18th Zsigmondy Colloquium 2023

BOOK OF ABSTRACTS

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PART I - TALKS

Aqueous self-assembly of 1-alkyl-3-methylimidazolium carboxylates, a new type of catanionic surface active ionic liquids

Jessica Bauhof¹, S. B. Wachsmann², T. D. Beuter¹, A. R. Raab², A. Zens², S.Laschat², T. Sottmann¹

¹ Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart ² Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart Presenting author e-mail: jessica.bauhof@ipc.uni-stuttgart.de

Keywords: Catanionic SAILs, self-assembly, liquid crystals

The aqueous behavior of 1-alkyl-3-methylimidazolium carboxylates $[C_n mim][C_{m-1}COO]$, which are a new type of salt-free catanionic surface active ionic liquids (CASAILs), were studied using surface tension measurements, polarized optical microscopy (POM), dynamic differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS). From the analysis of the surface tension data we inferred a strong and linear decrease of log(cmc) for increasing both the carboxylate anion and imidazolium cation chain length due to the increasing hydrophobic effect. Surprisingly, the chain length of the carboxylate anion has a stronger impact than the chain length of the imidazolium cation, indicating its greater surface activity and tendency to form micelles. The minimum head group area amin = 58 ± 5 Å² was found to be independent of the cation/anion chain length and much smaller than that of even single 1-alkyl-3-methylimidazolium bromide surfactants. The surfactant molecules are densely packed at the air-water interface, which is due to both the strong electrostatic attraction between the two oppositely charged ionic heads and van der Waals interactions between anionic and cationic alkyl chains [1]. Using POM and DSC, it was found that these novel catanionic surfactants form a lamellar structure (L_{α}) at higher concentrations (\geq 30 wt.%). The periodicity of the surfactant bilayers, as shown by SAXS measurements, decreases with increasing temperature due to the stronger interdigitation of the hydrocarbon chains as well as the decreasing orientational long-range order.



Figure 1. a) Surface tension γ of 1-alkyl-3-methylimidazolium carboxylates $[C_n mim][C_m \ _1COO]$ as a function of the surfactant concentration c at 25 °C in a semi-logarithmic representation. Increasing the cation chain lengths at constant m = 10 shifts the $\gamma(c)$ -curves and thus the cmc to lower concentrations. b) Contact preparation of $[C_{12}mim][C_{11}COO]$ at 22.5 °C, Maltese crosses indicate a lamellar phase.

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Aescin-Induced Temperature-Dependent Self-Assembly of Lipid Bicelles

<u>*Tim Julian Stank*¹</u>, and Thomas Hellweg ^{1,2}

¹Physical and Biophysical Chemistry, University Bielefeld, Bielefeld, Germany Presenting author e-mail: tim_julian.sta@uni-bielefeld.de

Keywords: phospholipids, saponins, self-assembly, bicelles, SAXS

The horse chestnut (*Aesculus hippocastanum*) seed extract has proven useful in clinical therapy and is also being investigated for its potential anti-carcinogenic properties. The main active ingredient, β -aescin, is used as an anti-oedema agent in the treatment of chronic venous insufficiency. [1, 2] In the context of pharmacological activity, the interaction of the biosurfactant β -aescin with biological membranes is of great interest. [2, 3]

In our present work, the temperature-dependent interaction of high amounts of β -aescin with the lipid DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine) was investigated by small-angle Xray scattering (SAXS) and UV-vis turbidity measurements. At temperatures above the phase transition temperature ($T_m \approx 41.3$ °C) aescin-stabilised DPPC bicelles assemble into extended bilayers and at higher temperatures into larger multilamellar structures. The self-assembly and final morphology are highly dependent on the phospholipid-to-aescin ratio and the actual temperature. It was also found that all structural changes are completely reversible by cooling to the initial temperature.



Figure 2. SAXS curves of DPPC samples with 20 mol%, 25 mol% and 30 mol% β -aescin content at temperatures from 35 – 80 °C. Samples were heated or cooled (20 °C min⁻¹) from the previous to the indicated temperature (red or blue number) and measured for 7h after 30 min equilibration time.

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Solvent effect on asphaltene flocculation: Insights of solubility from Static Multiple (SMLS) and Dynamic (DLS) Light Scattering

Ronald Marquez^{1,4*}, Jesús Ontiveros⁴, Nicolas Sanson^{1,3}, François Lequeux^{1,3}, Véronique Nardello-Rataj⁴, and Valérie Molinier^{1,2}

¹Laboratoire commun TotalEnergies/ESPCI, Physico-Chimie des Interfaces Complexes, CHEMSTARTUP, RD 817, Lacq F-64170, France

²TotalEnergies Onetech, Pôle d'Etudes et de Recherche de Lacq, B.P. 47, 64170 Lacq, France

³Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL University, Sorbonne Université, CNRS UMR 7615,

75005 Paris, France

⁴Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

Presenting authore-mail: ronald.marquez@univ-lille.fr

Keywords: Asphaltenes, Aggregation, Nanoaggregates, Flocculation, Static Multiple Light Scattering, Dynamic Light Scattering

This work investigates the impact of the solvent medium on the flocculation behavior of asphaltenes. The asphaltenes onset of precipitation in a mixture of decalin and dodecane was determined by two kinds of measurements. On the one hand, Static Multiple Light Scattering (SMLS) was used to obtain the transmission and backscattering profiles of the samples as a function of time, and on the other hand, by dynamic light scattering (DLS) to assess the asphaltene particle size distribution. The concentrations studied were 0.05 wt.% asphaltenes and dodecane/decalin mixtures with 0, 30, 40, 50, 60, 80 and 100 wt.% dodecane. The onset of flocculation was found at 50% dodecane by visual observation (modified ASCI), by changes in the transmission and backscattering profiles, and by changes in the aggregate size by DLS. The results demonstrate that the average size of asphaltene particles in decalin at low dodecane concentrations ranges from 8 to 12 nm, but progressively increases with the addition of dodecane until their precipitation starts when aggregates are around > 5000 nm. Moreover, a bimodal particle distribution occurs between 40 and 60 wt.% dodecane corresponding to nanoaggregate and cluster aggregation states, according to the literature [1,2]. These findings provide valuable insights into the solvent-mediated dynamics of asphaltene aggregates and the complex interplay between asphaltene molecules in different applications, such as flow assurance and petroleum emulsions formation.



Figure 3. Flocculation of asphaltenes in decalin/dodecane measured with DLS (Top) and SMLS (Lower panel) **References**

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Back to the Future: Fatty acids, the green genie to design smart soft materials

<u>Anne-Laure FAMEAU¹</u>

¹INRAe, Lille, FRANCE

Presenting author e-mail: <u>anne-laure.fameau@inrae.fr</u>

Keywords: fatty acids; responsive foams; capillary suspension; liquid marbles

All of the physical matter around us is composed of atomic or molecular building blocks. Controlling the assembly of these building block units holds the key for producing materials with new properties. Our research is focused on the self- and directed assembly of matter at all length scales, i.e. from molecular to macroscopic scale. We are interested in multiscale approaches to understand the interactions, which govern the assembly of colloids both in bulk and at interfaces. We develop new strategies to control the interactions and design responsive materials based on fatty acids. These systems could find applications in a wide range of industrial and environmental processes such as in food, cosmetics, crude oil treatment and extraction.

Soft materials, such as foam, liquid marbles and emulsion systems, which respond to external stimuli, are on the leading edge of materials research. The macroscopic responsivity relies on the ability to react at microscopic or mesoscopic scales. Stimuli-responsive surfactants that can change their structure in response to a trigger such as pH, temperature or light have attracted great attention due to their versatile applications in various fields. A change in the molecular structure of the surfactant activated by stimuli can affect the self-assembled structure in water and the interfacial activity, which can in turn tune the macroscopic properties such as emulsion and foam stability. Responsive foams correspond to foams for which stability can be reversibly tuned between ultrahigh stability and immediate destabilization under stimuli [1]. We will illustrate how we can use fatty acids, which are green anionic surfactants, to produce multi-stimuli responsive self-assemblies, liquid marbles and foams [2-8]. Other technologically important materials are made by assembling colloidal particles into structures that often start with simple chains or filaments. A variety of techniques are available to assemble particles into chains, but so far it has proven challenging to make permanent chains that are flexible. We will present a new method for making highly flexible particle chains based on capillary attractions between particles coated with liquid fatty acids, which is broadly similar to the way sandcastles are bound by small volumes of liquid. We will illustrate how the lipid capillary bridges between colloidal nanoparticles can be used to provide new opportunities for assembling nanoparticles in the form of filaments, networks and self-repairing gels [9].

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Improving the Rheological Properties of Microemulsion Droplets using Thermoresponsive Block Copolymers

<u>Albert Prause</u>¹, Michelle Hechenbichler², Robert F. Schmidt¹, André Laschewsky^{2,3}, and Michael Gradzielski¹

¹Technische Universität Berlin, FG Physical Chemistry/ Molecular Material Science, Straße des 17. Juni 135, 10623 Berlin, Germany

²Department of Chemistry, Universität Potsdam, Karl-Liebknecht-Straße 24–25, 14476, Potsdam, Germany

³Fraunhofer Institute of Applied Polymer Research IAP, Geiselbergstraße 69, 14476 Potsdam, Germany

Presenting author e-mail: albert.prause@tu-berlin.de

Keywords: rheology, thermoresponsive polymers, microemulsion, light scattering, small-angle neutron scattering

The combination of polymers as thickener with microemulsions as carrier for hydrophobic substances results in an interesting colloidal system. A main interest is to control the structure and properties of those polymer-microemulsion systems by changing the different parameters, such as pH, salt, or temperature. Formerly, hydrophobically modified (HM) multiarmed polymers were investigated in mixtures with oil-in-water (O/W) microemulsions in respect to network formation and the resulting rheologic properties. Of special interest are hydrophobically modified thermoresponsive (HMTR) block copolymers in aqueous solution which can be used as thermo-active thickeners [1] or thermoresponsive amphiphiles for solubilization of hydrophobic molecules. However, the solubilization capacity of such systems is generally low. Hence, the combination with microemulsions (MEs) as carriers for hydrophobic substances results in loaded systems, where the rheologic properties of the microemulsion solution can be tuned and switched via temperature. A biofriendly microemulsion consisting of Tween20 (polyoxyethylene-(20)-sorbitan monolaurate) as surfactant, 2-ethylhexyl-glycerol as cosurfactant, isopropylpalmitate as oil and water as solvent was used.

Accordingly, various ME–polymer mixtures were studied for which three different block copolymer architectures of BAB*, B_2AB^* , and $B(AB^*)_2$ type were employed. Here, "B" represents a permanently hydrophobic, "A" a permanently hydrophilic, and "B*" a TR block. For the TR-block, three different poly(acrylamide)s, namely poly(*N*-*n*-propylacrylamide) (pNPAm), poly(*N*,*N*-diethylacrylamide) (pDEAm), and poly(*N*-isopropylacrylamide) (pNiPAm), were used, which all exhibit a lower critical solution temperature (LCST). For a well selected ME concentration, these block copolymers lead to a viscosity enhancement with rising temperature [2]. This phenomenon is caused by the formation of a transitory network mediated by TR blocks, as evidenced by the direct correlation between the attraction strength and the viscosity enhancement. For applications requiring a high hydrophobic payload, which is attained via microemulsion droplets, this kind of tailored temperature-dependent viscosity control of surfactant systems should therefore be advantageous.

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Ionisation and swelling behaviour of weak polyampholyte core-shell networks – a Monte Carlo study

Christian Strauch¹, Stefanie Schneider¹

¹Insitute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D 52056 Aachen Presenting author e-mail: <u>strauch@pc.rwth-aachen.de</u>

Keywords: polyampholyte microgels, Monte Carlo simulation

Polyampholyte microgels revers their charge from positive to negative with increasing pH, which makes them promising candidates for drug delivery systems and sensors. In our work, we investigated core-shell polyampholyte networks with an equal number of basic monomers (shell) and acidic monomers (core) using molecular modelling and Monte Carlo simulations. We were able to determine the ionisation of acidic and basic monomers independently and with spatial resolution with respect to the center of mass of the polymer network. These quantities are not accessible in classical titration experiments.[1] In salt-free solution and under good solvent conditions, we systematically varied the pK-values of the acid and calculated the degree of ionisation as a function of pH. The ionisation of acid and base is influenced by the presence of the other species. Depending on the difference of the two pK values, this mutual influence varies from small $(pK_a(acid) \gg pK_a(base))$ to very pronounced $(pK_a(acid) < pK_a(base))$. The influence of the other species is less pronounced than for alternating polyampholyte networks, but still present despite the spatial separation into core and shell. Density profiles show an interpenetration of core and shell at intermediate pH. With increasing pH, the swelling of the network shows a U-shaped transition from swollen over collapsed to swollen, which is typical for polyampholyte microgels^[2] and is an approximately linear function of the total polymer charge. Adding salt decreases the influence of the microgel concentration on the swelling and decreases the width of the pH regime of the collapsed state.



Figure 4. Cross-sections of a core-shell network with increasing pH (above) and different ΔpK at pH 7 (below) ($\Delta pK = pK_{0,base} - pK_{0,acid}$).

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Novel PVA-hydantoin and its stable embedding in biocidal cryogels exploiting phase-separation

Vanessa Rosciardi^{1,2}, Damiano Bandelli², Gavino Bassu^{1,2}, Ilaria Casu², and Piero Baglioni^{1,2}

¹CSGI-Center for Colloids and Interface Science, University of Florence, Italy ²"Ugo Schiff" Chemistry Department, University of Florence, Italy Presenting author e-mail: vanessa.rosciardi@unifi.it

Keywords: PVA, esterification, cryogel, phase-separation, hydantoin, anti-bacterial

Poly (vinyl alcohol) (PVA) gels prepared via freeze-thawing are widely applied in the biomedical field and are appealing candidates as wound dressing materials. Their functionalization with highly selective biocidal molecules can further improve the benefits of their application.

In this contribution, the synthesis of a novel hydantoin-functionalized PVA (H-PVA-hyd) is proposed. Changes in its conformation and water solubility were investigated, and an upper functionalization limit, above which the polymer is no longer suitable for the formulation of cryogels, was detected. The H-PVA-hyd polymer was stably embedded in biocidal cryogels by exploiting phase-separation mechanisms, and the permanence and distribution of the biocidal functionality after complete swelling were investigated via ¹H-NMR and FT-IR microscopy.

The activated H-PVA-hyd cryogels have been tested against *B.subtilis* and the outcomes were analyzed by direct observation of the bacterial population via confocal laser scanning microscopy (CLSM). The systems in which a phase-separating polymer was introduced prior to gelation resulted to be the most effective (up to 90% bacterial killing rate), as a consequence of their better retainage towards the biocidal H-PVA-hyd polymer (up to 99% of the polymer introduced in the formulation). The proposed phase-separation strategy could be extended to different polymeric gel systems when the efficient embedding of functionalized chains without recurring to chemical crosslinking is needed.

A versatile synthetic platform for amphiphilic nanogels: tailoring network hydrophobicity to biomedical applications

Clara López Iglesias^{1,2}, Ante Markovina¹, Alexandra Gruber¹ and Daniel Klinger¹

¹Freie Universität Berlin, Department of Biology, Chemistry and Pharmacy, Institute of Pharmacy, ²Universidade de Santiago de Compostela (Spain), I+D Farma (GI-1645), iMATUS, IDIS

Presenting author e-mail: claralopez@fu-berlin.de

Keywords: nanogels, amphiphilic, drug delivery

Polymeric nanogels are promising candidates for delivery applications but are mostly restricted to hydrophilic drugs. To overcome these limitations, we have developed nanogels with precisely tunable amphiphilicity.^[1] These nanocarriers combine two crucial characteristics within one colloidal system: a hydrophilic polymeric matrix for biocompatibility and flexibility, as well as randomly distributed hydrophobic groups throughout the network to form hydrophobic domains for encapsulation of hydrophobic drugs.^[2]

Preparation of such amphiphilic nanogels represents a significant synthetic challenge: Existing emulsion-based approaches can show dramatic variations in the nanogels' colloidal features upon changing the hydrophilic/hydrophobic ratio. Consequently, this should be avoided to ensure comparability between nanogels of different amphiphilicity and allow accurate determination of structure-property relations. To address this challenge, we have developed a new versatile synthetic method that uses a master batch of reactive precursor nanogels for subsequent functionalization with mixtures of hydrophilic/hydrophobic moieties.^[1] By this, we could de-couple the interior network functionality from the colloidal properties and systematically investigate their potential for biomedical applications. Regarding parenteral delivery, we examined the influence of nanogel amphiphilicity on the protein corona and the resulting cellular uptake.^[3] In combination with the determination of loading and release profiles of various hydrophobic drugs, we have identified suitable carrier structures for such delivery applications. Regarding topical applications, we have examined the influence of network amphiphilicity on the nanogels' mechanical properties and the resulting ability to transport model drugs to the viable epidermis.^[4]



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Hydrogels and water-in-water emulsions from chiral chromonic liquid crystals

<u>Pérez-Calm, A., 1</u> Kolen'ko, YV.,² Christophe, B.,¹ Esquena, J.¹ and Rodríguez-Abreu, C.¹

¹Instituto de Química Avanzada de Cataluña (IQAC-CSIC) and Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), Jordi Girona 18-26, 08034, Barcelona, Spain.

