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Observation of single-molecules at interfaces: fundamentals and applicationsAndrei Honciuc¹¹Zurich University of Applied Sciences, ZHAW

Quantitative measurement of the molecular mobility at interfaces is essential towards understanding interfacial phenomena. Surfactant and polymers adsorb and undergo 2-dimensional diffusion at solid-liquid interfaces. Their diffusion can be very difficult to measure by macroscopic, statistically averaging, methods. In contrast, *in situ* single-molecule tracking reveals a new mechanistic understanding of the 2-dimensional diffusion process. It turns out that the lateral motion of the surfactant and polymer on surfaces follows a complex mechanism of hopping, long flights and molecular conformation changes between adsorption sites. This complex behavior is dictated by the interfacial energy landscape, the interaction strength between solvent molecules with the surface and solute. Using total internal fluorescence microscopy (TIRFM) we were able to observe and track single-molecules at liquid-solid interfaces and reveal the complexity of their motion. From their lateral mobility we were able to quantitatively measure the local hydrophobic interaction and hydrogen bonding strength with the surface in the presence of solvent. From the local interaction of the adsorbed molecules we were able to map the surface energy landscapes. Furthermore, surface energy gradients were used towards directional bias and propulsion of small objects, such as nanoparticles.

Generating anisotropic microstructures in colloidal gelsJan Vermant¹¹Department of Materials, ETH Zurich

Gelling colloidal suspensions constitute an important class of soft matter with a wide range of advanced technological and biomedical applications. Examples include many consumer user products, materials for 3D-direct printing, tissue scaffolding or even in molecular gastronomy. The wide range of utilisation of these materials is the result of the solid-like behaviour at rest due to their flocculated structure, combined with their ability to liquefy when subjected to mechanical stress. Understanding, predicting and controlling these properties remains however difficult. Different models have been proposed to relate the suspension microstructure to properties, based on either fractals, percolation or glassy dynamics, but invariably assuming essentially isotropic structures, even when the materials are flowing.

In the present work we demonstrate the so far unaccounted presence of spectacular anisotropy in the mechanical response of a pre-sheared gel, with especially the elastic moduli differing by as much as two orders of magnitude. We link the development of properties and the underlying thixotropic response to the microstructural evolution. Gels are intrinsically inhomogeneous and a deformation can be expected to be localised in the weaker regions of the structure, whereas stronger regions will get even more condensed. The destruction of the structure can hence be expected to be anisotropic. This may be similar to the localization mechanism underlying the Payne effect in filled rubbers, albeit with some subtleties: The vorticity inherent to a shear flow causes a continuous break-up and subsequent re-aggregation leading to a local compaction and a increasingly heterogeneous structure. Under an imposed low shear rate the microstructure of aggregated suspensions can also be highly anisotropic in nature which will be shown using data on both 2D and 3D suspensions. We will also show that flow fields are more effective than using intrinsically anisotropic non-spherical building blocks.

The microstructural anisotropy relaxes slowly upon cessation of flow. For suspensions in thermosetting or thermoplastic matrices, the anisotropic microstructure could be locked in to create novel functional soft materials with anisotropic mechanical, thermal or optical properties. Both shear rate and time upon cessation could be used to tune the properties of such materials. In connecting the flow-induced microstructure of these types of soft materials to their nonlinear rheology the anisotropic microstructure is an essential or even crucial element, especially when important non-hydrodynamic contributions are present.

Stimuli-Responsive (Bio)Hybrid Coiled Coil Peptide-Polymer MicrogelsVitaliy Kolesov¹, Harm-Anton Klok¹ *¹EPFL Lausanne

Microgels are solvent-swollen polymer or mixed polymer-inorganic hydrogel particles with sizes from ca. 10 nm to 10 μ m, which have the interconnected cross-linked structures suitable for loading or entrapment of therapeutic agents, dyes, and other molecules. There are two ways of introducing stimuli-responsiveness into polymeric microgels—via inherent properties of polymerized monomers or by the incorporation of reactive cross-linking agents. However, the common problem with such type of particles is that they often do not provide the possibilities for fine tuning of their stimuli-responsive properties. One step forward in the evolution towards better, more advanced polymeric microgels would be the development of specific polymers or cross-linkers, adjustable according to the needs of every particular problem. One such type of promising adjustable cross-linking moieties may be based on the use of the peptide superstructures such as coiled coils.[1] The advantages of peptides in this role are numerous: They may possess simultaneously responsiveness to changes in pH, temperature or ionic strength, and, when disassembled, can act as target-recognizing, target-binding or membrane-penetrating units.[2–4]

In this work we describe the first proof of concept for the synthesis of coiled coil peptide-containing microgel particles. pH-triggered disassembly or swelling of microgel particles was observed with circular dichroism and dynamic light scattering experiments.

[1] Woolfson, D. N. Adv. Protein Chem. 2005 Vol. 70, pp 79–112.

[2] Mason, J. M.; Arndt, K. M., ChemBioChem 2004, 5 (2), 170–176.

