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Polymers & Colloids, Lecture **562**

On the Ripening of Emulsions, Vesicles and Nanoparticles

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Ostwald ripening is a common coarsening mechanism for phases fragmented to small submicron dimensions. Driven by interfacial energy, larger particles grow at the expense of smaller ones, that dissolve. For emulsions, this coarsening mechanism is well established. In emulsion systems with saturated surfactant films, the effective interfacial tension can be identified from Helfrich's curvature energy. The tension here is relatively small, allowing for accurate measurements of the ripening rate using time resolved small angle neutron scattering with proper contrast.[1] In vesicle systems, the situation is less clear. Vesicle dispersions are often very stable, and claims of thermodynamic stability have been made, based on the observation that the size distribution does not evolve with time. However, this can be understood from the fact that within the harmonic approximation, the vesicle curvature energy is independent of the vesicle size and, consequently, offer no driving force for ripening. Interestingly, when including higher order terms, curvature energy is expected to lead to an anti-coarsening where small vesicles grow at the expense of larger ones.[2] Thus, allowing for a narrowing of an initially broad size distribution into a more narrow steady state width determined by fluctuations. Amorphous solid nanoparticles are related to emulsions and are prone to undergo Ostwald ripening. Crystalline nanoparticles, on the other hand, are not. The difference, which is related to the actual mechanism by which the particles grow and dissolve, will be discussed in the light of recent experimental data.

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Polymers & Colloids, Poster Talk **563**

New Structures from Artificial Phospholipids

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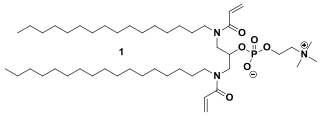
Our group has recently presented two approaches for the formation of 3D structures from artificial phospholipids: one involving polymerizable phospholipids and the other involving the Cu(I)-Huisgen-Sharpless click reaction.

Polymerization of phospholipids has been achieved with reactive groups at the end of the acyl chains, near the backbone and at the head group of phospholipids. So far no polymerization occurred from the backbone itself: with PanAc-PC-PanAc (**1**), acryl amide groups were introduced thank to the secondary amines in the chains [1].



In a second project, the 1,3 dipolar cycloaddition reaction was explored in order to link together several liposomes. Complementary phospholipids were introduced: one vesicle containing phospholipids with an azido moiety and the other vesicle containing an alkyno moiety. Both phospholipids were incorporated in a 10 % ratio in eggPC liposomes to create giant unilamellar vesicles [2].

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Polymers & Colloids, Poster Talk **564**

Reversible Selective Binding and Release of Small Molecules from Thin Polymer Coatings

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Our research aims to design thin coatings with reversible specific affinity to trigger molecules. This approach is inspired by natural systems that change their structure and function in response to trigger molecules in their environment. An inspiring example is nitrogen monoxide that serves as a messenger molecule in the human body by selectively inducing various reactions, which lead to a change in the structure, function and/or catalytic activity of proteins.
Selectivity and reversibility of the coatings is realized by using supramolecular crosslinking of functionalized polymers. The use of non-covalent interactions allows the fast and reversible change in polymer structure in response to the selective binding of small (gas) molecules (Figure 1).

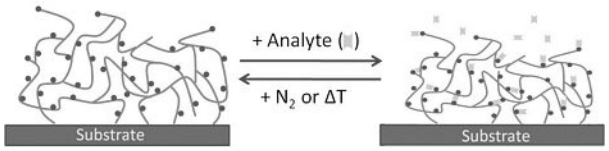

Figure 1: Reversible selective binding and release of small molecules.

The reversible binding/detaching of the gas molecules as well as conformational density changes in the polymer network are analyzed using methods like FT-IR, AFM, UV-Vis spectroscopy and the TInAS adsorption sensor.[1] One possible application of these selective polymers is thin coatings for both sensing and delivering functional substances.

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Polymers & Colloids, Poster Talk **565**

Novel hyaluronic acid-antioxidant conjugates for osteoarthritis therapy

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One of the actual therapies for osteoarthritis is the intra-articular injection of very high molecular weight hyaluronic acid (HA), but because of its limited retention time, a high number of injections are needed [1]. In order to reduce the frequency of injections, we follow a strategy to protect the HA from the occurring oxidative stress on HA by covalent grafting of antioxidant moieties.

For this, an improved HA-antioxidant coupling method in water has been developed based on [2, 3]. Five hyaluronic acid conjugates were prepared and characterized by ^{1}H-NMR. The amount of conjugated antioxidants was quantified by UV-spectroscopy, the antioxidant activity of the novel products evaluated by a DPPH test, the viscosity by rotational rheology and the mass weight by size-exclusion chromatography coupled with a multi angle light scattering detector. The different conjugates showed a wide range from 0.1-71% (mol. COOH) of grafting. Antioxidant activities increased between 10-60%, while a loss of polymer viscosity between 10-95% and mass weight loss of 0-70% compared to the non-conjugated HA were observed. The effect of the antioxidant molecular structure on the grafting efficiency and the effect of the grafting percentage on the viscosity will be presented. Mass weight maintenance of the grafted polymers in an oxidant environment (In Vitro and Ex Vivo) will also be shown.

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Polymers & Colloids, Poster Talk **566**

Polyacrylamide hydrogels with gradients in mechanical stiffness for differential cell response

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Hydrogels are crosslinked polymer materials able to absorb large amounts of water. Their resemblance to the extracellular matrix makes them interesting materials in the area of tissue engineering, where they have gained significant importance over the past decade. It is of particular interest to understand how tissue cells interact with their surroundings. Multiple studies have shown that cells are able to feel the physical properties such as mechanical stiffness and roughness of the culture substrate [1].

With this motivation, we aimed at the development of a single-step method to produce polyacrylamide hydrogels with a spatial gradient in mechanical properties. The proposed method is based on the controlled feeding of the hydrogel precursor solution, thereby changing the total monomer concentration over the feeding time. With programmable syringe pumps, we modified the total monomer content of the precursor solution from 16 wt% down to 4 wt%, which resulted in a gradient in compliance ranging from 200 kPa down to 20 kPa. Tuning the feeding profile, we achieved to produce gradient of different lengths, ranging from ca. 1 cm down to 2.5 mm.

Upon treatment with collagen I, the substrates were rendered biocompatible and allowed around 30% of seeded human foreskin fibroblasts to attach to the hydrogel surface within 1 hour. Fibroblast spreading proved to be position dependent on substrates with a spatial gradient in mechanical properties after 2 to 4 hours: at the stiff end, the cells were already well spread, while they still had a rounded morphology and a low area on the soft end.

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Polymers & Colloids, Poster Talk **567**

Towards 2D Polymers with Anthracene-Bearing Monomers

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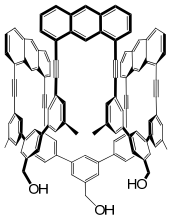
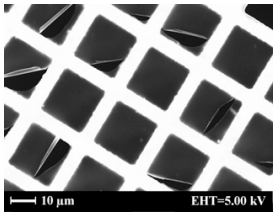
Two-dimensional (2D) polymers are free-standing monolayers with long-range internal order formed by covalent binding of monomers [1]. In this study, the air/water interface is used as a substrate for inducing lateral order among the monomers. The anthracene-bearing macrocycle **M3** is an amphiphilic monomer [2] which is used for polymerization.



M3 Macrocycle



SEM image of the spanned film

Upon formation of a macroscopically homogenous film on the Langmuir trough, anthracene photodimerization was used to covalently connect the adjacent monomers at the interface. *In-situ* fluorescence spectroscopy indicates the consumption of the anthracenes upon photoirradiation near the expected maximum. Scanning electron microscopy (SEM) images of the spanned polymer show its free-standing nature.

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Polymers & Colloids, Poster Talk **568**

Development of a light responsive membrane for controlled transdermal drug release

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Neonatal caffeine therapy for new-borns suffering apnea is known to have a beneficial impact on the rate of survival without disability of preterm infants.[1] Therefore, a responsive membrane adapting its caffeine mass transfer rate triggered by en external stimulus could be a key unit of a transdermal caffeine delivery system.[2]

The goal of this project is the development of a highly flexible and light responsive membrane which is able to change its mass transfer rate of an aqueous caffeine solution. Spirobenzopyran (**SP1)** is known to undergo reversible photo-induced heterolytic ring opening accompanied by an increase of polarity under UV-irradiation. To benefit from that polarity change, a porous PC membrane was coated with **SP1** and HEMA via a plasma induced surface graft-polymerization process. Contact angle measurements showed a contact angle (CA) of 105 ° at daylight and a lowered CA of 90 ° under UV irradiation. The resistance of the coated membrane towards caffeine solution was found to be 91'000 s/cm at day light whereas a resistance of only 12'000 s/cm was measured for the same membrane under UV light.