²International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga s/n, 4715-330 Braga, Portugal.

Presenting author e-mail: adria.perez@igac.csic.es

Keywords: perylene diimides, chiral chromonic liquid crystals, hydrogels, water-in-water emulsions

Chromonic liquid crystals are lyotropic mesophases formed by water-soluble planar polyaromatic compounds [1]. Herein, we describe the preparation and characterization of a chiral chromonic perylene diimide (PDI) functionalized with two terminal alanine groups, hereinafter (Ala)₂PDI. This planar molecule self-assembles in water at very low concentrations forming face-to-face columnar aggregates that evolve at higher concentrations to chiral nematic (above 12.5 wt%) and hexagonal mesophases (above 30 wt%). This is to our knowledge the first anionic perylene diimide forming chromonic mesophases.

Moreover, birefringent low molecular weight hydrogels were prepared by adding small amounts of glucono- δ -lactone (GdL) to nematic chromonic mesophases [2]. The nematic arrangement was retained, as revealed by SAXS measurements, but with an increase in the spacing between molecular stacks that resulted from swelling with water during gelation. Interestingly, the as-formed hydrogels were temperature-responsive, as the columnar stacks were disrupted upon heating.

Polymer-(Ala)₂PDI mixtures in water were also investigated. Notably, the (Ala)₂PDI nematic phase separated out in the presence of dextran (MW 86,000) and polyethylene glycol (MW 10,000) forming birefringent biphasic water-in-water emulsions. A similar behavior was observed using a non-gellable cationic PDI with the same polymers, which not only formed biphasic but also triphasic aqueous systems, suggesting that polymer-induced aqueous phase separation is a general phenomenon for chromonic PDIs. These results suggest that (Ala)₂PDI nematic phases can serve as soft templates in the preparation of biocompatible, temperature-responsive hydro- and microgels for drug delivery applications.



Figure 5. Graphical abstract.

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Why do hollow Microgels suppress Crystallization? – A Simulation Study

Tom Höfken¹, Alexander Petrunin¹, Stefanie Schneider¹ and Andrea Scotti¹

¹Institute of Physical Chemistry, RWTH Aachen, Germany Presenting author e-mail: <u>hoefken@pc.rwth-aachen.de</u>

Keywords: Microgels, Hollow Spheres, Binary Mixture, Crystallization, Molecular Dynamics

For some time, a well-established model system for soft colloidal particles have been microgels, cross-linked polymer networks swollen in a good solvent. Due to microgels being in the nano- to micrometer size-range their dynamics and properties can be nicely investigated using optical methods. Especially studying their phase behavior may yield valuable insights into the connection between properties of individual particles and system relevant quantities.

An immense variety of differently structured microgels have been experimentally realized. A most promising possibility among those internal architectures are hollow microgels, which contain a spherical cavity in their core. In general, hollow microgels are easier to deform and compress than their solid counterparts. Furthermore, it has been shown, that, unlike regular microgels, they do not crystallize [1]. The absence of crystallization is studied experimentally, by investigating binary mixtures containing regular and hollow microgels of the same size. It appears that a sufficient percentage of hollow microgels suppresses the formation of crystals. We perform molecular dynamic simulations to try to locate the microscopic origin of this observation.

On the one hand, we compare the effective pair potential acting between regular and hollow microgels (see Fig 1). Interactions of the hollow microgel are energetically more favorable, as they are mainly compressing the cavity instead of the polymer-network. On the other hand, we also studied a concentrated many-body system, containing multiple regular microgels interacting with one hollow microgel. At high concentration the hollow microgel is deformed first, which introduces a size- and shape-polydispersity to the system. We suggest these strongly aspherically deformed hollow microgels are the key to explain their role in suppressing the crystallization of the system.



Figure 6. Interaction potential between two regular; two hollow; and in-between a regular and a hollow microgel as a function of their normalized distance.

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Particle Stabilized Bicontinuous Emulsions: Basic Science for Sustainable Materials

Martin F. Haase¹

¹Utrecht University

e-mail: m.f.haase@uu.nl

Bicontinuous Interfacially Jammed Emulsion Gels (bijels) are self-assembled soft materials composed of two interpenetrating fluid networks. The bicontinuous fluid arrangement of a bijel is obtained by kinetically arresting the spinodal phase separation of two immiscible liquids [1]. To this end, particles attach to the interface and stabilize an oil/water channel system via interfacial jamming. The final bijel is tri-continuous, because oil, water, and the layer of colloids are all continuous. This unique architecture facilitates applications of bijels as separation membranes [2, 3], microreactors [4], and energy-storage devices [5]. Here, we employ solvent transfer induced phase separation (STrIPS) [6,7] to form bijels with nanostructured domains. We will discuss the postprocessing of bijels to enable their use as materials for sustainable technologies.



Figure 7. The nightmare of each plumber is a large network of entangled and branched pipes. Here, this assembly is realized for pipes with diameters of a few hundred nanometers.

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Nanoparticles/microgel hybrids as catalytically active Pickeringemulsifier

Martin Bick¹, Thomas Hellweg¹

¹Bielefeld University, Physical and Biophysical Chemistry, Bielefeld, Germany Presenting author e-mail: <u>Martin.Bick@uni-Bielefeld.de</u>

Keywords: Microgels, Pickering-emulsions, Catalysis

Pickering-emulsions are dispersions that are stabilized by particles absorbing at the liquidliquid interface. One class of particles that can stabilize these kinds of emulsions are microgels. When using thermoresponsive microgels, an emulsion can be obtained that can be broken on demand by changes in the temperature.[1] If an acid- or base-function is copolymerized into the microgel, an additional pH-sensitivity can be obtained. [2] This behavior makes these systems interesting as a medium for chemical reactions that involve both water and oil soluble components.[3]

For the use of microgels as a carrier for nanoparticles acid functions can be copolymerized to act as anchor points for the metal. Microgels, that can stabilize emulsions have to satisfy different attributes. A key parameter for the stabilization is the deformability of the microgel.[4] Therefore, very loosely crosslinked microgels are necessary to stabilize emulsions.

In this work a microgel was designed that can host catalytically active palladium nanoparticles while being able to stabilize Pickering emulsions. To obtain a microgel that can satisfy the needs for both features a core-shell structure was chosen. The core consists of N-*n*-propylacrylamide (NnPAM) as a monomer. Methacrylicacid (MAA) was copolymerized into the core to serve as anchor points for palladium nanoparticles and to gain a pH-responsiveness. The shell was synthesized with N-isopropylmethacrylamide (NIPMAM) as the monomer. After successful incorporation of palladium nanoparticles, as a model reaction a Suzuki-Miyaura-coupling reaction was performed in a methyl-*tert*-butyl ether in water emulsion. The reaction was successfully carried out and the product could be separated by breaking the emulsion.

Figure 8. A) *A water in MTBE emulsion during the catalysis. B) The same system broken after the catalysis. C) The different components after phase separation.*



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Amphiphilic Nanogels as Versatile Stabilizers for Pickering Emulsions

<u>Ruiguang Cui¹</u>, Ante Markovina¹ and Daniel Klinger¹

¹Freie Universität Berlin, Department of Biology, Chemistry and Pharmacy, Institute of Pharmacy, Königin-Luise-Str. 2–4, 14195 Berlin

Presenting author e-mail: <u>ruiguang.cui@fu-berlin.de</u>

Keywords: Pickering emulsion, amphiphilic, nano-/microgels, phase inversion, Flory-Huggins parameter, water-in-oil emulsion

Nano-/microgels are increasingly investigated as soft colloidal stabilizers in Pickering emulsions (PEs). These flexible and swollen colloids behave differently than traditionally used solid nanoparticles, where emulsion type is determined by the particles' well-defined contact angle at the oil/water interface. In contrast, soft nano-/microgels can deform at the oil/water interface due to their swelling. In most cases, the hydrophilic networks of nano-/microgels cause their preferential swelling in the water phase, leading to oil-in-water (O/W) emulsions. For water-in-oil (W/O) emulsions, the internal networks of the nano-/microgels need to be more hydrophobic to ensure successful stabilization. However, up to now, accurately correlating network hydrophobicity to complex interfacial swelling profiles and the resulting emulsion type is still challenging. This can be attributed to the synthetic difficulties in accurately controlling the network hydrophobicity in such colloidal particles.

To address this challenge, we have developed a versatile method for preparing a library of amphiphilic nanogels (NGs) with accurately tuned network hydrophobicity but similar colloidal features. [1-2] Our synthetic approach is based on network functionalization of reactive NG precursors with various ratios of hydrophilic and hydrophobic (dodecyl amine - DODA) moieties. For NGs with DODA contents from 0 - 40 mol%, the influence of network hydrophobicity on emulsion properties was examined. It was found that W/O emulsions are preferentially formed with increasing NG hydrophobicity, oil polarity, oil/water ratio, and temperature. Intriguingly, the phase inversion behaviors can be explained quite well by the difference in the Flory-Huggins parameter of NGs with water and with oil ($\chi_{water} - \chi_{oil}$). Carefully balancing these parameters even allows the formation of W/O emulsions from non-polar cyclohexane. Moreover, W/O high internal phase emulsions (HIPEs) can be prepared and transferred into solid porous materials by polymerizing the oil phase. Overall, we envision this strategy to serve as a platform for accurately tuning the properties of PEs to advanced applications such as interfacial catalysis, biomaterials, and drug delivery.



Figure 9. Network hydrophobicity in amphiphilic nanogels controls the type of Pickering emulsion.

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Unusual gold nanoparticle-antibody interactions

<u>Helena Mateos¹</u>

¹Dipartimento di Chimica, Università di Bari and CSGI, 70125, Bari, Italy Presenting author e-mail: <u>helena.mateos@uniba.it</u>

Keywords: Immunoassay, colloidal stability, protein corona, DLS, TEM, antibody aggregation

The formation of an antibody (Ab) protein corona around gold nanoparticles (AuNPs) stabilizes AuNPs avoiding their aggregation also at high ionic strength and can be obtained by the simple mixing of Abs and AuNPs [1]. In this work we report the uncommon interactions between AuNPs and the Ab against L1 Cell Adhesion Molecule (L1CAM).

At low ionic strength the addition of rabbit monoclonal Abs against L1CAM protein induces immediate coagulation of AuNPs. This is surprising since usually the addition of proteins to colloidal gold forms a stable protein corona. The combination of extinction spectra, DLS and TEM shows the coexistence of small AuNPs clusters coated by Abs and micron size Ab aggregates. Moreover, SLS measurements show that Ab self-interactions are attractive (second virial coefficient B2<0) and induce very slow Ab self-aggregation.

As seen in Figure 1, the addition of NaCl to obtain high ionic strength fully reverts the AuNPs coagulation and dissolve the aggregates (repulsive Ab interactions (B2>0)). This was rationalized by considering the favorable binding of Abs on the gold surface already paid the entropic penalty associated to Ab-Ab aggregation.

This phenomenon agrees with very old reports on AuNP coagulation induced by the immunoglobulins present in the cerebrospinal fluid of patients suffering neurosyphilis or multiple sclerosis [2]. It is reasonable to hypothesize that other antibodies share this unusual behavior so this work may assist in the interpretation of "anomalous" results that might otherwise be attributed to errors in the fine-tuning of AuNPs-Abs conjugation protocols.



Figure 10. Effect of the addition of NaCl to a sample of AuNPs-antiLCAM seen visually from the pictures of the samples, TEM micrographs and UV-vis absorbance spectra.

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Introducing nanoscale pores into complex hierarchical materials by using sol-gel chemistry and evaporation induced self-assembly

Joanna J. Mikolei¹, Marcelo Ceolin² and Annette Andrieu-Brunsen¹

¹Technical University of Darmstadt, Chemistry, Darmstadt, Germany ²Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas; Universidad Nacional de La Plata and CONICET, Argentina

Presenting author e-mail: joanna.mikolei@tu-darmstadt.de

Keywords: hierarchical mesoporous systems, control of the nanopore formation, EISA-process, paper-based hybrid material, sol-gel chemistry

Pores in mesoporous materials can be functionalized with for example stimulus responsive polymers, which allows to mimic natural processes like controlled ion transport, as well as to optimize ion separation and sensing.^[1] Based on the evaporation induced self-assembly (EISA) process mesoporous thin films can be deposited at smooth homogenous surfaces like glass.^[2] In this work we transfer the well-established EISA process to the very hierarchically structured material paper as well as to cotton threads to design and control their nanoscale porosity in a defined manner. Due to their structure, paper sheets as well as cotton threads inherit capillary forces driven microfluidic fluid flow. Based on the capillary fluid flow the sol-gel solution is transported inside the papers and the threads next to the deposition of the solution on the paper and thread surface. This influences the mesopore formation during EISA process. We were able to understand the interplay between the polycondensation, mesopore formation and the capillary fluid flow during the dip-coating while performing argon gas adsorption, small angle x-ray scattering as well as TEM measurements. This finding allows us to tune the EISA process in paper with respect to these parameters. Due to the adjustment of the template concentration with respect to the capillary flow velocity mesopores are formed onto paper as well as onto cotton threads. This is of great importance in the field of gating, sensing and separation issues as well as for controlling the paper microfluidic properties^[3, 4], which opens the possibility to use paper/threads as a high-tech material.



Figure 11: Interplay between fluid transport velocity, precursor condensation and critical micellar concentration for mesopore formation during EISA based paper dip-coating process.

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Bioceramic nano- and microparticles as components tissue engineering

Bogdan Parakhonskiy, Anatolii Abalymov, Nooshin Asadi, Louis Van der Meeren, Andre Skirtach

Ghent University, Proeftuinstraat 86, Ghent, 9000, Belgium Presenting author e-mail: bogdan.parakhonskiy@ugent.be

Keywords: Calcium carbonate; mineralization; particles; drug delivery; enzymes

Hydrogels, which are versatile three-dimensional structures containing polymers and water, are very attractive for use in biomedical fields, but they suffer from rather weak mechanical properties. In this regard, designing hydrogel-based biomaterials with cell-binding sites, tunable mechanical properties and complex architectures as a powerful tool to control cell adhesion and proliferation for tissue engineering.

In our study, we use the bioceramic colloidal micro/ nanoparticles as a key component of such a system. Particles containing various ratios of Ca^{2+}/Mg^{2+} with sizes ranging from 1 to 8 µm were prepared and mixed with gellan gum (GG) solution to study the in-situ formation of hydrogel-particle composites. The particles provide multiple functionalities: 1) they efficiently crosslink GG to induce hydrogel formation through the release of the divalent cations (Ca^{2+}/Mg^{2+}) known to bind to GG polymer chains; 2) they enhance mechanical properties of the hydrogel from 2 up to 100 kPa; 3)particles provide a delivery function, where loading efficiency and loading capacity are depending on particle size, time of enzyme loading, and various container compositions and enzyme concentrations 4) the samples most efficiently promoting cell growth were found to contain two types of minerals: calcium carbonate and hydromagnesite, which enhanced cells proliferation and hydroxyapatite formation.



Figure 12. Schematic of the functional colloids preparation and their application

A refined way of synthesis and particle modification (Fig 1) allows preparing the enzyme delivery system with functionalized protection layers as well as a diagnostic platform that can provide surfaceenhanced Raman scattering effect (SERS). Our results reveal that the size of particles influences their morphology and this, in turn, affects the activity of the encapsulated enzymes.

The presence of a therapeutic effect on osteoblastic cells coupled with a relatively high loading capacity, biocompatibility, and ease of fabrication suggests that the developed carriers are promising candidates for efficient drug delivery, especially in the field of bone reconstruction.

How Salts Affect the Activity of Urease

<u>Mert Acar¹</u>, Federico Rossi² and Pierandrea Lo Nostro¹

¹ Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Sesto Fiorentino, Italy ² Department of Earth, Environmental and Physical Sciences, University of Siena, Italy

Presenting author e-mail: mert.acar@unifi.it

Keywords: hofmeister series, enzymes, urease

In this study, we explore the effects of electrolytes on urease, an enzyme that catalyzes the hydrolysis of urea with a resulting pH increase in unbuffered aqueous solutions.

Chemistry and biology are strongly ion specific. Why is the interplay between Na^+ and K^+ inside/outside cells so crucial? Why does only lithium among the alkali metal ions works so well to treat bipolar illness? The answers to these questions have to do with specific ion effects.

