

<p>Polymers, Colloids Interfaces PCI01</p> <p>Single Particle Tracking in Colloidal and Granular Matter under External Load</p> <p>Günter K. Auernhammer</p> <p>Max Planck Institute for Polymer Research</p> <p>The mechanical properties of aggregated colloids depend on the mutual interplay of interparticle potentials, contact force, aggregate structure and material properties of the bare particles. We will discuss the interplay between the various possible modes of motion in a couple of examples. We investigated colloidal films [1, 2] made from monodisperse poly-methyl-methacrylate (PMMA) particles (diameter: 1.6 μm) via nanoindentation in combination with confocal microscopy. The mechanical properties were correlated with the three dimensional aggregate structure as well as the individual displacements of the particles. From the microscopic reorganizations the average strain field was calculated. We analyzed the differences between amorphous [1] and semi-crystalline assemblies [2]. Fluorescently labeled polydisperse silica particles (average diameter 7 μm) were hydrophobized with long alkyl chains and dispersed in an index-matching liquid [3]. The particles show a weak attraction. Photobleaching the central plane of individual particles generates an optical anisotropy without changing particle interaction. This allows following the trajectories and rotation of single particles [3, 4].</p> <p>[1] M. Roth, C. Schilde, P. Lellig, A. Kwade, and G. K. Auernhammer; □ Eur. Phys. J. E 35, 9801 (2012). [2] M. Roth, C. Schilde, P. Lellig, A. Kwade, G. K. Auernhammer; □ Chem. Lett. 41 (10), 1110-1112 (2012). [3] Jennifer Wenzl, Ryohei Seto, Marcel Roth, Hans-Jürgen Butt, and Günter K. Auernhammer; □ □ Granul. Matter, (2012), DOI 10.1007/s10035-012-0383-7. [4] M. Roth, M. Franzmann, M. D'Acunzi, M. Kreiter, and G. K. Auernhammer; □ □ arXiv:1106.3623v2 [cond-mat.soft] (2011).</p>	<p>Polymers, Colloids Interfaces PCI02</p> <p>Motion and Balance of Complex Fluids on the Nanoscale</p> <p>Annette M. Schmidt*</p> <p>¹Universität zu Köln, Chemistry Department Luxemburger Str. 116, D-50939 Köln</p> <p>We consider a material to be soft when it easily and readily adapts to an external stress. Nevertheless, time-dependent and viscoelastic processes, as prominent in many polymer- and colloid-based materials, are important for the performance of a large number of materials. When taken into account properly, dynamic processes in complex fluids, solutions and melts can be exploited for novel adaptive and responsive systems.^[1]</p> <p>The talk will summarize examples from our lab demonstrating the potential of dipolar nanoparticles and their tailored interaction with polymer matrices and external fields for the investigation of the quasi-static^{[2],[3]} and frequency-dependent^{[4],[5]} nanorheological properties of soft matter. The dynamic behavior of ferromagnetic hybrid structures can further be adopted for swimming objects that can be propelled by chemical fuel under very low Reynolds number conditions.</p> <p>[1] R. Messing, A. M. Schmidt, <i>Polymer Chem.</i> 2011, 2, 18. [2] N. Frickel, R. Messing, A. M. Schmidt, <i>J. Mater. Chem.</i> 2011, 21, 8466. [3] L. Roeder, P. Bender, A. Tschöpe, R. Birringer, A. M. Schmidt, <i>J. Polym. Sci., Part B: Polym. Phys.</i> 2012, 50, 1772. [4] M. Feyen, E. Heim, F. Ludwig, A. M. Schmidt, <i>Chem. Mater.</i> 2008, 20, 2942. [5] F. Ludwig, A. Guillaume, M. Schilling, N. Frickel, A. M. Schmidt, <i>J. Appl. Phys.</i> 2010, 108, 033918.</p>
<p>Polymers, Colloids Interfaces PCI03</p> <p>Peptide Nucleic Acid Modified Gold Nanoparticles and their Assembly on Surfaces</p> <p>Philipp Anstaett,¹ Yuanhui Zheng,² Thibaut Thai,² Alison M. Funston,² Udo Bach,² Gilles Gasser¹</p> <p>¹ Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland, gilles.gasser@aci.uzh.ch ² Monash University, Clayton, Victoria 3800, Australia, udo.bach@monash.edu</p> <p>DNA-modified gold nanoparticles (AuNPs) have been applied for a wide range of applications including nanofabrication.[1] However, due to the inherent charge of the phosphate backbone of DNA, their assembly requires the presence of ions to shield their charges. The preparation of AuNP assemblies in the absence of ions would be of great interest, e.g. for investigation of electrostatic phenomena. Peptide Nucleic Acids (PNAs) are non-natural DNA analogs with a peptide backbone instead of phosphoribose. As PNAs are electrostatically neutral, they can form assemblies in absence of ions. Unfortunately, PNAs strongly destabilize colloidal AuNP solutions. Here, we present a novel approach which allows the preparation of stable PNA-modified AuNPs by first stabilizing them with a thiolated polyethylene glycol carboxylate. PNAs can then be attached via mono- or trithiol linkers. The PNA-modified nanoparticles are able to form assemblies in absence of any additives, including ions, as demonstrated by scanning electron microscopy of PNA-modified particles assembled onto PNA-modified gold surfaces.</p> <p>[1] Y. Zheng, C. H. Lalander, T. Thai, S. Dhuey, S. Cabrini, U. Bach, <i>Angew. Chem. Int. Ed.</i> 2011, 50, 4398–4402. [2] P. Anstaett, Y. Zheng, T. Thai, A. M. Funston, U. Bach, G. Gasser, <i>Angew. Chem. Int. Ed.</i> 2013, 52, 4217–4220.</p>	<p>Polymers, Colloids Interfaces PCI04</p> <p>Failure of DLVO theory at distance of few nanometers: a colloidal probe study</p> <p>Mohsen Moazzami Gudarzi, F. Javier Montes Ruiz-Cabello, Plinio Maroni, Michal Borkovec</p> <p>Department of Inorganic, Analytical, and Applied Chemistry, University of Geneva, Sciences II, CH-1211 Geneva 4, Switzerland</p> <p>In the realm of forces among surfaces, the classical theory of DLVO has been able to reasonably predict the interaction among colloidal particles. However, many non-DLVO interactions have been proposed to be in action among surfaces including, but not limited to, ion-ion correlation, ion-specific interaction, hydration forces, and hydrophobic interaction postulating invalidity on DLVO theory especially at high ionic strength [1]. Interactions between sulfate polystyrene latex in monovalent electrolyte were investigated using colloidal probe atomic force microscopy [2]. Probing the forces from low to high ionic strength, transition from long-range repulsion to short-range attraction was detected. At intermediate ionic strength (50–250 mM), electrostatic repulsion screened enough to observed secondary minimum in force curves. The data agreed well with DLVO theory prediction without including any additional forces till the separation distance of 2–3 nm. In order to calculate the effective Hamaker constant between the particles, the forces around the secondary minimum was used for fitting using DLVO theory. Using the average Hamaker constant ($3.6 \pm 0.2 \times 10^{-21}$ J), one can precisely calculate the surface potential by fitting data with DLVO theory. The surface potential agreed well with Gouy-Chapman model at the moderate ionic strength. Thus the surface forces can be modeled with good agreement with classical DLVO theory up to 3 nm.</p> <p>[1] M. Bostrom, D. R. M. Williams, B. W. Ninham, <i>Phys. Rev. Lett.</i> 2001, 87, 168103. [2] M. Borkovec, I. Szilagyi, I. Popa, M. Finessi, P. Sinha, P. Maroni, G. Papastavrou, <i>Adv. Colloid Interf. Sci.</i> 2012, 179-182, 85-98.</p>

Polymers, Colloids & Interfaces

PCI05

Nacre-like composite materials produced via magnetically-controlled phase separation of sol-gel process

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Naturally occurring materials and structures have been always inspired scientists, who tried to either replicate or mimic them. Examples include gutta-percha, wood, opals, bones and nacre. The latter has gained considerable interest in the last few years. Naturally occurring nacre is made of thin hexagonal platelets of aragonite, having a size of 10–20 μm and a thickness of 0.5 μm held together by a bio-polymer. In this work we have prepared a new ceramic-polymer composite material inspired by the structure of nacre. This material is made from a monolithic skeleton of silica platelets in a size range of 20–30 μm and a thickness of $\sim 1 \mu\text{m}$ reinforced by a polyetheramines based polymer. The silica platelets have been produced via a modification of the magnetically controlled phase separation in sol-gel process previously developed in our laboratories. In this process polymer-magnetite nanoparticles produced via miniemulsion polymerization have been dispersed in an acidic solution where PEG and the silicon precursor TMOS have been previously dispersed. The obtained solution was then transferred to a mold and placed between the poles of an electromagnet. As shown in literatures the application of a rotating magnetic field leads to the formation of sheet-like structures. In our case we decided to rotate the sample inside a uniaxial magnetic field to mimic a rotating field. Once the monolith was formed it was functionalized with (3-aminopropyl)-triethoxysilane in order to promote the attachment of the polymer to the surface during the impregnation step. The obtained structures have been analyzed with SEM microscopy and mechanical compression test before and after the polymer impregnation step. We have shown that the radial velocity plays an important role in the formation of the platelets structure and of the initial anisotropic mechanical properties of the materials. The impregnation step enhances these properties by making the material more stable.

Polymers, Colloids Interfaces

PCI06

Purely peptidic amphiphiles: from self-assembled structures to gene delivery

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In modern pharmaceutical applications, carrier systems are indispensable due to their manifold benefits such as protection of active pharmaceutical ingredients against degradation, reduction of side effects, and improvement of bioavailability.¹ Polypeptides are a particular interesting carrier material because of their natural building blocks. We designed small amphiphilic peptides by combining a hydrophobic sequence, inspired by gramicidin A, and hydrophilic oligo amino acids such as glutamic acid, lysine and acetylated lysine. The generated self-assembled structures range from micelles and vesicles to spherical multicompartement micelles, named peptide beads.² The obtained structures are a function of the hydrophilic to hydrophobic ratio, the degree of acetylation and the stabilizing intra- and intermolecular interactions.

At present, we are optimizing the multicompartement micelles structure towards gene therapy.³ Therefore, we loaded peptide beads with plasmid DNA (pDNA) which has to be delivered into the cell nucleus. The results show high loading efficiency, uptake in different cell lines and no indication of a toxic effect. Furthermore, we demonstrated gene silencing in Huh7 cells through the peptidic carrier system, based on the successful delivery of pDNA, the expression of shRNA, and its subsequent cleavage into siRNA. In summary, the investigated peptidic material represents a new tool for gene delivery.

[1] N. Larson and H. Ghandehari, *Chem. Mater.* **2012**, *24*, 840.[2] T. B. Schuster, D. de Bruyn Ouboter, E. Bordignon, G. Jeschke and W. Meier, *Soft Matter* **2010**, *6*, 5596.[3] D. de Bruyn Ouboter, T. B. Schuster, V. Shanker, M. Heim and W. Meier, *submitted 2013*.

Polymers, Colloids Interfaces

PCI07

Polymer-Mediated Delivery of Therapeutic Coiled CoilsAna Maria Raduta¹, Sebastian Hanke², Katja M. Arndt², Harm-Anton Klok¹¹Ecole Polytechnique Fédérale de Lausanne (EPFL), Polymer Laboratory,
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Coiled coil domains are involved in a variety of biological regulation and fusion processes where coiled coil oligomerization results in either “active” or “inactive” multiprotein complexes that can subsequently turn “on” or “off” biological pathways.¹ As a consequence, coiled coil sequences with a higher binding affinity to the target than the wild type sequence can competitively inhibit or disrupt such oligomerization process, which makes them of interest as putative therapeutic entities, or “molecular switches”.

Here we present the preparation of poly(2-hydroxypropyl methacrylamide) (PHPMA) conjugates in which the peptide is attached via a redox or pH sensitive linker to the polymer backbone. As an example, this project uses the AFosW peptide, which can form a stable heterodimeric complex with a wild type cJun peptide derived from the oncogenic activator protein 1.² The polymer conjugation enhances the stability of the peptides in circulation and can improve cellular uptake whereas the pH and reduction sensitive linkers were designed to allow release of the free peptide within the cell. In addition we will report the in vitro studies of the cell uptake and efficacy of AFosW – polymer conjugates.

Financial support from the European Science Foundation (P2M exchange grant) is gratefully acknowledged.

