19TH ZSIGMONDY COLLOQUIUM@HENKEL

Book of Abstracts

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- Zsigmondy Talks

ZSIGMONDY TALKS

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Equilibrium phase behavior and dynamic interfacial properties of rhamnolipid and ethoxylate mixtures

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Keywords: *biosurfactants, microemulsions, adsorption*

Microbial biosurfactants, such as rhamnolipid, are considered as a greener alternative to fossil-based surfactants because they are made from renewable resources in a biological process [1]. But the simple drop-in replacement of fossil-based surfactants with biosurfactants in applications leads to a loss of performance in most cases. Hence, new synergistic surfactant combinations with biosurfactants must be identified. For the optimization of such system, not only equilibrium properties must be studied, but also the dynamic interfacial properties are highly relevant depending on the typical time scale of the respective application [2].

Therefore, we combined the biosurfactant rhamnolipid with potentially renewable ethoxylates and investigated their properties at different time scales. We found that efficient microemulsions emerge with rhamnolipids and hydrophobic ethoxylates in equilibrium. These ethoxylates however are slow in their adsorption to interfaces, whereas a high ratio of rhamnolipid accelerates the adsorption. Having understood the surfactant systems with pure substances, we then analyzed the technical systems. The fatty alcohol and higher ethoxylated species in technical ethoxylates lead to a different behavior at interfaces in equilibrium and non-equilibrium conditions.

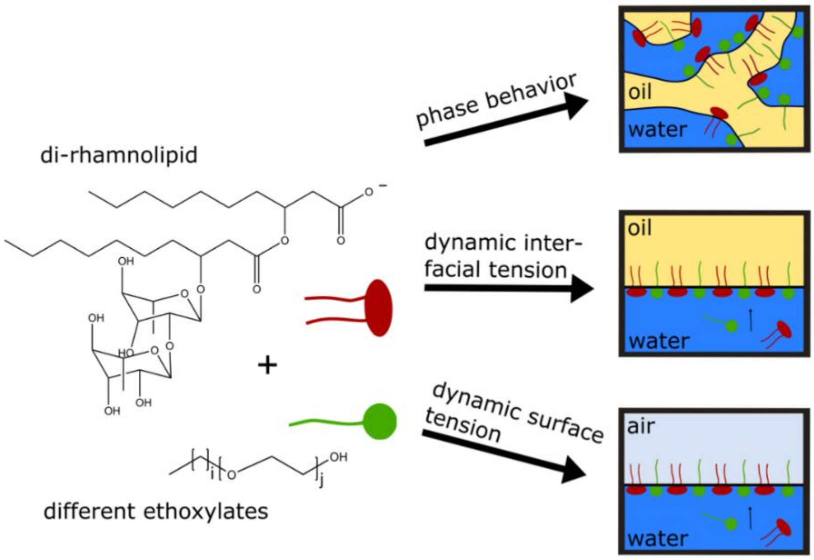

Figure 1. *outline of the talk*

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Combining SAXS and statistics to study self-assembly of surfactants from renewable resources

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Keywords: SAXS, sustainable surfactants, self-assembly, statistics

Surfactants from renewable resources are developed to replace petrochemical surfactants. Their attractiveness is explained by their biodegradability, low toxicity and their environmental friendliness but they are also known to present interesting solution self-assembly properties, controlled by temperature, pH or type of ion[1].

The most common methods employed to study the self-assembly properties of surfactants in solution are surface tension, light and X-rays scattering. However, when surfactants are obtained from renewable resources, the actual raw samples are not pure[2], but they are in fact a mixture of a number of structurally-related molecules that may have an impact on the self-assembly properties. The use of DLS or surface tension measurement is then not advised because complex morphologies and impurities can introduce biases. On the other hand, X-ray scattering is the most suitable analytical technique for a number of reasons (provided a reasonable number of coexisting phases): fast acquisition (from ms to s scale), information on size, morphology and interactions, statistically meaningful, high throughput equipment available.