[3] Kim, J.-S. et al. PNAS 2005, 102 (9), 3248–3253.

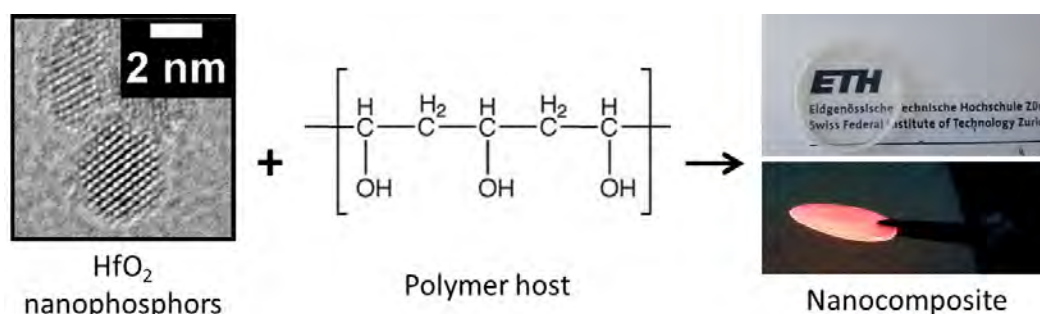
[4] Zhang, Z.; Zhu, W.; Kodadek, T., Nat. Biotech. 2000, 18 (1), 71–74.

Organic-Inorganic Nanocomposite Scintillators: $\text{HfO}_2\text{:Eu}$ Luminescent Nanoparticles Embedded into Polymer Films

Alessandro Lauria¹, Julia Carpenter¹, Irene Villa², Anna Vedda², Markus Niederberger¹, Walter Caseri^{1*}

¹ETH Zurich, ²University of Milano-Bicocca

Hafnium dioxide with luminescence activated by rare earth ions is an interesting material for phosphor and scintillator applications, due to its very high density and chemical stability. Since the synthesis of macroscopic single crystals of HfO_2 is not achievable with conventional methods, we synthesized $\text{HfO}_2\text{:Eu}$ nanoparticles of about 3 nm through a colloidal nonaqueous synthesis based on the reaction of metal alkoxide precursors with benzyl alcohol.¹ In order to be employed in scintillator materials, able to convert ionizing radiation (X-ray, γ -ray) into visible light, it is required to minimize the detrimental scattering of the emitted light, associated with the powder form of the active material.²



Here, we report the preparation of organic-inorganic transparent and luminescent nanocomposites, obtained by embedding stabilized HfO_2 phosphor nanoparticles into polyvinyl alcohol films, used as passive host thanks to the high transparency of this organic matrix in the UV and visible spectral range. The optical transparency of the nanocomposite materials have been investigated by UVVis absorption, and the luminescence efficiency was studied by radio- and photoluminescence measurements.

[1] Alessandro Lauria, Irene Villa, Mauro Fasoli, Markus Niederberger and Anna Vedda, *ACS Nano*, **2013**, 7(8), 7041-7052

[2] Dorota Koziej, Alessandro Lauria, and Markus Niederberger, *Advanced Materials*, **2014**, 26, 235-257

Modeling multiradicals in bulk crosslinking copolymerizationStefano Lazzari¹, Giuseppe Storti¹¹ETH Zurich

Since the seventies, multiradicals (active chains with multiple active sites) have been considered to have an important role in bulk crosslinking copolymerization, as they are expected to play a key role in the gel formation process.¹ The first model dealing with such species has been proposed by Zhu and Hamielec²: along with a series of simulation results, the Authors proposed a simplistic criterion to identify if multiradicals should be accounted for when modeling a generic crosslinking system. Such criterion is based on the ratio between two rate constants, propagation and bimolecular termination: when the ratio is larger than a critical value, multiradicals have to be considered, along with the corresponding additional computational effort. Despite its relevance, this criterion was seldom used in following modeling literature: multiradicals were either included, pointing out that they realistically will be formed close to the gel point,^{3, 4} or ruled out without a preliminary quantitative check of their relevance^{5, 6}.

In this work, the role of multiradicals in polymer systems underlying crosslinking reactions is further examined and a new criterion aimed to elucidate the actual need of such complication is proposed. Instead of involving rate constants only, such criterion is based on the probability for an active chain to crosslink to another active chain, accounting for all possible kinetic events. This way, a more effective criterion is developed, involving also process conditions, such as the initial amount of crosslinker or the monomer dilution. As a matter of fact, it turns out that multiradicals play a role at both high and low crosslinker contents. By comparative evaluation of two kinetic models, accounting for and neglecting multiradicals, the corresponding discrepancies in terms of gel point predictions have been used to quantify the actual need of the more detailed modeling.