Effects of electrolytes on enzyme kinetics cannot be accounted for by non-specific Coulombic interactions. In fact, specific ion effects in proteins and enzymes are extremely important and may determine remarkable changes in protein folding, stability, solubility, aggregation, fibrillation, and action kinetics [1,2]. Moreover, understanding how ions regulate enzyme activities is crucial for the development of enzyme-based formulations and for biotechnological applications.

This work aims at determining and understanding how the electrolytes affect urease activity. We exploit the autocatalytic behavior of urease in nonbuffered solutions and focus on the pH clock reactions to investigate the specific ion effects on the clock time (see Figure 1). To estimate the process rate, the pH change is followed as a function of time, and the normalized differences in the clock time and the maximum rates were compared. Finally, the concentration dependence of the observables is analyzed and discussed in terms of specific ion-enzyme interactions and hydration.

Our results show that cations and anions have different effects on the enzyme activity and do not share the same interaction mechanisms. The data are discussed in terms of the kosmotropic/chaotropic nature of the ions. These findings offer important insights into the mechanism of the enzyme's activity, and into the nature of ion-enzyme interactions.



Figure 13. pH versus time plot showing the clock time of the blank solution. Inset shows the first derivative $(\partial pH/\partial t)$ values versus time of the same plot.

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Enhanced Solubilization of Fragrances in Solutions of Sugar Surfactants in Mixtures of Deep Eutectic Solvents (NADES) and Water.

Tomáš Omasta 1, Anton Michel 1 and Michael Gradzielski1

¹Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin, Germany

Presenting author e-mail: <u>t.omasta@tu-berlin.de</u>

Keywords: solubilization, fragrances, NADES, sugar surfactant, terpenes

Solubilization of fragrances in aqueous solutions has been already studied for a long time[1]. Interestingly, such fragrances can be also solubilized in natural deep eutectic solvents (NADES), a novel class of polar solvents that has the potential to become a non-toxic and cheap alternative to conventional organic solvents, ionic liquids, or even water.

As a result of our experiments, the NADES based on choline chloride and urea, dubbed "reline", is a good candidate for solubilizing fragrances. Both components, choline chloride, and urea are inexpensive and widely used in agriculture[2]. We were able to widen the limited scope of reline-soluble surfactants with sugar surfactants. They are already being industrially produced from biomass and are readily biodegradable[3]. More specifically, we examined and characterized numerous glucosides to dissolve terpenes and other fragrances. With specific formulations, we achieved to dissolve terpenes such as limonene, α -pinene, eucalyptol, or *p*-cymene up to 25 wt% of the total mixture mass, see Figure 1.

All components were chosen thoroughly with an emphasis on biocompatibility, biodegradability and their low price. Interestingly, controlled water content not only enhances the solubility of fragrances but also affects the internal structure and viscoelastic properties of the final formulations, see Figure 1. Such property could find application in cosmetics and pharmaceuticals in form of creams and topical drug delivery.



Figure 14. Left: Chemical structures of four terpenoids (limonene, a-pinene, eucalyptol and p-cymene) and their sources in nature (lemons, pines, eucalyptus, cumin). Right: SANS of eucalyptol solution (200 mM) in reline with different D_2O content (ISIS).

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Ion Effects in Colloidal Science - beyond simple Electrostatics

<u>Dominik Horinek¹</u>, Author² and Author^{1,2} (12pt Times Roman, Italics)

¹Institute of Physical Chemistry, University of Regensburg, D-93040 Regensburg Presenting author e-mail: <u>dominik.horinek@ur.dem</u>

Keywords: salts effects, ion effects, Hofmeister series

Salts play an important role in many colloidal systems. They screen electrostatic interactions and ions are attracted or repelled interfaces. Since the early days of colloidal science, the explanation of salt effects gave rise to many well know models, for example the iconic DLVO theory. In these models for charged particles, the Coulomb interaction always plays a dominant role. But ion effects cannot be understood solely based on electrostatics, especially effects that are specific for a certain anion, cation, or combination thereof. For small ions, for example from the alkali metal or halide groups, some key principles have been understood like the concepts of strong vs. weak hydration or the ordering of these ions in the Hofmeister series. In recent years a new class of ions has been the topic of interest: ions that are much larger in size and are at the same time multiply charged. These "nanoions" have special properties in the way they bind to interfaces and solutes. For this class of ions, the theoretical understanding is much less developed.

In my talk, I will give a short overview of established theories and discuss models that go beyond electrostatics. Results from molecular dynamics simulations, which are a very powerful method for the study of ions in colloidal and interfacial systems, will be presented.

Origin of the Shift Between Macro-and Microrheology

<u>Robert F. Schmidt ¹</u>, Henrik Kiefer ², Michael Gradzielski ¹, Roland Netz ²

¹ Stranski-Laboratorium, Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin ² Institut für Theoretische Physik, Freie Universität Berlin, 14195 Berlin

Presenting author e-mail: <u>r.schmidt.1@tu-berlin.de</u>

Keywords: rheology, microrheology, hydrogel

Classical macrorheology experiments require comparatively large sample volumes and the accessible frequency range for oscillatory measurements is limited to lower values up to 100 Hz. Microrheology can overcome these limitations by determining rheological properties from the movement of microscopic tracer particles inside the sample. The particle mean-squared displacement (MSD), which is experimentally accessible through dynamic light scattering (DLS) can be converted into the complex shear modulus G^* using the generalized Stokes-Einstein equation (GSER) [1].

We compared the results from macro- and microrheological measurements of aqueous solutions of poly(ethylene oxide) (PEO) for different tracer particle sizes and for a wide range of viscoelasticities to test the validity of the GSER. Similar to previous investigations, agreement is generally good for samples with intermediate viscoelasticity [2]. However, we have found that for very low and very high viscous samples, microrheology yields an overestimation and underestimation of the dynamic modulus G^* , respectively.

Following the work of Fan et al. [3], we attribute these discrepancies between the two methods to the formation of a spherical shell around the tracer particles with a local viscosity that is different from the bulk. This decrease or increase in the local viscosity can be explained by depletion or accumulation of polymer around the tracers. We found that the properties of the shell depend on the length of the polymers, as well as their concentration.





Figure 15. A) The data from macrorheology (lines: G', broken lines: G'') and microrheology (circles: G', triangles: G'') are shifted against each other. B) The shift is explained by the formation of a spherical shell of lower or higher local viscosity compared to the bulk.

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Dynamic light scattering, rheology and simulations of Interpenetrating network microgels

Elisa Ballin¹, Roberta Angelini^{2,3}, Lorenzo Rovigatti^{2,3} and Barbara Ruzicka^{2,3}

¹Department of chemistry "Ugo Schiff" University of Florence, CSGI and University of Perugia ²Consiglio Nazionale delle ricerche CNR-ISC ³Department of Physics, Sapienza University of Rome

Presenting author e-mail: elisa.ballin@unifi.it

Keywords: IPN microgels, PNIPAM, PAAc, Rheology, DLS, Simulations

Soft colloids have recently attracted great attention both in fundamental studies and applications thanks to their deformability, elasticity and interpenetrable nature, providing a very rich phenomenology. Among soft colloids, microgels, particles composed of chemically crosslinked polymer networks, are very enthralling due to their hybrid nature which combines the properties of polymers and colloids.

Herein we focus on a colloidal suspension of poly(N-isopropylacrylamide) (PNIPAM) microgel [1] and on colloidal suspensions of interpenetrated polymer network (IPN) microgels made of PNIPAM and poly(acrylic acid) (PAAc) [2]. PNIPAM microgels change their affinity with the solvent as the temperature changes; the addition of the second network of PAAc makes IPN microgels sensitive also to pH. Moreover, these systems undergo to a phase transition passing from a liquid to an arrested state as a function of concentration.

The study aims to verify the influence that different contents of N,N'-methylbisacryla mide (BIS), the crosslinker used to polymerize the PAAc network, have on the swelling behaviour, the dynamics and the viscoelastic properties of the systems. To this purpose, concentration, temperature and pH-dependence of the dynamic of four different IPN microgel solutions is carefully investigated through Dynamic Light Scattering (DLS) and rheology. The swelling behaviour of PNIPAM and IPN microgels is also studied performing molecular dynamics simulations. This *in silico* study on microgel particles is divided in three phases. As a first step the swelling behaviour of a microgel particle composed of single-network is studied. Then it is analysed how the swelling capability is affected by the introduction of a second neutral interpenetrated network that does not respond to temperature changes. Eventually the effects that a second charged network introduces on the swelling behaviour is investigated.

Both experimental and simulation data allow to conclude that the different concentrations of BIS have a strong effect on the swelling capability of IPN microgels and on the softness of their structure. Particularly a higher concentration of BIS reduces the swelling capability of microgels particles as a function of temperature. Moreover, also the slowing down of the dynamics up to the formation of an arrested state is influenced by the BIS concentration. Results suggest that a higher concentration of BIS shifts the transition to an arrested state to higher concentrations of IPN solutions. These findings open the way to further investigation on the role that topological constrains have on the interactions between microgel particles and how they influence the transition to arrested states.

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Programmable morphology-determined total internal reflection of light by multi-phasic colloids

Bradley D. Frank¹, Pablo Simón Marqués¹, and Lukas Zeininger¹

¹Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany

Presenting author e-mail: Bradley.Frank@mpikg.mpg.de

Keywords: Adaptive optical colloids, micro solar concentrators

Adaptive optical materials capable of reversible dynamic alteration respond to desired stimuli, collecting and transducing information as light. Materials with one or more interfaces can modulate their intrinsic optical properties or utilize morphological transformation to adapt the behavior of light. The chemical orthogonality of Janus droplets connects nano-scale chemical events into a structural response that is sensitive, inexpensive, and quick. Utilizing this chemo-morphological coupling, the detection of e.g., antibodies, pathogens, enzymes, PFAS, and metal ions, have been reported.

While the connection between environmental change and droplet morphology is established, a method for simple and quick measurement of polydisperse samples is required. Spherical Janus colloids with a morphology-tunable internal optical interface can totally internally reflect light dependent on morphology. Gravity-aligned Janus droplets with an internal refractive index contrast induce environmental and structural effects that contribute mutually to programmable optical behaviors. We investigate total internal reflection at the internal droplet interface, and the resulting morphology-determined anisotropy of both incident (Figure 1a) and emissive light (Figure 1b).

Janus emulsion droplets concentrate incident solar light as total internal reflection, demonstrated as photocatalytic microreactors (Figure 1a), where the collection of light and oxygenrich fluorocarbon phase increase reaction yield to 89% from 5% in bulk conditions.[1] We directly measure the anisotropic morphology-determined emission band around dyed Janus droplets with a rotating fluorescence microscope to verify analytical and simulated experimental insight (Figure 1c,d). Using this angular emission, we present a ratio-metric sensing scheme to measure monolayers of polydisperse emulsion droplets responding to their chemical environment. Further engineering of volume ratio, refractive indices, and radiative emission transfer are used to control the signal-to-no ise ratio. Our findings constitute a comprehensive adaptive optical system, where optical effects determined by droplet structure and the local environment will enable the generation of tailored particles [2], and transduction of nano-scale effects into collective macro-scale information.



Figure 16. a) Schematic for total internal reflection of incident (a) and emissive light (b) within bi-phasic Janus colloids. c) Optical and fluorescence micrographs of angle-dependent dyed Janus droplet emission. d) Overlaid simulated incident and emissive light intensity maps for three different Janus morphologies.

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Polymer Brush/Gold Nanoparticle Composite Materials: Controlling the Structure of Components and Composite with Ion-Specific Effects

Philipp Ritzert¹, Lorena Šimunić¹, Olaf Soltwedel¹, Stephen Hall², and Regine v. Klitzing ¹

¹Soft Matter at Interfaces, Institute for Condensed Matter Physics, TU Darmstadt, 64289 Darmstadt, Germany ²ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot Oxfordshire, OX11 0QX, UK

Presenting author e-mail: philipp.ritzert@pkm.tu-darmstadt.de

Keywords: functional materials, polymer brush, thin film, gold nanoparticle, structure formation

The Nanocomposite materials based on inorganic gold nanoparticle (AuNP) inclusions inside an organic matrix (e.g. polymer brushes) are employed in various fields: medical technology, catalysis, materials engineering. Combining the properties of both material classes facilitates high versatility of mechanical, optical and chemical properties, while simultaneously covering obvious drawbacks, e.g. stability of one compound.

To provide the wide range of applications, nanocomposite materials usually require a specific internal structure. Yet, the understanding of the formation of internal structure and control over formation process is still lacking. Therefore, we aim to provide an approach to manufacture nanocomposite materials with controlled structure.

Our model system utilizes various sodium salts (anion: F, Cl, Br, I, SCN) as stimuli for the assembly of citrate-capped gold nanoparticles in a poly-(N-isopropylacrylamide) brush. In a first step, we characterize the effect of sodium salts on pure AuNP suspensions. In a second step, we investigate adsorption parameters of AuNPs from suspension to brush, e.g. adsorption time. The third step involves the structure control of the composite materials with the characterized stimuli, similar to previous works [1]. Optical measurements reveal distinct differences between the sodium ions and concentration dependent aging behavior, as exemplified for AuNP suspensions in Figure 1.



Figure 17. AuNP (5 nm) suspensions with varying salt type and concentration: directly after mixing (upper) and 12 h later (lower). The samples are ordered from left to right with increasing salt concentration and ion size of the sodium salt (F, Cl, Br, I, SCN).

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Tailoring Non-Ionic Microgel Swelling by Nano-Ion Binding

Jasmin Simons¹, Max Hohenschutz¹ and Walter Richtering¹

¹ Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany

simons@pc.rwth-aachen.de

Keywords: Microgels, Chaotropic Effect, Nano-Ion, Swelling Behavior

Microgels are mesoscopic, three-dimensional crosslinked polymer networks, which are swollen in a good solvent. Their ability to react to external stimuli like temperature, ionic strength, pH and pressure makes it possible to adjust their physicochemical properties reversibly. Moreover, encapsulated solutes can strongly affect the properties of microgels in solution. Microgels are widely used as carriers for active substance for example, in biomedical or catalytic applications. [1]

As model solutes, nanometre-sized ions, such as the polyoxometalate $SiW_{12}O_{40}^{4-}$ (SiW) and the boron cluster $B_{12}I_{12}^{2-}$ (BI) have recently gained much attention due to their propensity to adsorb to non-charged soft matter interfaces owing to a water-mediated driving force, called the chaotropic effect. Superchaotropic nano-ions have thus emerged as potentially useful soft matter additives as they assemble with non-ionic solutes and convey their inorganic traits (for example catalytic) to the soft matter material. [2,3]

This leads us to explore the influence of SiW and BI on the swelling behaviour of non-ionic pNiPAM microgels by light and small angle x-ray scattering. We show that millimolar amounts of SiW induce swelling of the microgel below the volume phase transition temperature (VPTT), while BI swells the microgel above the VPTT. At higher concentrations of SiW the microgels were found to collapse even below the VPTT. In comparison to a 5 %-crosslinked microgel, ultra-low crosslinked microgel exhibit dramatically increased swelling/deswelling with nano-ion concentration. By choice of the nano-ions it is thus possible to tune the swelling behaviour of non-ionic pNiPAM microgels in solution. Swelling and deswelling are due to an electrostatic mechanism and can be switched by adjusting the pH for SiW.



Figure 18. Hydrodynamic radius r_H of a microgel with 5 % cross-linker at different concentrations of (a) HSiW, and (b) NaBI as a function of temperature T. Molecular structures of SiW and BI are inserted, respectively in (a) and (b). The arrows depict the swelling trend with concentration.

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Phase Separation in Wetting Ridges of Sliding Drops on Soft and Swollen Surfaces

Lukas Hauer^{1,2}, Zhuoyun Cai², Artem Skabeev³, Doris Vollmer¹ and Jonathan T. Pham²

¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany ²Department of Chemical and Materials Engineering, University of Kentucky, Lexington, USA ³Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich Schiller University Jena, Lessingstrasse 8, 07743 Jena, Germany

Presenting author e-mail: <u>hauerl@mpip-mainz.mpg.de</u>

Keywords: Wetting, Elastocapillary, Phase Separation, Polymer Gels

Sessile drops on soft substrates can induce capillary-mediated phase separation of free polymers (oligomers) in wetting ridges. However, direct observation of the free chain accumulation in the wetting ridge under dynamic wetting conditions is still lacking. Detailed information on the reorganization of the chains is critical to assess the functionality and durability of the substrate.

In this talk, I discuss wetting ridges on soft and swollen substrates (elastomers) during forced wetting. Confocal microscopy and fluorescence dyes on the free and crosslinked chains enable discrimination between the phases. This directly resolves the network and free chains temporally and spatially around the three-phase contact zone during wetting. Water drops are slid on the surface of lightly crosslinked PDMS surfaces (60:1, weight ratio crosslinker to PDMS chains), and swollen with silicone oil (10 to 16 times the dry network volume). We find that the two phases (oil and network) separated to a differing degree, depending on the sliding speed and the amount of swollen oil. A diffusion-advection model that considers the chemical potential in the respective phases is developed and validated with experimental data. The model helps to explain I) the degree of phase separation, and II) the mobility of the silicone oil in the PDMS network.