Here, we show how high throughput SAXS using synchrotron (ESRF) radiation allowed to study about 400 samples of raw surfactants from renewable resources, prepared by varying different conditions like pH, storage time and temperature, purification, concentration and dilution. The large number of experiments allows to perform a statistical study correlating each parameter to the size, shape and core-shell structure of self-assembled aggregates, after fitting each SAXS profile with known numerical model (core-shell ellipsoid of revolution).

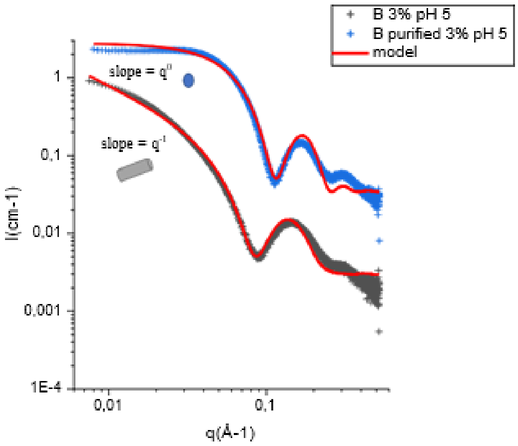

Figure 1. *SAXS fittings of a sphere and a cylinder shape*

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Inkjet-printed nanocomposites of hybrid nanoparticles and polyvinyl alcohol

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Keywords: nanocomposite, printed electronics, recycling, sinter-free, adhesion, conductive

Electrically conductive structures can be made from metal-based inks/pastes by inkjet or screen printing. Inkjet printing saves material and can produce structures with high precision but requires colloidally stable particles, which in commercial inks often carry insulating organic ligands. A post-treatment is necessary to obtain conductive structures, which limits the choice of substrate and applicability. Hybrid nanoparticles with metal cores and a conductive polymer as ligand shell do not require sintering and are conductive after the solvent evaporation. [1,2]

Limitations of such hybrids include weak adhesion on glass or polyethylene terephthalate and limited stability in water. Here, we investigate nanocomposites of hybrid nanoparticles in matrices of insulating polyvinyl alcohols (PVA) with different molecular weights and degrees of hydrolysis. We created inkjet-printable nanocomposites with large filling ratios, printed them, and characterized their electrical resistivity, adhesion, bendability, stretchability, and stability in water.

The colloidal stability of the hybrid particles was not affected by the addition of PVA, and we were able to print nanocomposites with up to 10 vol% PVA. A fraction of 5 vol% PVA in the composite increased the adhesion; surprisingly, the addition of 10 vol% highly hydrolyzed PVA even increased the conductivity. The composites remained stable after 500 bends to 3.1 cm^{-1}, and the relative resistances remained between 0.9 and 1.4 after 500 cycles to 10 % strain. The addition of PVA also increased the stability in water.

We will discuss a possible phase separation due to interactions between PVA and the conductive polymer PEDOT:PSS that the particle carry as a ligand, which could explain increases in conductivities. Finally, we demonstrate that it is still possible to redisperse the particles from the nanocomposite and recycle them.

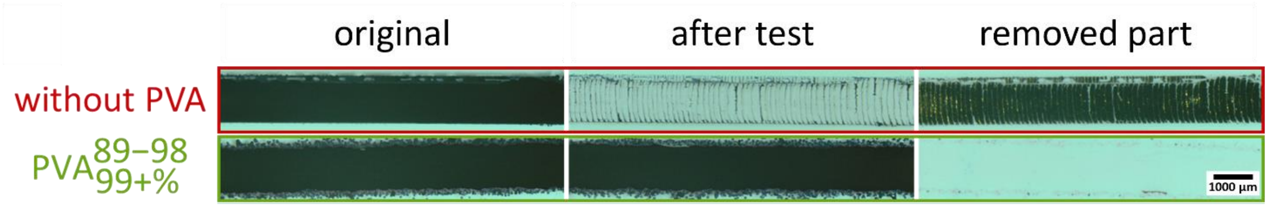

Figure 1. *Adhesion test of inkjet-printed nanocomposites of hybrid particles without and with 10 vol% PVA (M_w = 89.000 – 98.000; 99+ % hydrolyzed).*