[1] (a) A. Lupas, *Trends Biochem. Sci.* **1996**, *21*, 375; (b) B. Apostolovic, M. Daniai, H.-A. Klok, *Chem. Soc. Rev.* **2010**, *39*, 3541[2] J. M. Mason, M. A. Schmitz, K. M. Muller, K. M. Arndt, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 8989.

Polymers, Colloids Interfaces

PCI08

Low-Temperature Preparation of Carbon Nanosheets from Hexa(ethynylene) AmphiphilesStephen Schrettl¹, Holger Frauenrath^{1*}¹École Polytechnique Fédérale de Lausanne (EPFL)
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Carbon nanostructures constitute promising components for high performance composites and mitigating their poor dispersibility in organic matrices should allow for the preparation of novel types of electronically active nanocomposites.^{1,2} However, the high-energy processes typically employed for their production impede the tailored preparation of carbon nanostructures with controlled morphology and chemical functionalization. In this context, we developed a novel strategy for the low-temperature wet-chemical preparation of carbon nanostructures based on the synthesis, self-assembly, and subsequent mild carbonization of oligoynne amphiphiles as reactive molecular precursors.³

Here, we demonstrate that these amphiphiles are unique molecular carbon precursors suitable for the preparation of carbon sheets at the air-water interface. To this end, a concise synthetic route allowed for the gram-scale synthesis of amphiphiles that resemble fatty acids but comprise a reactive, “carbon-only” hexayne segment. At the air-water interface these reliably self-assemble into films with a thickness on the molecular length scale containing a densely packed domain of the reactive, carbon-only rod segments. UV irradiation then served as a mild external stimulus for the carbonization of the reactive molecular precursors, leading to novel carbon sheets with extended lateral dimensions and a thickness on the order of a few nanometers.

[1] T. N. Hoheisel et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 6496.[2] S. Schrettl, H. Frauenrath, *Angew. Chem. Int. Ed.* **2012**, *51*, 6569.[3] R. Szilluweit et al., *Nano Lett.* **2012**, *12*, 2573.

<p>Polymers, Colloids Interfaces PCI09</p> <p>Synthesis of monolayer metal-organic polymer/copolymer sheets</p> <p><u>Zhikun Zheng</u>,* Antonella Rossi, Junji Sakamoto and A. Dieter Schlüter</p> <p>Laboratory of Polymer Chemistry, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zurich</p> <p>The current interest in graphene, a naturally occurring two-dimensional polymer (2DP), makes it clear that there is no organic synthetic method available that would allow accessing a laterally infinite, one-monomer unit thick, freestanding, unimolecular network with a defined internal periodicity (2DP).^[1] Here we present a general method for the synthesis of metal-organic sheets that may qualify as 2DPs.^[2] It rests on the connection of monomers at air-water interface with metal ions. These sheets obtained are one-monomer unit thick and are mechanically stable enough to be spanned over $20 \times 20 \mu\text{m}^2$ holes. Interestingly, transmetallation of Zn^{2+} in Zn-based sheets to Fe^{2+} (Co^{2+}, Pb^{2+}) can be achieved on the cm^2-sized scale.^[3] The extent of the transmetallation can be controlled by varying reaction time. Assuming that the transmetallation is a random process, this allows access to sheets with a random distribution of two different metals in the netpoints. In the terminology of linear polymers this is reminiscent of random copolymers, thus we are dealing with random metal-organic sheet copolymers until transmetallation is finished. Furthermore, area-selective transmetallation of Zn-based sheets with appropriate masks leads to arrays of chemical patterns alternatingly containing Zn^{2+} and Fe^{2+}-based netpoints. Looking at such sheets with the eyes of a polymer chemist one may consider them as two-dimensional analogues of block copolymers.</p> <p>[1] J. Sakamoto, J. Van Heijst, O. Lukin, A. D. Schlüter, <i>Angew. Chem. Int. Ed.</i> 2009, <i>48</i>, 1030. [2] (a) T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto, A. D. Schlüter, <i>Angew. Chem. Int. Ed.</i> 2011, <i>50</i>, 7879, (b) Z. Zheng, T. Bauer, A. Rossi, P. Payamyar, J. Sakamoto, A. D. Schlüter, <i>submitted</i>. [3] Z. Zheng, L. Opilik, W. Liu, P. Ceroni, R. Zenobi, J. Sakamoto, A. D. Schlüter, <i>manuscript in preparation</i>.</p>	<p>Polymers, Colloids Interfaces PCI10</p> <p>Controlling the microstructure and charge carrier transport of solution-processed semiconducting polymers</p> <p>A. Gasperini¹ and K. Sivula¹</p> <p>¹Laboratory for Molecular Engineering of Optoelectronic Nanomaterials, ISIC-SB-EPFL, Station 6, 1015 Lausanne, Switzerland.</p> <p>Conjugated polymers have emerged as viable candidates for the fabrication of solution-processed electronic devices. Given their semicrystalline nature, controlling microstructure and performance of these materials has remained a fundamental challenge. In particular, poly[2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene], PBTTT, has shown an exceptional charge carrier mobility due to its rigid conjugated backbone that gives a highly crystalline structure.¹ However, variations in observed microstructure and performance of this material are currently of great interest. Here we describe general strategies that allow the tuning of crystalline domain size observed in thin film devices. First, by precisely varying the population of chain lengths (MW) in the thin film and characterizing the resulting microstructure (by AFM, GIXS) and mobility, we demonstrate control over the morphology and gain insight into the factors required for state-of-the-art performance in this class of materials. We further show it is possible to drastically improve the mobility in low MW films by over three orders of magnitude by adding only small amounts of high MW material, suggesting that long chains strongly affect the intermolecular interactions at grain boundaries, changing both morphology and charge transport. In an effort to unravel the roles of inter- and intra-chain transport on the overall mobility we also synthesized a prototype PBTTT polymer made of short and fully conjugated moieties linked to each other by flexible chains. Impacts of our bottom-up approach to improve performance of both photovoltaic and transistor devices fabricated from rigid and flexible PBTTT will be subjects of discussion.</p> <p>[1] McCulloch, I.; Heeney, M.; Bailey, C <i>Nat. Mater.</i> 2006 <i>5</i>, 328 – 333</p>
<p>Polymers, Colloids Interfaces PCI11</p> <p>Dielectric elastomers put to work</p> <p><u>Dorina M. Opris</u>,^a Simon Dünki,^a Frank Nüesch,^a Jose E. Q. Quinsaat,^a Yee Song Ko,^a Silvain Michel,^a Carmen Racles,^b Maria Cazacu^b</p> <p>^aEmpa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstr. 129, CH-6800 Dübendorf, Switzerland Institution ^bPetru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania</p> <p>Dielectric elastomer actuators are flexible and stretchable capacitors that elongate when charged.^[1] The elongation and the reliability of such actuators depend on the dielectric material as well as the electrode material used. While elastomers with low modulus of elasticity and increased permittivity allow actuations at lower electric fields, the electrode material can have a direct impact on the actuator lifetime and reliability as well as on the energy consumption.^[2]</p> <p>This presentation will show how with specially designed elastomers an actuator can be operated at lower electric fields.^[3]</p> <p>References</p> <p>[1] R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph, <i>Science</i>, 2000, <i>287</i>, 836–839. [2] S. Michel, B. T. T. Chu, S. Grimm, F. A. Nüesch, A. Borgschulte, D. M. Opris, <i>J. Mat. Chem.</i> 2012, <i>22</i>, 20736-20741. [3] M. Molberg, D. Crespy, P. Rupper, F. Nüesch, J.-A. E. Månson, C. Löwe, D. M. Opris, <i>Adv. Funct. Mater.</i> 2010, <i>20</i>, 3280-3291; D. M. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, <i>Adv. Funct. Mater.</i> 2011, <i>21</i>, 3521-3539.</p>	<p>Polymer Science PCI12</p> <p>Perforated Bicontinuous Cubic Phases with pH-Responsive Topological Channel Interconnectivity</p> <p><u>Alexandru Zabara</u>,^a Renata Negrini,^a Ozana Onaca-Fischer,^b Raffaele Mezzenga^{a*}</p> <p>^aETH Zürich, Food & Soft Materials Science, Schmelzbergstrasse 9, LFO E23, 8092 Zürich, SWITZERLAND ^bUniversity of Basel, Department of Chemistry Klingelbergstrasse 80, 4056 Basel, SWITZERLAND</p> <p>Lyotropic liquid crystals are at the frontline of current research for release of target therapeutic molecules due to their unique structural complexity and the possibility of engineering stimuli-triggered release of both hydrophilic and hydrophobic molecules. One of the most suitable lipidic mesophases for the encapsulation and delivery of drugs is the reversed double diamond bicontinuous cubic phase, in which two distinct and parallel networks of water channels percolate independently through the lipid bilayers, following a Pn3m space group symmetry. In the unperturbed Pn3m structure, the two sets of channels act as autonomous and non-communicating three-dimensional transport pathways. Here, we introduce a novel type of bicontinuous cubic phase, where the presence of OmpF membrane proteins at the bilayers provides unique topological interconnectivities among the two distinct sets of water channels, enabling molecular active gating among them. By a combination of small angle x-ray scattering, release and ion conductivity experiments, we demonstrate that -without altering the Pn3m space group symmetry or the water channels diameter-, the newly designed perforated cubic phase attains transport properties well beyond those of the standard mesophase, allowing a faster, sustained release of bioactive target molecules. By further exploiting the pH-mediated pore-closing response mechanism of the protein, we also provide the perforated mesophase with a pH-triggered ON-OFF opening of the pores, enabling a fine modulation of the transport properties by only moderate changes in pH, which could open unexplored opportunities in the targeted delivery of bioactive compounds.</p>

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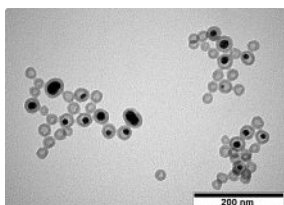
One-pot synthesis of antimicrobial Ag@SiO₂ nano-rattle through the microemulsion approach

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Silver cations and silver nanoparticles (AgNPs) are gaining an increasing interest in medical applications due to their multidirectional activity and a broad antimicrobial spectrum.^[1] Encapsulation into inorganic nanocontainers, such as silica, might provide not only protection for the AgNPs from unwanted interactions with the surrounding environment, but also a mean for a functionalization of the wall of the nanocapsules.

The purpose of this project is to develop a one-pot synthesis and encapsulation of silver nanoparticles into silica hollow spheres (Ag@SiO₂) via the microemulsion approach. Initially, silver cations are reduced inside reverse micelles. Then, hydrolysis and polycondensation of silica precursors on the boundary phase of the micelle leads to the formation of nano-rattles (Figure 1). The characterization of nanoparticles is carried out using TEM, HRSEM, EDS, XRPD, IR, TGA, ICP, DLS and zeta potential measurements. The antimicrobial activity of Ag@SiO₂ is tested against *E. coli*.

Figure 1. TEM image of Ag@SiO₂ nano-rattles.

- [1] Eckhardt S., Brunetto P. S., Gagnon, J., Priebe M., Giese B., Fromm, K. M., *Chem. Rev.*, **2013**, DOI: 10.1021/cr300288v.

Polymers, Colloids Interfaces

PCI14

Protection and Deprotection of DNA – High Temperature Stability of Nucleic Acid Barcodes for Polymer Labeling

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Nucleic acids are the information carriers of all known life forms and have the ability to store more information per volume space than magnetic domain. This makes DNA most suited for nanobiotechnology,^[1] encrypted barcoding and as an anti-counterfeit tag of consumer goods. The vulnerability of nucleic acids to hydrolytic damage, oxidation and alkylation requires well controlled DNA storage conditions, ideally dry and at low temperatures.^[2] Similarly, ancient DNA is best recovered from permafrost samples^[3] or following desiccated storage in amber and fossils.^[4] Within these fossils a dense diffusion layer separates the desiccated DNA specimen from the environment. The here presented work shows how a simple encapsulation of DNA in silica particles mimics these fossils and protects DNA from severe environmental attack.^[5] We demonstrate that silicate and hydrofluoric acid chemistry is compatible with nucleic acid analysis via quantitative real-time PCR. We also display how silica protected DNA can be made compatible with injection molding at 200°C enabling the barcoding of polymers.