Figure 19. Phase separation in moving wetting ridge. Left, schematic of the oligomer fluxes. Right, confocal image of the wetting ridge where red is the dye in the separated silicone oil and orange the network-oil mixture.

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Gelatin Methacryloyl and Dextran Aqueous Two-Phase Systems: journey from solution to hydrogel state

Evdokia Stefanopoulou^{1,2}, Ghazi Ben Messaoud^{1,2}, Horst Fischer ³and Walter Richtering ^{1,2}

¹Institute of Physical Chemistry, Landoltweg 2, 52074, RWTH Aachen, Germany ²DWI-Leibniz Institute for Interactive Materials, Forckenbeckstraße 50, 52074, Aachen, Germany ³Department of Dental Materials and Biomaterials Research (ZWBF), Paulwelsstraße 30, 52074, RWTH Aachen University Hospital, Germany

Presenting author e-mail: stefanopoulou@pc.rwth-aachen.de

Keywords: gelatin methacryloyl, segregative phase separation, porous hydrogels, sheared hydrogels.

Aqueous two-phase systems (ATPS) are involved in various applications from artificial extracellular matrices and cell carriers to microfluidics, membranes and hydrogels [1]. Understanding the process of phase separation and optimizing the conditions under which this can occur has a great impact on the properties of the targeted application.

In this work, an ATPS based on gelatin methacryloyl (GelMA) and dextran is employed, in order to produce porous hydrogels. GelMA is a polyampholyte that constitutes the gelling phase and dextran is a neutral polysaccharide used as a sacrificial template to produce the pores in the hydrogel. Segregative phase separation of the two polymers in solution is triggered by approaching the isoelectric point (IEP) region of the synthetized GelMA, through acidification or by adding salt to the system. The demixing occurs as a result of the decrease of GelMA's charge density. The phase diagram of GelMA/dextran is determined and demonstrates that the binodal line shifts to lower components' concentrations when the pH is near the IEP [2]. Turbidity increase is also indicative of the demixing of the two polymers in solution state, which can be observed by UV-Vis Spectroscopy.

The second part of this study concerns the development of hydrogels from the ATPS system by photo-crosslinking of the GelMA phase during the phase separation to quench the microstructure. The hydrogels are prepared by either casting at rest or under shear in situ using UV-rheology. The porosities and microstructures that are achieved vary from porous or interconnected to fibrous or band-like after applying shear. Rheology allows us to further optimize the microstructure and obtain information about the gelation kinetics and mechanical properties of the hydrogels. Confocal laser scanning microscopy (CLSM) is also utilized to probe the produced microstructures, where clearly one can distinguish between nucleation and growth or spinodal decomposition as the phase separation mechanism. Although an unstable mechanism, the latter provides us with an interconnected microstructure, which is reproducible and is considered optimal for future cell applications.



Figure 20. Hydrogels' microstructures that have been achieved: Bicontinuous and regular pores by casting at rest. Bands and fibers by UV-rheology. The GelMA phase is labelled red and dextran is the dark phase.

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Α

Azobenzene Functionalized, Multi-responsive Polymers: Exploring (Counter-) Intuitive Cloud Point Shifts

<u>René Steinbrecher</u>¹, Peiran Zhang², André Laschewsky^{1,3} and Christine M. Papadakis²

¹University of Potsdam, Institute of Chemistry, Potsdam-Golm, Germany ²Technical University of Munich, Physics Department, Garching, Germany ³Fraunhofer Institute for Applied Polymer Research IAP, Potsdam-Golm, Germany

Presenting author e-mail: rene.steinbrecher@uni-potsdam.de

Keywords: multi-responsive polymers, azobenzene, counterintuitive behavior

We explore multi-responsive polymers, which combine thermo-responsive and photoresponsive properties. A priori, such systems have the advantage that both temperature and light are non-invasive and independent triggers. Furthermore, such stimuli are fast and simple to apply. For achieving thermo-responsive behavior, alkyl substituted acrylamide copolymers are used. Further, the azobenzene moiety is incorporated as photoactive group. Its reversible trans-cis isomerization is a well explored process which modulates its hydrophobicity. This effect has been used to increase the lower critical solution temperature (LCST) transition of water soluble polymers after irradiation, typically by around 5 °C, in an extreme case up to 14 °C [1]. Yet, the effect of the azobenzene moiety has not been fully understood, and even a counterintuitive decrease of the LCST transition temperature after irradiation was reported. However, these shifts are generally even smaller [2,3].

Based on a rational design, we prepared several copolymer sets that show, against the common knowledge, opposite directions of photo-induced LCST shifts depending on their azobenzene content. In a specific case, we achieved a decrease of almost 10 °C after UV-irradiation. Such an exceptionally huge counterintuitive effect of azobenzene trans-cis isomerization has not yet been reported before.

We will present the synthesis and characterization of the thermo- and photo-responsive copolymers as well as the effect of cyclodextrin on the LCST transition. Figure 1 summarizes the (counter-) intuitive cloud point (CP) shift behavior.



Figure 21. Difference ΔT_{cp} cis-trans after 15 min of irradiation at 365 nm (LED). Aqueous solution (1 g/L) of copolymers polymerized from N-ethyacrylamide (NEAm), dimethylacrylamide (DMAm) or methylacrylamide (MAm) with azobenzeneacrylamide (AzAm).

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Supraparticles on beads for supported catalytically active liquid metal solutions – the SCALMS suprabead concept

<u>Philipp Groppe¹</u>, Thomas Zimmermann¹, Nnamdi Madubuko², Theodor Raczka¹, Marco Haumann², Karl Mandel^{1,3} and Susanne Wintzheimer^{1,3}

¹Department of Chemistry and Pharmacy, Professorship for Inorganic Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstraße 1, 91058 Erlangen, Germany ²Lehrstuhl für Chemische Reaktionstechnik (CRT), Friedrich-Alexander-Universität Erlangen-

Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany ³Fraunhofer Institute for Silicate Research ISC, Neunerplatz 2, 97082 Wuerzburg, Germany

Presenting author e-mail: philipp.groppe@fau.de

Keywords: suprabeads, supraparticles, supported catalytically active liquid metal solutions (SCALMS), catalysis, novel materials, colloid characterization

In this work, a novel Gallium-Platinum (GaPt)-based supported catalytically active liquid metal solution (SCALMS) material is developed by exploiting the suprabead concept: Supraparticles, i.e. micrometer-scaled particles consisting of nanoparticles assembled by spray-drying, are bound onto millimeter-scaled beads. The approach achieves the enlargement of the entities' size into the millimeter region while ensuring the maintenance of the unique properties of the µm-scaled particles. The created material provides the catalytic properties of a GaPt nano-alloy and is tested in the industrially relevant propane dehydrogenation (PDH) reaction.[1]

The use of supraparticles as catalyst materials offers a vast combination variety of different materials in one system.[2] By this, it enables the entrapment of the catalytic species into a mesoporous support framework (herein: GaPt inside silica (SiO₂)). Especially, as Ga shows poor pore intrusion for commonly used support materials due to its high surface tension and particle size [3], the entrapment via spray-drying is a promising strategy to ensure stability of the catalytic species during reaction. The suprabead concept lifts the whole entity to an applicable size regime circumventing typical problems like size-dependent pressure drops in the fixed-bed reactor. This usually limits the advantage of micron-sized materials in such applications. The highlights of the herein presented concept are the entrapment of Ga particles inside a porous SiO₂ framework by exploiting spray-drying and the fabrication of the multicomponent suprabead as a catalyst entity, both shown for the first time. By galvanic displacement of Pt into the Ga nanoparticles a SCALMS material is created. This novel system provides superior catalytic properties of the GaPt nanomaterial compared to typical, established GaPt-SiO₂ materials in PDH reaction.[3] Furthermore, it shows excellent stability of the catalytic species due to the entrapment inside the SiO₂ framework and easy handling due to its size in the millimeter-range.

The concepts of Ga entrapment by means of spray-drying and the fabrication of functional suprabeads, both combined in this work, offer a new approach for generating catalytically active materials and extend the applicability of µm-scaled particles in catalysis and many other fields.

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Drying of Monolayers of Core-Shell Microgels

Julian Ringling¹, Keumkyung Kuk¹, Vahan Abgarjan¹ and Matthias Karg¹

¹Heinrich-Heine-Universität Düsseldorf Presenting author e-mail: <u>julian.ringling@hhu.com</u>

Keywords: hard-core soft-shell microgel, monolayer compression & drying, microstructure at interfaces, microgel-substrate interaction, isostructural phase transition

Hard-core soft-shell microgels are interesting colloids with the potential to be used in medicine or as model systems to understand crystallization and melting processes [1]. They spread at flat fluid interfaces and self-assemble into 2D monolayers in which the cores do not touch directly due to shell-shell repulsion. Compression of the monolayer allows control over the inter-particle distance by compressing the soft and deformable shell [2]. Such monolayers are commonly studied via transfer onto a substrate using a Langmuir-Blodgett trough, followed by microscopy techniques (SEM or AFM) to investigate the microgel arrangement [2, 3].

Our group has previously investigated silica-core PNIPAM-shell microgel monolayers in situ at the air/water interface, using a Langmuir trough combined with small-angle light scattering [4]. Contrary to literature reports [2,3], no isostructural phase transition was observed at the air-water interface, while dried monolayers exhibited the characteristic microgel clustering [4].

To gain insights into the behaviour of microgels during drying, we monitored the process in situ using light microscopy. Here we present evidence of structural changes in microgel monolayers during the drying process and their dependence on substrate hydrophobicity and microgel cross-linking density.



Figure 22. Microgel monolayer drying on a hydrophobic substrate. The monolayer is drying towards the left side, where the meniscus is visible. The centre shows a thin water film remaining in the PNIPAM shells with a decreasing thickness towards the dried region on the right side. Scale bar = $10 \mu m$.

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Magnetic In Situ Determination of Surface Coordination Motifs by Utilizing the Degree of Particle Agglomeration

<u>Andreas Wolf 1,2</u>, Andreas Zink ¹, Lisa M. S. Stiegler ³, Robert Branscheid ⁴, Benjamin Apeleo Zubiri ⁴, Stephan Müssig ¹, Wolfgang Peukert ³, Johannes Walter ³, Erdmann Spiecker ⁴ and Karl Mandel ^{1,2}

¹ Department of Chemistry and Pharmacy, Professorship for Inorganic Chemistry, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Egerlandstraße 1, 91058 Erlangen, Germany

² Fraunhofer Institute for Silicate Research ISC, Neunerplatz 2, 97082, Wuerzburg, Germany

³ Institute of Particle Technology (LFG), (FAU), Cauerstraße 4, 91058 Erlangen, Germany

⁴ Institute of Micro- and Nanostructure Research (IMN), (FAU), Cauerstraße 3, 91058 Erlangen, Germany

Presenting author e-mail: <u>andreas.j.wolf@fau.de</u>

Keywords: superparamagnetic iron oxide nanoparticles (SPIONs), magnetic particle spectroscopy (MPS), agglomeration, colloidal surface chemistry, cation coordination

Most analytical techniques used to study the surface chemical properties of superparamagnetic iron oxide nanoparticles (SPIONs) are barely suitable for in situ investigations in liquids, where SPIONs are mostly applied for hyperthermia therapy, diagnostic biosensing, magnetic particle imaging or water purification [1,2]. Magnetic particle spectroscopy (MPS) can resolve changes in magnetic interactions of SPIONs within seconds at ambient conditions. Herein, we show that by adding monoand divalent cations to citric acid capped SPIONs, the degree of agglomeration can be utilized to study the selectivity of cations towards surface coordination motifs via MPS. A favored chelate agent, like ethylenediaminetetraacetic acid (EDTA) for divalent cations, removes cations from coordination sites on the SPION surface and causes redispersion of agglomerates. The magnetic determination thereof represents what we call a "magnetically indicated complexometric titration". The relevance of agglomerate sizes for the MPS signal response is studied on a model system of SPIONs and the surfactant cetrimonium bromide (CTAB). Analytical ultracentrifugation (AUC) and cryogenic transmission electron microscopy (cryo-TEM) reveal that large micron-sized agglomerates are required to significantly change the MPS signal response. With this work, a fast and easy-to-use characterization method to determine surface coordination motifs of magnetic nanoparticles in optically dense media is demonstrated.



Figure 23. MPS signal can resolve changes in surface chemistry that trigger agglomeration.

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Influence of uniaxial compression on soft colloidal monolayer

Vahan Abgarjan¹, Keumkyung Kuk¹ and Matthias Karg¹

¹Heinrich-Heine-Universität Düsseldorf Presenting author e-mail: <u>vahan.abgarjan@hhu.de</u>

Keywords: colloidal monolayer, in-situ characterisation, real-time investigation

Controlled assembly of molecules and colloids into two-dimensional structures has inspired the fields of surface functionalization to produce nanocoatings and develop functional materials [1]. The importance and understanding of soft colloids increased over the past decade due to their soft properties and unique interfacial phase behaviour. The Langmuir-Blodgett technique is widely used for investigations of the assembly behaviour of colloids at various interfaces, in which their compression isotherms are studied in terms of surface pressure Π as a function of interfacial area. Structural information of order and distances at different phases was achieved by other methods such as atomic force or light microscopy and small-angle x-ray/light scattering (SAXS/SALS). [2-5]

Our group previously studied various colloidal monolayers via in-situ SALS on a Langmuir trough (LT) [5]. This study provided us with the first insights into the real-time structural development of colloidal monolayers. In this work, we used micron-sized hard-core soft-shell microgels [6] and monitored the compression process and the resulting response of the monolayer using our in-situ setup (LT-SALS). We want to highlight and discuss further results from previous investigations with a focus on compression parameters like speed and relaxation time.



Figure 24. Left: compression isotherm (surface pressure Π against normalized area A/A_0) of a hard-core soft-shell microgel monolayer at the air/water interface with corresponding diffraction pattern from SALS at various Π . Scale bars correspond to 10 mm. Right: Connection of the radial profiles from SALS images (colour-coded intensity against the magnitude of the scattering vector q) with the corresponding Π .

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From Cellulose Model Surfaces to Elastic Papers

<u>Cassia Lux¹</u>, Sabrina Kerz¹, Catarina Ribeiro², Micha Tsintsaris¹, Robert Stark² and Regine von Klitzing¹

¹Department of Physics, Technische Universität Darmstadt, Darmstadt, 64289, Germany

²Department of Materials Science, Technische Universität Darmstadt, Darmstadt, 64287, Germany

Presenting author e-mail: <u>cassia.lux@pkm.tu-darmstadt.de</u>

Keywords: cellulose model surfaces, PNIPAM microgels, core-shell particles, elastic moduli

Paper is a hierarchical material based on cellulose which allows functionalization on different length scales. The resulting multilateral use is especially crucial with regard to reducing plastic use and waste and replacing it with renewable and biodegradable resources. A novelty in terms of mechanical robustness and controllable fluid mechanics are elastic papers, prepared through the functionalization of the paper fibers with polymeric particles that concentrate at the fiber-fiber-crossing points.

In this work, two types of polymeric particles are used, elastomeric core-shell particles and PNIPAM microgels. In order to study the particle adsorption, planar cellulose model surfaces are prepared to mimic the surface of a cellulose fiber. The elastomeric particles have a pH-responsive polycation shell while the PNIPAM microgels are overall positively charged. Their adsorption to the negative charged cellulose surface is studied in dependence of e.g. pH-value.

The question we address is how the properties of the cellulose surface and the particles affect the contact area between both, and what effect the adsorption has on the elastic behavior of both of the particles. Additionally, the force necessary to move the particles on the cellulose model surface is studied by peak force tapping mode (AFM).



Figure 25. Graphical depiction of how the flexibility of paper can be increased. By incorporating elastic particles in the cellulose fiber network, a lateral force can lead to a shear in the particles and a parallel aligning of the fibers, leading to a higher stretchability.

Synthesis of micro rods and observation of rolling motion

<u>M. Wittmann¹</u>, I. Kulic² and J. Simmchen¹

¹Technische Universität Dresden, Department of Physical Chemistry, 01069 Dresden/Germany ²Institut Charles Sadron, MCUBE, 67034 Strasbourg/France

Presenting author e-mail: <u>martin.wittmann@tu-dresden.de</u>

Keywords: micro rod, synthesis, micro swimmer, rolling

While many procedures have been developed for the growth of homogeneous nano meter sized rods, the synthesis of micro rods is still challenging. Here, common synthesis concepts and driving forces for growth of one-dimensional micro particles are summarized for different materials. The concepts include anisotropic growth guided by the crystal structure, a solution liquid solid process or a template and can be applied for a large range of different materials (Figure 1).[1]

Finally, the synthesized rods are applied as micro rollers propelled by a chemical reaction imitating the motion of influenza viruses on cell membranes[2] or an external flow. While similar concepts have been discovered using artificial macroscale rods,[3] the occurrence of gliding and rolling motion on the microscale without application of external fields has not yet been discovered. Here, we analyze the influence of the distance to the substrate and discuss potential influences on the behaviors.