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Crystallization-driven Gelation and Solvent Exchange towards Sustainable, Thermally-stable and Flame-retardant Polymer Aerogels

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Keywords: Thermoreversible gel, aerogel, poly(lactide), solvent exchange, stereocomplex

Aerogels are a diverse class of highly porous materials with intrinsic properties such as low density, high specific surface area, low thermal conductivity, low sonic velocity, ultra-low dielectric constant, etc., obtained by replacing liquid from the corresponding gels with air.[1] Semicrystalline polymers can form thermoreversible gels in organic solvents by crystallization, where tiny crystallites constitute the physical cross-links of the three-dimensional polymer network.[2] These thermoreversible organogels can be converted to aerogels by either supercritical drying or freeze-drying. The popularization of freeze-drying in aerogel preparation has simultaneously boosted the use of solvent exchange strategies before solvent extraction from polymer gels. However, the possibility to tune the thermal, mechanical and other properties of polymer aerogels by modifying the crystallization and solvent exchange conditions has been least explored.

Herein, we show facile and sustainable methods to enhance the poly(lactide) (PLA) aerogel properties. PLA is a commercially important biodegradable polymer that exists in two enantiomeric forms, poly(L-lactide) and poly(D-lactide). We devise a facile strategy for the stereocomplex (SC) formation between these enantiomers in the gel state in order to enhance the thermal and mechanical properties of PLA aerogels. A unique morphology is obtained for SC aerogel (Figure 1a).[3] By modifying the solvent exchange step that follows the thermoreversible gelation, bio-resourced molecules such as chitosan, sodium alginate, and phytic acid are assembled onto the PLA gel framework in a layer-over-layer (LoL) fashion, which greatly improves the flame-retardant properties of the aerogel (Figure 1b).

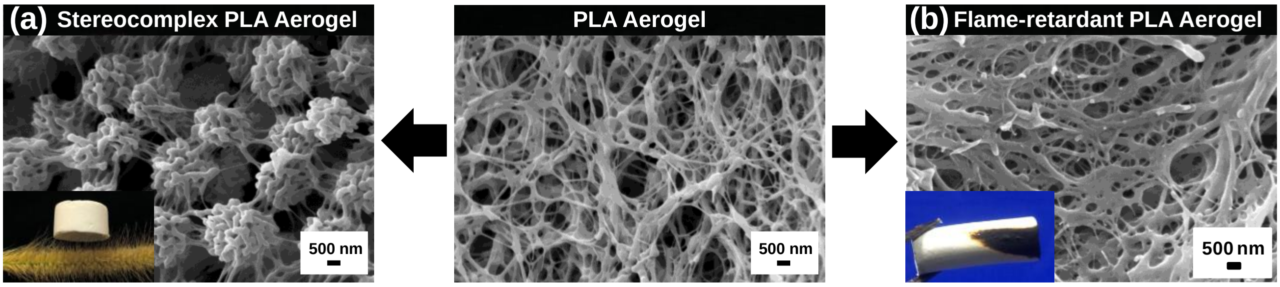

Figure 1. *Morphology of PLA aerogel after (a) the SC formation and (b) the LoL assembly.*

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Synergism and kinetics of lipase-peptide systems for solid fat removal at low temperatures

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Keywords: Solid fat, lipase, peptide, low temperature

The effect of both chemistry and temperature in cleaning processes is critical to the removal of solid and liquid fats from substrates. While liquid fats are removed by forming emulsions, solid fats must first be melted at high temperatures ($T > 50°C$) to be emulsified. [1] However, this process requires a considerable amount of energy to heat the cleaning liquid, which is not sustainable. Therefore, new ways to remove solid fats at low temperatures ($T < 30°C$) are needed. Lipase-catalyzed fat hydrolysis, which is well known from literature, is used for this purpose. [2] This approach is extended by the addition of novel peptides to promote the removal of solid fats in a sustainable manner.