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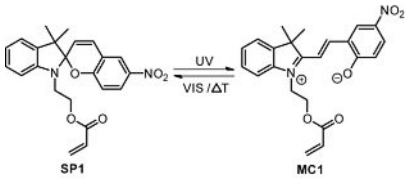

Polymers & Colloids, Poster Talk **569**

Towards new polymeric materials based on poly(*m,p*-phenylene) by Suzuki polycondensation

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Polyarylenes are known to have a broad variety of useful properties for technical applications.[1] Polyarylenes are however poorly soluble in general and therefore need to be modified with long flexible side chains for solubility during synthesis and processing. The main drawback of this modification is the dilution and deterioration of the desirable properties intrinsic to the polymer backbone.[2] It would therefore be of great interest to remove these side-chains after processing of the material. In the present study, two different polyphenylenes (**3a** and **3b**) with removable side-chains were synthesized by Suzuki Polycondensation (SPC) (Figure 1). A parent polyphenylene was then prepared from the precursor polymers by "shaving" the side chains either thermally or chemically.[3]

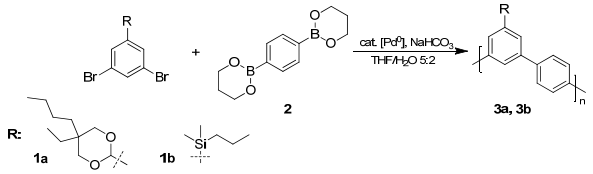

Figure 1. SPC synthesis of soluble precursor polymers with removable side-chains.

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Polymers & Colloids, Talk **570**

Stability of colloidal suspensions in the presence of multivalent ions

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Multivalent ions strongly modify interactions between charged interfaces; therefore, such ions represent important additives to control aggregation or deposition of colloidal particles. In the present study, surface potentials and colloidal stability of charged polystyrene latex particles modified with amidine or carboxylic groups on their surfaces were investigated in the presence of oppositely charged polyacrylates and polyamines by electrophoretic mobility and dynamic light scattering.

Multivalent oligomers of low valency destabilize the particles by screening the charge of the particle surface similarly to the effect of simple salt. The slow and the fast aggregation regimes are separated by the critical coagulation concentration (CCC). Oligomers with higher valency induce a charge reversal of the particles. Close to the charge reversal point, the aggregation is rapid while the suspension becomes stable away from this point. At high oligomer concentrations, the aggregation becomes rapid again due to screening induced by the increased concentration of counter ions of the oligomers. With increasing valency of the oligomers, the CCC corresponding to the first fast aggregation regime shifts towards lower concentrations according to the Schulze-Hardy rule. Since these oppositely charged systems (amidine latex – polyacrylate and carboxylic latex – polyamine) behave entirely analogously, we suspect that the observed trends are generic.

The stability data of any valency can be well described by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) indicating that the interactions are governed by attractive van der Waals and repulsive electrostatic double layer forces. This fact has two main implications. First, additional non-DLVO forces are mostly unimportant. Second, DLVO theory can be used to make reliable predictions of suspension stability in systems containing multivalent ions.

Polymers & Colloids, Talk **571**

Synthesis of helical, substituted polybenzamides

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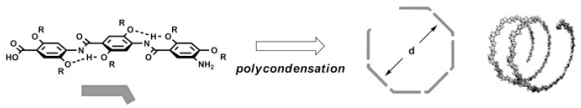
We present the synthesis of substituted aromatic amino acids and their subsequent oligomers as rigid precursors for the preparation of helical polybenzamides. Due to their chain stiffness, shape persistence and intramolecular hydrogen bonding patterns substituted aromatic oligoamides are highly interesting tools for the construction of nanoscopic objects.[1] Our group has already established an automated solid supported synthesis allowing for sequence control[2] and facile preparation of a vast number of differently substituted oligomers. Additionally, organo-soluble poly(*p*-benzamide)s have been investigated.[3]
In this project, disubstituted monomers based on 4-amino-2,5-dihydroxybenzoic acid and 5-amino-2,4-dihydroxybenzoic acid have been synthesized. Combining the ability of intramolecular hydrogen bond formation with sequence control leads us to angled, rigid oligomers which will later on ensure the development of helical polymers during polycondensation. Altering the number of linear and bent monomers within the oligomeric precursor enables us to tune the diameter of the helix.



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Polymers & Colloids, Talk **572**

Synthesis and controlled immobilization of amphiphilic block copolymers on solid supports

S. Toughraï[1], J-L. Perin[1], C.K. Pandiyarajan[2], N. Bruns[1], W. Meier[1]

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The functionalization of surfaces using biomimetic block copolymer membranes aims at developing smart surfaces for biotechnological applications such as biosensing. Instead of lipid membranes, amphiphilic block copolymer membranes were chosen as mimics of biological membranes due to properties such as tunable thickness, chemical and mechanical stability, lower permeability, fluidity, mobility, etc. Upon insertion of membrane proteins, these systems could allow for the preparation of mechanically and chemically robust and air-stable biosensor devices. 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 hydrophilic part of the brushes renders the surface smoother and more hydrophilic, whereas the hydrophobic part results in a rougher, more hydrophobic surface. The thickness was measured layer by layer by surface plasmon resonance (SPR), with an overall thickness of 39 nm. 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.

Polymers & Colloids, Talk **573**

Preparation and Characterization of Functional Silica Coated Superparamagnetic Iron Oxide Nanoparticles (SPIONs)

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The present study highlights a novel approach towards the synthesis and characterization of functional silica coated superparamagnetic iron oxide nanoparticles (SPIONs). Chemical hydrolysis followed by condensation of the 3-aminopropyltriethoxysilane and tetraethyl orthosilicate (APTES/TEOS) mixture in the presence of SPIONs led to the production of magnetic silica nanoparticles containing primary amino groups on their surface. Many different samples were synthetized and the study focused upon the preparative aspect and characterization of the silica coated SPIONs in terms of their size, morphology, surface properties, and magnetic responses as determined using electron microscopy (TEM), dynamic light scattering (DLS), inductively coupled plasma optical emission spectrometry (ICP-AES), UV-Visible spectrophotometry (UV-VIS) and vibrating sample magnetometry (VSM). It was observed that depending on the mass ratio of the starting materials (either magnetic (SPIONS) or non-magnetic (TEOS and APTES)) the magnetic properties and surface charge of the obtained nanoparticles could be controlled between different sample batches. Due to the magnetic properties and the presence of the primary amino groups on their surface, these magnetic silica nanoparticles can be manipulated for grafting polymers, target peptides, dyes and others biomolecules in order to obtain stable and high quality of functionalized nanoparticles for biomedical and biochemical applications in therapy and diagnostics.

Polymers & Colloids, Talk **574**

Facile Synthesis of Silica Micro-rods

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The use of nano-building blocks as fillers to enhance the property of composites is a topic of great interest. The most used nano-blocks are spherical nanoparticles, which can be prepared using a variety of methods. Nevertheless, there is a growing interest in the use of anisotropic building blocks, such as nanotubes, platelets, rods, ellipsoids, etc. In this work we propose a new and reliable method for the production of large quantities of magnetic silica micro-rods. This method is based on the spinodal decomposition of a silica precursor leading to a bicontinuous phase, the structure of which is controlled by the incorporation of polymer-magnetite nano-spheres with the aid of an external magnetic field. Our system is based on the silica precursor TMOS and the polymer PEG, which undergoes a phase separation following a spinodal decomposition due to the chemical cooling induced by the condensation polymerization of the silica precursor. Polymer-magnetite nanoparticles are incorporated in the silica rich phase due to the strong affinity of the magnetite to the silica precursor. The accumulation of the nanocolloids in the silica rich phase during the spinodal decomposition leads to the formation of long rod-like structures in the presence of an external magnetic field, which form a monolith. At the end of the reaction, the application of strong ultrasonication leads to the disintegration of the monolith and to the recovery of the rods. Different parameter such as rods diameter and length can be tuned by varying reactant concentration, the applied magnetic field and the sonication time. The applied magnetic field has an enormous influence on the length of the produced rods and depending on the kind of field applied, homogeneous or alternating, the length can be varied by more than two orders of magnitude.