Figure 26. SEM images of different micro rods (A: MnO₂, B: SiO₂, C: ZnO).

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Trapped and alone: clay-assisted aqueous graphene dispersions

<u>Oren Regev¹</u>, Lucas Cullar² and Istvan Furo^{1,2}

¹ Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 8410501, Israel.

² Division of Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, Stockholm SE-1044, Sweden.

Presenting author e-mail: <u>oregev@bgu.ac.il</u>

Keywords: Graphene, exfoliation, trapping, kinetically arrest, dispersion, thermal conductivity.

Dispersing graphene sheets in liquids, in particular water, could enhance the transport properties (like thermal conductivity) of the dispersion. Yet, such dispersions are difficult to achieve since graphene sheets are prone to aggregate and subsequently precipitate due to their strong van der Waals interactions. Conventional dispersion approaches, such as surface treatment of the sheets either by surfactant adsorption or chemical modification, may prevent aggregation. Unfortunately, surfactant- assisted graphene dispersions are typically of low concentration (< 0.2wt%) with relatively small sheets (<1 μ m lateral size), while chemical modification is punished by increased defect density within the sheets. We investigate here a new approach in which the concentration of dispersed graphene in water is enhanced by the addition of a fibrous clay mineral, sepiolite.[1] As we demonstrate, the clay particles in water form a kinetically arrested particle network within which the graphene sheets are effectively trapped (Figure 1). This mechanism keeps graphene sheets of high lateral size (~4 μ m) dispersed at high concentrations (~1 wt%). We demonstrate the application of such dispersions as cooling liquids for thermal management solutions, where a 26% enhancement in thermal conductivity is achieved compared to that in a filler-free fluid.[2]



Figure 1. cryo-SEM imaging of trapped graphene (star) in sepiolite network.

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A straightforward strategy to construct Molybdenum nitride nanoparticles as advanced sulfur host for Li-S batteries

Yael Rodriguez-Ayllon^{1,2}, Xuefeng Pan^{1,2}, Dongjiu Xie^{1,2}, and Yan Lu^{1,2,*}

¹Department for Electrochemical Energy Storage, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany ²Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

Presenting author e-mail: yael.rodriguez-ayllon@helmholtz-berlin.de

Keywords: Transition metal nitride, nitridation-free synthesis, Poly(ionic liquid)s, Li-S batteries.

Transition metal nitrides (TMNs) are attractive for cutting-edge energy storage technology owing to their unique electronic structure, superior electrical conductivity, chemical, and mechanical stability [1,2]. Nevertheless, the complex synthesis pathway via ammonia-based reduction compromises environmental stewardship and makes large-scale production off-target [3]. Herein, a straightforward approach to construct nano-structured C@Mo₂N without external nitridation via the colloidal route using an imidazole-based Poly(ionic liquid)s (PILs) [4] as an N-rich template is revealed (Figure 1).

The morphology of C@Mo₂N, as well as the composition and crystallite size of Mo₂N were tuned by controlling the calcination temperature. The different C@Mo₂N were used as a sulfur host for Lithium-Sulfur batteries (LSBs) cathode. The C@Mo₂N-600/S cathode discloses the best electrochemical performance, with a reversible specific capacity of 845 mAh g⁻¹ over 150 cycles at 0.2 C. The novel strategy for constructing C@Mo₂N nanoparticles presented herein could pave the way for the fabrication of other state-of-art TMNs such as C@VN.



Figure 27. Synthesis pathway for the fabrication of nano-structured C@*Mo*₂*N without external nitridation.*

Acknowledgements: The authors acknowledge Bundesministerium für Bildung und Forschung (BMBF, Federal Ministry of Education and Research) for financial support on the SkaLiS project.

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PART II - POSTERS

Switchable Nanoparticle Superstructures

Cathrin Kronenbitter¹, Helmut Cölfen¹

¹University of Konstanz, Universitätsstraße 10, 78457 Konstanz, Department of Chemistry cathrin.kronenbitter@uni-konstanz.de

Keywords: smart material, poly(2-oxazoline)s, magnetite, gold nanocubes, superstructures

In recent years, so-called smart polymers have been extensively investigated for their phasetransfer ability in fields such as medicine as drug delivery molecules. The temperature-responsive poly(2-ethyl-2-oxazoline)s are among these smart polymers, since thev undergo а hydrophilic/hydrophobic phase-transition in water at a characteristic temperature, called lower critical solution temperature (LCST). Due to their straightforward synthesis and post-synthesis modification, as well as tunable LCST properties, they are interesting for their medical application due to their biocompatibility, phase transition at certain temperatures and their easy adjustment through functional groups. ^[1] In combination with inorganic nanoparticles such as magnetite or gold nanocubes, they generate smart materials with a broad field of possible applications.^[2]

The main topic of this project can be divided into different subtopics, as shown in the overview Figure 1. The synthesis of temperature-responsive block-copolymers (TRP) with different linker groups (e.g. -COOH) and the synthesis of anisotropic nanoparticles (e.g. magnetite, gold nanocubes). Furthermore, these nanoparticles are functionalized via different methods with the TRP. With a change in stimulus, in this case temperature, the TRP change their conformation and initiate a temperature-induced destabilization of the nanoparticles. Due to this destabilization, ordered superstructures are created by self-assembly. Especially due to the size- and shape-dependent properties of anisotropic nanoparticles as building blocks, the collective properties in the ordered superstructures are of particular interest.



Figure 28. Schematic overview of the formation of temperature-responsive block-copolymer assisted switchable nanoparticle superstructures.

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Encapsulating hydrophobic cargoes in amphiphilic nanogels: Systematic studies on Nile red microenvironment via fluorescence spectroscopy

<u>Ante Markovina¹</u>, Clara López Iglesias ^{1,2}, N. Nirmalananthan-Budau³, U. Resch-Genger³ and Daniel Klinger¹

¹Institute of Pharmacy, Freie Universität Berlin, Königin-Luise Str. 2-4, Berlin D-14195, Germany ²Department of Pharmacology, Pharmacy and Pharmaceutical Technology, I+D Farma (GI-1642), iMATUS and IDIS, Universidade de Santiago de Compostela, 15782 Santiago, Spain ³Biophotonics Division, Federal Institute of Materials Research and Testing, BAM, Berlin, Germany

ante.markovina@fu-berlin.de

Keywords: amphiphilic, nanogels, drug delivery, spectroscopy, drug microenvironment

Amphiphilic nanogels (ANGs) are designed to contain hydrophilic networks with hydrophobic nanodomains that allow for the encapsulation of water insoluble drugs. We recently have reported a facile synthetic strategy to prepare ANGs with varying degrees of amphiphilicity and an isotropic distribution of the hydrophobic nanodomains (shown by SAXS). ^[1] In addition, we could show that ANGs can encapsulate highly hydrophobic payloads like Nile red. Here, loading contents and release kinetics depend on type and quantity of hydrophobic groups in the network. While we suggest that this can be attributed to different interactions between hydrophobic payload and hydrophobic nanodomain, a clear insight into the underlying mechanisms remains to be determined.

To address this challenge, we have conducted systematic studies on loading Nile red into ANGs of varying amphiphilicity. Utilizing the solvatochromic character of the hydrophobic dye, we investigated its behavior within the polymer network via fluorescence spectroscopy. By analyzing the emission spectra and quantifying the quantum yield of the dye within the nanogels, we were able to probe the polarity of its microenvironment. In addition, deconvolution of emission bands and fluorescence lifetime studies showed different species of Nile red in ANGs. We suggest that these can be related to different microenvironments and aggregation phenomena. Overall, our studies revealed a strong influence of cargo concentration and network amphiphilicity on the molecular structure of the loaded dye. These insights are the foundation for adjusting specific release profiles.



Figure 29. A versatile synthetic platform for amphiphilic nanogels: tailoring network hydrophobicity to study Nile red microenvironment.

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Statistical Design of Adhesion Experiments

<u>Agnes Specht¹</u>, Dominik Krämer¹, Nicolas Helfricht¹, and Georg Papastavrou¹

¹ Physical Chemistry II, University of Bayreuth, Germany Presenting author e-mail: <u>agnes.specht@uni-bayreuth.de</u>

Keywords: big data, statistics, atomic force microscopy, adhesion

In our fast-paced world, *big data* is omnipresent in practically all aspects of human life. Massive amounts of data became indispensable in various fields such as energy, health care, and finance. In scientific research, automated measurement protocols allow as well for generating large amounts of data. Automation includes acquiring, processing, and analyzing data in this context.

However, the statistical design of experiments is crucial when generating datasets with statistical meaning. The aim must be not only to create large datasets but meaningful ones, also in terms of time constraints. Therefore, the choice of a suitable sample size is of crucial importance. A balance must be struck between meaningful statistics and saving time and resources. Thus, the question of "how much data is enough?" is pertinent, but often neglected.

In this research project, direct force measurements [1] are performed by atomic force microscopy (AFM) [2] using the colloidal probe technique [3-5]. Adhesion forces are measured between a colloidal particle and a chemically functionalized glass substrate.[6, 7] A statistical evaluation of the adhesion force is performed. Different measurement spots and particles are investigated, always considering deviations within the experimental setup. For all datasets, the optimum sample size is calculated by means of statistical tools in order to guarantee statistically valid experiments. Moreover, we elucidate the mechanisms leading to the variation in the adhesion forces, such as roughness of the colloidal particles or heterogeneity of the sample.



Figure 30. Process of the reversible immobilization of microparticles using micro-channeled cantilevers.

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Core/shell nanoparticle formation by coprecipitation

Bastian Roedig¹, Dominik Zahneweh¹, Diana Funkner¹ and Werner Kunz¹

¹ University of Regensburg, Institute for Physical and Theoretical Chemistry, Regensburg, Germany

Presenting author e-mail: <u>bastian.roedig@chemie.uni-regensburg.de</u>

Keywords: nanoparticle, colloid, self-assembly,

Coupled chemical reactions are known to be able to produce ordered patterns under certain conditions far from thermodynamic equilibrium. Such phenomena can be exploited to obtain complex mineral structures, as reported for self-assembled crystalline carbonates and amorphous silica composites. [1] The dynamic pH-based coupling underlying the formation of these inorganic composites can be extended to produce core-shell nanostructures of functional materials. Specifically, the concept was applied to synthesize fluorescent silica-coated quantum dots in a simple one-pot procedure at ambient conditions based on the coupled co-precipitation of metal chalcogenides and silicate. This straightforward approach can likely be generalized to produce a wide variety of functional nanoparticles with possible applications in the areas of optics, energy storage, catalysis, and beyond.

This way, silica-coated transition metals (Mn, Co, Ni, Cu, Zn, Cd), sulfide, phosphate, carbonate, and oxide NPs can be prepared. It resulted in particle sizes from 30 nm up to 400 nm depending on the synthesis approach and other added substances during synthesis, with quantum dot sizes between 4 nm and 10 nm. In addition, surface modifications with different covalent binding silanes or adsorbed polyelectrolytes provided electrosteric stabilization in physiological buffers and could enable cell tests with the produced NPs. [2]



Figure 31. Coupled coprecipitation of cadmium sulfide and silica.

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Effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution

<u>Pablo A. Alvarez Herrera¹</u>, Geethu. P. Meledam¹, Cristiane Henschel², Leonardo Chiappisi³, André Laschewsky² and Christine M. Papadakis¹ ¹TU Munich, School of Natural Sciences, Garching, Germany ²Institut of Chemistry, University Potsdam, Potsdam-Golm, Germany ³Institut Laue-Langevin, Grenoble, France.

Presenting author e-mail: pablo.alvarez@ph.tum.de

Keywords: Amphiphilic diblock copolymers, pressure, SANS.

Amphiphilic diblock copolymers feature self-assembly behavior in aqueous solution. For example, poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) (PMMA-*b*-PNIPAM) forms spherical core-shell micelles upon heating above the cloud point of PNIPAM [1]. It was previously found that pressure enhances the hydration of PNIPAM homopolymers in aqueous solution [2]. However, the effect of pressure on the micellar structure of PMMA-*b*-PNIPAM is still unknown.

In this contribution, we determine the temperature-pressure phase diagram of a 5 wt % solution of PMMA₂₁-*b*-PNIPAM₂₈₃ in D₂O by turbidimetry. Furthermore, we characterize its micellar structure by small-angle neutron scattering (SANS). Temperature-resolved experiments were carried out at 0.1 MPa (atmospheric pressure) and 75 MPa (Fig. 1a-c). At 0.1 MPa, we find that the micellar shell strongly dehydrates after crossing the co-existence line. At 75 MPa, on the contrary, the micellar shell remains hydrated and the micelles are highly-correlated (Fig. 1d). Accordingly, pressure arises as promising tool for tailoring the structure of the micelles.



Figure 32: a) Phase diagram of a 5 wt% solution of $PMMA_{21}$ -b-PNIPAM₂₈₃ in D_2O determined by turbidimetry. The SANS measurements are indicated with spheres. (b-c) SANS profiles for the temperature scans at b) 0.1 MPa and c) 75 MPa. d) Schematic representation of the effect of pressure and temperature on the micellar structure of PMMA₂₁-b-PNIPAM₂₈₃ in D_2O .

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From Waste Treatment to Water Treatment: Phase Behaviour of Humic Acid - Quaternized Chitosan Complexes

Mingyu Yuan¹, Heriberto Bustamante² and Michael Gradzielski¹

¹Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany ²Sydney Water, Parramatta NSW 2125, Australia Presenting author e-mail: <u>m.yuan.1@campus.tu-berlin.de</u>

Keywords: polyelectrolyte, aggregation, water treatment

The complexation/coagulation induced by cationic polyelectrolyte (PE) is considered to be an effective method to deal with humic acid (HA) in conventional water treatment process. That is important as HA exists ubiquitously in aquatic environments as a degradation product of plants and it can negatively affect the quality of drinking water. [1]

In this study, phase behaviour of HA and different PEs has been studied recently by us with a focus on the PE chain structure effects. Specifically, regarding PEs we have developed various modified cationic (quaternized) chitosan (qCs), which are derived from natural waste to develop an environmentally friendly solution. [2] A combination of SLS, DLS, and confocal microscopy is utilized to probe the colloidal morphology of the formed HA-qCs aggregates as a function of mixing ratio. It was observed that by tailoring the degree of quaternization, a shift of phase diagram can be found with predictable aggregate structures. This insight from colloid science is promising to optimize water treatment process in industrial fields.



Figure 33. Reaction Scheme for the quaternization of chitosan and the ζ -potential for complexes of modified quaternized chitosan(qCs) and PDADMAC with humic acid at varying charge ratio Z = [+]/[-].

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A Comparative Macrorheology Study of Bovine Submaxillary Mucin and Washes from Nasal Epithelial Cultures for Characterization as a Potential Airway Mucus Model System

<u>Hanna Rulff¹, Annalisa Addante², Anita Balázs², Sara Timm³, Matthias Ochs⁴, Marcus A. Mall²,</u> Michael Gradzielski¹

¹ Institute for Chemistry, Technische Universität Berlin, Berlin, Germany; ² Department of Pediatric Respiratory Medicine, Immunology and Critical Care Medicine, Charité - Universitätsmedizin Berlin; ³ Core Facility Electron Microscopy, Charité - Universitätsmedizin Berlin; ⁴ Institute of Functional Anatomy, Charité - Universitätsmedizin Berlin; ^{2, 3 and 4} Corporate member of Freie Universität Berlin and Humboldt-Universität zu Berlin, Berlin, Germany

Presenting author e-mail: <u>hanna.rulff@campus.tu-berlin.de</u>

Keywords: mucus, macrorheology, model

Airway mucus provides important protective functions in health. Abnormal viscoelasticity due to increased mucus concentration and crosslinking between secreted mucin polymers is a characteristic for a spectrum of muco-obstructive lung diseases such as cystic fibrosis (CF) [1]. As human samples are subject to interindividual variations and only available in limited quantity, suitable and easily accessible airway mucus model systems are required.

Bovine submaxillary mucin (BSM) is molecularly closely related to human airway mucus and has natural gel-forming properties due to its polymeric structure containing glycoproteins [2]. BSM shows concentration-dependent changes in viscoelasticity [3]; moreover, it is commercially available and easy to prepare in quantities sufficient to perform comprehensive measurements under different experimental conditions. Therefore, BSM could be appropriate for investigating and refining it as a potential mucus model system.