To perform the aforementioned calculations, a 4-D population balance equation model, accounting for multiradicals in bulk crosslinking copolymerization, has been developed and solved by Numerical Fractionation⁵ combined with the method of moments. In particular, chain length, bridges, pendant double bonds and number of active sites per chain have been used as internal coordinates. Besides the usual generation number, N_{gen} , also the maximum amount of active sites per chain, N_{rad} , has been estimated by numerical experiments. The developed model has been applied to the simulation of the bulk copolymerization Methyl-methacrylate (MMA)/Ethyleneglycol-dimethylacrylate (EGDMA) at 70°C, using literature parameter values.

[1] Kuchanov, S. I.; Pismen, L. M. *Vysokomol Soedin A* 1971, 13, (9), 2035-.

[2] Zhu, S.; Hamielec, A. E. *Macromolecules* 1993, 26, (12), 3131-3136.

[3] Hernandez-Ortiz, J. C.; Vivaldo-Lima, E.; Penlidis, A. *Macromolecular Theory and Simulations* 2012, 21, (5), 302-321.

[4] Iedema, P. D.; Hoefsloot, H. C. J. *Macromolecules* 2004, 37, (26), 10155-10164.

[5] Kizilel, S.; Perez-Luna, V. H.; Teymour, F. *Macromolecular Reaction Engineering* 2009, 3, (5-6), 271-287.

[6] Kizilel, S.; Papavasiliou, G.; Gossage, J.; Teymour, F. *Macromolecular Reaction Engineering* 2007, 1, (6), 587-603.

Short Poster Presentations: Polymers, Colloids Interfaces

Christian Hinderling¹

¹Zurich University of Applied Sciences, ZHAW

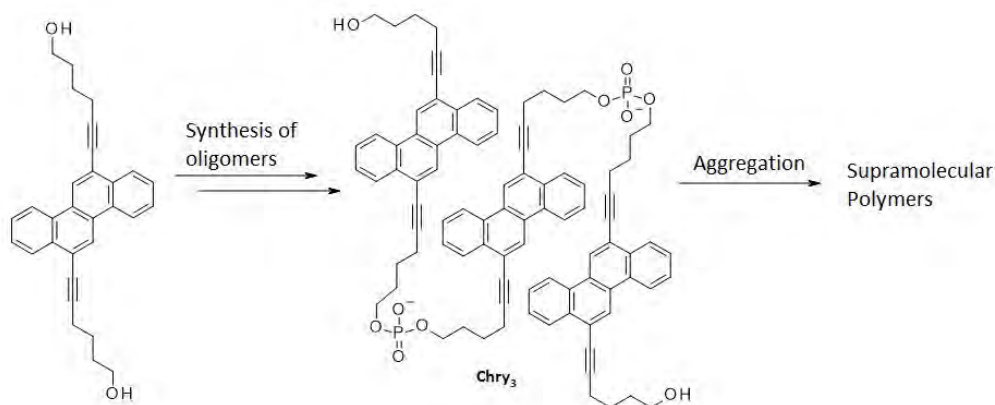
Short Poster Presentations, 3min each:

- Yee Song Ko, EPFL Lausanne
«Poleable nanoparticles as fillers towards non-linear optically active actuators» [PI-031]
- Chiara Gstrein, ETH Zurich
«Microenvironment of the Interior of Dendronized Polymers» [PI-032]
- Justyna Kowal, University of Basel
«Functional Surface Engineering by Insertion of Membrane Protein into Solid-Supported Polymer Membranes» [PI-033]
- Caroline Bösch, University of Berne
«Formation of supramolecular polymers by chrysene oligomers» [PI-034]
- Lei Wang, EPFL Lausanne
«Cyanine Dye Polyelectrolytes for Organic Bilayer Solar Cells» [PI-035]

Formation of supramolecular polymers by chrysene oligomersCaroline Bösch¹, Robert Häner¹ *¹University of Berne

Supramolecular assembly of π -conjugated systems is of large interest due to the possibility to use them in electronic devices.[1] Chrysene is a polyaromatic hydrocarbon which has been studied e.g. for organic light-emitting diodes (OLEDs).[2] In continuation of our previous work involving the supramolecular polymerisation of pyrene oligomers [3] an oligomer consisting of three chrysenes linked by phosphodiester was synthesised (Chry₃).

UV-Vis measurements show that aggregates of Chry₃ are formed in aqueous medium. This is illustrated by general hypochromicity, a change in vibronic band intensities and, in particular, the appearance of a red-shifted absorption band in the $S_0 \rightarrow S_2$ transition. The data suggest the formation of J-aggregates. The formation of supramolecular polymers is further studied by temperature-dependent absorption- and fluorescence measurements, and by atomic force microscopy (AFM). Results will be shown.



[1] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.*, **2005**, 105, 1491 – 1546.

[2] A. S. Ionkin, W. J. Marshall, B. M. Fish, L. M. Bryman, Y. Wang, *Chem. Commun.*, **2008**, 2319 – 2321.

[3] M. Vyborni, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri, R. Häner, *Angew. Chem. Int. Ed.*, **2013**, 52, 11488 – 11493.