Polymers & Colloids, Lecture **575**

Responsive polymersomes and nanocapsules as robust and tunable carrier systems

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UV-crosslinkable polymersomes based on the self-assembly of amphiphilic block copolymers have been developed incorporating the reversible pH sensitive polydiethylaminoethyl-methacrylate (PDEAM) and photocrosslinkable poly-dimethyl-maleic imidobutyl methacrylate (PDMIBM) as hydrophobic components.[1] While pH sensitive polymersomes usually disassemble upon acidification, ours show a definite and reversible swelling, since the cross-linked membrane remains intact. It will be shown that these vesicles provide a very good basis for a synthetic bionanoreactor. [2] Furthermore, we used surface-initiated RAFT polymerization to synthesize narrowly distributed hollow nanocapsules (PtBMA-*co*-PDMIPM-*b*-PHPMA) employing silica nanoparticles as sacrificial templates and 2,3-dimethyl maleic imidopropyl methacrylate as a photo cross-linker. [3] In addition, a method was developed to bi-functionalize mesoporous silica nanoparticles (MSN) by combining ATRP and RAFT polymerization techniques which allows to anchor two hetero-polymers onto the surface of MSN. Thus, the pH sensitive polymer polyDEAEMA has been grafted which can act as gatekeeper to control the loading and release of guest molecules by changing pH value, whereas the hydrophilic poly-HPMA was used to enhance the hydrophilicity and biocompatibility of MSN.

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Polymers & Colloids, Talk **576**

Measuring single nanoparticle wetting properties

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Nanoparticles (NPs) at fluid interfaces are central to a rapidly increasing range of nanotechnological applications, including drug delivery [1], functionalized NPs for uptake through biological membranes [2], emulsion stabilization [3] and the fabrication of nano-composite materials [4]. Despite large body of work devoted to micro- and nanoparticle adsorption and self-assembly at fluid interfaces [5], understanding wetting at the single-nanoparticle level is an unresolved issue and is essential in designing NP-building blocks with controlled surface properties. We present here an approach based on freeze-fracture and cryo-scanning electron microscopy, which greatly surpasses the current state-of-the-art, and pushes the boundaries of true single-nanoparticle contact angle measurements to the 10-nm range, relevant for applications [6]. We demonstrate measurements on hydrophilic and hydrophobic, organic and inorganic NPs. This approach poses no constraints on the choice of liquid phases and thus is generally applicable to many systems of fundamental and applied interest.

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Polymers & Colloids, Talk **577**

***In vivo* imaging of oral enzyme activity in the gastrointestinal tract – application to celiac disease**

Gregor Fuhrmann and Jean-Christophe Leroux

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Therapeutic enzymes are administered orally to treat several diseases, such as pancreatic insufficiency and lactose intolerance. Oral application of proline-specific endopeptidases (PEPs) is one of the potential adjuvant therapeutic approaches for celiac disease (CD), a highly prevalent (1%) immunogenetic enteropathy induced by wheat proteins (*i.e.,* gluten) [1]. PEPs can efficiently cleave gluten peptides minimizing toxicity for CD patients. However, PEP's oral activity may be impaired due to pH changes and digestive enzymes along the gastrointestinal (GI) tract. In this work a convenient and non-invasive assay to monitor the activity of PEPs in real time *in vivo* in the GI tract was developed [2]. Subsequently, PEP-polyethylene glycol (PEP-PEG) conjugates were prepared and their stability monitored *in vitro.* The PEP-specific peptide sequence LPYPQP was labeled with a fluorescent dye and corresponding quencher. Peptide and enzymes were orally administered to rats and upon cleavage fluorescence emission was detected and analyzed using an *in vivo* imaging system. This study incorporated PEPs from *Flavobacterium meningosepticum* (FM) and *Myxococcus xanthus* (MX). *In vivo*, FM PEP showed significant gastric activity compared to MX PEP. Coadministration of an antacid drug (*i.e.,* magaldrate) significantly ameliorated gastric activity of MX PEP due to increased pH and/or inhibition of stomach proteases. In the small intestine, comparable fluorescence signals were observed for both PEPs. PEGylation of the enzymes significantly improved the PEPs' activity under simulated GI conditions.
This work was financially supported by the SNSF (310030_135732).

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Polymers & Colloids, Talk **578**

PHEMA polymer brushes functionalized with RGD peptide at different depths to evaluate cell adhesion

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This presentation reports the preparation of polymer brush coated substrates in which RGD peptides are integrated at different depths to study cell adhesion. Two main characteristics of surface initiated atom transfer radical polymerization (SI-ATRP) were exploited. First, the catalytically controlled growth of the polymer chains was used to tune precisely the thicknesses of the polymer brushes for which the brush conformation was reached through a high grafting density of the initiator of the polymerization. Secondly, the "living" characterizer of the SI-ATRP allowed the functionalization of a first polymer brush layer with a peptide before the growth of a second layer. 2-Hydroxymethacrylate was chosen as a monomer for its well-known nonbiofouling abilities and the numerous available hydroxyl groups of its side chains giving great opportunities of post-modification. A peptide containing the RGD (arginine-glycine-aspartic acid) sequence was immobilized on the brushes to promote cell adhesion due to the specific binding of the integrin receptors of the cells. The influence of the depth of the RGD sequence in a nonbiofouling background was investigated by the culture of cells on the surfaces. Cell densities counts and immunofluorescence staining were performed on the cells. The results showed that there was a maximum depth at which the cells could not reach anymore the adhesion sequence. The studied platform is of great interest as the top layer is available for any kind of postmodification such as the introduction of another peptide containing a cell recognized sequence or the integration of drugs.

Polymers & Colloids, Talk **579**

Twofold Light and Magnetic Responsive Behavior in Nanoparticle-Lyotropic Liquid Crystal Systems

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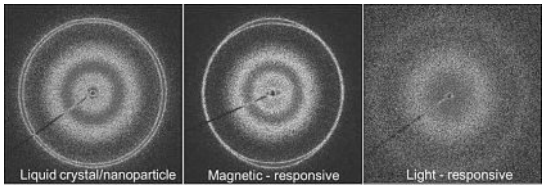
We demonstrate the dual magnetic and light responsive nature of hybrid mesophases constituted by Fe_3O_4 nanoparticles dispersed in lipid-based lyotropic liquid crystals (LC). When subjected to an external magnetic field in the mesophase isotropic state, the nanoparticles aggregate and orient along the magnetic field direction, and upon cooling the system through the disorder-order transition, the aggregates drive the orientation of the mesophase via heterogeneous nucleation[1]; furthermore order-disorder transitions in the lipidic mesophase can be triggered by Fe_3O_4–induced photothermal effect under visible light exposure[2]. Both the orientational order and the photothermal effect of the hybrid mesophase can be tuned by the nanoparticle content, offering a general route for controlled assembly of complex fluids with combined magnetic and light responsiveness.



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Polymers & Colloids, Talk **580**

Upconversion in Polymeric Solids

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The present work introduces new polymeric materials that enable low-power light upconversion by triplet-triplet annihilation (TTA-UC) using a combination of inorganic complexes (Pd porphyrin) as sensitizers and diphenylanthracene derivatives as emitters. This phenomenon has recently been transposed into rubbery polymers. Realizing the importance of dye concentration, polymer properties and morphology, a series of upconverting polymer films and nanoparticles were made, employing both glassy and rubbery matrix materials. We probed whether tethering multiple diphenylanthracene moieties, either in small molecules or as pendant groups in macromolecules, would affect their propensity for triplet-triplet annihilation. Homopolymers and copolymers bearing diphenylanthracene side chains were made by controlled polymerization methods, i.e. reversible addition-fragmentation chain transfer polymerization and ring-opening metathesis polymerization. This general design strategy was found to mainly circumvent the problems associated with phase-separation of the dyes and the polymer matrix in the solid. Diphenylanthracene dimers were synthesized and incorporated in various matrices. The upconversion of the different components synthesized were investigated in the presence of Pd octaethylporphyrin in both solution and solid-state. Our investigation of structurally varied materials based on the same chromophore system is beginning to shine light on the parameters that govern energy transfers between the chromophores (e.g. dye content, confinement, glass transition temperature, etc.), and therefore the overall efficiency of the upconversion process.

Polymers & Colloids **581**

Organisation of colloidal nanoparticles for use as metamaterials

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The field of metamaterials has exploded in the decade since the term was first introduced. Meaning literally 'beyond materials', it is used to describe materials whose properties, unlike conventional ones, are derived largely from their sub-wavelength structure rather than their composition. These properties, such as negative refractive indices, cloaking, and perfect lensing, which do not exist in nature, can now be regularly observed in the microwave and infrared regions of the electromagnetic spectrum. However, one of the major challenges facing the community is the reduction in scale that is required to shift these special effects into the visible domain.

One solution is the organisation of colloidal metallic nanoparticles into specific structures such as planar layered arrays [1] and spherical core-shell nanoclusters [2] which allow the optical properties to be tailored to meet specific design requirements. A wide variety of applications can be envisaged for these structures which are fabricated using bottom-up self-assembly techniques including surface chemistry modification and the layer-by-layer assembly of polyelectrolytes. Cloaking properties have been predicted for the core-shell nanoclusters while the layered arrays have been investigated as SERS substrates. The flexibility and versatility of the fabrication process provides numerous advantages over more traditional top-down techniques, allowing the down-scaling that is required to be achieved and true bulk metmaterials in the optical regime to be prepared.