Primary human nasal epithelial cells (hpNEC) produce mucus [4] that can be collected from the apical surface of cultures grown at air-liquid interface. The mucus washes show similar viscoelastic properties like human sputum which are adjustable via different experimental procedures and treatments. This makes the hpNEC mucus promising to study as a possible mucus model system more closely resembling human lung mucus.

Performing macrorheological measurements with several mucus samples is shown to be a robust and reproducible technique [1] to study their viscoelastic properties. We investigate the successive approximation of human, bovine and hpNEC mucus in their viscoelastic behavior and the relative importance of storage and loss modulus by variation of concentration to mimic different disease stages [5] and by addition of other components (salt [6], osmolyte, proteases, therapeutic treatment) to BSM and hpNEC mucus washes.

By evaluating the data obtained from Scanning Electron Microscopy (SEM) measurements of the solutions above we can additionally conclude the network structure on a nanoscale and complete and compare to the rheological data.

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Development of ultrasonic cavitation assisted geraniol nanoemulsion stabilized using lecithin-saponin based mixed biosurfactant system

Amit Kumar^{1,2}, S. K. Mehta² and Michael Gradzielski¹

¹Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Straße des 17. Juni 124, Sekr. TC7, Technische Universität Berlin, D-10623 Berlin, Germany ²Department of Chemistry, Panjab University, Chandigarh, 160014, India

Presenting author e-mail: <u>amit.kumar.1@campus.tu-berlin.de</u>

Keywords: Saponin, lecithin, essential oil, nanoemulsion, biosurfactant

The stabilization of nanoemulsion (NEm)-based systems using synthetic binary emulsifiers has been thoroughly researched [1]. Nevertheless, the desire for natural ingredients among consumers has resulted in the replacement of synthetic surfactants with natural alternatives, including proteins, phospholipids, saponins, etc., especially in agri-food-based applications. Our objective is to study the characteristics of a mixed binary lecithin-saponin biosurfactant system at varying concentration ratios r(1:0, 3:1, 1:1, 1:3, 0:1) with a total surfactant concentration of 1% (w/w). To accomplish this, various NEm of Geraniol were prepared using the probe ultrasonication technique and then their stability was tested against various environmental stress factors (storage, ripening, pH, temperature, and salt effect).

The use of a mixture of lecithin and saponin as a biosurfactant mixture resulted in a decrease in droplet size of NEm as compared to a NEm made with only one type of emulsifier (r(1:0) or r(0:1)). The storage stability of the NEms was tested, and it was found that only those made with pure lecithin (r(1:0)) or a mixture of lecithin and saponin at ratios of r(3:1) and r(1:1) were stable against creaming and phase separation. When tested for salt tolerance, the mixed biosurfactant system was found to be more stable against NaCl up to 300 mM compared to pure lecithin. However, for pH stability, only lecithin stabilized NEm at r(1:0) was stable over a wide range of pH (2-10), whereas mixed biosurfactant NEms was stable only in the pH range of 5-10.

These findings suggest that only specific mixed ratios of lecithin and saponin, such as r(3:1), can improve the overall stability of geraniol nanoemulsion. Overall, the binary lecithin-saponin-based biosurfactant system was found to be less suitable than the sole lecithin stabilized NEm r(1:0), but was more effective than the sole saponin stabilized NEm; r(0:1).



Fig.1 Fabrication of Geraniol Nanoemulsion

Acknowledgments: The authors acknowledge DAAD and DST for the fellowship. **References**

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Characterization and drug release behaviour of conductive hydrogel

<u>Yining Sun¹, Michael Gradzielski¹</u>

¹Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin, Germany

Presenting author e-mail: yining.sun@campus.tu-berlin.de

Keywords: Hydrogel, Drug release, Conductivity

An environmentally sensitive drug delivery hydrogel with good biocompatibility and degradability are recognized as a potential biomedical technology for treating diseases. Electrically controllable drug release can provide precise control by tuning current and duration of the electric field [1]. Herein, a conductive hydrogel was prepared by using quaternized chitosan grafted with polyaniline (QCSPA), polyvinyl alcohol (PVA), and boronic acid (BA) as shown in Figure 1. The QCSPA/PVA/BA hydrogel is dynamically crosslinked by borate ester and ionic interaction, which can endow conductive and pH-sensitive properties. The crosslinking and drug release mechanisms were studied by using rheology, electrochemistry, small angle scattering (SAS), and conductivity for understanding the relations between hydrogel structure and physical-chemical properties. By tuning the composition of the system and the electrically field, drug release profiles ranging from slow elution to rapid release can be achieved, which could provide a potential application of an electroactive drug release hydrogel.



Figure 34. Structural description of QCSPA/PVA/BA hydrogel.

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SmartBrane: Microgel-based Membranes for Low Temperature Fuel Cells and Application in Catalysis

Jonas Runge¹, Stefanie Uredat¹, Maxim Dirksen¹, and Thomas Hellweg¹

¹*Physical and Biophysical Chemistry, Bielefeld University, Bielefeld, Germany*

jonas.runge@uni-bielefeld.de stefanie.uredat@uni-bielefeld.de

Keywords: microgels; smart membranes; UV cross-linking; catalysis

Membranes are used in water treatment, chemical sensing and separation. They can be prepared with different cross-linking methods: chemical cross-linking, electron beam cross-linking, and UV cross-linking. We have prepared UV cross-linked membranes consisting of poly-(N-isopropylacrylamide) (PNIPAM) based copolymer microgels and the secondary cross-linker 2-hydroxy-4-(methacryloyloxy)-benzophenone (HMABP).[1] These microgel-based membranes exhibit a change of resistance at the volume phase transition temperature (VPTT) of the originally used microgels (figure 1). Moreover, silver nanoparticles were successfully incorporated and the catalytic activity was examined with UV-Vis spectroscopy.

Within this project, we aim at preparing microgel-based membranes for low-temperature fuel cell applications and for chemical catalysis systems. Especially for the fuel cell application the volume phase transition temperature (VPTT) of the membrane has to be around 80-90°C. Based on our previous work, we intend to use UV-crosslinking to prepare such high VPTT membranes. In electrochemical devices, these membranes will regulate ion flow and prevent over-temperature. Furthermore, we want to examine the distribution of the copolymers in the microgel and the membranes using contrast variation SANS.



Figure 35. Resistance as a function of temperature for a membrane with 4 mol% HMABP commoner content. The shown measuring cycle consists of a heating curve (red) and a cooling curve (blue). Additionally, a swelling curve (green) of the corresponding microgel obtained from photon correlation spectroscopy measurements is shown.[1]

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Chemical cross-linked microgel membranes

Stefanie Uredat¹ and Thomas Hellweg¹

¹*Physical and Biophysical Chemistry, University Bielefeld, Bielefeld, Germany*

stefanie.uredat@uni-bielefeld.de

Keywords: microgel, smart membrane, chemical crosslinking, glutaraldehyde

Smart membranes can be used for many applications like water treatment, chemical sensing and separation. Most membranes are fabricated on the substrate they are used on. To extend the field of usage freestanding membranes are desired to be able to transfer them to arbitrarily shaped surfaces. There are different methods to crosslink the microgel particle into a membrane: electron beam cross-linking, UV cross-linking or chemical cross-linking.[1,2] Glutaraldehyde is useful in construction of functional polymeric materials from proteins and other molecules that contain amino groups because it can attack on the primary amines and e.g. link microgel particles into a membrane.[3,4]

In this work freestanding membranes are prepared by chemical crosslinking of copolymer microgels with glutaraldehyde. The microgels are synthesized via surfactant-free precipitation polymerization of the comonomer N-(3-aminopropyl)methacrylamid-hydrochloride (APMH) with N-isopropyl-acrylamide (NIPAM). A variant of the evaporating drop method is used to create the membranes. Therefore, the microgel was dried on a PTFE substrate and the glutaraldehyde was spread on this microgel layer. After a few hours the substrate was submerged in water to detach the membranes. The membranes float on the water-air interface. Hence, they could easily be transferred to e.g. a silicon wafer for further investigations. The microgels were investigated by photon correlation spectroscopy whereas the membranes were investigated by atomic force microscopy.



Figure 36. Freestanding microgel membrane on the water surface (left) caught on a silicon wafer in wet (middle) and dry state (right).

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Controlled Self-Assembly of Anisotropic Metal Nanoparticles into Colloidal Binary Mesocrystals

<u>Nick Sokov¹</u>, Simon Schnitzlein¹, Guillermo Gonzalez-Rubio¹ and Helmut Cölfen¹

¹University of Konstanz, Universitätsstraße 10, 78457 Konstanz, Department of Chemistry nick.sokov@uni-konstanz.de

Keywords: mesocrystals, surface ligands, gold nanocubes, silver nanocubes

In recent years, intense research efforts have been dedicated to understanding the co-assembly of different colloidal nanoparticles into complex superstructures with emerging and unique physicochemical properties. In this context, mesocrystals represent a distinctive class of structured material in which crystalline faceted nanoparticles organize themselves following a defined pattern that results in long-range atomic ordering in at least one dimension.^[1] Thereby, mesocrystals can display directional, enhanced, or emerging properties not observed in non-mesocrystalline assemblies.^[2] Unfortunately, it is challenging to fabricate mesocrystals consisting of two or more components due to different attractive van der Waals interactions between nanoparticles with various compositions. To face this challenge, it is fundamental to control the effective screening of attractive forces. Notably, this can be achieved by covering the surface of nanocrystals with surface ligands capable of providing desired repulsive interactions via steric or electrostatic repulsion.^[3] In this sense, we have developed a method for the synthesis of surface ligands bearing different surface linkers (i.e., to strongly bind the nanoparticle surface, such as thiol and amine moieties) and polymer chains (i.e., to impart tunable steric repulsions, such as polystyrene). Using such designed polymeric ligands as colloidal stabilizing agents, we demonstrated the controlled stabilization of gold and silver nanocubes in different organic medium (e.g., THF, chloroform, toluene), where they can later be successfully co-assembled into binary mesocrystals through an oil-in-water emulsion technique. The nature of the surface ligand (i.e., surface linker and polymer chain) and slow evaporation of the oil from the droplets are critical for the formation of ordered gold and silver mesocrystals. Thereby, we reveal the potential of the described self-assembly strategy for the fabrication of binary mesostructures, which should be implemented to obtain compositionally more complex superstructures.



Figure 37. Schematic overview of binary mesocrystals.

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Investigations of the Formation Kinetics of Interpolyelectrolyte Complexes (IPECs) from Linear Polyelectrolytes

<u>Christoph Brückner¹</u>, Michael Gradzielski¹

¹ Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, Straße des 17 Juni 124, 10623 Berlin, Germany

Presenting author e-mail: <u>christoph.brueckner@tu-berlin.de</u>

Keywords: polyelectrolytes, complexes, kinetics

The phase behavior and structures of interpolyelectrolyte complexes (IPECs) have been studied intensely for many years [1] and in general are rather well understood, even if sometimes it is not easy to ascertain thermodynamic equilibrium for observed nanostructures. Though extensive studies on the static, thermodynamic behavior have been performed, little is known about the actual kinetic pathways taken during the formation and ageing process.

We have been studying the kinetics of two homopolymers, namely the weak polyanion sodium polyacrylate (NaPA) and the strong polycation poly(diallyldimethylammonium chloride) (PDADMAC) by probing the effect of molecular weight, charge mixing ratio (z), pH, salt effect and total concentration. Here, the lowest molecular weight of NaPA (5.1 kDa) used for complexation with PDADMAC (8.5 kDa) is in terms of repeating units of symmetric size, whereas with increasing NaPA molecular weight the relation becomes more asymmetric. Since light scattering is very sensitive to changes in molecular weight, we performed kinetic studies by means of stopped-flow in static and dynamic (DLS) detection mode to follow the early stage formation processes.

We could find and confirm that the pathways taken strongly depend on the charge mixing ratio identifying 3 distinct kinetic responses [2]. Most significant, complexation performed under stochiometric charge mixing conditions results largely in coacervation which is featured by typical bell-shaped curve. In this context, condensation towards coacervation appears to follow an universal mechanism and is rather independent on the molecular weight as indicated in figure 1. The addition of small ions results for all z-ratios in coacervation with identical scaling for the decaying process underlining the meaning of short-range attractions for an universal coacervation mechanism.



Figure 38:. Relative intensity curves for mixtures of PDADMAC (8.5 kDa) with NaPA of varying molecular weight at equimolar charge mixing condition (z = 1.0) at pH 10.

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Tailoring the microstructure of octylmonoglucoside microemulsions with geraniol: a systematic SANS study

<u>Florian Trummer¹</u>, Otto Glatter², Oliver Lade³, Cosima Stubenrauch ¹, Thomas Sottmann¹

¹Universität Stuttgart, Institut für Physikalische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart ²TU Graz, Institut für Anorganische Chemie, Stremayrgasse 9/IV, A-8010 Graz ³Provadis School of International Management and Technology, Faculty of Computer Science and Business Informatics, Industriepark Höchst, D-65926 Frankfurt a.M.

Presenting author e-mail: <u>florian.trummer@ipc.uni-stuttgart.de</u>

Keywords: Microemulsions, SANS, microstructure, quaternary systems

Microemulsions have been under investigation for several decades and their properties are of exceptional interest in materials research, pharmaceutical applications and many other fields [1]. Systems composed of water – oil – nonionic surfactant are commonly referred to as 'ternary systems' and their phase behaviour is well-established. In most applications, temperature is used to tune the microstructure and thus the properties of a given system, starting from oil-in-water (O/W) over bicontinuous all the way to water-in-oil (W/O) microemulsions. When polyethylene glycol alkyl ethers (C_iE_j) are used as surfactant, an increase in temperature leads to the dehydration of the hydrophilic head group and thus to a change of the mean curvature *H* of the surfactant monolayer: one observes the mentioned transition from an O/W (H > 0) to a W/O (H < 0) microemulsion, with a bicontinuous microemulsion (H = 0) at the phase inversion temperature (PIT).

When the petrochemical-based C_iE_j surfactants are replaced with *n*-alkyl glucoside surfactants, which are biodegradable, low-toxic and made from renewable resources, temperature is no longer an effective tuning parameter to drive the system through the phase inversion due to their hydrophilicity. Hence, a fourth component, a hydrophobic co-surfactant, is added to change the mean curvature *H* from positive to negative.

Here, we investigated the behaviour of water- and oil-rich as well as symmetric microemulsions composed of water – cyclohexane – *n*-octyl- β -D-glucoside (β -C₈G₁) – geraniol. The addition of the co-surfactant geraniol changes the composition of the interfacial film, which, in turn, changes the microstructure of the system with a bicontinuous microemulsion (H = 0) at the phase inversion composition (PIC). Studies of the phase behaviour, complemented by NMR [2,3] and SANS measurements, allow us to extract the quantitative relationship between the film composition and the mean curvature of the surfactant monolayer. The SANS data were analysed with the Generalised Inverse Fourier Transformation (GIFT) technique [4] to extract the particle shape and thus the mean curvature *H*. Going from droplet microemulsions towards the bicontinuous state, a preference for unidimensional micellar growth via cylindrical structures is seen, as well as micellar interactions due to critical fluctuations close to the near critical boundary.

We show that the influence of the temperature in ternary systems and that of the co-surfactant in quaternary systems is quantitatively equivalent, as long as the appropriate reduced tuning parameters are chosen.

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Waveguiding complex particles as light funnels

<u>Yuzi Hong¹</u>, Agata W. Baryzewska¹ and Lukas Zeininger¹

¹Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

Presenting author e-mail: <u>Yuzi.Hong@mpikg.mpg.de</u>

Keywords: complex colloids, emulsions, surfactants, sensors, bacteria, refractory optics

Sensors enable to transduce information from biological and chemical environment. By incorporating stimuli-responsive surfactants to complex emulsions, we can induce morphological changes or a tilting of droplet out of their gravitational alignment in response to the presence of specific chemical or biological analytes. A temperature-controlled miscibility and phase-separation of fluorocarbons (F) and hydrocarbons (H) can be exploited to produce structured complex emulsion droplets of H and F in water (W). By varying the interfacial tensions using surfactants, the geometries of such droplets can be alternated between encapsulated (F in H and H in F) and Janus configurations. This morphology changing property of Janus droplets combines with the unique optical properties of complex emulsions as a new platform for chemo- and bio-sensing applications. When exposed to specific analytes in response to pH changes, or visible light, these complex emulsion droplets invert morphology. Capturing the readout of this morphological information requires robust droplet-based sensing platforms.

To obtain an in-situ readable signal in response to changes in shape or alignment, we explore new pathways for optical signal transduction. Particularly, by adjusting the refractive indices of the two constituent phases of our complex colloids, a new level of light propagation control was achieved inside the emulsion droplets. We also add emissive dyes that partition selectively into one of the two immiscible phases of the complex emulsion to create fluorescence sensor readouts.

