloric acid solution. The anisotropic structure can then be hardened by depositing via a sol gel process either the same material of the nanoparticles or a different one, by simply immersing the monolith in a solution of the sol-gel precursor. After removing of the hydrogel by thermal treatment a hard porous monolith can be obtained. The resulting materials have a complex and organized structure, which was studied and characterized using SEM microscopy and mercury porosimetry.