Microenvironment of the Interior of Dendronized PolymersChiara Gstrein¹, Baozhong Zhang¹, A. Dieter Schlüter¹ *¹ETH Zurich

Dendronized polymers (DPs), which consist of a linear polymer chain and a dendron on each backbone repeat unit, are ideal candidates for the study of loading, transporting and releasing guest molecules, which potentially have various biological applications.[1] The microenvironment inside DPs is of obvious interest because of its significant role in the guest uptake. Further, the microenvironment near the core of DPs will provide valuable information regarding the structural compactness of DPs, especially for high generations (G3).

The microenvironment of a dendritic structure is not directly reflected by its chemical structure. For example, the micropolarity of the interior of Fréchet dendrimers has been reported as similar to a very polar solvent, DMF, despite the fact that the dendrimer only consists of rather nonpolar moieties.[2] Moreover the microenvironment of Fréchet dendrimers changes upon the generation discontinuously in non-polar solvents, which is in line with the transformation from an extended to a more globular shape.

Herein, we present the synthesis of a new series of DPs with a solvatochromic chromophore (*p*-nitroaniline) covalently attached to one of the G1 branches of each backbone repeat unit, allowing the other G1 branch to be further developed to higher generations (Figure 1). UV-vis spectroscopical studies of these DPs in various solvents reveal the internal micropolarity, which will shed some light on the loading abilities of DPs with similar chemical structures. Furthermore, the generation dependency of the microenvironment will also be presented.

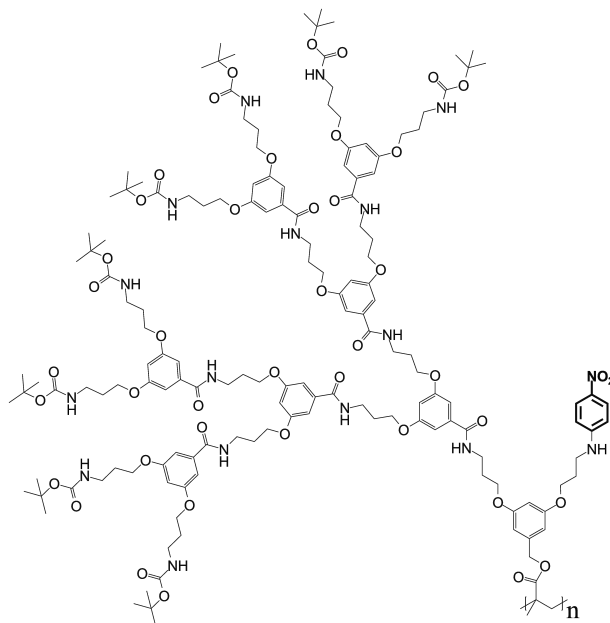
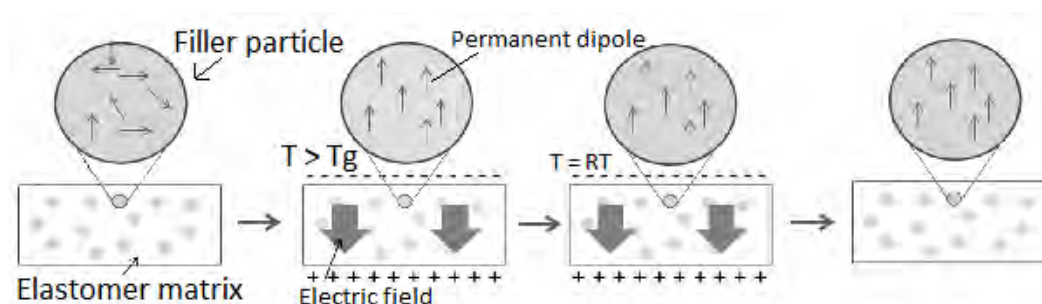


Figure 1 – Chemical structure of a new dendronized polymer of the fourth generation, carrying a nitroaniline moiety near the core at each backbone repeat unit.

- [1] A. D. Schlüter, J. P. Rabe, *Angew. Chem. Int. Ed.* **2000**, 39, 864-883.; H. Frauenrath, *Prog. Polym. Sci.* **2005**, 30, 325-384.; G. Fuhrmann, J.-C. Leroux et al., *Nat. Chem.* **2013**, 5, 582-589.
[2] C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1993**, 115, 4375-4376.

Poleable nanoparticles as fillers towards non-linear optically active actuatorsYee Song Ko¹, Dorina Opris², Frank Nüesch² *¹EPFL Lausanne, ²EMPA Dübendorf

Research on dielectric elastomer actuators (DEAs) focuses mainly on the enhancement of the permittivity (ϵ) as it linearly increases actuation displacement. [1] Most recent developments include the grafting of polar molecules onto the elastomer backbone to increase the intrinsic matrix permittivity. [2] In the field of non-linear optics, the poling of polymers containing polar molecules is a well-established method to create non-linear optical (NLO) materials. [3] The alignment of the dipole in an amorphous polymer is done in a high electric field at temperatures above its glass transition temperature (T_g) followed by freezing of the oriented material by cooling below T_g while the electric field is maintained. Poleable elastomers can be realized by blending high T_g polymeric nanoparticles into an elastomer matrix. The poling of such an elastomer is schematically illustrated below.