- [1] A. V. Pinheiro, D. R. Han, W. M. Shih, H. Yan, *Nat. Nanotechnol.* **2011**, 6, 763 – 772.
 [2] J. G. Baust, *Biopreserv. Biobanking* **2008**, 6, 251.
 [3] E. Willerslev, A. J. Hansen, J. Binladen, T. B. Brand, M. T. P. Gilbert, B. Shapiro, M. Bunce, C. Wiuf, D. A. Gilchinsky, A. Cooper, *Science* **2003**, 300, 791-795.
 [4] H. N. Poinar, M. Hoss, J. L. Bada, S. Paabo, *Science* **1996**, 272, 864-866.
 [5] D. Paunescu, R. Fuhrer, R. N. Grass, *Angew. Chem. Int. Ed.* **2013**, 52, 4269 – 4272.

Polymers, Colloids Interfaces

PCI15

Modification of proteins with PEG-based comb-shaped polymers

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As biotherapeutics, proteins are attracting significant attention due to their high biological activity and specificity. However, therapeutic proteins, in their unmodified form, can display several drawbacks including poor stability, short biological half-lives, and immunogenicity. Conjugating polymers to proteins is an effective means to overcome these limitations. In this work, we have examined a “polymer engineering” approach for tuning the bioactivity of protein–polymer conjugates by manipulation of architecture and the conformation of polymer chains grown from the surface of proteins. We have prepared >100 well-defined conjugates of the model protein α -chymotrypsin (α -CT) or an anticancer enzyme L-asparaginase (ASNase) with PEG-based comb-shaped polymers (poly (oligoethyleneglycol monomethylether methacrylate) (pOEGMA)). The grafting density, backbone length, and side-chain length of the polymer were adjusted to control the properties of the polymer layer on the surface of proteins. The properties of the conjugates were characterized by ¹H-NMR spectroscopy, SEC, UV-Vis spectroscopy, antigenicity, bioactivity, etc.^[1] Within a certain regime, conjugates displayed molecular sieving properties which led to high catalytic activity (towards small molecules) and simultaneously very low antigenicity. This effect is inaccessible using other modern PEGylation strategies or using conventional linear polymers. In forthcoming experiments, selected conjugates composed of pOEGMA and ASNase will be evaluated *in vivo*. This “polymer engineering” approach may be applicable to a large class of protein drugs and provides a general modification methodology for improving their pharmacological profiles. This work was supported by Sassetta Stiftung and the China Scholarship Council (CSC).

References:

- [1] M Liu, P Tirino et al, *Adv. Funct. Mater.*, **2012**, DOI: 10.1002/adfm.201202227

Polymers, Colloids Interfaces

PCI16

Synthesis and Functionalization of Silver Nanoparticles for the Preparation of High Dielectric MaterialsJose Enrico Q. Quinsaat^{1,2}, Dorina M. Opris¹, Frank A. Nüesch¹, Heinrich Hofmann², Paul Bowen², Andrea Testino³.¹Empa, Laboratory for Functional Polymers, Überlandstr. 129, 8600 Dübendorf, Switzerland²Ecole Polytechnique Fédérale de Lausanne (EPFL), Materials Institute, Powder Technology Laboratory (LTP), 1015 Lausanne, Switzerland³Paul-Scherrer-Institut, Chemical Processes and Materials, 5232 Villigen, Switzerland

Silver nanoparticles (AgNPs) have gained a lot of attraction for its array of properties that can be tuned through the control of size and morphology offered by the polyol synthesis.¹ The high polarizability of AgNPs allows to increase the dielectric constant ϵ of polymer based nanocomposites such as polydimethylsiloxane (PDMS)/AgNPs. However, the production of AgNPs in large quantities (10-100 g) is required for further composite testing and current batch methods yield poor quality products upon increasing the batch volume. In this work, we demonstrate the polyol synthesis of AgNPs using a segmented flow tubular reactor (SFTR)² that provides the possibility of producing AgNPs at a larger scale and maintaining high product quality. We also show the effect of nanoparticle surface modification on the dielectric properties of pellets composed of modified AgNPs.³

- [1] B. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem. Eur. J.* **2005**, 11, 454.
 [2] A. Aimable, N. Jongen, A. Testino, M. Donnet, J. Lemaitre, H. Hofmann, P. Bowen, *Chem. Eng. & Technol.* **2011**, 34(3), 344.
 [3] J.E.Q. Quinsaat, F. A. Nüesch, H. Hofmann, D. M. Opris, *RSC Adv.* **2013**, DOI: 10.1039/c3ra23192e.

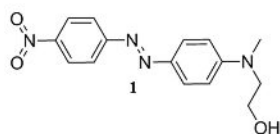
Polymers, Colloids Interfaces

PCI17

Encapsulation of Permanent Dipoles using Miniemulsion PolymerizationYee Song Ko, Monica Circu, Frank A. Nuesch, Dorina M. Opris

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Miniemulsion polymerization is used to encapsulate molecules with large permanent dipole moments into polymers with high glass transition temperatures [1]. Particles with size distributions in the nanometer range were obtained. The effect of the filler on particle size distribution, permittivity and other physical properties of the host material are investigated, using a modified version of the commercially available molecule Disperse Red One (1) as filler.



[1] K. Landfester, *Angew. Chem., Int. Ed.*, **2009**, 48, 4488

Polymers, Colloids Interfaces

PCI18

DNA hybrids structure formationDawid Kedracki, Ilyès Safir, Jancy Abraham, Corinne Vebert-Nardin

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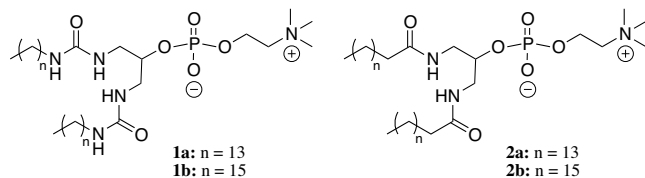
Relying on the achievement of a general mechanism to eventually solve critical biological and medical issues through the observation and manipulation of biochemical mechanisms, we are investigating the structure formation and modes of interaction of DNA hybrids, in particular copolymer self-assembly and crystallization as well as interpolyelectrolyte complex formation. We are predominantly focusing on reaching a comprehensive understanding of the organization of these peculiar macromolecules which can undergo specific interactions such as biological recognition to ultimately establish a general process of their association.

Polymers, Colloids Interfaces

PCI19

Synthesis and Characterization of Artificial PhospholipidsDennis Müller¹, Andreas Zumbuehl¹¹Department of Chemistry, Chemin de Musée 9, 1700 Fribourg, Switzerland

Organic chemistry is an attractive tool to study the properties of phospholipid vesicles: by changing the key parts of phospholipid molecules a deeper understanding of the balance of physical forces at play can be gained. This is important for the optimization of the release properties of mechanosensitive liposomes [1].



Here, a new urea-type phospholipid **1** will be introduced. The synthesis as well as the monolayer and bilayer biophysical characterization of the bis-urea phospholipids **1a** and **1b** [2] will be compared to natural lipids as well as to the artificial 1,3-diamino phospholipids **2a** and **2b** [3].

- [1] M. N. Holme, I.A. Fedotenko, D. Abegg *et al.*, *Nat Nanotechnol* **2012**, 7, 531.
 [2] D. Müller, *in preparation*.
 [3] I. A. Fedotenko, P.-L. Zaffalon, F. Farvager, A. Zumbuehl, *Tetrahedron Lett* **2010**, 51, 5382.

Polymers, Colloids Interfaces

PCI20

On the self-assembly interplay of liquid crystals with patchy nanoparticlesStefan Guldin¹, Kellen Harkness¹, Francesco Stellacci¹¹Department of Materials Science, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.

Over the past decade, mixed ligand self-assembly has become a powerful tool to control the spatial arrangement of patches (e.g. stripes or Janus-like) on gold nanoparticles (NPs) [1]. This mechanisms of molecular self-assembly is driven by the dissimilarity in chain length of binary ligand mixtures. This leads to additional conformational entropy terms in the interplay between conformational entropy-driven stabilisation and enthalpy-driven minimisation of the domain interfaces [2]. Implications of ligand patches on the sub-2 nm length scale are numerous, ranging from NP solubility [3] to solid-liquid interactions [4], cell penetration [5] and chemical sensing [6].

The interplay of patchy NPs with liquid crystal (LC) mesogens represents a novel platform to further understand the crosstalk of two self-assembling systems with widespread applications. In this paper I will report on aspects of NP solubility in LCs that is mediated by ligand stripes acting as mesogen anchoring docks [7] as well as ferroelectric aspects of LC/NP assemblies arising from Janus-like ligand formation that induces a permanent dipole moment [8].

- [1] A.M. Jackson *et al.*, *Nature Mater.* **2004**, 3, 330-336.
 [2] C. Singh *et al.*, *Phys. Rev. Lett.* **2007**, 99, 226106.
 [3] A. Centrone *et al.*, *PNAS* **2008**, 105, 9886-9891.
 [4] J.J. Kuna *et al.*, *Nature Mater.* **2009**, 8, 837-842.
 [5] A. Verma *et al.*, *Nature Mater.* **2008**, 7, 588-595.
 [6] E.S. Cho *et al.*, *Nature Mater.* **2012**, 11, 978-985.
 [7] J. Milette *et al.*, *J. Mat. Chem.* **2011**, 21, 9043-9050.
 [8] L. Lopatina *et al.*, *Phys. Rev. Lett.* **2009**, 102, 197802.

Polymers, Colloids Interfaces

PCI21

Electrospun Nanofibers for Functional Food Packaging

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In recent years, several active food packaging systems have been developed to extend the shelf-life of food. Such active packaging systems are designed to release or adsorb substances into or from the packed food or its surrounding environment [1]. Several systems releasing antioxidants and antimicrobials such as essential oils, bactericides, organic acids or enzymes were tested [2].

Very recently, the application of electrospun nanofiber membranes for active food packaging has been investigated. Such membranes provide a couple of advantages such as very high specific surfaces, the possibility to design porous structures, and a simple incorporation of active substances.

Currently, we are incorporating volatile actives into nanofibers as cyclodextrin complexes. We are studying the release rate, the homogeneity of active distribution, the total capacity and the endurance of the material depending on the presence and type of cyclodextrin complexes. In contrast to a very promising study by Kayaci and Uyar [3] a nozzle-less electrospinning technique is applied with the potential for a large scale production as required for the packaging industry.

- [1] D.A. Pereira de Abreu, J.M. Cruz, P. Paseiro Losada, *Food Rev. Int.* **2012**, 28, 146.
 [2] F. Kayaci, A. Celebioglu, Z. Aytac, T. Uyar, *COST FA0904 Int. Workshop Waedenswil* March 21-22, **2013**
 [3] F. Kayaci, T. Uyar, *Food Chem.* **2012**, 113, 641

Polymers, Colloids Interfaces

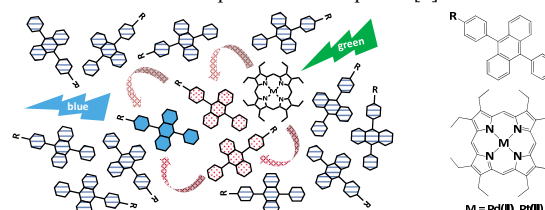
PCI22

Low-power photon upconversion in molecular glass materials

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Low-power photon upconversion (UC) via triplet-triplet annihilation (TTA) is a nonlinear process converting incident radiation into higher energy light using relatively low power densities ($< 100 \text{ mW cm}^{-2}$). TTA-UC systems usually consist of a two organic dyes: a sensitizer, harvesting incoming light and an emitter. Most UC dye-pairs have been investigated in solution. However, in the last years, several solid-state polymer and non-polymer-based UC materials and material concepts have been reported [1].



Here, we present emitter-based molecular glasses (MGs) as a new strategy for solid-state upconverting materials. Green to blue upconverting 9,10-diphenylanthracene-based MGs serving simultaneously as palladium- or platinum porphyrin-based sensitizer hosts were produced and found to exhibit a stronger UC compared to the crystalline, mixed dye components. The influence of morphology, sensitizer type and concentration on the TTA-UC efficiency was also investigated. MGs are believed to kinetically hamper porphyrin aggregation and thus promote efficient upconversion. Furthermore, these materials benefit from general MG-properties, such as melt processability and high transparency.

- [1] Y. C. Simon, C. Weder, *J. Mater. Chem.* **2012**, 22, 20830.