Gaining control over the potential of these micro-colloids to manipulate light in form of waveguides paves the way towards the development of easily deployable modular droplet-based sensing layers for optical sensors. As such, modular sensing layers based on complex droplets hold promise to decrease the signal-to-noise ratio in several established refractive index-based sensing technologies, including total internal reflection fluorescence microscopes or dual polarization interferometers. Based on the unique chemical-morphological-optical coupling inside these complex emulsions, new sensor paradigms for the rapid and sensitive detection of various chemical and biological analytes, including a record-breaking detection scheme targeting the common foodborne pathogens *Salmonella Typhimurium, Listeria monocytogenes* and *E. coli* were developed. One of the leading advantages of this optical transducer is low cost and ease of preparation enabling the development of new and improved emulsion technologies including in environmental protection, medical diagnostics and industrial monitoring applications.

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Tailor-made cobalt hexacyanoferrate nanocubes: adjustable building blocks towards binary Prussian Blue Analogue mesocrystals

Simon Cardinal¹, Frederic Hallmann¹, Elrike Reinalter¹, Julian Schlotheuber¹ and Helmut Cölfen¹

¹University of Konstanz simon.cardinal@uni-konstanz.de

Keywords: cobalt hexacyanoferrate, prussian blue analogues, nanocubes, mesocrystals

Prussian Blue Analogues (PBA) are a promising class of functional materials with remarkable electrocatalytic properties. To enhance their catalytic activity, PBA nanomaterials can be synthesized with selectivity towards size and morphology. Furthermore, anisotropic PBA building blocks may be assembled into mesocrystals *via* oriented attachment to exploit directional properties. Here we show the citrate-mediated synthesis of uniform cobalt hexacyanoferrate (CoHCF) nanocubes in the absence of organic ligands. In addition, we show the formation of monomeric and binary mesocrystalline structures.

The applied synthetic approach is based on nucleation control *via* temporary cobalt ion complexation. We found that the relative amount of citrate, the total reactant concentration, and the temperature have a direct impact on the nanocubes' size and surface texture in consistency with the classical nucleation theory (CNT). We further found that by introducing nickel ions mixed nickel-cobalt hexacyanoferrate (NiCoHCF) nanocubes with different compositions can be obtained. In addition, we observed the *in-situ* formation of micron-sized mesocrystalline clusters at sufficiently high ionic strengths combined with relatively large amounts of citrate in accordance with the DLVO theory. Furthermore, we prepared two-dimensional mesocrystalline films *via* solvent evaporation by exploiting the so-called "coffee-ring effect". Additionally, we were able to produce binary mesocrystalline films from CoHCF and nickel hexacyanoferrate (NiHCF) nanocubes. The NiHCF nanocubes were synthesized using a similar synthetic approach adapted from literature.[1] Consequently, three-dimensional binary PBA mesocrystals may be accessible as well.

Our findings provide a straightforward approach to synthesize CoHCF and NiCoHCF nanocubes with adjustable size and surface texture towards their assembly into monomeric and binary mesocrystalline structures. The advantage of our systems is that no organic ligands are involved in the synthesis. Hence, no electrically insulating layer is present on the nanocubes' surface or between the individual building blocks of the formed mesocrystals which is desirable for electrocatalytic applications. The presented results may also be applicable to other materials of the PBA family and provide a pathway towards new functional materials for application in electrocatalysis.

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Supersaturation of Curcumin in Micellar and Plant Protein-based Systems

Lea Rohr¹, Michael Schmidt² and Werner Kunz¹

¹Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany

²Institute of Materials Resource Management, University of Augsburg, D-86159 Augsburg, Germany

Presenting author e-mail: lea1.rohr@ur.de

Keywords: Curcumin, surfactant, supersaturation, pea protein isolate

Curcumin is an umbrella term for a group of polyphenols called curcuminoids. Curcumin is extracted from the plant Curcuma Longa L. (C. Longa) and is mostly known for its bright yellow colour. In addition to its use as a dye, curcumin is an interesting bioactive compound that has antioxidant, anti-inflammatory and antiviral properties. [1] However, due to its poor water solubility, its bioavailability is low and the health beneficial properties are compromised. Therefore, it is of great interest to increase the solubility of curcumin in aqueous systems, for example, by designing protein-based carrier systems. [2]

A non-equilibrium state of solubilised curcumin is achieved either by encapsulating the polyphenol in pea protein or by micellar solubilisation followed by dilution with water. In both cases, precipitation occurs in the initially transparent (micellar solution) or translucent (protein-based solution) solutions within 24 hours, reaching a minimum that corresponds to thermodynamic equilibrium. This behaviour determines the use of the formulations. The supersaturated state of curcumin could be interesting for pharmaceutical applications regarding drug delivery systems. The thermodynamically stable state of the solubilised curcumin could find application in food colouration.

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Thermal phase separation approach towards structurally-defined multicompartment hydrogel microreactors

<u>Y. K. Xil,</u> B. D. Frank¹, M. Antonietti¹, L. Zeininger^{*1},

¹Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces Am Mühlenberg 1, 14476 Potsdam, Germany

e-mail: <u>Lukas.Zeininger@mpikg.mpg.de</u>

Keywords: Liquid-liquid phase separation; Aqueous two phase systems; Compartment hydrogel microreactors, Enzyme cascade reactions

Emulating the inspirational regulatory capabilities of natural systems, the construction of multicompartment microreactors to perform multistep biochemical cascade reactions in one pot has attracted substantial attention. Spatially localizing reaction centers enables a regulation of the diffusion pathways of substrates, intermediates, and products, as well as control over constructive and destructive interference of active reaction centers, such as enzymes. In addition, higher local substrate and catalyst concentrations within the confined space of a microreactor can effectively tune reaction kinetics by overcoming unfavorable thermodynamics of the bulk environment. Consequently, having fine control over the compartmentalization of active reaction centers within multiphasic microreactors constitutes an exciting avenue to impart materials with regulatory capabilities.

We demonstrate a thermal phase separation protocol for the continuous generation of complex calcium alginate-based enzyme-loaded biomimetic microreactors. The gelation of alginatecontaining emulsion droplet templates is achieved employing a novel freeze-thaw approach, which can be applied to both the scalable batch production as well as precise microfluidic methods. By using aqueous complex emulsion droplets loaded with hydrophilic polymer mixtures as colloidal tectons for gelation, a method for the controlled and uniform construction of structurally defined hydrogel particles with multiple internal compartments was realized. Controlling time and temperature to influence segregative phase separation of the internal droplet phases enables the design of complex microreactors with a defined size and number of microcompartments. Phase-selective partitioning of enzymes within the individual phases of the particles enables multistep cascade reactions to occur simultaneously. The resulting biomimetic hydrogel microreactors enable effective transport of reactants, while distinguished compartments offer desirable micro-environments to control and tune reaction product generation in high efficiency, negating mutual interference. Consequently, combined with the insights into the optimization of enzyme cascade reaction kinetics inside artificial soft microreactors we provide a new avenue toward the facile batch generation of synthetic hydrogel cascade microreactors.

Designing sustainable Microgel-stabilized Pickering-like Liquid crystal droplets for optical sensing of chemical and biological analytes

<u>Shikha Aery</u>^{1,2,3}, Adele Parry², Andrea Araiza-Calahorra², Stephen D Evans², Helen Gleeson², Abhijit Dan³, and Anwesha Sarkar²

¹ Institute of Physical Chemistry, RWTH Aachen University, 52074, Germany
² University of Leeds, Leeds, LS2 9JT, UK
³ Panjab University, Chandigarh, 160014, India

Presenting author e-mail: <u>aery@pc.rwth-aachen.de</u>

Keywords: Liquid crystal, Plant protein, Microgel, Emulsifier

Liquid Crystal (LC)-in-water emulsions are new generation optical sensors, consisting of micrometer-sized LC droplets dispersed in aqueous media. [1] They are widely used in highly sensitive detection of a range of chemical and biological analytes. [2,3] In presence of analytes, the LC droplets undergo ordering transition resulting in a change of optical appearance observed under Polarized optical microscope. But due to various factors such as instability to coalescence, inability of bigger droplets to undergo analyte induced-transition, the bare LC emulsions show poor shelf-life and fail to provide reliable results for quantitative analysis of targeted analytes, thus making them unfavourable for the use in clinical settings. [4]

Herein, we investigated the design of a new sustainable emulsifier produced from industrial byproduct for LC emulsions. For this study, we used plant-based protein, a byproduct from starch industry (Potato protein, PoP) [5] and corresponding physically cross-linked microgel (Potato protein microgel, PoPM) [6] to prepare emulsions and studied their effectiveness in terms of their stability and response to analytes via polarised microscopy. It was observed that both PoP and PoPM adsorb at LC-water interface with reduction of interfacial tension and uniformly coat the droplets observed using confocal microscopy. However, the PoPM-coated droplets showed better stability than PoP-coated droplets caused by irreversible Pickering stabilization of droplets with PoPM particles. Further, Pickering LC droplets showed $5\times$ lower detection limit to model analyte (surfactant) as a result of difference in interaction behaviour of analyte with protein and microgel. Also, highly monodisperse and ultra-stable Pickering LC droplets were obtained using microfluidics (~ 15 μ m) which eliminated the effect of polydispersity on the reliability of response and exhibited same response to chemical as well as biological analytes. The study concluded that the microgels are better emulsifiers and the eco-friendly Pickering emulsions provide a sustainable alternative to LC stabilization which can be used in clinical settings and other sensing applications.

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Block Copolymer-based Photosensitizer Carrier Systems for Advanced Antimicrobial Photodynamic Therapy

<u>Max Müller</u>¹, Kawaljit Kaur¹, Raphaëlle Youf², Mareike Müller¹, Gilles Lemercier³, Tony Le Gall², Tristan Montier², and Holger Schönherr¹

 ¹ Physical Chemistry I & Research Center of Micro- and Nanochemistry and (Bio)Technology (Cμ), University of Siegen, Adolf-Reichwein-Straße 2, 57076 Siegen, Germany.
² Univ. Brest, INSERM, EFS, UMR 1078, GGB-GTCA, F-29200 Brest, France.
³ Université de Reims Champagne-Ardenne, BP 1039, CEDEX 2, 51687 Reims, France.

Presenting author e-mail: <u>max.mueller@uni-siegen.de</u>

Keywords: Block copolymer, Photosensitizer, Antimicrobial photodynamic therapy (aPDT)

Photodynamic therapy (PDT) using photosensitizers has become an essential tool in cancer therapy and has been expanded to treat multi-resistant microbial infections.[1] However biological accessibility, biocompatibility and solubility of photosensitizers in aqueous and biological media constitute major challenges, which may be addressed exploiting encapsulation strategies based on biocompatible block copolymers (BCPs) [2]. Herein we report on the encapsulation of Ru-based photosensitizers (PS) into BCP-based micelles and vesicles to develop a biocompatible on-demand release system for the treatment of localized microbial infections. Different Ru-based PS are encapsulated into tailor-made PEG_{114} -*block*-PLA_x and PEG_{114} -*block*-PCL_x assemblies (PEG: poly(ethylene glycol), PLA: poly(lactic acid), PCL: poly(ε -caprolactone)). In particular, PS encapsulation, the influence of the PS on the size of assemblies and the bacterial enzyme-mediated PS release were studied. In addition, the efficiency of singlet oxygen generation upon irradiation is studied for neat, encapsulated and released PS. This approach may overcome key drawbacks of conventional PS by safeguarding high local concentrations inside the nanocarriers.



Figure 39. Size distribution of PEG₁₁₄-b-PLA₄₀₀ vesicles (left, inset: SEM data), fluorescence intensity of singlet oxygen sensor green vs. irradiation time for released and encapsulated photosensitizer (right).

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Enhancement of Water Solubilization of Quercetin by Meglumine and Deprotonation Order Determination Method with COSMO-RS

<u>Adrien Fusina^{1,2}</u>, Didier Touraud², Véronique Nardello-Rataj¹ and Werner Kunz²

¹Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France ²Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany

Presenting author e-mail: adrien.fusina@chemie.uni-regensburg.com

Keywords: Quercetin, Meglumine, Water-solubilization, pKa, COSMO-RS

Quercetin is a well-known flavonoid, a natural molecule found in many plants, fruits, and vegetables, with numerous health benefits [1]. Like other polyphenols, quercetin is very poorly watersoluble. One way to enhance this solubility without co-solvent or complex structuration is to increase the pH to form polyphenates, but it often leads to oxidation of the compound and does not suit biological applications (physiological pH = 7.4).

The addition of meglumine, an aminocarbohydrate derived from glucose, was found to be able to enhance the water-solubility of quercetin among other polyphenols, at any given pH value from approximately one unit above the first pKa [2]. A compromise was found between solubility enhancement and reasonable stability against oxidation for quercetin at pH 8.

The solubilization mechanism is believed to be a proton exchange between the hydroxyl groups of quercetin and the amine group of meglumine, resulting in a salt formation. Hydrogen bonding of water molecules with the hydroxyl groups of meglumine brings hydration and enables the breaking of the π -stacking of quercetin. In this regard, one crucial parameter to consider is the order of deprotonation of the hydroxyl groups of quercetin and its pKa values. Since the latter are particularly challenging to measure due to quick oxidation, there is no real agreement in the literature. Thus, we developed a method based on pKa calculation with COSMO-RS software for every possible combination of deprotonation states of quercetin [2].



Figure 40. Solubilization of quercetin as a function of pH and meglumine concentration (A), schematic representation of solubilization mechanism (B), and determined deprotonation order of quercetin (C).

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Natural Rubber Derived Heparin-Mimicking Polyampholytes - Synthesis, Structural Transformation and Charge Regulation

Katarzyna Byś¹, Pablo M. Blanco¹, Peter Košovan¹, Mariusz Uchman¹

¹Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 12840 Prague 2, Czech Republic

Presenting author e-mail: byk@natur.cuni.cz

Keywords: polyelectrolyte, polyampholyte, charge regulation

Highly sulfated heparin-mimicking polyelectrolytes effectively act as anticoagulants with tailorable structure and tunable sulfation degree. This versatility has prompted the scope of their biomedical applications. However, the complex charge regulation of the polymer chain and the mechanisms controlling the structure of such polymers remain unclear.

Sodium poly((sulfamate-carboxylate)isoprene) is a natural rubber-derived high-charge-density polyelectrolyte containing two negatively charged groups of different pH sensitivity at the same monomeric unit. The pH-dependent sulfamate group, which resembles the one found in heparin, undergoes N-S bond cleavage in acidic pH, which leads to the chemical transformation into a polyzwitterionic poly((amino-carboxylate) isoprene). [1-3].

To evaluate the pH induced change of ionization, mechanism of structural transformation, and charge regulation of such polymer we conducted a post-polymerization modification of cis-1,4-polyisoprene to obtain poly((sulfamate-carboxylate) isoprene). The reaction was followed by acid-induced cleavage of over 90% of the N-S bonds and ultimately lead to the chemical transformation into a polyzwitterionic poly((amino-carboxylate) isoprene. The structure of both hydrophilic polymers and the cleavage of sulfamate groups were confirmed by ¹HNMR, FTIR, elemental analysis, pH-dependent zeta-potential and dynamic light scattering measurements. The total charge on the polymer was determined by potentiometric titration and based on those results we performed molecular dynamics simulations to gain insights into the polyelectrolyte charge regulation. Additionally, we investigated the biocompatibility of the polymers by MTT assays and confirmed their anticoagulating heparin-mimicking behavior by activated partial thromboplastin time (aPTT) measurement.

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Trimer polymer nanoparticles: tuning the angle distribution during synthesis

<u>Gabriel A. A. Monteiro¹</u>, Lisa Bernhard¹, Sabrina Brusch¹, Remo Stark¹ and Alexander Wittemann¹

¹Colloid Chemistry, University of Konstanz, Universitätsstraße 10 78464, Konstanz, Germany Presenting author e-mail: <u>gabriel.monteiro@uni-konstanz.de</u>

Keywords: nanoparticles, anisotropic particles, polystyrene latex, seeded polymerization, colloidal molecules, dumbbells

Anisotropy is one of the main variables determining the hydrodynamics of colloidal particles [1]. The importance of the morphology inspired the development of strategies to prepare complexshaped particles [2]. Such strategies include using phase separation seeded polymerization, a technic used to obtain polymer dumbbells. Dumbbells are among the most explored anisotropic morphologies for polymer nanoparticles and can be a starting point for more complex architectures. The phase separation route to obtain dumbbells consists of disrupting the monomer-polymer mixture in a seed sphere swollen with monomer, yielding a liquid protrusion on its surface. This disruption is achieved thermally, what also polymerizes the monomer and creates a solid lobe on the seed's surface. This process can be repeated and yield a second protrusion to produce more complex morphologies. Such morphologies are expected to be determined by a property gradient between the two seed dumbbell lobes. Said gradient can be based on crosslinking densities [3] or surface wettability, with the latter still to be demonstrated. Controlling the gradient between the two dumbbell sides could lead to particles with higher anisotropy and aspect ratio, thus expanding their rich phase behavior [1, 2].