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Polymers & Colloids **582**

Functional dielectric elastomers put to work

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The search for better performing materials to be used in dielectric elastomer actuators (DEA) increased significantly in the last years mainly due to their high application potential. DEA are stretchable capacitors which change their shape with voltage. They are made of a thin elastomeric film coated on both sides with compliant, flexible, and stretchable electrodes. When charged, the opposite charges on the electrodes squeeze the elastomeric film which results in its elongation perpendicular to the applied electric field. Applications of DEA as actuators, generators and sensors are hindered by the high driving voltage still required for operation.

Several approaches are followed in order to reduce the driving voltage, such as increasing the permittivity and decreasing the modulus of elasticity of the elastomer or reducing the thickness of the dielectric film. Our approach is to develop more performing materials by increasing the permittivity. This is achieved by attaching polar groups to the silicone polymer chain and by blending it with conductive particles (polyaniline and silver nanoparticles) which are coated with an insulator shell prior blending.

This presentation will show the electromechanical properties of some new polar silicones and of silicone composites containing conductive fillers.

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Polymers & Colloids **583**

Silver Nanoparticles as Filler in Polydimethylsiloxane Composites

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Silver nanoparticles (AgNPs) have attracted considerable attention due to their catalytic, electronic and optical properties which differ from bulk. The "polyol" synthesis has emerged as a convenient way of preparing AgNPs and tuning their properties such as size and shape [1]. Because of their high polarizability, the dispersion of AgNPs into a polymeric matrix leads to an enhancement in the dielectric constant (ε) of the resulting material. This approach is of considerable attraction for preparing dielectric elastomer actuators.

In this work, AgNPs were prepared and their electronic properties used to increase the ε of polydimethylsiloxane (PDMS) by blending which normally is ε = 2.3. Prior to the dispersion into the polymeric matrix, the AgNPs require an initial silica coating via hydrolysis of tetraethoxysilane (TEOS) to prevent possible percolation leading to electric shortcuts. Furthermore, the silica surface has to be subjected to hydrophobic treatment in order to ensure a good dispersion of the AgNPs in PDMS. The surface can be hydrophobized by either grafting an alkyl chain or an initiator which can be used to initiate a surface polymerization such as ATRP [2]. Upon cross-linking of PDMS, it was possible to obtain elastomeric films which can be used for further investigation as prospective flexible electronics components.

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Polymers & Colloids **584**

Biopolymeric Shuttles for Targeted Delivery of Polyoxometalates

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Biopolymers, such as chitosan and its derivatives, are highly promising substances for drug delivery applications due to their biocompatibility und degradability. We used carboxymethyl-chitosan (CMC) to encapsulate a variety of polyoxometalates (POMs) and to safely shuttle them to their cellular destination. POMs are well known for their antiviral and antitumoral activities, but applications are still hindered by their adverse effects. However, cell viability tests show that POM toxicity is significantly decreased after their embedding in a biopolymeric matrix.[1] Furthermore, with a wide range of analytical methods we could show that the POMs are quantitatively encapsulated in the polymeric matrix while still keeping their original structure. The nanocapsules have an average size of around 120 nm and show a very homogenous morphology. The uptake of the nanocomposites and their localization in the cells was investigated by confocal laser scanning microscopy and the results were additionally confirmed by TEM imaging.[2] All in all, we could show that the incorporation of POMs into biopolymeric matrices is a first step to fully explore the biomedical features of these potential inorganic drugs, and fine-tuning approaches for chitosan-based matrices are now in progress.

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Polymers & Colloids **585**

Homotelechelic olefin metathesis polymers via copolymerization

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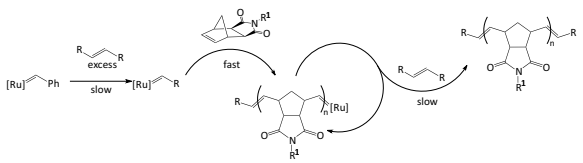
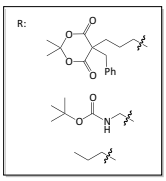
Today, well defined ruthenium catalysts are widely used and commercially available for the synthesis of olefin metathesis polymers. They offer high stability, high reactivity and a good control over molecular weight and molecular weight distribution especially for the living ring opening metathesis polymerization (ROMP). Functional group tolerance is one of the major advantages of ROMP compared with other polymerization techniques. However, focal or terminal functional group placement remains difficult due to the limited number of reactions that result in functional initiation or termination of the living polymer chains. Here we show that a better understanding of the reactivity, selectivity and kinetics of these catalytic systems immediately leads to new highly efficient methods for the prefunctionalization and functional termination of polymers.





Polymers & Colloids **586**

Orthogonal Functionalization of Multifunctional Ring-Opening Metathesis Polymers – A Combination of ROMP and CuAAC

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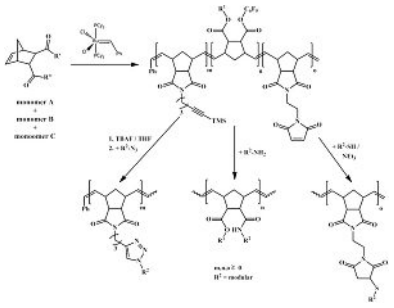
Our research aims at the development of a robust synthetic technique that will allow multiple orthogonal post-polymerization modifications of highly functionalized copolymers synthesized via living Ring-Opening Metathesis Polymerization (ROMP). For a variety of post-polymerization modifications, reactions fulfilling the 'Sharpless criteria' of a 'click-reaction' (activated esters, alkynes, maleimides etc.) are needed, to ensure a homogenous functionalization of each chain.



In particular the combination of ROMP and copper catalyzed azide-alkyne cycloaddition (CuAAC) has been a challenge so far. Organic azides are not tolerated by the ruthenium carbene initiators and non-protected alkynes react with its propagating species leading to broad molecular weight distributions. To overcome this limitation, several monomers bearing a sterically hindered terminal alkyne have been synthesized and, after the polymerization step, deprotected and functionalized.

Via copolymerization of these functional monomers with a water-soluble monomer, the conjugation of the resulting polymers with for example proteins or antibodies can be performed, giving access to a broad variety of biomedical applications.

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Polymers & Colloids **587**

Efficient Amine End Functionalization of Living Ring Opening Metathesis Polymers

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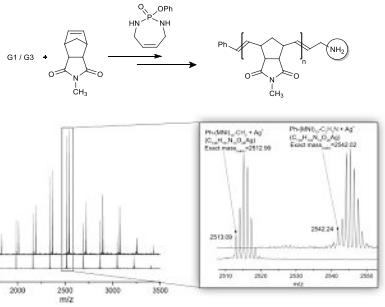
There are several methods for chain end-functionalization of living ring opening metathesis polymers, one of which is the 'Sacrificial Synthesis' strategy developed by our group. In this strategy, a sacrificial block is polymerized onto the main polymer and then cleaved to yield the desired functionality at the chain end of the polymer. Our group has successfully synthesized alcohol and thiol monotelechelic polymers by this method. Here, we present the synthesis of amino end-functionalized polymers. Amines are very useful nucleophiles that can readily be further functionalized. More complex polymeric architectures are thus readily accessible.



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Polymers & Colloids **588**

Twisting structure of amyloid fibrils emerges as a compromise between competing forces

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Under abnormal circumstances, normally soluble proteins may aggregate and form highly stable filamentous structures, known as *amyloid fibrils*. Such structures play a central role in neurodegenerative disorders such as Alzheimer's, Parkinson's and Huntington's diseases, to cite but a few examples [1]. Because of the heterogeneity in sequence of the several proteins able to undergo a disorder-leading fibrillation process, it has been proposed that such ability is a general property of polypeptides, and systematic in vitro experiments have shown that even disease-unrelated proteins form fibrils and probed their structure features. Some recent experiments focusing on β-lactoglobulin fibrils showed that they are made of several inter-twisting filaments organized in ribbon-like structures, thus showing a *pitch*, i.e. a period in length, which depends on the width of the ribbon and on the concentration of salt added in the solution [2, 3]. Here, we propose a simple model where the filaments are considered as chains made of springs and charged beads, whose interaction is implemented by means of the Poisson-Boltzmann equation. In spite of its simplicity, the model turns out not only to capture the physics of the system, but also to quantitatively describe the experimental data.