Polymers, Colloids & Interfaces

PCI23

Asymmetric functionalization of shape-anisotropic polymer nanoparticles

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In the research of nanoparticles in the last years, much attention has been devoted to the synthesis of anisotropic nanoparticles, also called Janus Nanoparticles. Anisotropy may be provided in different ways, usually either in terms of non-homogeneous surface functionalization, or as compartmentalized internal structure. These special features render the nanoparticles much more interesting than their isotropic counterparts, especially regarding their self-assembling properties. In this work, a two-step emulsion based polymerization has been applied to synthesize shape-anisotropic dumbbell nanoparticles, which size and morphology can be tuned by changing the process parameters.

Narrowly distributed surfactant-free polystyrene nanoparticles are used as seeds. They are coated with a random copolymer of styrene and 3-trimethyl-oxysilyl propyl acrylate (MPS), bringing silane groups on the surface of the seeds. The particles are then swollen with a monomer solution before a second polymerization. Due to the hydrophilic shell on the surface of the nanoparticles, the newly formed polymer is bulging out of the seeds, giving birth to dumbbell-like nanoparticles. The resulting nanoparticles are not only anisotropic in shape, but also in term of surface chemistry. The first bulb is bearing silane groups coming from the MPS, while the second is only made of polystyrene. This specific feature can be used to further asymmetrically functionalize the dumbbells. Silane chemistry can be applied, which will result in the functionalization of the first hemisphere only. Superparamagnetic iron oxide nanoparticles (SPIONS) can be coated by surfactant having silane group, offering the possibility to attach SPIONS only to one bulge. The same approach could be used for platinum nanocrystals, leading to particles that can be used as Janus nanomotors in H_2O_2 solution.

Polymers, Colloids Interfaces

PCI24

THz Time Domain and Transient Absorption Spectroscopy of Charge Carrier Dynamics in Conjugated Polymers

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Understanding the process of charge generation in polymer:fullerene bulk heterojunction (BHJ) blends is the key to improve the efficiency and the performance of organic solar cells [1]. There is still a lot of debate about the origin of free charges inside the blended materials. According to a simple picture, the exciton after travelling to an interface, undergoes charge separation to a Coulomb bound charge-transfer state which relaxes in 100 fs to its lowest vibrational level. After a time scale of 5 ns the bound charges can geminately recombine or completely separate to the polymer and fullerene phases². Recently a more complex mechanism has been experimentally proven: the free charges are created after exciton quenching in a time shorter than 100 fs from hot delocalized charge transfer states before relaxation [2], [3]. The charge separation happens in a mixed phase where the polymer and the fullerene are not pure and completely separated [4]. We use transient absorption spectroscopy in order to gain more insight to the dynamics of charged and neutral excited states and THz time domain spectroscopy to have more information on the lifetime of generated charge carriers and on recombination dynamics. In particular, we studied thin films of neat and blended (with fullerene) conjugated donor-acceptor copolymers: PBDTPD, PBTTT, PBDTPD:PCBM, PBTTT:PCBM changing the excitation wavelength and the laser intensity.

- [1] S. H. Park et al., *Nat. Photonics* (2009), **3**, 297
 [2] Ian A. Howard et al., *J. Am. Chem. Soc.* (2010), **132**, 14866
 [3] A. A. Bakulin et al., *Science* (2012), **335**, 1340
 [4] F. C. Jamieson et al., *Chem. Sci.* (2012), **3**, 485

Polymers, Colloids Interfaces

PCI25

Simulations of Breakage and Restructuring of Colloidal Aggregates in the Presence of Repulsive Interactions

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Understanding the effect of interactions on the breakage of colloidal clusters is of crucial importance to better design nanoparticles re-dispersion and coagulation processes. In this work the breakage and restructuring of colloidal aggregates under shear were analyzed by means of Stokesian Dynamics simulation. A library of clusters made of identical spherical particles covering a broad range of masses and fractal dimension values (from 1.8 to 3) have been generated by means of a combination of several Monte-Carlo methods. The hydrodynamic interactions among the particles have been accounted for by Stokesian Dynamics. DLVO theory has been used to describe the interparticle interactions, while contact forces, described by means of discrete element method, have been included to provide the clusters with realistic structural rigidity. The aggregates breakage process was investigated by exposing them into a well-defined shear forces, generated under both simple shear conditions and elongational flow. To investigate the evolution of aggregate size and morphology, respectively, the mean radius of gyration and the cluster fractal dimension were monitored during the breakup process [1]. Considerable attention has been given to understand the effect of electrostatic repulsive interactions on both the breakage rate and restructuring of the aggregates. It has been found that the presence of repulsive interactions strongly enhances the breakage rate of clusters. A simplified semi-empirical equation has been proposed to account for this effect.

[1] Y.M. Harshe, M. Lattuada, *Langmuir*, **2012**, *28*, 283.

Polymers, Colloids Interfaces

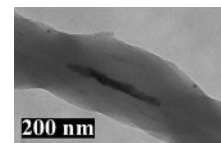
PCI26

Inorganic transcription of organic fibers for hollow silica structures

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In this work we report the fabrication of tubular silica structures via transcription of organic self-assemblies. Anionic surfactant-templated route has been widely used for fabrication of rod-like mesoporous silica with chiral helical channels using positively charged organosilane as co-structuring directing agent [1]. From another point of view, organic material self-assemblies can be used as a scaffold for introducing special shape, porosity and functionality into inorganic structures [2]. We observed the formation of organic fibers in a mixed solution of L-Arginine and C₁₄-L-AlaA anionic surfactant. By adding BTEE (Bis-triethoxysilyl-ethylene) as a silica precursor and TMAPS (N-Trimethoxysilylpropyl-N,N,N-trimethylammonium chloride) as a co-structuring directing agent, we solidified the fibers inside silica structures besides formation of helical channels at their surface. The shapes and sizes of the silica structures and the hollow parts were very sensitive to the syntheses' parameters such as pH, gel aging time and stirring rate.



TEM image of a calcined SiO₂ structure; the hollow part and surface channels are partially filled with gold.

[1] X. Wu, J. Ruan, T. Ohsuna, O. Terasaki, and S. Che, *Chem. Mater.*, **2007**, *19*, 1577.

[2] Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, S. Shinkai, M. Sano, and J. Hojo, *Chem. Commun.*, **1998**, *0*, 1477.

Polymers, Colloids Interfaces

PCI27

Natural channel protein inserts and functions in an artificial, solid-supported bilayer membrane

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Lipid cell membranes selectively control the transport by their specific proteins; however, insertion of such proteins has never been achieved in a stable, solid-supported artificial membrane [1]. Although an amphiphilic block copolymer is a relatively stable substitute for a lipid, and there were successful incorporations of membrane proteins in polymer vesicles and free-standing membranes, they lack the desired stability for extended study or practical applications [2][3]. We show the first, preliminary model of a channel protein that is incorporated in a much more stable polymer, tethered, solid-supported bilayer membrane (TSSBM). A variation in electrical conductance during protein insertion and atomic force microscopy (AFM) images together established the unequivocal functional incorporation of membrane proteins in a polymer TSSBM. For the unique variation in conductance in a TSSBM, a model describing channel protein mediated ion transport was introduced. This protein-inserted polymer TSSBM will serve as a promise tool for biological studies and applications.

[1] K. Murata, K. Mitsuoka, T. Hirai, T. Walz, P. Agrek, J. B. Heymann, A. Enge, Y. Fujiyoshi, *Nature* **2000**, *407*, 599.

[2] W. Meier, C. Nardin, M. Winterhalter, *Angew Chem Int Edit* **2000**, *39*, 4599.

[3] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, *Proc. Natl. Acad. Sci. U. S. A.* **2000**, *104*, 20719.

Polymers, Colloids Interfaces

PCI28

Preparation of novel composite materials via CO-Coagulation of NPs

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Since the term 'nanocomposites' has been proposed for the first time by Theng in 1970, the science dealing with these materials has arisen at the border of different areas of knowledge.

Numerous procedures for the preparation of nanocomposite materials have been investigated in order to generate materials with controlled features, which is still one of the great challenges in nanotechnology.

The purpose of this work is to use the extended and large knowledge of self-assembly behavior of spherical nanoparticles and its dependence on interparticle interactions, developed in the last few decades, for the preparation of various polymeric nanoparticles and the investigation of their self-assembly, to generate hybrid nanostructured composites.

Immiscible compounds with different properties have been co-coagulated at nanometer scale to obtain a final material with improved mechanical properties. Heterocoagulation of large and small oppositely charged colloid particles, accompanied by spreading of small beads over the surface of large spheres, has been chosen as assembly process, since it represents a promising strategy for the achievement of a uniform distribution of the components in the final material. The technique was thus applied to the synthesis of core-shell clusters with a soft rubbery shell and a rigid core. These clusters have then been precipitated and subsequently annealed, giving rise to a nanostructured polymeric composite.

Playing with size and nature of filled and filler compound it is thus possible to test the impact resistance improvement in the different cases. This simple technique for the preparation of composite ordered materials can be extended to several different kinds of nanoparticles.

Polymers, Colloids Interfaces

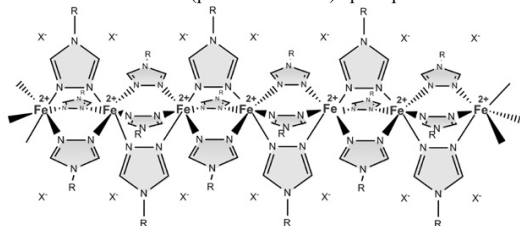
PCI29

Iron(II) triazole spin-crossover polymers in solution

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Spin-crossover, i.e. the change from low to high spin, can arise near room temperature which is of potential use for displays and data storage [1]. Of particular interest are Fe^{II} complexes (Figure), where linearly arranged Fe^{II} ions are bridged by triazole ligands and non-coordinating anions compensate the charge [2]. These complexes show thermochromism (pink → colorless) upon spin-crossover.



We investigated such compounds in different solvents. In solutions of DMF the equilibrium between the coordinated and free ligands was explored in detail revealing that these complexes form polymers also in solution. However, it appears that ligand-to-metal ratios above 3 are required to include all iron atoms in fully developed polymeric structures.

Notably, solutions in toluene showed a dependence of the spin-crossover temperature on the amount of water. As a consequence, while anhydrous solutions were colorless at room temperature, exposure to humidity lead to a color change to pink.

[1] O. Kahn et al., *Science*, **1998**, 279, 44.[2] P. J. van Koningsbruggen et al., *J. Mater. Chem.*, **1997**, 7, 2069.

Polymers, Colloids Interfaces

PCI31

pH responsive PEG-*b*-PMCL-*b*-PDMAEMA triblock copolymers for protein therapy¹Daniela Vasquez; Yves Matter; Cornelia Palivan and Wolfgang MeierDepartment of Chemistry, University of Basel, Klingelbergstrasse 80 CH-4056
Basel, Switzerland

The design of nanocarriers with improved properties in terms of encapsulation efficiency is an important key in modern medicine for drug and gene delivery research. While a considerable number of studies are reporting the self-assembly of amphiphilic diblock, and symmetric triblock copolymers to generate supramolecular nanocarriers, the morphology of these assemblies for asymmetric triblock copolymers has been reported only by very few studies [1]. Here, we present the self-assembly process of asymmetric triblock copolymers PEG-*b*-PMCL-*b*-PDMAEMA in terms of the morphology, encapsulation of proteins, and their stimuli responsive properties. We selected PEG-*b*-PMCL-*b*-PDMAEMA based on their biocompatibility and biodegradability which will support their further medical applications. We analyze the pH- and chain length- effect on the architecture and properties of a library of PEG-*b*-PMCL-*b*-PDMAEMA copolymers by SLS/DLS, TEM and SEM. Different morphologies have been found at different pH values and chain lengths: micelles, worms and vesicles; they change with pH both the aspect and the ratio between different assemblies. The encapsulation/release of Albumin isotiocyanate conjugate of bovine (BSA-FITC) inside/from the polymer supramolecular assemblies can be modulated as a function of pH and chain length. In this respect, our polymer assemblies deliver their content "on demand", which support their further medical applications.

[1] Y. Matter, R. Enea, O. Casse, C. C. Lee, J. Baryza, W. Meier, *Macromolecular Chemistry and Physics*. **2011**, 212 (9), 937.