Synthesis and characterization of the nanoparticles, as well as preliminary results of a poleable DEA are being presented. It will be shown, that a material with a novel mixture of mechanical and optical properties can be obtained using this route.

[1] Federico Carpi, Danilo De Rossi, *IEEE Transactions on Dielectrics and Electrical Insulation*, **2005**, 12, 835-843.

[2] Björn Kussmaul, Sebastian Risse, Guggi Kofod, Rémi Waché, Michael Wegener, Denis N. McCarthy, Hartmut Krüger, Reimund Gerhard, *Advanced Functional Materials*, **2011**, 21, 4589-4594.

[3] Siegfried Bauer, *Journal of Applied Physics*, **1996**, 80, 5531-5558

Functional Surface Engineering by Insertion of Membrane Protein into Solid-Supported Polymer Membranes

Justyna Kowal¹, Julia Kowal¹, Dalin Wu¹, Henning Stahlberg¹, Cornelia Gabriela Palivan¹, Wolfgang Meier¹ *

¹University of Basel

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 self-assemble in membranes with higher mechanical stability, greater thickness and rigidity, while remaining fluid enough to incorporate proteins.^[1]

We present a new method to prepare functional, solid-supported polymer membranes based on amphiphilic block copolymers membranes,^[2] in which membrane proteins have been inserted. Well organized membranes of a diblock copolymer with poly(2-methoxyl-2-oxazoline) (PMOXA) as hydrophilic domain, and poly(dimethylsiloxane) (PDMS), as hydrophobic domain were prepared through Langmuir-Blodgett and Langmuir-Schaefer monolayer transfer techniques. The membranes were homogenous, with a thickness of approximately 12 nm, as established by AFM, and ellipsometry. The incorporation of the nucleotide-modulated potassium channel (MloK1 from *Mesorhizobium loti*)^[3] into solid-supported polymer membrane was triggered with Bio-Beads, which destabilized both the protein and the membrane, and supported the protein insertion in the hydrophobic domain of the membrane. Successful and functional insertion of the protein was established by fluorescence microscopy, and conductance measurements. This method is straightforward and uses mild conditions, which support further development for medical applications.

[1] X. Y. Zhang, P. Tanner, A. Graff, C. G. Palivan and W. Meier, *Journal of Polymer Science Part a-Polymer Chemistry* **2012**, 50, 2293-2318.

[2] J. Kowal, X. Zhang, I. A. Dinu, C. G. Palivan and W. Meier, *ACS Macro Letters* **2014**, 3, 59-63.

[3] J. Kowal, M. Chami, P. Baumgartner, M. Arbeit, P.-L. Chiu, M. Rangl, S. Scheuring, G. F. Schröder, C. M. Nimigean and H. Stahlberg, *Nature Communications* **2014**, 5, 3106.

Cyanine Dye Polyelectrolytes for Organic Bilayer Solar Cells

Lei Wang¹, Frank Nüesch², Roland Hany², Christian Hinderling³ *

¹EPFL Lausanne, ²EMPA Dübendorf, ³Zurich University of Applied Sciences, ZHAW

Polyelectrolytes are promising materials for applications in organic electronic devices such as organic light-emitting diodes, thin-film transistors and organic photovoltaic (OPV) cells. Their tunable solubility in polar and nonpolar solvents allows the fabrication of multilayer devices by solution casting methods, where the second active layer material is coated from an orthogonal solvent onto the underlying layer.

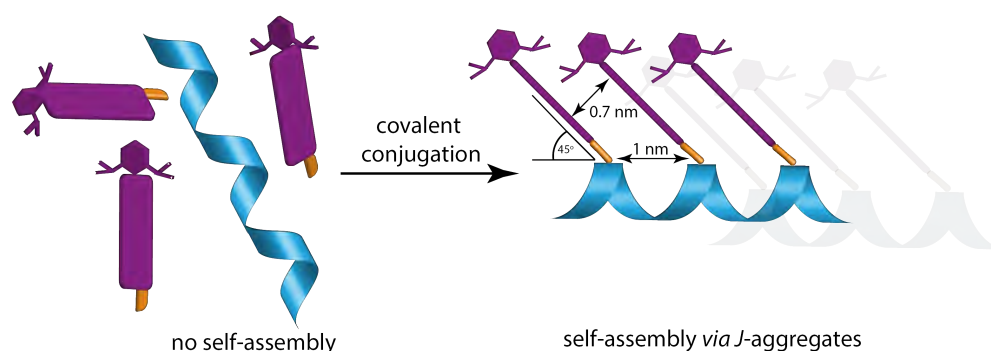
Here, we demonstrate a versatile synthetic approach for cyanine polyelectrolytes consisting of an anionic sulfoethyl methacrylate / methacrylate backbone and either pentamethine or trimethine cationic cyanine counter ions with contents up to 50% of polymer repeating units. The synthesis route consists of a thermal radical copolymerization, followed by deprotonation of sulfonic acid and a salt metathesis reaction to incorporate the dye. These materials were characterized by NMR, TGA, AFM and UV and exhibit good film forming property and largely reduced solubility in apolar solvents, such as chlorobenzene. Simple cyanine polyelectrolytes / PCBM bilayer solar cells were fabricated in an all-solution-processed approach and cell performances were optimized systematically regarding cyanine content, active layer thickness and buffer layer materials.