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Polymers & Colloids **589**

Polymorphic fibril formation of Aβ42: Observation of secondary nucleation

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The process of Amyloid-β (Aβ) fibril formation plays a central role in initiating the cascade of pathological events that ultimately lead to Alzheimer's disease (AD). However, the molecular mechanisms of Aβ fibrillzation and how this process contributes neurodegeneration in AD remain unknown. In this study, we investigated the detailed mechanism of Aβ fibril formation under controlled aggregation condition and starting with preparation of very defined hydrodynamic Aβ species [1]. Here we present a detailed mechanistic model that provides novel insight into the mechanism Aβ42 fibril formation and the molecular basis underlying different structural transitions in the amyloid pathway. Our results demonstrate that the oligomeric state of the starting materials, ratio of monomeric to aggregated forms of Aβ42 and occurrence of secondary nucleation events are key determinants of Aβ fibrils polymorphism. We demonstrate that monomeric Aβ42 plays an important role mediating structural transitions on the amyloid pathway and provide direct evidence demonstrating that Aβ42 fibrillization occurs by a combination of nucleated polymerization and secondary nucleation mechanisms.

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Polymers & Colloids **590**

Dewetting-Driven Hierarchical Self-Assembly of Small Semiconductive Molecules [1]

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Solution processing of organic molecules for optoelectronic applications requires the deposition of functional materials on predefined surface areas. To achieve this goal for the PCBM/cyanine dye materials combination, we use the process of liquid-liquid dewetting on microcontact-printed substrates. Characteristic to liquid-liquid dewetting are PCBM droplets floating on the lower cyanine liquid surface during spin coating and solvent evaporation. The lateral dimensions of these lenses in the final film can be controlled by the film thickness [2] giving this system a tunable length scale (λ). On the other hand, microcontact printing fixes an energetic periodicity (π) on the surface. We examine to what extent the local deposition of small organic semiconductors can be controlled by varying these length scales. We observe transitions from one wetting morphology regime to another, and the surface pattern can selectively be replicated when the system's characteristic decomposition wavelength (λ) matches with the pattern periodicity (π). Contact line pinning of the evaporating PCBM droplet onto the underlying substrate structure determines precisely where PCBM is deposited. Here, we combine self-assembly with micro-contact printing to organize small semiconducting molecules materials into a 1D or 2D photonic crystal lattice.

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Polymers & Colloids **591**

Misfolding and aggregation of human β2-microglobulin probed by chemical protein synthesis

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Human β2-microglobulin (β2m) deposits as amyloid fibrils within joints during long-term hemodialysis treatment. Despite the devastating effects of dialysis-related amyloidosis, a full understanding of how fibrils form from soluble β2m remains elusive. Previously, it was inferred that *cis*-to-*trans* amide bond isomerization of the *cis*-Pro32 residue triggers a transition of the native form of β2m into an aggregation-prone conformer. We used chemical synthesis to prepare a series of analogues of β2m in which Pro32 residue was systematically substituted with several analogues, including 4-(*R*)-fluoroproline (**fpr**), 4-(*S*)-fluoroproline (**Fpr**), α-methylproline (**Mpr**) and *D*-proline (**Dpr**), which have different propensities to adopt either a *cis* or *trans* conformation of the prolyl amide bond. We find that such substitutions indeed affect *cis*-to-*trans* populations of conformers when inserted into the β2-microglobulin polypeptide chain, and the resulting molecules exhibit different tendencies to aggregate with a gradually increasing trend **Pro** ≈ **fpr** < **Fpr** < **Mpr** < **Dpr**. Thus, our data confirm the hypothesis that amide bond isomerization of Pro32 plays a key role in this process. The effects of Pro32 substitutions on the early stages of protein aggregation by unnatural amino acids as well as structural features of the chemically synthesized proteins will be presented.

Polymers & Colloids **592**

Disulfide Reduction During the Trafficking of Cationic Polymers

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ETH Zürich, Department of Chemistry and Applied Biosciences, Institute of Pharmaceutical Sciences, Zürich, 8093, Switzerland

Disulfide bonds are increasingly being introduced into cationic gene-delivery systems to reduce toxicity by promoting bio-degradation [1] [2]. However, a detailed understanding of disulfide reduction during the cellular trafficking of such systems is missing. To this end, a redox-sensitive cationic probe was prepared by coupling boron-dipyrromethene dyes covalently to a poly(amido amine) dendrimer via labile disulfide bonds. In this system, the fluorescence of the dye molecules was self-quenched, while upon disulfide bond cleavage fluorescence is quantitatively restored. This probe was then used as a model cationic gene delivery system to analyze disulfide reduction in different cell lines (see Figure). The polyionic nature of gene delivery polymers was found to exert an interesting micro-environmental effect on the disulfide bonds, thereby significantly altering their properties. Our findings also highlight the important role of extracellular thiols in disulfide exchange, a result which sheds new light onto the role of disulfide reduction on transfection efficacy and on the mechanism of cytotoxicity of bio-reducible cationic polymers. This information can be used to rationally improve the uptake/toxicity profile of this important class of excipient.

Analysis of disulfide reduction during the cellular trafficking of model gene delivery systems.

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L. Brülisauer gratefully acknowledges a doctoral fellowship from the Scholarship Fund of the Swiss Chemical Industry (SSCI).

Polymers & Colloids **593**

Molecular Sieving Via "Smart" Protein PEGylation

Mi Liu, P Tirino, M Radivojevic, J C Leroux, Marc A Gauthier*
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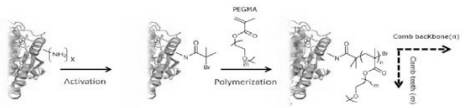
In this contribution, we explore the possibility of tuning the bioactivity of protein–polymer conjugates by adjusting polymer architecture and consequently polymer conformation [1]. In this study α-chymotrypsin was selected as model protein onto which PEG-based comb-polymers with different backbone and side-chains lengths were grown by controlled radical polymerization [2,3]. The enzymatic activity of the protease towards a variety of substrates with differing sizes was exploited to analyze the diffusion properties of the surface-grafted polymer coating. Over 100 unique protein–polymer conjugates were prepared within a three-dimensional parameter space to investigate the influence of polymer architecture and conformation on the bioactivity of α-chymotrypsin.



Polymer architecture and conformation were found to be important parameters in bioconjugate design. A change of polymer conformation from *star* to *rigid worm* to *flexible worm* greatly influenced the diffusion properties of the polymer layer. In the rigid worm regime, a 100% active (vs. native) conjugate was prepared and the latter was completely insensitive to the addition of glycoprotein inhibitors. This work is currently being transposed to the "smart" PEGylation of therapeutic enzymes. This work was partly supported by the China Scholarship Council (CSC).

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Polymers & Colloids **594**

Liquid-phase deposition of freestanding copper foils and supported copper thin films and their structuring into conducting line patterns

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As the feature size of electronic devices is constantly reduced, also their individual components need to be downscaled. Entering submicrometer dimensions it becomes important to control the evolving microstructure of the conducting copper-traces and copper-lines which nowadays seems to be difficult to achieve with the current deposition technologies. Therefore the development of new deposition processes is of tremendous importance for the fabrication of future microelectronic devices. Here we present a novel and profoundly simple electroless, non-aqueous deposition technique applicable to the preparation of freestanding submicron thin copper foils as well as to copper-supported thin films involving the reaction of copper (II) acetylacetonate with benzyl alcohol at 140°C in an oil bath[1].

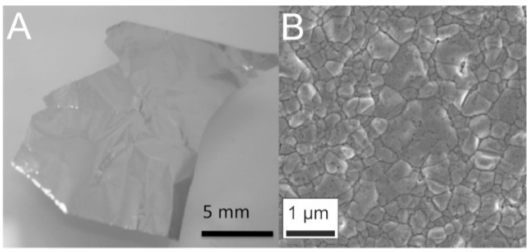

Figure 1. A: Picture of the freestanding copper foil. B: SEM micrograph of the copper foil surface.

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Polymers & Colloids **595**

Synthesis and assembly of ultrathin tungsten oxide nanowires

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Synthesis and assembly of ultrathin nanowires are highly important in nanoscience and nanotechnology [1-2]. In this work, a surfactant-assisted nonaqueous sol-gel method was developed for the synthesis of highly uniform, ultrathin tungsten oxide nanowires with diameters of about 1.7 nm and extremely high aspect ratio (Figure a). After a post functionalization step, the nanowires can be dispersed in chloroform, forming a completely colorless, transparent solution (Figure b). The uniformity, the high aspect ratio and the excellent colloidal stability of the nanowires makes them a good candidate for the study of alignments of nanowires and lyotropic inorganic liquid crystal behavior.

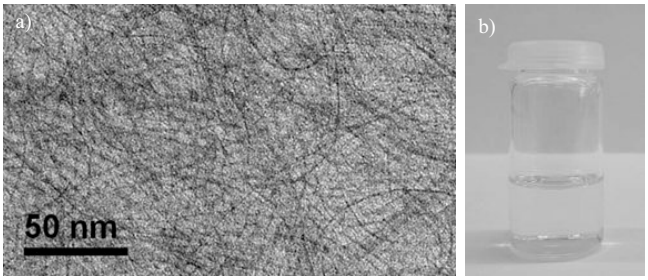

Figure: a) TEM image of the tungsten oxide nanowires; b) photograph of the tungsten oxide nanowires dispersed in chloroform.