Polymers, Colloids Interfaces

PCI30

Light-triggered release from responsive amphiphilic conetworksKatrin Schöller^{a,c}, Lukas Baumann^{a,c}, Sabrina Küpfer^a, Damien de Courten^{b,d}, Martin Wolf^b, René M. Rossi^d, Lukas J. Scherer^{a*}^aEmpa, Swiss Federal Laboratories for Materials Science and Technology,
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To avoid apnea, preterm neonates are treated nowadays with caffeine either orally or via infusion. A controlled release and thus a constant up-take of caffeine by the neonates is desired and can be achieved by a transdermal drug-release system with a light-responsive membrane as smart release unit. Here we report the synthesis of a nanophase-separated amphiphilic conetwork where photochromic spirobenzopyran comonomers are entrapped in its hydrophilic domains via copolymerization. The obtained transparent membranes became dark-red after irradiation with UV-light (Fig. 1). Furthermore, the caffeine permeability of an aqueous solution increased up to 40%.

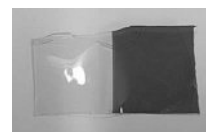


Figure 1. Spirobenzopyran-modified amphiphilic conetwork before (left side, transparent) and after illumination with UV-light (right side, dark red).

Interestingly, a reversed and much more pronounced permeability change (up to 1000%) was found, when the light-responsive amphiphilic conetworks were coated on track-etched polyester membranes via a "grafting through" approach. Due to the easy processing of such membranes, polymerization parameters can be tuned depending on the application.

Polymers, Colloids Interfaces

PCI32

Polymers, Colloids Interfaces

PCI32

Solid-supported planar polymer membranes as the platforms for protein incorporationJustyna Kowal^a, Wolfgang Meier^a^aDepartment of Chemistry, University of Basel, Klingelbergstrasse 80
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Amphiphilic block copolymers are of great interest because they are well suited to mimic biological macromolecular amphiphiles. In contrast to natural phospholipids, amphiphilic block copolymers are characterized by higher mechanical stability, greater thickness and rigidity, while remaining fluid enough to incorporate proteins.

We present a model system based on amphiphilic copolymers used to prepare a solid-supported polymer membrane, as the platform for protein incorporation.¹ Well organized membranes of a diblock copolymer with poly(2-methoxyloxazoline) (PMOXA) as hydrophilic domain, and poly(dimethylsiloxane) (PDMS), as hydrophobic domain were prepared through Langmuir-Blodgett and Langmuir-Schaefer monolayer transfer techniques. Characterization, performed by means of surface analysis tools (AFM, ellipsometry), showed that the obtained membranes were homogeneous, with a thickness of approximately 14 nm.

The incorporation of the potassium channel (MloK1 from *Mesorhizobium loti*) into solid-supported polymer membrane was induced by Bio-Beads method. Successful insertion of the protein was followed by fluorescence microscopy, conductance measurements, as well as by AFM.

[1] Belegriou, S.; Dorn, J.; Kreiter, M.; Kita-Tokarczyk, K.; Sinner, E.-K.; Meier, W. *Soft Matter* **2010**, 6, 179.

Polymers, Colloids Interfaces

PCI33

Poly (N-isopropylacrylamide-co-tris-nitrilotriacetic acid acrylamide) for molecular recognition

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Tris-nitrilotriacetic acid (tris-NTA) exhibits high binding affinity for histidine (His) peptides and His-tagged proteins [1]. Here, a library of functional polymers, poly (N-isopropylacrylamide-co-tris-nitrilotriacetic acid acrylamide)s [poly (Nipam-co-trisNTAam)s] were synthesized and well characterized. These copolymers exhibit pH-dependent thermal-responsive properties. When the pH is above 3, no thermal response was observed. The coordination of Cu^{2+} to the polymers was confirmed and almost 100% Cu^{2+} loading efficiency was observed for the polymers, with each one having a different trisNTA content. The Cu^{2+} -loaded polymers bind with His₆ peptides and His-tagged proteins. The binding stoichiometry of His₆ to Cu^{2+} -loaded trisNTA on copolymers is 1:1. Fast release of the His₆ and His-tagged proteins was achieved by the addition of EDTA or imidazole.

[1] S. Lata, *J. Am. Chem. Soc.* **2005**, 127, 10205.

Polymers, Colloids Interfaces

PCI34

Scaling properties of DNA at high concentrations studied by AFM

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DNA is a very important object of study for geneticists and biologists as well as for physicist. DNA is a polymer that can adopt many different topological conformations starting from linear and circular to supercoiled and knotted form, making it an ideal object to test theories over a wide flexibility range [Fig.1]. It is important to study the role of topology of objects at high concentrations to understand more about processes such as DNA migration in electrophoresis gel or DNA compaction in Viral capsids. Therefore a better experimental and theoretical understanding of basic properties of such systems is highly important [1,2].

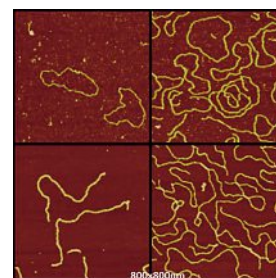


Fig.1 A typical image of 2.7kb DNA in circular and linear forms at low and high concentrations

[1] G. Witz, K. Rechendorff, J. Adamcik and G. Dietler, *Phys. Rev. Lett.* **2008**, 101, 148103.[2] G. Witz, K. Rechendorff, J. Adamcik and G. Dietler, *Phys. Rev. Lett.* **2011**, 106,248301.

Polymers, Colloids Interfaces

PCI35

Protein Nanoreactors and Native Enzymes for Controlled Radical Polymerization in Aqueous Solution

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Atom transfer radical polymerization (ATRP) has emerged as one of the most powerful synthetic techniques in polymer science. Similarly to other controlled radical polymerization (CPR) methods, it allows the synthesis of polymers with predetermined molecular weight, narrow molecular weight distribution, as well as desired composition and molecular architecture.¹ An environmentally friendly alternative to conventional catalysts in many areas of synthetic chemistry are enzymes. However, no natural protein or enzyme was known to be able to catalyse ATRP, despite the fact that Nature offers a wide variety of metal-containing enzymes and proteins. We are studying conjugates of ATRP catalysts and proteins, e.g. in order to confine ATRP to the cavity of a protein cage. We successfully grafted ATRP catalysts into the thermosome (THS), an archaeal chaperonin, and used the resulting conjugates as nanoreactors for ATRP polymerization.² In the course of this project, we discovered that the heme proteins hemoglobin (Hb) and horseradish peroxidase (HRP) catalyse (ARGET) ATRP and termed them ATRPases.³ In a comparison with conventional ATRP, our THS system as well as the ATRPases permit significant reduction in the concentration of residual transition metal catalysts in polymers synthesized by this means.

[1] K. Matyjaszewski, *Macromolecules* **2012** 45, 4015-4039[2] K. Renggli, M. Nussbaumer, N. Bruns, *Polym. Prepr.* **2012** 53, 294-295[3] S. Sigg, F. Seidi, K. Renggli, T. B. Silva, G. Kali, N. Bruns, *Macromol. Rapid Commun.* **2011** 32, 1710-1715

Polymers, Colloids Interfaces

PCI36

Fiber-matrix interface study in supramolecular self-healing based composites

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In 2010 Montarnal et al.[1] combined the chemistry of epoxides with supramolecular chemistry, and thus developed a polymer which network is constituted by both chemical and supramolecular bonds (hydrogen bonds) and which displays a self-healing behavior.

The interaction of these polymers with long fibers (glass fibers) as well as the possibility of achieving self-healing at the matrix-fiber interface has been evaluated by means of pull-out tests and SEM analysis (see Figure 1), using 125µm diameter glass fibers.

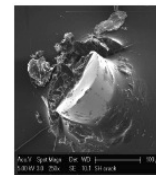


Figure 1: Example of SEM image of glass fiber embedded in the polymeric matrix.

Moreover, several ratios between covalent and supramolecular bonds in the polymer are evaluated, to analyse their influence on the healing behaviour.

[1] D. Montarnal, F. Tournilhac, M. Hidalgo, L. Leibler, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, 48, 1133.

Polymers, Colloids Interfaces

PCI37

Preparation and Characterization of Polymer Blends Based on Polyisobutylene-Oligopeptide Conjugates

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β -sheet-forming oligopeptides can be used to tailor the thermomechanical properties of synthetic elastomers in versatile ways due to their hierarchical structure formation similar to the one observed in structure proteins [1]. We prepared two series of polymer blends of polyisobutylene- and polystyrene-oligopeptide conjugates with an identical number of either two or three alanine residues in the oligopeptides, in which the polyisobutylene (PIB) serves as the soft segment, the polystyrene (PS) serves as an incompatible glassy reinforcement, and the monodisperse, chiral, and β -sheet-forming oligopeptides Ala_n from both molecules provide the possibility to co-assemble at the interface of the PIB/PS domains. The properties of these two series of polymer blends, such as the secondary structure formation in the solid state and in organic solvent, thermal properties, morphologies, as well as rheological properties were investigated. Moreover, the polymer blends with three alanine residues were systematically compared to the polymer blends of PIB-Ala₃-Ac and PS amine by rheological tests. Both the storage and loss modulus of the polymer blends increased when the oligopeptide segments were present in the PS-based additives.

[1] E. Croisier, S. Liang, T. Schweizer, J. Cugnoni, V. Michaud, H. Frauenrath, **2013**, manuscript in preparation.

Polymers, Colloids Interfaces

PCI38

Stiffness Evaluation of Cell-Adhesive Polymer Brushes by Atomic Force MicroscopySolenne Desseaux¹, Kislou Voitchovsky², Harm-Anton Klok¹¹Polymers Laboratory, ²Supramolecular Nanomaterials and Interfaces Laboratory, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

This poster reports the preparation of non fouling polymer brushes functionalized with RGD and their analysis by Atomic Force Microscopy in order to determine their stiffness. The cell adhesive platform is made of polymer brushes of 2-hydroxyethylmethacrylate (HEMA) and poly(ethylene glycol) methacrylate (PEGMA) functionalized with a peptide containing the RGD (arginine-glycine-aspartic acid) sequence. HEMA and PEGMA are monomers known for their non fouling properties while the RGD peptide was immobilized on the brushes to promote cell adhesion due to the specific binding of the integrin receptors of the cells.^[1] Atomic Force Microscopy was employed to measure the Young Modulus of these polymer brushes through indentation experiments, and compare their respective stiffness. Brushes functionalized with RGD and non modified brushes were analyzed. It was found that the post-modification step has a significant effect on the stiffness of the brushes. We also studied the influence of the thickness of the brush layer on the stiffness of the coating using polymer brushes of various thicknesses. Finally cells were seeded on the cell adhesive platform and their proliferation and behavior on each type of polymer brush coating was observed by immunofluorescence.

[1] Tugulu, S. *et al.*, *Biomaterials* **2007**, 28, 2536–2546

Polymers, Colloids Interfaces

PCI39

Inverse Miniemulsion Radical Polymerization as a Facile Method for the Synthesis of Stimuli-Responsive Nanogels at Room Temperature

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Inverse miniemulsion radical polymerization is extensively used in the preparation of polymeric micro- and nanogels [1]. In this type of synthesis, monomers, crosslinkers and initiator are dissolved in aqueous phase, which is in turn dispersed in organic phase, forming nanosized droplets stabilized by the surfactant and lyophobic. Polymerization proceeds within each droplet thus allowing the final nanoparticle to be direct replica of the initial droplet in size and chemical composition.

Nanogels based on poly(N-(2-hydroxypropyl) methacrylamide) and poly(N-isopropylacrylamide), PHPMA and PNIPAM, respectively, were synthesized with help of inverse miniemulsion radical polymerization. The synthesis, driven by redox initiator, ammonium persulfate / tetramethylethylenediamine, was finished within 30 min at room temperature. The final nanogels were supremely water-dispersible and had uniform size and distribution, with size strongly dependent on the parameters of inverse emulsion, especially water-to-oil ratio. The developed method is advantageous over higher temperature inverse miniemulsion polymerization of PHPMA and precipitation polymerization of PNIPAM, as it allows the direct in-situ incorporation of protein / growth factor molecules without damaging their structure. Paired with the temperature-sensitive properties of PNIPAM (which can be varied with help of co-monomer, e.g. PEGMA) and stimuli-responsive properties of crosslinkers (e.g. N,N'-Bis(acryloyl)cystamine), we get fast and facile method for the synthesis of stimuli-responsive nanocontainers for the delivery of biological molecules.

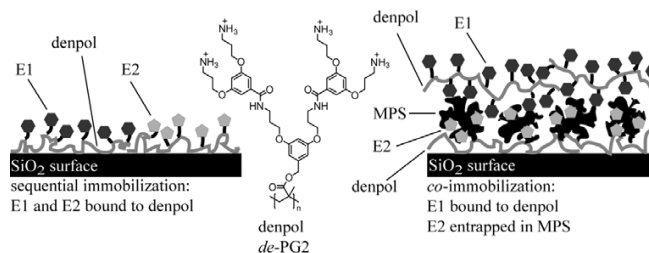
[1] I. Capek, *Adv. Colloid Interface Sci.* **2010**, 156, 35.