Tunable aggregation of sterically demanding peryleneimides induced by the conjugation with rigid oligoproline scaffolds.

Urszula Lewandowska¹, Long Chen², Klaus Müllen², Helma Wennemers¹ *

¹ETH Zurich, ²Max Planck Institute, Mainz, Germany

Precise control over the incorporation of functional building blocks into larger, organized systems has enormous potential for material science. Efforts have been made to create well ordered, functional structures based on DNA scaffolds and polypeptide backbones which can be easily decorated with the desired functionality.¹⁻³ Until now the use of rigid, non-selfaggregating scaffolds for such purposes has been limited.



Functionalizable, azidoproline-containing oligoprolines direct the self-assembly of π -conjugated systems as they adopt (already at a short chain lengths of six residues) the conformationally well-defined polyproline II (PPII) helix, in which every third residue is stacked on top of each other in a distance of ~ 1 nm.⁴ Covalent conjugation of this rigid peptidic scaffold with π -systems which do not self-assemble on their own allowed for the hierarchical supramolecular aggregation of hybrid molecules in solution and on the solid support. Thus, the use of functionalizable azidoproline (Azp) rich oligoproline as scaffolds constitutes new and efficient approach to the design of the self-assembly of functional π -conjugated systems as precise control over the molecular design enables control over the aggregation process.

[1] Grimsdale A. C. Müllen, K. *Angew. Chem., Int. Ed.* **2005**, 44, 5592–5629.

[2] Kumar R. J., MacDonald J. M., Singh Th. B., Waddington L. J. Holmes, A. B. *J. Am. Chem. Soc.* **2011**, 133, 8564–8573.

[3] Tovar, J. D. *Acc. Chem. Res.* **2013**, 46, 1527–1537.

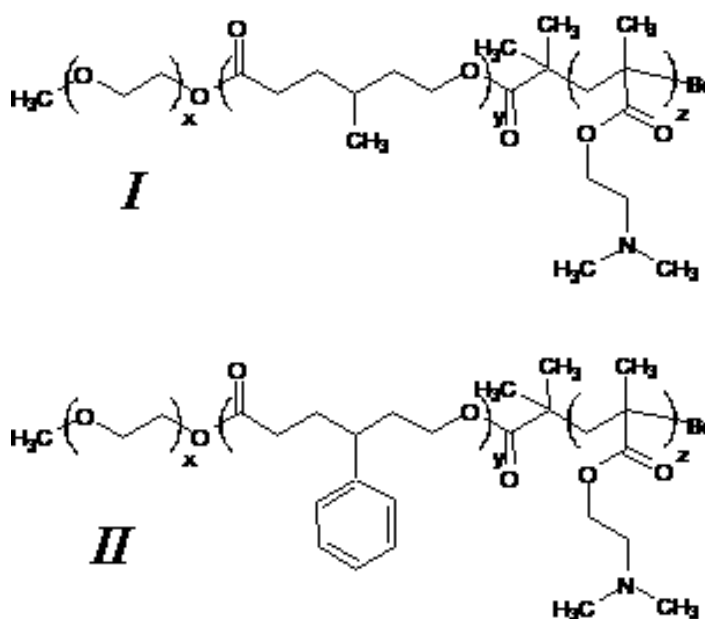
[4] M. Kümin, L. S. Sonntag, H. Wennemers, *J. Am. Chem. Soc.* **2007**, 129, 466–467.

Effect of hydrophobicity on nanoparticle formation: a case of ABC asymmetric triblock copolymers

Evgeniia Konishcheva¹, Cornelia Gabriela Palivan¹, Wolfgang Meier¹ *

¹University of Basel

Asymmetry in biological lipid membranes plays a crucial role in insertion and orientation of membrane proteins. Stoenescu and co-workers [1] have shown self-assembly of asymmetric amphiphilic triblock copolymer into nanoparticles that provided a directional insertion of Aquaporin 0. Orientation of asymmetric copolymers mainly depends on the nature and length of hydrophilic parts. However, to the best of our knowledge, influence of hydrophobicity of the central hydrophobic block on the nanoparticle formation has never been studied. In this presentation, we investigated two asymmetric triblock copolymers: mPEG₄₅-b-PMCL₁₁₀-b-PDMAEMA₃₇ (I) and mPEG₄₅-b-PPhCL₁₀₀-b-PDMAEMA₃₀ (II). The crucial difference in the structures is the presence of more hydrophobic phenyl group in case of II. Both polymers assemble into nanoparticles by co-solvent method. The self-assembly behavior of these polymers has been investigated using DLS and TEM. Copolymer I has longer hydrophobic B block (110 vs. 100 units) and hydrophilic PDMAEMA C block (35 vs. 30 units) compared to copolymer II. Nevertheless, DLS data and TEM images confirmed that copolymer I formed smaller nanoparticles. Thus, hydrophobic nature of the central block plays a crucial role in the self-assembly process of asymmetric mPEG-b-PMCL/PPhCL-b-PDMAEMA copolymers.