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Polymers & Colloids **596**

Nanoparticle-based Multicomponent Aerogels

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Nanoparticle (NP) based aerogels offer a sophisticated route to low density and high surface area materials. Characteristic of such a modular approach is the outstanding control of composition, crystallinity, porosity and functionality, depending on the NP building blocks. In particular, applications in the area of photocatalysis[1] and luminescence[2] have been reported recently.

In this work titania NPs are used as building blocks for photocatalytically active aerogels. The titania structure serves as matrix for the incorporation of different other nanoparticles, offering possibilities for the improvement of the photocatalytic properties and possibilities for the implementation of further functionalities, e.g. magnetic properties. The figure shows a monolithic anatase-magnetite-gel.

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Polymers & Colloids **597**

Nanostructured Materials for Organic Photovoltaics

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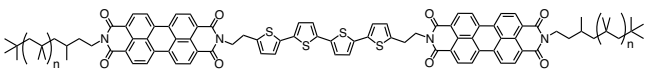
Charge separation in organic photovoltaics devices takes place at an interface between n- and p-type semiconductors.[1] To maximize that interface within the active film, bulk heterojunctions can be kinetically formed by mixing the two components in order to form an interpenetrating network.[2] However, bulk heterojunctions do not have an ideal morphology; moreover, they are metastable and may, therefore, change over time. The key to prepare thermodynamically stable ordered heterojunctions is to covalently link the n- and p-type semiconductors and achieve a sufficiently good internal order.[3] In this context, we prepared a triblock copolymer comprising a central perylene-quaterthiophene-perylene triad that serves as the optoelectronically active part, substituted with poly(isobutene) chains that brings order at the nanoscale via microphase segregation. We investigated its spectroscopic properties as well as phase morphology in thin films.



Triblock copolymer containing an n-p-n triad substituted with poly(isobutene).

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Polymers & Colloids **598**

Synthesis of Uniform Oligomethacrylates by Template Polymerization

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The preparation of synthetic polymers with exact control over chain length and monomer sequence is one of the long-standing challenges in polymer science. To date, no efficient, general synthetic strategies are available that allow access to uniform, sequence defined synthetic polymers. This study aims to synthesize uniform, sequence defined oligo- and polymethacrylates following the synthesis of the peptide template, template polymerization and replica release.

The peptide template for the synthesis of the proposed uniform methacrylates was prepared by acylation of oligoserine synthesized by Fmoc solid phase peptide synthesis. Free radical and controlled radical polymerization of the methacryloyl groups that are appended to the serine side chains results in a ladder oligomethacrylate with defined chain length by the peptide template. The synthetic replica is released from the peptide template by cleavage of the ester bonds that connect the template and replica. Transesterification is particularly attractive as they allow generating libraries of uniform methacrylates with different side-chain functionalities by variation of the alcohol that is used in the cleavage reaction.

Polymers & Colloids **599**

Controlled Radical Polymerization in Protein Nanoreactors

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By confining chemical reactions to a nanoscale volume it is possible to tune reactions and investigate them at the level of a single molecule, where catalytic and also mechanistic characteristics can be explored. Nanoreactors hold promise for applications ranging from selective and size-constrained organic synthesis to biomedical advances (e.g., artificial organelles, biosensing) and as analytical tools for the study of reaction mechanisms.[1] For our purposes, we used a protein cage from the Archaea *Thermoplasma acidiphilum* (THS). We encapsulated a catalyst for atom transfer radical polymerization (ATRP) inside this cage. By adding monomers to this system we retrieved polymeric products, making our nanoobject a nanoreactor.
Atom transfer radical polymerization (ATRP) demonstrably represents one of the most important synthetic techniques known to polymer science. Just as with other methods of controlled radical polymerization, it permits synthesis of polymers with a more defined distribution of molecular weight, with good control.[2] ATRP is a reaction mediated by a metal complex, with copper-based catalysts being used most often.
In a comparison with conventional ATRP, our THS system permits significant reduction in the copper concentration in polymers synthesized by this means. Furthermore, a THS nanoreactor allows for the synthesis of well-defined polymers in aqueous solution, because ATRP inside a protein cage enhances the degree of control of ATRP.

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Polymers & Colloids **600**

Shear Stress Sensitive Nanocontainers for Targeted Drug Delivery

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[3]University Hospitals of Geneva, Rue Gabrielle-Perret-Gentil 4, CH-1211

The lack of biomarkers in critically stenosed arteries demands the development of alternative methods for targeted drug delivery during heart attack. A delivery vector such as shear stress sensitive 100 nm diameter vesicles fulfils the criteria of releasing the drug at the site of constriction but not in the lower shear environment of the systemic vessels. The validity of such vesicle formulations can be assessed by applying predefined shear stresses using a rheometer.

100 nm unilamellar vesicles containing 50 mM 5(6)-carboxyfluorescein were prepared from 30 µmol of the artificial amide-bearing phospholipid Pad-PC-Pad[1] by the thin film method[2]. The resulting liposomes were diluted in HEPES buffer containing 4 g/L human serum albumin (HSA). A Bohlin CVO 120 Rheometer was used to assess release of a fluorescent dye induced by applying a predetermined shear stress of 0, 0.5, 1, 3 or 5 Pa 1 min to 3 mL aliquots of vesicle suspension at 37 °C. Release was analysed using a 96-well fluorescence plate reader.

Pad-PC-Pad vesicles were found to release an additional 3%, 6%, 13% and 16% of their payload at 0.5, 1, 3 and 5 Pa respectively. Shear stresses in the vascular system occur in the range of 0-1.5 Pa, whereas in constricted coronary arteries they have been reported to exceed 10 Pa. The release profile suggests that this formulation fulfils the criteria of specific release of contents under elevated shear stress, as found in constricted coronary arteries.

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Polymers & Colloids **601**

Simulation study on the structural and rheological properties of ferrofluids

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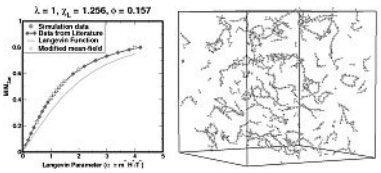
Ferrofluids are colloidal suspensions of magnetic nano-particles which find applications in various fields spanning from electronic devices to medicine [1]. We are studying the anisotropy of magnetoviscous effect (MVE) with a model system [2, 3] using Langevin dynamics simulations. We compare our results with experiments on cobalt-based ferrofluids [4]. To understand the



(a) Magnetisation curve (b) Ring formation in cobalt ferrofluids

Figure 1: (a) Magnetisation curve of the system with $\lambda = 1$, (b) Ring formation in cobalt nano particles in the absence of magnetic field.

origin of anisotropy of MVE, we are now focusing on the microstructure and viscosity of the fluid with the change in orientation of magnetic field.

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Polymers & Colloids **602**

Synthesis and Assembly of Janus-like Nanoparticles

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In recent years, the synthesis of Janus (i.e., double faced) nanoparticles attracted much scientific interest, as their very special structure confers them unique properties, which render them very promising for many applications. The work presented here focuses on two new strategies to prepare Janus nanoparticles in large amounts in an efficient and controlled manner. Both strategies are based on miniemulsion techniques, which permit to create dispersions of particles with medium to high concentrations. The first strategy for the preparation of organic/inorganic Janus nanoparticles relies on the simultaneous miniemulsification of an organic monomer and of a silica precursor. By controlling the composition of the mixture, the polymerization conditions and the condensation of silica precursor, particles with different morphologies can be created, including core-shell and asymmetric Janus particles. A second strategy is based on miniemulsifying blends of incompatible polymers dissolved in a common solvent, followed by solvent evaporation, leading to Janus particles with different morphologies, depending on the operating parameters and starting materials. The incorporation of iron oxide nanocrystals inside the particles to introduce magnetic properties to the composite particles, and in particular their confinement in one of the polymer phases, has been also investigated.

Polymers & Colloids **603**

Controlling the surface exchange on gold nanorods

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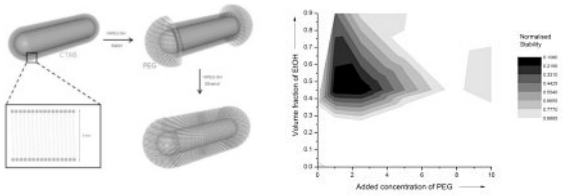
Adolphe Merkle Institute, University of Fribourg, Rue Ancienne Papeterie, Marly CH1723, Switzerland

Gold nanorods (GNRs) exhibit more complex surface chemistry than their spherical counterparts, resulting in the need for challenging surface functionalization procedures [1]. Often, the extent of functionalization is uncertain and the optimal parameters for surface coverage while maintaining colloidal stability are unknown [2], therefore a more rigorous approach was taken and the phase diagram of colloidal stability was generated.