Polymers, Colloids Interfaces

PCI40

Enzyme immobilization with a dendronized polymer for surface-localized cascade reactionsAndreas Küchler¹, Hanna Gustafsson², A. Dieter Schlüter¹, Krister Holmberg², Peter Walde¹¹Polymer Chemistry, Department of Materials, ETH Zürich, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland²Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

The second generation dendronized polymer (denpol) *de*-PG2 has been used successfully for the immobilization of enzymes on SiO₂ surfaces through the biotin-avidin linker system, thereby allowing the *sequential immobilization* of two different types of enzymes (E1 and E2) for catalyzing a cascade reaction [1, 2]. With the same denpol and with mesoporous silica (MPS) particles, spatially controlled *co-immobilization* of enzymes is possible. In both cases, strong adherence of the denpol to the silicate is crucial.



[1] S. Fornera, T. Bauer, A. D. Schlüter, P. Walde, *J. Mater. Chem.* **2012**, 22, 502.

[2] S. Fornera, P. Kuhn, D. Lombardi, A. D. Schlüter, P. S. Dittrich, P. Walde, *ChemPlusChem* **2012**, 77, 98.

Polymers, Colloids Interfaces

PCI41

MOLECULAR ORDERING OF IONIC LIQUIDS AT SOLID INTERFACES

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Ionic liquids (ILs) are salts naturally liquid at room temperatures. We have studied the ordering of several ILs in contact with different surfaces using the Atomic Force Microscopy. Both the IL layers in close contact with the surface and the subsequent layers have been studied [1].

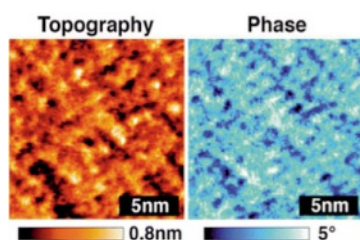


Figure 1: Imaging of superficial IL layer at the surface of mica. The image was achieved in amplitude modulation using a particularly soft cantilever.

The effect of an electrical perturbation on the ordering of these ILs has also been studied using both external electric fields and ferroelectric surfaces.

[1] Segura, J. J.; Elbourne, A.; Wanless, E. et al. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3320.

Polymers, Colloids Interfaces

PCI42

Chitin nanowhisker derivatives for drug delivery system applications

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Chitin is a renewable and abundant natural resource, with a marine production of at least 2.3 million metric tons per year [1], therefore practical applications of chitin are desired to multiply and improve. The present study applies and evaluates different published procedures regarding the derivatization of chitin in order to develop a drug delivery system. The goal was to introduce two functionalities on the chitin structure, one to bind the drug and the second to bind an arginine-rich peptide residue, with the purpose of enhancing membrane and skin permeation [2]. The first step was a partial deacetylation of chitin [3], which generated surface charges in order to facilitate the individualization of chitin nanowhiskers. The final compound had peptide arms for better membrane and skin permeation as well as carboxyl groups available as sites for drug binding. Our current efforts focus on the optimization of the synthesis and the use of artificial membranes for testing the membrane permeation as function of the nanowhisker size. The conclusions from the experiments will determine the final synthesis strategy.

- [1] C. Jeuniaux, M.F. Voss-Foucart, *Biochem. Syst. Ecol.* **1991**, *19*(5), 347
 [2] B. Rothbard, S. Garlington, Q. Lin, T. Kirschberg, E. Kreider, P.L. McGrane, P.A. Wender, P.A. Khavari, *Nat. Med.* **2000**, *6*(11), 1253
 [3] Y. Fan, T. Saito, A. Isogai, *Carbohydr. Polym.* **2010**, *79*, 1046

Acknowledgement: We acknowledge the financial support of Sciex-NMS grant 12.072.

Polymers, Colloids Interfaces

PCI43

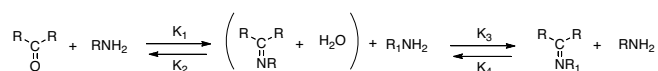
Dynamic Libraries for the synthesis of new combinatorial materials

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Combinatorial materials science offers an exciting experimental strategy for rapidly surveying a wide array of materials chemistries in order to process variables coupled to the screening of structure and properties. Adapting approaches used in synthetic organic chemistry for applications such as pharmaceutical sciences and chemical discovery, materials scientists have developed a variety of approaches to create libraries in the solid state in order to rapidly examine a broad range of materials characteristics; the ultimate hope is to accelerate the discovery of new materials and/or new materials properties[1].

Here we present a set of new dynamic silica nanoparticles synthesized using different dynamic libraries having as common feature the possibility to form a reversible iminic bond. We investigate the assemble/disassemble/exchange of the libraries and their dynamic arrangement on the surface.



[1] Rajan, K., *Annu. Rev. Mater. Res.* **2008**, *38*, 299.

Polymers, Colloids Interfaces

PCI44

Functional surfaces through biomimetic block copolymer membranes

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¹University of Basel, Department of Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

²Université de Genève, Département de Chimie Physique, 30 Quai Ernest Ansermet, CH-1211 Genève 4

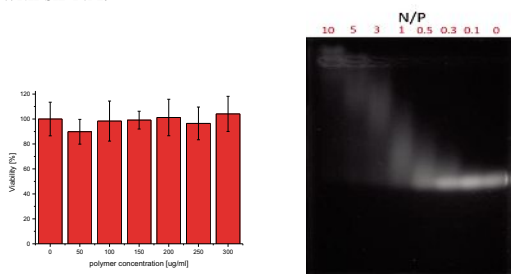
The functionalization of surfaces using biomimetic block copolymer membranes aims at developing smart surfaces for biotechnological applications such as biosensing. Instead of lipid membranes, amphiphilic block copolymer membranes were chosen as mimics of biological membranes due to properties such as 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. ABA-triblock copolymer membranes were successfully prepared and characterized by using two synthesis strategies: the “grafting-from” approach with surface-initiated ATRP from gold supports, and the “grafting-to” approach with Langmuir-Blodgett transfer on germanium supports. Protein insertion experiments were performed by using impedance spectroscopy for gold surfaces and by in-situ ATR-FTIR for germanium surfaces. Results with in-situ ATR-FTIR show the presence of the protein on the polymeric membrane. 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 Interfaces

PCI45

siRNA delivery system based on diblock polymer PMOXA-PBLAD.L.Wu, P. Baumann, M. Nussbaumer, C. G.Palivan,
W.P.MeierPhysical Chemistry Department, University of Basel, Klingelbergstrasse 80,
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siRNA is ideal candidate for treatment of gene deficiency, due to its ability to efficiently silence specific genes by the mechanism of RNA interference. However, there are various limitations for a direct administration of siRNA, such as impossibility to penetrate cell membrane and low stability. An alternative to support siRNA uptake is to use polyion complexes formed by siRNA and oppositely charged polycations^{1, 2}. Here, we synthesize PMOXA-*block*-PBLA (poly(2-methyl-2-oxazoline)-*b*-poly(γ -Benzyl-L-Aspartic Acid)) first, in order to obtain an effective polycations for delivery of siRNA, the polycations PMOXA-*block*-Pasp(DET) are obtained and characterized by NMR and GPC after chemical modification. The cell toxicity proves that polycations are not toxic and electrophoresis proves they complex with siRNA.

[1] Kensuke Osada, *Adv Polym Sci.* **2006**, 202, 113.[2] Hiroyasu Takemoto, *Biomaterials.* **2010**, 31, 8097.

Polymers, Colloids Interfaces

PCI46

Surface forces across ionic liquids: an atomic force microscopy study

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Ionic liquids (ILs) are pure salts with melting point below 100°C. During the past years they attracted considerable interest among the scientific community on account of their unique physico chemical properties (i.e. low flammability and vapor pressure, high thermal and chemical stability) and their “tuneability”, the ability to tune them through systematic variation of cation’s and anion’s structure and combination [1].

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

Silica and latex particles of different diameter (3-10 µm) have been employed to study colloidal behavior in different ionic liquids and ionic liquids-water mixtures, in order to elucidate an eventual structure dependent behavior. In pure ionic liquid step-like force profiles are detected, showing layering of IL’s molecules on the surface.

[1] K. Ueno, H. Tokuda and M. Watanabe, *Phys. Chem. Chem. Phys.*, **2010**, 12, 1649-58[2] W. A. Duker, T. J. Senden, R. M. Pashley, *Nature*, **1991**, 353, 239-41[3] I. Popa, P. Sinha, M. Finessi, P. Maroni, G. Papastavrou, M. Borkovec, *Phys. Rev. Lett.*, **2010**, 104, 228301-4

Polymers, Colloids Interfaces

PCI47

Aggregation of colloidal particles induced by metal ions of different valence

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The stability of colloidal suspensions plays an important role in many industrial processes e.g. paper, paint and cosmetics industry. It is well-known that ions of higher valence adsorb on oppositely charged surfaces, which changes their charging properties in significant way [1]. In the present work the aggregation of a negatively charged colloidal particle was investigated in the presence of inorganic salts containing metal ions of different valence. Electrophoretic mobility (EM) and time-resolved dynamic light scattering (DLS) measurements were performed.

To prevent the hydrolysis of metal ions and to provide sufficient charge on the particles, the pH was adjusted to 4.0 in all measurements. From the EM measurements one can see that, monovalent ions (NaCl, KCl, CsCl) screen the charge of the particle, the di- (MgCl₂, CaCl₂, BaCl₂) and trivalent (LaCl₃, [Co(NH₃)₆]Cl₃, [Ru(NH₃)₆]Cl₃) ions neutralize the surface at the isoelectric point (IEP), while in the case of ZrCl₄ the counterion can overcharge the surface at a certain concentration. The DLS results are in good agreement with the DLVO theory. Close to the IEP due to the neutral particles and the dominating van der Waals forces all suspensions are unstable, while away from the IEP due to the repulsive electric double-layer forces the stabilities increase. Increasing the valence of the counterions the critical coagulation concentrations, which separates the fast and the slow aggregation regimes, decrease.

[1] I. Szilágyi, A. Sadeghpour, M. Borkovec, *Langmuir*, **2012**, 28(15), 6211-5

Polymers, Colloids Interfaces

PCI48

Specific artificial organelles detoxify superoxide radicals in cells

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Basel, Switzerland

Cell dysfunctions play an important role in many diseases, such as Parkinson’s disease, arthritis, cancer, and many more. Therefore, a major goal in medical research is to repair cell dysfunction directly at the source of origin. A promising strategy to efficiently lower cell dysfunctions is achieved by the development of artificial organelles inspired from cell organelles that implant in cells as cell implants to treat pathological conditions or to add new functionalities to cells. Several attempts have been made to encapsulate or entrap enzymes, proteins or mimics in polymer compartments, but only a few of these claimed artificial organelles were active in cells and none was proven to mimic a specific, natural organelle. We show that an artificial organelle comprising two kinds of enzymes that work in tandem in a polymer vesicle, with a membrane rendered permeable by inserted channel proteins, mimics a specific natural organelle. Uptake, absence of toxicity, and in situ activity in cells exposed to oxidative stress demonstrated that this artificial organelle efficiently detoxified superoxide radicals and H₂O₂ after endosomal escape. In conclusion, the feasibility of this system opens a new frontier in future medicine to develop other “cell implants” for cell dysfunction.

Polymers, Colloids Interfaces

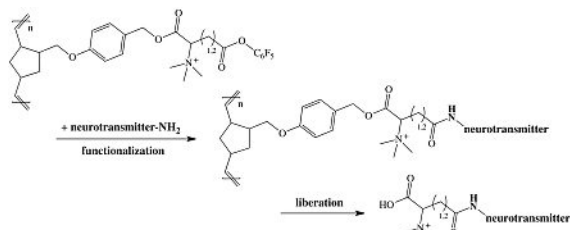
PCI49

Multifunctional Polymers for the Analysis of Brain Neurotransmitters

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A robust synthetic technique that will allow for multiple orthogonal post-polymerization modifications of highly functionalized copolymers, synthesized via living Ring-Opening Metathesis Polymerization (ROMP), has been developed in our group.¹ Taking advantage of this model, a functional polymeric resin can be used to purify and quantify mono-amine neurotransmitters contained in e.g. microdialysis samples of animal brains.