Phase separation seeded emulsion polymerization was employed using dumbbells as seed particles to obtain colloidal trimer nanoparticles. These particles exhibit high degrees of anisotropy and linearity between their three lobes (Figure 1 (A)), what is attested by their angle distribution (Figure 1 (B)). Expanding the investigation, the morphology was controlled for different samples using the surface wettability gradient between their seed dumbbells' lobes. avoiding the use of crosslinking agents. Presenting such a route to trimer polymer colloids opens perspectives for their preparation in large scale, paving the way to their organization in superstructures in the future.



Figure 41 - (A)Scanning electron microscopy image of PS trimers and (B) their angle distribution.

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Surface-topography quantification of DNA functionalized colloids via super-resolution microscopy

Bahar Rouhvand¹, Barbara Malheiros¹, I.K.Voets¹, P Zijlstra¹, P.Moerman¹

Eindhoven university of technology, Eindhoven, The Netherlands

<u>b.rouhvand@tue.nl</u>

Keywords: Colloids, DNA, Super resolution microscopy, Self assembly

DNA coated colloids are promising building blocks for the self-assembly of functional materials such as photonic and mechanical metamaterials. However, a lack of insight into the microscopic structure of the DNA brush on the particles prevents the design of optimal building blocks. By employing Stimulated emission depletion (STED) super-resolution microscopy, we can visualize the surface of DNA coated colloids on a nanoscale level for the first time, which enables us to study spatial heterogeneities in the DNA grafting density. Moreover, using an imager strand that hybridizes to the particles' DNA we probe the brush's accessibility. We correlated our measurements on the microscopic structure of the brush to the assembly dynamics of the particles and ask how spatial heterogeneities affect the particle crystallization (See figure 1). We also compare DNA distributions on the particles synthesized with click chemistry to those produced using Biotin-Avidin chemistry, to shed light on why only the click particles crystallize.

Our results may help target assemblies that were not previously accessible by leveraging control over spatial heterogeneities through understanding the mechanisms of DNA-mediated interactions between particles.



Figure 42. Heterogeneities in the DNA distribution on the surface of 1 µm polystyrene particles, synthesized in different ways. The streptavidin based DNA-coated particles show large fluorescence intensity fluctuations compared to high grafting density click particles indicating a more heterogeneous surface

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Designing gastric stable adsorption layers by whey protein-pectin complexation at the oil-water interface

<u>Hao Li</u> and Paul Van der Meeren

Particle and Interfacial Technology Group (PaInT), Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000, Gent, Belgium

Presenting author e-mail: Hao.Li@UGent.be

Keywords: Gastric digestion, protein emulsion, pectin, interfacial rheology

This work aims to design gastric-stable emulsions with food-grade biopolymers, using a novel multi-scale approach. The adsorption layer formation at the oil-water interface was based on opposite charge interactions between whey proteins and pectin (with different esterification levels) at pH 3.0 by a sequential adsorption method. The interfacial assembly and disassembly (interfacial complexation, proteolysis, and lipolysis) during in vitro gastric digestion were evaluated by quartz crystal microbalance with dissipation monitoring, zeta potential, dynamic surface tension, and interfacial dilatational rheology. Besides, the evolution of the particle size and microstructure of bulk emulsions during the digestion was investigated by static light scattering and light microscopy. Meanwhile, the release of encapsulated compounds was quantified. As compared with WPI-stabilized emulsions, the presence of an additional pectin layer can prevent or at least largely delay gastric destabilization (giving rise to coalescence or/and oiling off), thus limiting the premature release of encapsulated lipophilic compounds. Especially, the esterification degree of the pectin used was found to largely affect the emulsion stability upon gastric digestion.



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The characteristics of bubbles for encapsulation of ethylene gas

Zhanpeng Liu^{1,2}, Qiang Huang ¹ and Paul Van der Meeren ²

¹ School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, China

²Particle and Interfacial Technology Group (PaInT), Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000, Gent, Belgium

Presenting author e-mail: zhanpeng.liu@ugent.be

Keywords: ethylene, bubble, bubble gel, release, gas storage

Ethylene gas was introduced into bubble and bubble gel systems at room temperature and atmospheric pressure, achieving gas encapsulation, storage and release. The bubble system exhibited a better ethylene loading capacity with contents in the range of 25.3-44.2% (v/v), which was attributed to the different viscosity of the solutions, as revealed by the viscosity analysis, leading to different bubble diameters. The ethylene release kinetics investigation showed that approximately 50-80% of the ethylene was released from the bubble system in 60 h. After transformation to a bubble gel, the ethylene content significantly decreased from 0.51-0.57 to 0.18-0.23 mL/g_{carrier} because of bubble rupture and coalescence during gel formation. The bubble gel had a better performance for storage of ethylene during 28 days compared to the bubble system, which was ascribed to the gel coated and water layer around the bubble surfaces. As an effective carrier, a bubble gel is a desirable encapsulation matrix with potential in fruit ripening applications.



Figure 43. Schematic diagram of gas loading and storage in a bubble and bubble gel system.

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Time-Resolved Fluorescence Studies of Core-Shell Nanocapsules

<u>Nigar Hajiyeva¹</u>, Sergey I. Druzhinin¹, Aneta Medaj², Joanna Odrobińska-Baliś², Szczepan Zapotoczny² and Holger Schönherr¹

¹ University of Siegen, Physical Chemistry I & Research Center of Micro- and Nanochemistry and (Bio)Technology (Cμ), 57076 Siegen, Germany ² Jagiellonian University, Faculty of Chemistry, 30-387 Krakow, Poland

Presenting author e-mail: <u>nigar.hajiyeva@uni-siegen.de</u>

Keywords: amphiphilic polymer, core-shell capsule, oil water interface, nanoreactor.

The development of polymeric nanocarriers with a core-shell architecture has played a significant role in different fields, including medicine, chemistry, biotechnology and found its application in e.g. drug delivery, theranostics, imaging and chemical nanoreactors.[1] Ultrasmall confined volumes may afford a high local concentration of reagents that can be exploited to increase the reaction rate, selectivity and efficiency of chemical reactions.[2] This study focused on the fabrication of polymeric capsules templated on oil cores to form nanoreactors. Stabilizing cationic polyelectrolytes were synthesized by derivatization of PAH (poly(allylamine hydrochloride)) with GTMAC (glycidyltrimethylammonium chloride) and epoxyalkanes in a 2-step reaction.[3] Capsules, formed during sonication of the polyelectrolytes and hexadecane (HD) or octadecane, were loaded with the reporter dye Nile Red. The formation of capsules was confirmed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Dynamic light scattering and nanoparticle tracking analysis were used to determine the hydrodynamic diameter in a range of ~ 50 to 190 nm, depending on the core. The photostability of single Nile Red molecules and their characteristic lifetime ($\tau \approx 3$ ns) were determined in HD and after encapsulation by fluorescence lifetime imaging microscopy. The results confirmed that these nanocapsules may serve as stable nanocontainers for hydrophobic loads and can be used for further studies as nanoreactors.



Figure 44. a) Confocal fluorescence intensity and *b*) SEM images of PAH GTMAC C_{12} capsules.

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Determination of the molar mass of microgels using fluorescence microscopy

<u>Thomas Schmidt¹</u>, Moritz Becker², Frédéric Grabowski³, Andreas Jupke², Andrij Pich³ and Dominik Wöll¹

¹ Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen ² Aachener Verfahrenstechnik, RWTH Aachen University, Forckenbeckstraße 51, 52074 Aachen ³DWI - Leibniz-Institut für Interaktive Materialien, RWTH Aachen University, Forckenbeckstraße 50, 52074 Aachen

Presenting author e-mail: <u>Thomas.Schmidt@pc.rwth-aachen.de</u>

Keywords: Molecular mass determination, microgels, fluorescence microscopy, Nile Red labeling

Even though the molar mass M is one of the most important physicochemical quantities, the molar mass of microgels is often not determined since it is not a straight-forward task. We developed a facile method to estimate the molar mass of microgels using fluorescence microscopy. This method can be readily also applied to other (soft) objects. Mixing an aqueous microgel dispersion with a Nile Red solution in water we non-covalently labeled the microgels[1,2] and visualized them with good signal-to-noise-ratio. For our initial experiments, we used PVCL (poly(N-vinylcaprolactam))) microgels with a PGMA (poly(glycidyl methacrylate)) core.

We performed single particle tracking experiments to determine diffusion coefficients and determined the molar mass of the microgels by counting the number of microgels per volume taking into account the respective mass concentration of the solution. To verify that no other effects like surface interactions affect the calculation we made a dilution series and tested for linearity. We also measured in different distances to the surface to gain sufficient statistics. The number of microgels in dependence of the height above the cover slip is represented in *Figure 1* (exemplarily for one measurement). As visualized it might occur that some microgels stick to the cover slip surface. This effect has to be carefully accounted for.

To demonstrate the generality of the method, we used different microscopy setups like widefield fluorescence microcopy, spinning disc confocal microcopy and also a simpler fluorescence microscope without a laser excitation demonstrating that our method is applicable to different systems and not restricted to research groups specialized on fluorescence microscopy with the option of laser excitation.



Figure 45. Depiction of the number of microgels in dependence of the height above the cover slip surface.

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How Salmonella overcome the gastrointestinal mucus labyrinth

<u>Kevin Diestelhorst¹</u>, Fereshteh Ghazisaeedi ², Anton Klimek³, Sebastian Braetz², Karsten Tedin², Marie Weinhart^{1,4}, Roland Netz³, Marcus Fulde², Stephan Block¹

¹Institute of Chemistry and Biochemistry, Department of Biology, Chemistry, Pharmacy, Freie Universität Berlin

²Institute of Microbiology and Epizootics, Department of Veterinary Medicine, Freie Universität Berlin

³Institute of Theoretical Bio- and Soft Matter Physics, Department of Physics, Freie Universität Berlin

⁴*Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover*

Presenting author e-mail: <u>kevin.diestelhorst@fu-berlin.de</u>

Keywords: Mucus, Hydrogels, Salmonella

The glycans and glycoproteins on the surface of the intestinal mucosal barrier serve as sources of nutrients and ligands for microbiota and pathogens. Certain host cell metabolites attract bacteria, such as oxygen. However, only enteric pathogens like Salmonella typhimurium can penetrate the mucus layer and invade epithelial cells, disrupting the mucosal barrier. Therefore, it is important to study how enteric pathogens navigate, adhere, and approach the mucus layer in combination with their molecular mechanisms.

For this purpose, dynamic hydrogel as a barrier against infectious agents get investigated by using optical microscopy. The study aimed to investigate the motional behavior of Salmonella typhimurium in bulk solution compared to its behavior in the presence of mucus-producing epithelial cells HT29-MTX. Various mutants of Salmonella were examined, whereby the motility was influenced by changes to the complex flagellum structure, as well as the binding properties of the fimbriae to fucosylated components were affected. For this purpose, the 2D movement patterns and movement velocities are extracted and compared between the different mutants and conditions. Additionally, the study was expanded to include 3D movement analysis using z-stack imaging, which revealed that Salmonella typhimurium reaches the cellular layer via tunnel-like structures.

Effect of co-delivered L-ascorbate on storage stability and in vitro release of curcumin in chitosan-stabilized caseinate particles

<u>Xin Yin^{1,2,3}</u>, Muhammad Aslam Khan^{1,2}, Weining Huang^{1,2}, Ning Li⁴, Li Liang^{1,2*} and Paul Van der Meeren³

¹State Key Lab of Food Science and Technology, Jiangnan University, Wuxi, Jiangsu, China ²School of Food Science and Technology, Jiangnan University, Wuxi, Jiangsu, China ³Particle and Interfacial Technology Group, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Gent, Belgium ⁴Guangzhou Puratos Food Co., Ltd, Guangzhou, Guangdong, China

Presenting author e-mail: <u>xinxyin.Yin@ugent.be</u>

Keywords: binary particle; L-ascorbate; curcumin; co-delivery; stability; regulated release

The construction of binary particles has gained attention for their use for the co-delivery of hydrophilic and hydrophobic bioactive compounds^[1,2]. The objective of this work was to assess the effectiveness of an L-ascorbate loaded chitosan coating on co-delivered curcumin in the caseinate core, by evaluating their interaction, protective effect as well as release behavior during *in vitro* simulated digestion. Caseinate-chitosan particles were fabricated by a combined facile pH conversion and ionic gelation method. Circular dichroism and infrared spectroscopy indicated that the structural change of caseinate was inhibited after coating with chitosan, and their interactions included hydrogen bonding and electrostatic interaction. Electrostatic interaction occurred between L-ascorbate and chitosan, while hydrogen bonding primarily occurred between curcumin and caseinate. The particles could efficiently coencapsulate around 48% L-ascorbate and 96% curcumin and exhibited a regulated *in vitro* release behavior, with most of the release happening in the intestine. The L-ascorbate-loaded chitosan coating greatly improved the storage and irradiation stability of curcumin. The ABTS⁺⁺ scavenging ability of the co-delivered system was significantly improved compared with the two components alone and was basically unchanged during irradiation. These results can be used as a helpful guide for future research to optimize bilayer particles for co-delivery of multi-ligands with preventive health activity.



Figure 46. Graphical abstract of the present work.

References

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Modifying the structure and physicochemical properties of insoluble soybean fiber towards enhanced emulsion stability

Lihua Huang ^{1,2}, Yongjian Cai¹, Qiangzhong Zhao¹ and Paul Van der Meeren²

¹School of Food Science and Engineering, South China University of Technology, Guangzhou, 510641, China

²Particle & Interfacial Technology Group, Faculty of Bioscience Engineering, Ghent University, 9000, Ghent, Belgium

Presenting author e-mail: <u>lihua.huang@ugent.be</u>

Keywords: superfine grinding; steam explosion; enzymatic hydrolysis; insoluble soybean fiber; emulsion properties

Insoluble soybean fiber (ISF) extracted from *okara* can be used to stabilize emulsions ^[1, 2]. However, the previously described extraction method applied extreme conditions and was not suitable for industrial application. In the present work, various methods were utilized for the modification of the structure and physicochemical properties of ISF. Compared with the untreated ISF (UT-ISF), the viscosity was reduced for the ISF obtained after superfine grinding (SG-ISF). Steam explosion increased the water solubility but decreased the water holding capacity and swelling capacity of ISF (SE-ISF). Enzymatic hydrolysis removed the combined protein and enhanced the crystalline index. Emulsions containing UT-ISF and SG-ISF before or after enzymatic hydrolysis or SE-ISF presented large oil droplets and were unstable. SE-ISF after enzymatic hydrolysis (SE-E-ISF) produced emulsions with the smallest volume-weighted average diameter, but with the largest amount of flocculation, as well as the highest viscosity and viscoelastic modulus. Moreover, the SE-E-ISF stabilized emulsions exhibited an excellent storage stability. Hence, this synergistic extraction method of ISF was effective for enhancing the emulsion stability. The present study provides a novel way for the extraction of ISF and the utilization of *okara*.



Figure 47. Graphical abstract of the present work.

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Effect of type of initiator and purification on the properties of thermo-responsive PNIPAM microgels

Joanne Zimmer¹, Sebastian Stock¹, Souraj Mandal¹, Carina Schneider¹, Luca Mirau¹, Regine von Klizing¹

¹ Technische Universität Darmstadt, Institute for Condensed Matter Physics, 64289 Darmstadt, Germany

Presenting author e-mail: joanne.zimmer@pkm.tu-darmstadt.de

Keywords: microgels, PNIPAM, radical initiator, purification

Microgels (MG) are polymeric networks in the size range of micrometers boasting properties of both colloids and polymers. [1] In addition, MG can be surface active and are, thus, a valuable stabilizing agent e.g. in stabilizing foams. [2] Depending on their composition MG can respond to external stimuli such as temperature or pH. [1] An example of a thermo-responsive polymer is Poly(N-isopropylacrylamide) (PNIPAM). [3] PNIPAM MG can be synthesized by surfactant-free precipitation polymerization comprising monomers. the NIPAM crosslinker N,N'-methylenbisacrylamide (BIS) and a radical initiator. [4] Depending on the radical initiator, either negatively or positively charged MG are generated. The subject of this work is the evaluation of the MG charge on the thermo-responsive swelling behavior and elastic properties using Dynamic Light Scattering and Atomic Force Microscopy. In addition, the type of MG purification and its effect on the resulting MG properties is investigated. It was shown, that the presence of undesired lowmolecular weight products strongly impacts the MG interfacial adsorption behavior what we wish to understand. In this regard, sufficient removal was only achieved if, apart from the standard purification via dialysis, subsequent centrifugation steps were carried out. The MG bulk properties (hydrodynamic radius, Zeta-potential) remained unchanged before and after centrifugation.

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