We have shown that the simplified method to detoxify and stabilize GNRs with thiolated polyethylene glycol (PEG) is inadequate due to the properties of the stabilizing surfactant, cetyltrimethylammonium bromide (CTAB). The stability of the rods was mapped out over three variables: concentration of CTAB, PEG and ethanol. Through manipulation of the position in this phase diagram, we were able to ensure near-complete removal of CTAB via a two-step procedure, and investigate the stabilizing properties of the PEG on the surface of the gold nanorods.

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Polymers & Colloids **604**

Generation of Silver Nanoparticles in the Presence of Oligoproline Derivatives

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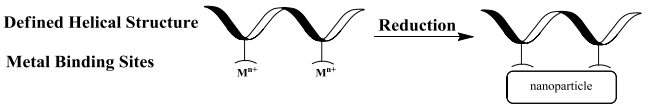
[1]ETH Zürich, Wolfgang-Pauli Strasse 10, CH-8093 Zürich, Switzerland

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 address this goal by utilizing functionalized oligoprolines that form a conformationally well-defined and rigid helical secondary structure (PPII) [2] as additives. Recently, we showed that by decorating this template with aldehydes which allow for *in situ* reduction of the silver ions, they act as scaffolds in the generation process and allow the formation of defined nanoparticles. [3]



We will report the results of the generation of nanoparticles with various oligoprolines as additives, which differ in the attached functional groups as well as in the length of the peptides 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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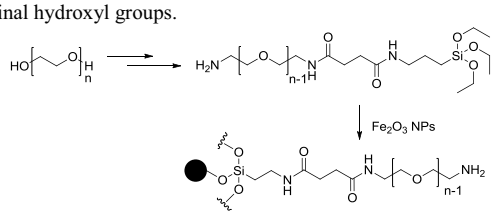
Polymers & Colloids **605**

Convenient synthesis of bifunctional amino-silyl-poly(ethylene glycol) for the coating of iron oxide nanoparticles

Solène Passemard,[1] Davide Staedler[1], Lucia Ucnova,[1] Lucienne Juillerat-Jeanneret[2] and Sandrine Gerber-Lemaire[1]
[1]EPFL, ISIC, Batochime, CH-1015 Lausanne, Switzerland
[2]University Institute of Pathology, CHUV, CH-1011 Lausanne, Switzerland

Poly(ethylene glycol) (PEG) oligomers are used extensively in biomedical applications due to their good solubility in water and many organic solvents, their lack of toxicity and their nonimmunogenicity.[1] The preparation of PEG-modified bio-materials, requires the preparation of PEG molecules displaying two reactive end functionalities, allowing conjugation to the biomaterials and further chemical derivatization.[2] Here we present a versatile route toward linear amino-silanized PEG through selective modification of the terminal hydroxyl groups.



The resulting activated PEG was applied to the functionalization of iron oxide nanoparticles designed for cancer diagnosis and imaging.[3]

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[2] Thompson, M.S; Valada, T.P.; Valada, M.L.; Lin, Y.; Riffle, J.S. Polymer **2008**, *49*, 345.
[3] We thank the European FP7 Research Project *NAMDIATREAM* (NMP4-LA-2010-246479, http://www.namdiatream.eu) and INTERREG IV France-Switzerland *NAOMI* for financial support.

Polymers & Colloids **606**

Vesicle-Assisted Enzymatic Synthesis of Conductive Polyaniline – Comparison of Two Different Heme Peroxidases

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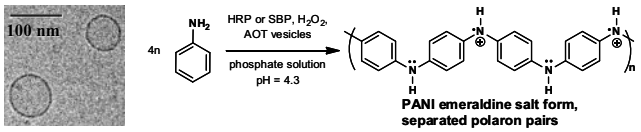
Polymer Chemistry, Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

Aniline can be polymerized to polyaniline (PANI) under mild conditions in aqueous solution at pH = 4.3 in presence of negatively charged vesicles and the enzyme horseradish peroxidase (HRP) and H_2O_2 as oxidant. The presence of the vesicles is crucial for the formation of the conductive emeraldine salt form of PANI.[1] The vesicles (i) increase the local concentration of the reacting aniline monomers, (ii) adsorb the positively charged HRP (pI = 9) (iii) promote mainly the *para*-addition of aniline and (iv) act as counterions. The use of vesicles formed from AOT (= bis-(2-ethylhexyl) sulfosuccinate) was found to be particularly promising to obtain in high yield a stable PANI-vesicle suspension.[2]

In order to understand the influence of the enzyme localization on the product formation, a comparison was made with soybean peroxidase (SBP) (pI = 3.9) under otherwise identical reaction conditions. Although both enzymes are very similar in structure and function, their different kinetic properties and localization significantly affected the aniline polymerization reaction in terms of yield and product properties.



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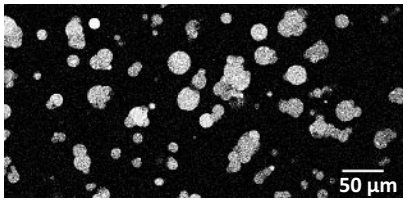
Polymers & Colloids **607**

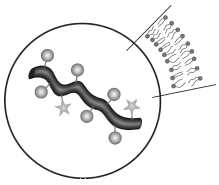
Encapsulation of a Dendronized Polymer-Enzyme Hybrid in Phospholipid Vesicles

Andrea Grotzky[1], Emiliano Altamura[2], Fabio Mavelli[2], Paolo Carrara[3], Pasquale Stano[3], A. Dieter Schlüter[1] and Peter Walde[1]

[1]Polymer Chemistry, Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland
[2]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, IT-70125 Bari, Italy
[3]Dipartimento di Biologia, Università degli Studi di Roma Tre, Viale Marconi 446, IT-00146 Roma, Italy

For efficient encapsulation of biomacromolecules inside phospholipid vesicles the method of vesicle formation is crucial.[1] Moreover, in the case of enzyme entrapment, the retention of the enzymatic activity is important for enzyme-catalyzed reactions inside vesicles. By covalently binding multiple copies of horseradish peroxidase[2] to a fluorescently-labeled dendronized polymer[3], high concentrations of the enzyme could be encapsulated inside phospholipid vesicles. It could be shown that the entrapped peroxidase remained catalytically active.





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Polymers & Colloids **608**

Towards 2D-Polymers: S-triazine-cored anthracene monomers for photo-polymerization reactions

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ETH Zurich, Polymer Chemistry, Department of Materials, Wolfgang-Pauli-Str. 10, 8093 Zurich

Recently, the first organic synthesis of a two-dimensional polymer was achieved by employing a specifically designed, C_3-symmetric monomer bearing photoreactive groups that can be converted into sheet-like polymers under UV-irradiation.[1]
This work has the aim of finding new possible monomers for the creation of two-dimensional polymers by using triazine-cored monomer structures. Monomers based on a triazine core have numerous advantages. In addition to the cheap and easy preparation of highly diverse structures, the triazine moiety is particularly suitable to generate desired supramolecular architectures required for solid-state polymerization reactions through its ability to experience supramolecular interactions.[2]

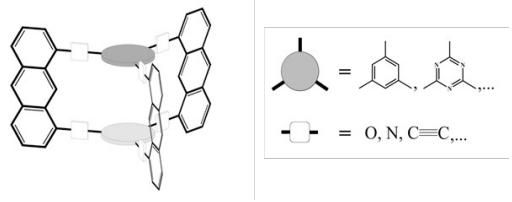


Figure 1. Monomer design

[1] P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Götzinger, A. D. Schlüter, J. Sakamoto, *Nat. Chem.* **2012**, *4*, 297-291.
[2] T. J. Mooibroek, P. Gamez, *Inorganica Chimica Acta* **2007**, *360,* 381–404.

Polymers & Colloids **609**

Towards two-dimensional polymers by photo-induced, topochemical polymerization

Andri P. Schütz, Patrick Kissel, Junji Sakamoto, A. Dieter Schlüter

[1]ETH Zurich, Polymer Chemistry, Department of Materials, Wolfgang-Pauli-Str. 10, 8093 Zürich

Lately, considerable interest was drawn to the naturally occurring two-dimensional polymer graphene. Its thermolytic or epitaxial synthesis precludes molecular design on demand as well as distinct, chemical modifications. We have synthesized an ordered, non-equilibrium, one-monomer-thick two-dimensional polymer beyond molecular dimensions,[1] which may serve in a later stage as ultra-thin membrane or molecular sieve. By crystallization of **1** (Figure 1), important intermolecular close-contacts are formed, which allow for a topochemical photo-induced [4+2] reaction. The polymerized crystals are delaminated by solvent-induction or microwave irradiation to obtain individual two-dimensional polymers as free-standing, mono- or oligolayered molecular sheets. Examination of these sheets is carried out by various microscopy techniques (SEM, AFM, TEM). The poster will give an up-to-date report on an improved monomer synthesis (g-scale), improved exfoliation procedures and advances on 2D polymer analysis.