Compared to the functionalization with reactive small molecules,² a sample containing various amines can now be bound to the polymeric resin, an excess of non-reactive sample be washed away, and the amines cleaved off as a purified and concentrated sample. Additionally, the quaternary ammonium group contained in the spacer unit acts as a sensitizer for subsequent mass spectrometric analysis, giving access to the quantification of neurotransmitter concentrations in the original sample.

- [1] M. Schäfer, N. Hanik, A. F. M. Kilbinger, *Macromolecules* **2012**, *45*, 6807.
 [2] P. Song, O. S. Mabrouk, N. D. Hershey, R. T. Kennedy, *Anal. Chem.* **2012**, *84*, 412.

Polymers, Colloids Interfaces

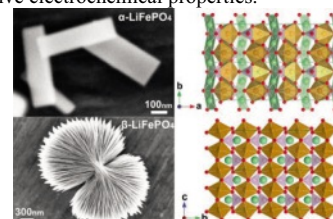
PCI50

Tailoring Two Polymorphs of LiFePO₄ by Efficient Microwave-assisted Synthesis for High-power Li-ion Batteries

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ETH Zurich, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

LiFePO₄, which has been extensively studied as a cathode material for power batteries in electric vehicles, typically crystallizes in the olivine-like phase (α -phase hereafter). When high pressure (65,000 bar) and elevated temperature (900 °C) is applied, α -LiFePO₄ transforms into high-pressure phase (β -phase hereafter) which, however, has been rarely considered because of its inactive electrochemical properties.



Here we report a facile approach to directly fabricating two polymorphs of LiFePO₄ under mild conditions. Employing microwave-assisted non-aqueous route, highly crystalline LiFePO₄ with either α - or β - phase can be efficiently synthesized within 3 minutes. Interestingly, without any templates or surfactants, the resulting LiFePO₄ presents various morphologies. Among all, hierarchical self-assembled bow tie-like microstructure is most appealing since it provides a cathode with novel structure (*i.e.* micro assembly composed of nanoparticles with open porous three dimensional structure) which is believed to be ideal for high-performance LIBs.

- [1] Carriazo, D.; Rossell, M. D.; Zeng, G. B.; Bilecka, I.; Emi, R.; Niederberger, M. *Small* **2012**, *8*, 2231

Polymers

PCI51

Monte Carlo simulations of polymers in confined geometriesMalinverni Duccio¹, De Los Rios Paolo¹

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 École Polytechnique Fédérale de Lausanne, EPFL
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Polymers in confined geometries are of growing interest in the fields of biophysics, physical chemistry, as well as in theoretical physics. Classical algorithms for sampling of long linear chain conformations in the canonical ensemble [2,3] break down in the limit of high-confined geometries, due to their prohibitively large rejection rates caused by the confinement [4].

We present a new algorithm, based on a decomposition of the trial moves according to the symmetry of the confining geometry, which allows a zero-rejection rate with respect to confinement. The main gain is a great decrease in correlation times of the Markov chain, which allow an efficient sampling of long chains in high confinement regime. Our current implementation allows off-lattice simulations of semi-flexible polymers subject to self-avoidance in D-slabs, and ongoing work is done to adapt the method to further geometries.

Preliminary results of semi-flexible DNA like polymers are presented, namely scaling behaviors in the Odjick regime for slab confinements, for varying persistence lengths and confinement scales. DNA chains ($l_p \approx 50\text{nm}$, $\varnothing \approx 2\text{nm}$) of lengths of up to 30 μm , consisting of up to 5000 cylindrical monomers can be simulated in different confinement setups.

- [1] Hsu H-P., Grassberger P., *J. Stat. Phys* **2011**, *144*
 [2] Kennedy T., *J. Stat. Phys* **2002**, *106*
 [3] Madras N., Sokal A.d., *J. Stat. Phys* **1987**, *50*
 [4] Micheletti C., et al., *Phys. Reports* **2011**, *504*
 [5] Reisner W., Pedersen J., Austin H., *Rep. Progress in Phys.* **2012**, *75*

Polymers, Colloids Interfaces

PCI52

Absolute aggregation rates of latex particles in ionic liquid / water binary mixtures

Désert A., Szabó T., Trefalt, G., Szilágyi I., Borkovec M.

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These last years, ionic liquids (ILs) – organic salts which are liquid at temperatures below 100°C – know a considerable academic and industrial development due to their very interesting properties (negligible vapor pressure, non-flammability, high thermal and chemical stability, etc.). Moreover many properties could be easily tuned through the choice of cation/anion pairs (especially the hydrophilic/hydrophobic balance) and by associating ILs with another solvent (like water to decrease viscosity and enhance conductivity). ILs could not only substitute volatile organic compounds in catalytic reactions, separations and extractions, but also be used in electrochemical devices (battery, fuel cells) or in other materials science purposes.

Because little is known concerning interactions between interfaces and ILs, nevertheless crucial for many applications, the present work proposes to provide answer elements by studying the colloidal stability of latex particles in binary mixtures of ILs/water using light scattering techniques. We focus on water-miscible and room temperature ILs with cations such as 1-butyl-3-methylimidazolium or 1-butylpyridinium, and anions such as dicyanamide or thiocyanate. To start, we have measured physical properties (density, refractive index and viscosity) of the ILs/H₂O mixtures on the entire concentration range. Then, aggregation rates of positive amidine and negative sulfate latex particles are measured by light scattering. First results show several phenomena: (i) low IL concentrations affect latex stability like a salt by screening charges up to reach a fast aggregation regime, (ii) then aggregation rates decrease with the IL amount but this apparent stabilization is simply due to a viscosity effect, (iii) and for some ILs, still taking account of the viscosity increase, particle stabilization can be finally observed at high IL concentrations.

Polymers, Colloids Interfaces

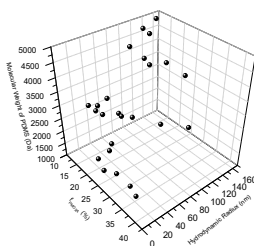
PCI53

Self-assembling behaviour of diblock PDMS-PMOXA polymers: structure influence

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Physical Chemistry Department, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Understanding the structural aspects that determine the self-assembly behavior of amphiphilic block copolymers is important, for generation of supramolecular assemblies with a desired architecture, specific for the intended applications. To the best of our knowledge, the relationship between the morphologies of supramolecular assemblies formed by self-assembly of amphiphilic copolymers structures and the molecular weight of both hydrophobic and hydrophilic block and their ratio has not been investigated. We synthesized a library of diblock poly(dimethylsiloxane)-*block*-poly(2-methyl-2-oxazoline) copolymers (PDMS-*b*-PMOXA) with various lengths of the hydrophilic and hydrophobic blocks. Various supramolecular assemblies (micelles, vesicles, worms or combination of them) have been obtained as function of the hydrophilic or hydrophobic block lengths investigated by light scattering and TEM. In addition, spin probe EPR provides new details regarding the structure of polymer membrane of vesicles.

[1] R.Hoogenboom, *Angew. Chem. Int. Ed.* **2009**, 48, 7978.

Polymers, Colloids & Interfaces

PCI54

Impact of glass transition on crystallization process of charged colloids

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We explore the phase behaviour of charged microgels at quasi-deionized conditions. At these conditions the microgels interact by long-range screened Coulomb interactions, which triggers the formation of crystalline phases over a large range of particle volume fractions.



Illustration 1: A set of samples characterized by increasing volume fractions (from left to right: 3.8%, 5.7%, 11%, 15%, 21%, 27%, 30% and 34%). Presence of a crystalline phase is evidenced by the iridescence.

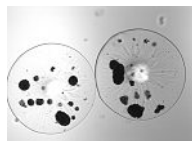
However, an increase in particle concentration also entails that the initial amorphous state, from which crystallization needs to arise, becomes increasingly frustrated. We investigate how both structural relaxation and elasticity of the amorphous phase impacts the crystal formation.

Polymers, Colloids Interfaces

PCI55

Development of new alginate-based Materials for Islets MicroencapsulationBorcard Françoise¹, Redouan Mahou¹, Elisa Montanari², Christine Wandrey¹¹SV-IBI-LMRP EPFL, CH-1015 Lausanne, ²Geneva University Hospital, CH-1211 Geneva

Alginate is a natural abundant polysaccharides showing high potential in medical uses for its ability to form hydrogel at mild pH and temperature and for its biocompatibility [1]. However, alginate polymers suffer from a lack of mechanical properties for long-term *in vivo* applications. In the present project, we propose to chemically modify alginate biopolymers [2] to improve its mechanical properties for the microencapsulation of Langerhans islets used in the treatment of diabete I.



Our goal is to covalently functionalize the alginate polymer with a poly(ethylene glycol) chain allowing the formation of a physical hydrogel and an additional chemical cross-linking increasing the physical stability of the capsules. Here the chemical synthesis of the modified alginate, the physical characterization of the polymers and finally the preliminary biological assays with islets are presented.

[1] Pawar, S. N.; Edgar J. K. *Biomaterials*, **2012**, 33, 3279-3305.[2] Mahou, R; Wandrey C. *Polymers*. **2012**, 4, 561-589.

Acknowledgement: We thank the commission of technology and innovation for the financial support.

Polymers, Colloids Interfaces

PCI56

Peptidic multicompartement micelles as a versatile carrier system

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Carrier systems are gaining more and more importance in the field of nanomaterials and medicine. To prevent drugs and prodrugs from degradation and to enable the delivery of fragile and insoluble substances sophisticated carrier systems are necessary. Polypeptides are promising candidates not only due to the well defined structure allowing selective functionalization but also because of the variety of their self-assemblies.¹ The use of short, purely peptidic amphiphiles to form multicompartement micelles, named peptide beads, is beneficial in several aspects. On the one hand the similar volume for both hydrophilic and hydrophobic payloads allows co-delivery. On the other hand they are biocompatible and biodegradable, a prerequisite for any advanced carrier system. Recently, we presented the incorporation of rose bengal and 5-carboxy-fluorescein into peptide beads.² As a further step towards a multifunctional and versatile co-delivery system, dyes of various hydrophobicities were embedded, namely: bodipy, dylight 488 and sulforhodamin B. We also successfully loaded the peptide beads with topotecan, an anti-cancer drug. Finally, we demonstrated the robust self-assembly properties of these peptides by embedding nanoscaled gold particles. The results showed highly ordered hierarchical superstructures, whereas the individual gold nanoparticles remain separated from each other by a thin peptide layer.³

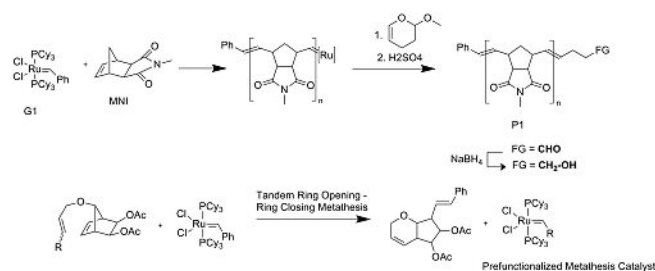
[1] W. Hamley, *Soft Matter* **2011**, 7, 4122.[2] C. Dittrich and W. Meier, *Macromol. Biosci.* **2010**, 10, 1406.[3] D. de Bruyn Ouboter, T. Schuster, S. Sigg and W. Meier, *submitted 2013*.

New Approaches Towards Telechelic Polymers by Ring Opening Metathesis Polymerization

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A new terminating agent for functional termination of ROMP polymers is reported. This new terminating agent provides an easy access to aldehyde and alcohol end functional polymers. We also demonstrate a highly effective tandem ring opening - ring closing metathesis strategy for the synthesis of new prefunctionalized metathesis catalysts in an atom economical reaction. Such new catalysts carrying various functional groups can further be used along with suitable terminating agents to synthesize heterotelechelic polymers in a straightforward manner leading to very high degree of end functionalities.



Scheme 1 : (top) Functional termination of ROMP polymers. (bottom) Tandem ring opening - ring closing metathesis strategy

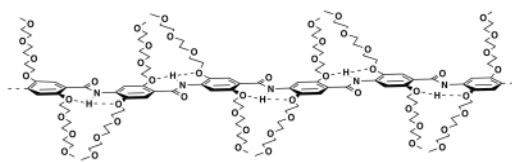
- [1] (a) Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M. *J. Am. Chem. Soc.* **2008**, *130*, 11040 (b) Kim, H.-S.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801. (c) Niethé, A.; Fischer, D.; Blechert, S. *J. Org. Chem.* **2008**, *73*, 3088.