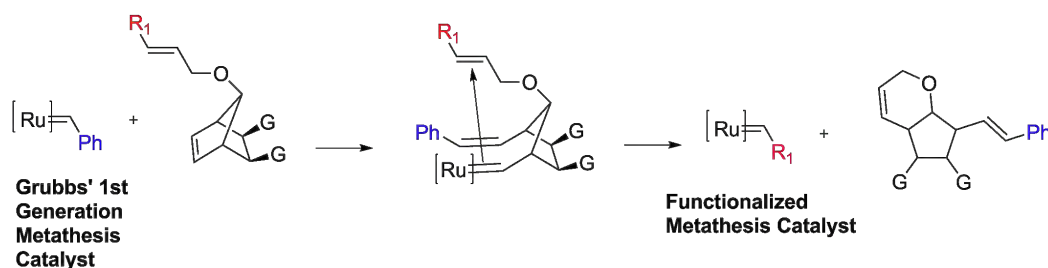
[1] R. Stoenescu, A. Graff, W. Meier, *Macromol Biosci*, **2004**, 10, 930-935.

Tandem Ring Opening-Ring Closing Metathesis for Synthesis of Functional Metathesis Catalysts

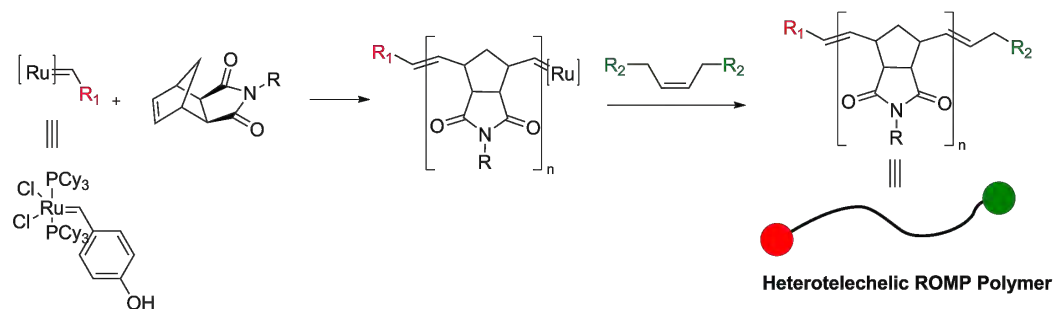
Amit Nagarkar¹, Andreas Kilbinger¹ *

¹University of Fribourg

We demonstrate a highly effective tandem ring opening - ring closing metathesis strategy for the synthesis of new prefunctionalized metathesis catalysts in an atom economical approach. This leads to new metathesis catalysts carrying easily functionalizable groups on the benzylidene ring. The ring opening-ring closing mechanism was confirmed by observing the ruthenium methylidene species by ¹H-NMR. The 4-hydroxy version of Grubbs' first generation metathesis catalyst was successfully synthesized using this method.



Such new catalysts carrying various functional groups can further be used along with suitable terminating agents to synthesize heterotelechelic ROMP (Ring Opening Metathesis Polymerization) polymers in a straightforward manner leading to very high degree of end functionalities. A heterotelechelic polymer carrying a easily functionalizable phenol functionality at one end and an acid functionality at the other end was synthesized and proved by MALDI-TOF spectrometry. This technique could be applied to synthesize a large library of heterotelechelic polymers extending the utility of ROMP in material science.



[1] Hilf, S.; Kilbinger, A. F. M. *Nature Chemistry* **2009**, 537. [2] Kim, H.-S.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, 116, 10801. [3] Niethe, A.; Fischer, D.; Blechert, S. *J. Org. Chem.* **2008**, 73, 3088. [4] La D. S.; Sattely E. S.; Ford J. G.; Schrock R. R.; Hoveyda A. H. *J. Am. Chem. Soc.* **2001**, 123, 7767-7778.