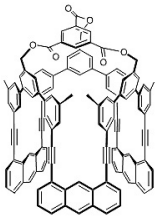


Figure 1: Monomer **1** for two-dimensional polymers.

[1] P.Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Götzinger, A. D. Schlüter, J. Sakamoto, *Nat. Chem.* **2012**, *4*, 297–291.

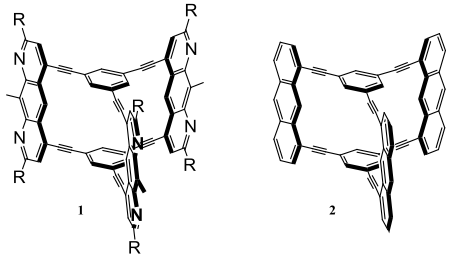
Polymers & Colloids **610**

Photoreactive Propeller-shaped Monomers for Topochemical Synthesis of 2D Polymers

Marco Servalli, A. Dieter Schlüter, Junji Sakamoto

ETH Zürich, Department of Materials, Laboratory of Polymer Chemistry, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland

We are exploring the rational synthesis of "one monomer unit thick" covalent network structures with translational periodicity (2D polymers) [1, 2]. In the present work, propeller-shaped monomers **1** and **2** bearing three anthracene moieties were rationally designed to form laminar single crystals, in which the anthracenes stack face-to-face in each layer. Once the monomers have crystallized in the expected manner, photo-irradiation of the single crystals is expected to induce the [4+4]-cycloaddition among the stacked anthracenes to directly convert the layers in the crystal to the corresponding 2D polymers. The monomer synthesis was performed by employing Sonogashira cross-coupling reactions of readily accessible building blocks.



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Polymers & Colloids **611**

μm²-Sized Freestanding Sheets and their cm²-Sized Multilayers on Solid Substrates

Zhikun Zheng,[1] Thomas Bauer,[1] Antonella Rossi,[2] Junji Sakamoto[1] and A. Dieter Schlüter[1*]

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[2]Department of Inorganic and Analytical Chemistry, University of Cagliari, 09100 Cagliari, Italy

Recently there is a vigorous research activity aiming at developing access to sheet-like polymers that are covalently bonded, one monomer unit thick, and exhibit internal periodicity. According to a recent definition, they are referred to as two-dimensional polymers (2DPs).[1] Feasible concepts were recently reported.[2,3]

Here we present our efforts to μm²-sized freestanding 2DPs and cm²-sized 2DPs on solid substrates. A set of D_{3h} and D_{6h} symmetric monomers with three and six 2,2':6',2''-terpyridineunits at the periphery were synthesized.[4] After polymerization of the monomers at the air/water interface in two dimensions with metal ions, they were transferred onto substrate of interest for UV-vis spectroscopy, XPS, AFM, optical microscopy, SEM and TEM measurements. The sheet can be put on top of one another, and thus create a transition from two-dimensional sheet to a (thin) three-dimensional layered material.

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Polymers & Colloids **612**

Single-molecule force spectroscopy: studying adhesion of dendronized polymers at molecular level

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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 [1].
Polymethacrylate-based dendronized polymers of different generations (PGn) adsorbed on four different surfaces were imaged with atomic force microscopy (AFM) in solution. Surface adhesion was investigated using single-molecule force spectroscopy (SMFS) by manipulating 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 materials properties at the molecular level. Difference in hydrophobicity of investigated surfaces clearly affects the surface-molecule interaction force.

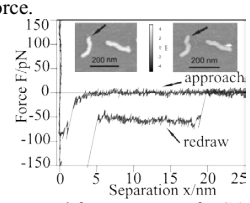

Fig 1. AFM height images and force curves of PG4 adsorbed on mica in solution at pH 4.

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Polymers & Colloids **613**

Studying the interactions between sulfate latex particles with adsorbed linear poly(ethylene imine) through a multiparticle colloidal probe technique

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Interaction forces between negatively charged particles with adsorbed cationic linear polyelectrolyte like linear poly(ethylene imine) (LPEI) were studied with atomic force microscopy (AFM) and electrophoresis. Forces were measured directly using the multiparticle colloidal probe technique. This technique allows attaching to the edge of the cantilever colloidal particles in the liquid suspensions ensuring in this way a large surface area during the experiment. It was found that the strength of the forces measured were dependent on the polymer dose. Indeed at very low doses the system shows a repulsive force given from the overlap of the diffuse part of the electrical double-layer around a charged surface. Getting close to the isoelectric point (IEP) the entire surface of the particle is going to be neutralized and this corresponds to a short range attractive Van der Waals force. The absence of additional electrostatic attractive forces due to patch-charge heterogeneities found in other particle-polyelectrolyte systems indicates that the adsorbed layer of LPEI has a high lateral homogeneity. Above the IEP a diffuse layer builds up again and the force switches from attractive to repulsive. This strength increases, increasing the amount of polymer adsorbed on the surface until this one has been saturated. In this case the magnitude of the force does not change anymore corresponding at a constant value of potential as a function on the polymer dose.

Polymers & Colloids **614**

Colloidal Particles Interactions in Aqueous Electrolytes and in Ionic Liquids Studied with Atomic Force Microscopy

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Interaction forces between colloidal particles dictate many important suspension properties, such as phase behavior, osmotic pressure, rheology or colloidal stability [1].

Atomic force microscopy (AFM) has been widely used to study interaction forces between particles and surfaces. In particular, the direct functionalization of the AFM cantilever with a colloidal probe [2] allows to measure directly the forces-versus-distance curves for different particle-particle and particle-surface systems [3,4].

Colloidal probes of silica and latex of different diameter (1-5 μm) are used to investigate colloidal behavior in aqueous electrolytes and in ionic liquids at different salt concentration. In the first case, at high ionic strength, Van der Waals forces can be estimated, while in the latter oscillatory solvation profiles are detected.

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Polymers & Colloids **615**

Self-Assembly of Chitosan-grafted-Oligonucleotides

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A suitable coupling between single stranded DNA fragments (ssDNA) and chitosan is expected to give rise to a novel biocompatible copolymer with a high potential for numerous applications. In this work, results on the synthesis and characterization of a self-assembling oligonucleotide-biopolymer hybrid are presented. For the first time, both biochemical and organic synthesis routes were combined to design an amphiphilic copolymer composed of a "water-loving" ssDNA fragment linked to a "water-hating" natural polymer backbone. The chemical characterization of the newly synthesized copolymers (chitosan-grafted-ssDNA (C-g-ssDNA)) was performed through the combination of conventional techniques such as FTIR, mass spectrometry to demonstrate the successful coupling between the natural polymer and ssDNA. C-g-ssDNA molecules self-assemble into water filled vesicle-like structures in dilute aqueous solution. The vesicular structure formation was characterized by fluorescence microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The time course of the release of an encapsulated water soluble dye from the inner aqueous pool of the vesicles was followed by fluorescence spectroscopy. The design of this fully biocompatible self-assembling material paves the way to several future uses e.g., as targeted drug delivery vehicle for sustained drug release and/or gene therapy just to cite few examples.

Polymers & Colloids **616**

XRD investigation of piezoelectric polymers as barrier materials for hydrogen storage

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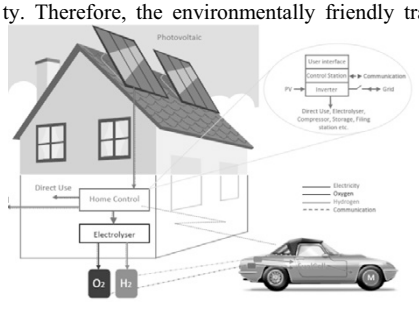
The largest sources of air pollution are power plants, industries and transportation emissions. Transportation is a key component of our society. Therefore, the environmentally friendly transportation system is of paramount importance for the decrease of emission. Our main affords are focused on the principle of the use of solar energy (collected on home roofs), which can be used to electrolyze water in order to produce H_2 and O_2. The idea is to compress these gases and stored locally, filled in car reservoirs and transposed to electricity for fuel cell driven cars. Safety related to hydrogen storage is a key topic. Therefore, the materials used in gas tanks have to be deeply characterized. Worldwide, significant developments are on-going to find alternatives to traditional stainless steel pressure tanks designed for use as on-board H_2 storage. For this purpose, the poly-vinylidene fluoride and its copolymers are investigated as material being extremely dense and as a pressure sensor. XRD methods establish the structure/property relationship for those systems. The films structure and in-situ HT-XRD studies will be discussed.



* Nano-Tera project **Greenpower:** http://www.nano-tera.ch/projects/411.php