Bis-TEGylated oligo- and polybenzamidés: Organo-soluble and shape-persistent building blocks for the assembly of supramolecules

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We present the polycondensation of perfectly planar, bis-substituted aromatic polyamides. With highly flexible triethylene glycol chains attached and conformational restriction through intramolecular, bifurcated hydrogen bonds these are- to our knowledge- the most shape-persistent yet organo-soluble polymers to date. Their tendency to aggregate could be proved in the dried state by Transmission Electron Microscopy (TEM). However, aggregation through aromatic interactions is prevented in solution as shown by Dynamic Light Scattering (DLS). With their unique features these rigid rods serve as well-suited candidates for the assembly of nanoscopic objects of different geometries, among these large tubular helices.



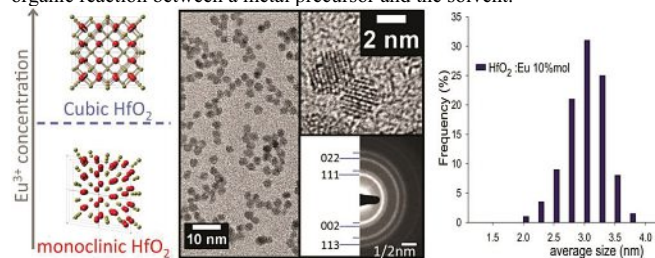
- [1] T. Yokozawa, T. Asai, R. Sugi, S. Ishigooka, S. Hiraoka, *J. Am. Chem. Soc.* **2000**, *122*, 8313.
[2] M. Schulze, B. Michen, A. Fink, A. F. M. Kilbinger, "Combining organo-solubility with shape-persistence: Bis-TEGylated poly(*p*-benzamide)s" **2013**, submitted.

Nonaqueous synthesis of cubic HfO₂ nano-phosphors: structural modification through Eu³⁺ incorporation.

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Nonaqueous routes to metal oxides are a valuable alternative to other "wet" methods where the formation of inorganic nanoparticles is promoted by an organic reaction between a metal precursor and the solvent.¹



Reacting Hf alkoxide with benzyl alcohol led to colloidal suspensions of crystalline HfO₂ with an average size of 3 nm. The doping with Eu ions was adopted to activate its red luminescence, stimulated both by UV light and X-rays. We investigated the structural modification occurring depending on the rare earth concentration in these nano-phosphors, i.e. the room temperature stabilization of cubic hafnia. The optical properties of the nano-powders have been investigated by radio- and photo-luminescence experiments, where specific features of Eu³⁺ luminescence sensitive to local crystal field have been employed for probing lattice modifications at the atomic scale.

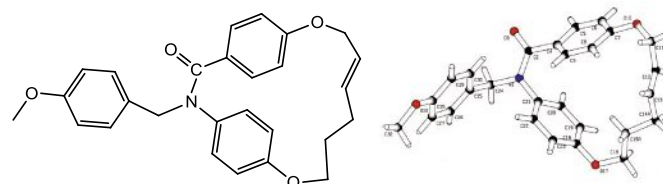
- [1] Niederberger M. and Garnweitner G., *Chem. Eur. J.* **2006**, *12*, 7282.

Olefinic Aramide Macrocycles for Ring-Opening Metathesis Polymerization of Aromatic Polyamides

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Due to mechanical properties and difficulties in processing, improvement of synthetic routes of aromatic polyamides is an important topic nowadays. Conventional polycondensation methods could be replaced with Ring-Opening Metathesis Polymerization (ROMP)^[1] to obtain polymers with high molecular weight and narrow polydispersity and even block copolymers. The geometry of the amide bonds in the monomer unit must be controlled and fixed to *cis*-conformation to allow the ring closing to obtain the cyclic monomer. The *p*-methoxybenzyl (PMB) protecting group is a suitable option for this synthesis since it can be easily removed under acidic conditions. The unprotected cyclic amide will isomerize to the *trans*-conformer thereby inducing a ring strain needed to perform ROMP. This property can be used to prepare macrostructures having different protecting groups with different lability which could provide shape control.



- [1] R. H. Grubbs, *Handbook of Metathesis*, Ed., Wiley-VCH, Germany, **2000**.
[2] H. M. König et al., *Org. Lett.* **2006**, *8*, 1819-1822.

Polymers, Colloids Interfaces

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Conjugates of polymers and protein cages by atom transfer radical polymerization

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Protein-polymer hybrid structures were synthesized by conducting atom transfer radical polymerization (ATRP) within a protein cage. The polymerization was initiated from a protein-bound initiator, therefore yielding protein-polymer conjugates. These hybrids are explored for drug delivery applications¹. The thermosome (THS) from *T. acidophilum* was used as protein cage². Cysteins within the cavity of THS were modified with a maleimide-functionalized ATRP initiator. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was polymerized by ARGET ATRP using Cu(II)HMTETA as catalyst and sodium ascorbate as reducing agent. As poly(DMAEMA) is a cationic polymer and as the THS has pores that are large enough to allow macromolecules to enter the protein cage, negatively charged siRNA was encapsulated into the cage by electrostatic interactions with the polymer³. The protein cage itself has also the advantage that it protects sensitive compounds against degradation, and it shields the positively charged poly(DMAEMA) from cells, which reduces the polymer's toxicity. Furthermore, THS can be genetically and chemically modified on the outer surface with targeting and activating ligands, such as cell penetrating peptides. Studies are currently underway to deliver siRNA and other drugs to cells with this polymer-protein hybrid.

- [1] M. Uchida et al., *Adv. Mater.* **2007**, 19, 1025-1042
 [2] N. Bruns et al., *Angew. Chem.* **2009**, 121, 5776-5779.
 [3] P. van de Wetering et al., *Bioconjugate Chem.*, **1999**, 10, 589-597

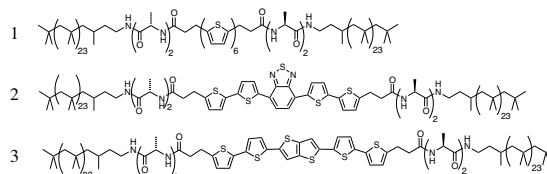
Polymers, Colloids Interfaces

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Organic Nanowires with Sexithiophene-Based π -Conjugated CoresRegina Hafner¹, Holger Frauenrath¹

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Organic nanowires may provide insights into the fundamental processes of charge generation and transport in organic semiconductors under nanoscopic confinement. We recently reported how 'well-defined' nanowires that comprise a single stack of π -conjugated segments at their core are obtained from oligopeptide-functionalized quaterthiophenes or perylene bisimide.¹⁻³ These nanowires were semiconducting, showed space-charge injection-limited conductivity behavior, and exhibited photo-current generation, relating their macroscopic electric properties to the spectroscopically characterized charge carriers.⁴ Here, we demonstrate that similar nanowires can be obtained from a variety of different π -conjugated segments, such as sexithiophene **1** or the corresponding derivatives **2** and **3** with benzothiadiazole or thienothiophene cores. This allowed us to obtain nanowires with tunable optical and electronic properties, as investigated by UV/Vis/NIR and CD spectroscopy.



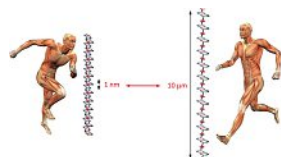
- [1] L. Tian et al., *Chem. Sci.* **2012**, 3, 1512-1521.
 [2] E.-C. Spitzner et al., Magerle, *ACS Macro Lett.* **2012**, 1, 380-383.
 [3] R. Marty et al., manuscript in preparation.
 [4] L. Tian et al., manuscript in preparation.

Polymers, Colloids & Interfaces

PCI63

Muscle-like Supramolecular Polymers: Integrated Motion from Thousands of Molecular MachinesGuangyan Du¹, Emilie Moulin¹, Nicolas Jouault², Eric Buhler^{2*} and Nicolas Giuseppone^{1*}

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 2 Matière et Systèmes Complexes (MSC) Laboratory, University of Paris Diderot – Paris VII, UMR 7057, Bâtiment Condorcet, 75205 Paris Cedex 13, France.



One of the current challenges in nanotechnologies consists in coupling together well-defined molecular machines, individually producing translational or rotational motions, in order to amplify their mechanical output by several orders of magnitude. Here we show that molecular double threaded rotaxanes – being mechanically interlocked and switchable by gliding between extended and contracted conformations – can be tailored with coordination functions and subsequently polymerized in the presence of metal ions. Characterizations by a combination of scattering techniques in solution reveal the formation of single-strand supramolecular polymer chains with very high molecular weights (up to 8.10^6 g.mol⁻¹). The subsequent pH modulation triggers cooperative nano-contractions (or extensions) of the individual rotaxanes resulting in an amplified motion of the muscle-like supramolecular chains with changes of their contour lengths by several micrometers.

- [1] G. Du, E. Moulin, N. Jouault, E. Buhler, N. Giuseppone, *Angew. Chem. Int. Ed.* **2012**, 51, 12504.

Polymers, Colloids Interfaces

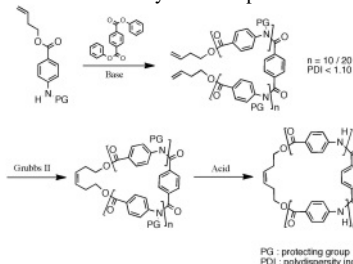
PCI64

Facile synthesis of giant shape persistent cyclic poly(*p*-benzamide)s

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Shape persistent macrocycles are of special interest due to their rigid backbone [1]. This rigidity often leads to self-aggregation into columnar stacks that can be used for transport processes and separation or as rigid scaffolds with well-defined cavities for catalytic or biomimetic applications. Highly effective preparations of large macrocycles presents a major challenge. Here, we present a facile synthesis for giant shape persistent cyclic poly(*p*-benzamide)s with narrow molecular weight distribution. Chain-growth polycondensation [2] that is known to yield polymers with narrow molecular weight distribution was used to polymerize *N*-protected but-3-enyl *p*-aminobenzoate using a bifunctional initiator. Cyclization was performed via ring-closing metathesis followed by acidic deprotection.



- [1] (a) C. Grave, A.D. Schlüter, *Eur. J. Org. Chem.* **2002**, 3075. (b) S. Höger, *Chem. Eur. J.* **2004**, 10, 1320. (c) W. Zhang, J.S. Moore, *Angew. Chem. Int. Ed.* **2006**, 45, 4416. (d) C. Storz, C.M. Hauke, A. Kühnle, A.F.M. Kilbinger, **2013 submitted**.
 [2] T. Yokozawa, T. Asi, R. Sugi, S. Ishigooka, S. Hiraoka, *J. Am. Chem. Soc.* **2000**, 122, 8313.

Polymers, Colloids Interfaces

PCI65

Ionic incorporation of cyanine dyes into a methyl methacrylate polymer for photovoltaic applicationsLei Wang^{1,2,3}, Christian Hinderling¹, Roland Hany², Frank Nüesch^{2,3}¹ZHAW, Life Sciences and Facility Management, 8820 Wädenswil, Switzerland²Empa, Laboratory for Functional Polymers, 8600 Dübendorf, Switzerland³Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, EPFL Station 12, CH-1015 Lausanne, Switzerland

Polyelectrolytes are promising materials for use in organic electronic devices such as organic light-emitting diodes, thin-film transistors and organic photovoltaics (OPV). Their solubility in polar solvents allows fabrication of multilayer devices by solution casting methods in combination with neutral organic molecules and polymers that are soluble in apolar solvents. In this approach, one alternates the polarity of the casting solvent to minimize disturbance of underlying layers.

Here, we demonstrate a strategy for the assembly of solution-processed organic bilayer solar cells using cyanine dyes as electron donors and a soluble fullerene derivative (PCBM) as electron acceptor. Cyanine dyes are actually organic salts (Cyanine⁺ Anion⁻) and have attracted interest for OPV applications [1]. We synthesized polyelectrolytes that consist of a polymer methyl methacrylate backbone containing sulfonic acid side groups. In a second step, the sulfonic acid was modified to the silver sulfonate, and then cyanine dyes were introduced via a salt metathesis reaction. The solubility of the resulting cyanine polyelectrolytes could be tuned by varying the degree of ionic groups. Thereby, polymers that are insoluble in apolar solvents, such as chlorobenzene, were obtained. We report on the use of these polyelectrolytes in simple bilayer cyanine dye / PCBM solar cells.

[1] R. Hany, B. Fan, F. A. de Castro, J. Heier, W. Kylberg, F. Nüesch, *Prog. Photovolt: Res. Appl.* **2011**, *19*, 851.