The role of peptides in the formation of silver nanoparticles

Matthias Messerer¹, Sonja Kracht¹, Matthieu Lang¹, Bernd Giese¹, Katharina Fromm¹ *

¹University of Fribourg

Several microorganisms reduce silver ions to silver nanoparticles (AgNPs). In some cases these reductions occur outside of the cell while electrons migrate from the inner cell membrane through peptides to the outside of the cell.^[1] We are studying this production of AgNPs using a model peptide that carries histidine as a silver binding amino acid and tyrosine as a source of electrons, generated by irradiation.^[2] The results are highly surprising:

1. Silver peptides do not produce AgNPs by electron transfer (ET)! Only after addition of chloride ions, which generate silver chloride imbedded into the peptide, AgNPs are formed.
2. In the first step AgNPs of about 120 nm size are formed within a few minutes. These particles decompose into particles of about 25 nm diameter. The UV spectra (surface plasmon resonance) of the AgNPs exhibit an isosbestic point that demonstrates a clean transformation of large into small nanoparticles. The reaction order and reaction rate of the formation and of the transformation can be measured.
3. We have also determined the influence of the pH, the concentration and the ratio peptide:silver:chloride on the formation of the AgNPs.
4. The generation of AgNPs by long distance ET differs from the „classical“ formation of AgNPs using inorganic or organic chemical reductants.

We will present a mechanistic picture for the explanation of these experimental results.

[1] Gemma Reguera, Kevin D. McCarthy, Teena Metha, Julie S. Nicoll, Mark T. Tuominen, Derek R. Lovley, *Nature*, **2005**, 1098-1101

[2] Kirsten Belser, Tünde Vig Slenters, conelious Pfumbidzai, Gregory Upert, Laurent Mirolo, Katharina Fromm, Helma Wennemers, *Angew. Chem. Int. Ed.* **2009**, 48, 3661-3664

Particle Aggregation in Ionic Liquids

Gregor Trefalt¹, István Szilágyi¹, Tamas Szabo¹, Anthony Désert¹, Tamas Oncsik¹, Michal Borkovec¹ *

¹University of Geneva

Aggregation of colloidal polystyrene latex particles was studied in room temperature ionic liquids (ILs) and their water mixtures by time-resolved light scattering techniques. A general trend in stability was observed when varying IL-to-water molar ratio. At low IL contents the aggregation rate coefficient is small, but it increases rapidly with increasing the IL content and reaches a plateau, see Figure 1. This behavior is similar as in the case of simple salts and can be understood within the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory. At even higher concentrations the rate slows down again. This re-stabilization behavior at higher concentrations is attributed to two effects, namely viscous and solvation stabilization. Viscous stabilization is important in highly viscous ILs, since the increase of viscosity slows down the diffusion of particles and hence decreases the aggregation rate. The solvation stabilization mechanism is attributed to system specific solvation forces and it becomes operational in almost pure ILs. This effect is probably related to the layering of ILs close to the surface, which has been already observed in other systems [1-3]. These stabilization mechanisms seem to be generic, since they were found in different ILs and for particles differing in surface functionalities and size.

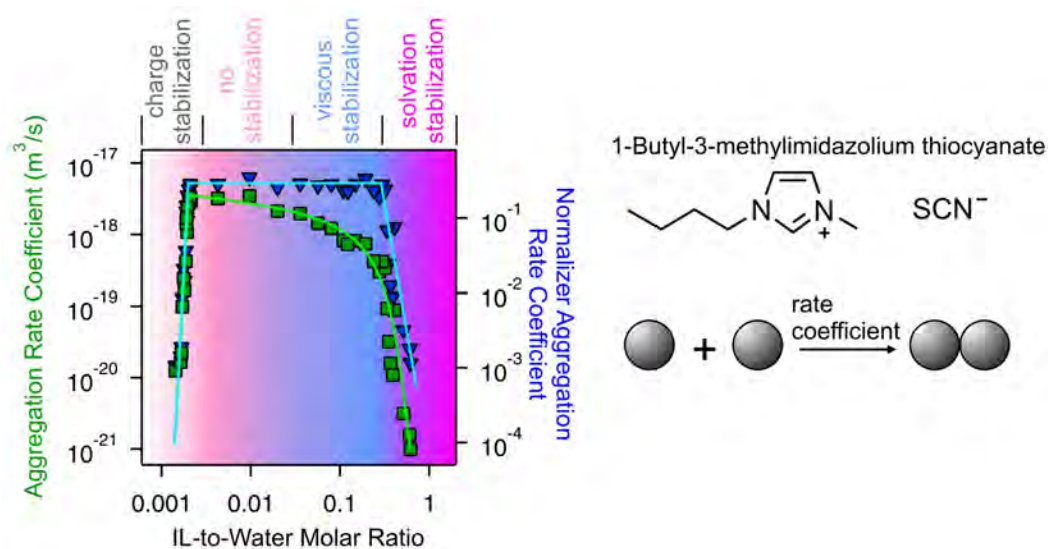


Figure 1: Absolute and normalized aggregation rate coefficients of sulfate latex particles in mixtures of 1-Butyl-3-methylimidazolium thiocyanate and water.

[1] Atkin, R.; Warr, G. G. *J. Phys. Chem. C* **2007**, 111, 5162-5168.

[2] Ueno, K.; Watanabe, M. *Langmuir* **2011**, 27, 9105-9115.

[3] Espinosa-Marzal, R. M.; Arcifa, A.; Rossi, A.; Spencer, N. D. *J. Phys. Chem. C* **2014**, 118, 6491-6503.