In this work, the desorption of solid fats was studied using the quartz crystal microbalance with dissipation monitoring (QCM-D). It was found that the characteristic time required for solid fat desorption is significantly reduced when small amounts of peptides are adsorbed onto the solid fat prior to lipase addition. This means that the order of addition plays a crucial role in this synergistic effect between lipase and peptide. Furthermore, it has been shown that the desorption time of the lipase-peptide systems is similar or even shorter than that of conventional lipase-surfactant systems. As a result, bio-based peptides can be considered as a sustainable alternative to conventional surfactants.

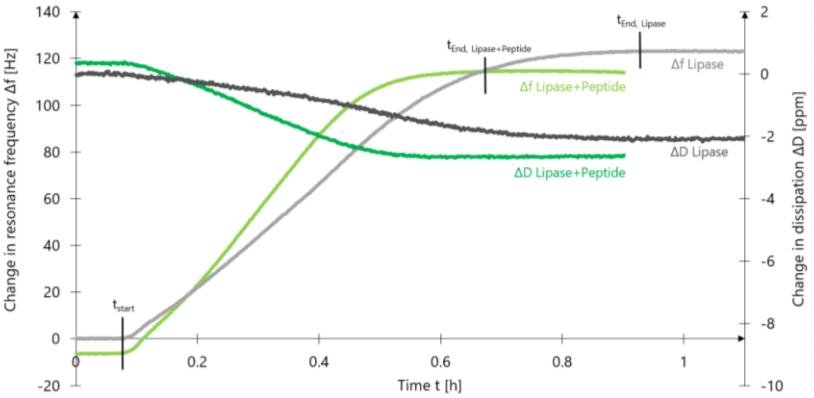

Figure 1. *QCM-D measurements with plotted desorption times for both lipase and lipase-peptide systems*

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Investigating the interactions between the biosurfactant rhamnolipid and cationic guar gum using light scattering based microrheology

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Keywords: polyelectrolyte, biosurfactant, interactions, microrheology, adsorption

Combinations of anionic surfactants and cationic polyelectrolytes are frequently used as ingredients in various applications. For example, in shampoos, they help to reduce the combing force of the hair and provide a smooth hair feeling. Laundry and cleaning applications typically contain ionic surfactants or surfactant mixtures and may also include cationic polyelectrolytes, which act as soil release polymers and prevent re-soiling.

The adsorption behavior of polyelectrolytes onto substrates is decisively controlled by the bulk interactions of mixtures of polymers and surfactants. These interactions have been extensively researched since the 1950s [1-3]. However, due to climate crisis, there is an urgent need to replace complex, well-established fossil-based systems with green and sustainable polymer-surfactant systems.

Conventional systems, which contain a cationic polyelectrolyte and anionic surfactants, have been extensively studied [4-6]. Recent studies have mostly focused on systems containing either a well-described biosurfactant or a well-described biopolymer. However, there is still a lack of research on combinations of both biopolymers and biosurfactants.

In this work, we investigated the interactions between a bio-based cationic derivate of hydroxypropyl guar and the biosurfactant rhamnolipid. To study the bulk behavior, among others, light scattering based techniques were used. In addition, rheological properties were accessed using microrheology. A quartz crystal microbalance with dissipation (QCM-D) was used to investigate the adsorption properties on model surfaces. Anionically modified gold surfaces were used to mimic the negatively charged surface of damaged hair. The bulk interaction properties were adjusted, resulting in a significant improvement in polymer deposition on the model surfaces compared to the pure polymer solution. It has been shown that there is a clear correlation between interactions in the bulk phase and the adsorption behavior.

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Using tetraPEG Hydrogels to Mimic the Properties of Mucus

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Keywords: mucus, hydrogel, rheology, tetraPEG, scattering

Mucus is a biological hydrogel found at surfaces in the human body, which serves critical functions such as protecting tissues from pathogens [1]. Mucus is mainly made from highly glycosylated polypeptides, called mucins, that are crosslinked via disulfide bonds. Understanding the physicochemical properties of mucus is challenging due to its complex hierarchal structure and limited sample availability. Conversely, tetraPEG hydrogels, prepared from mutually reactive 4-arm PEG precursors, have a near-ideal network structure, and clearly defined viscoelastic properties and are therefore well-suited for investigations of structure-dynamics relations of hydrogels [2].

Starting from an ideal tetraPEG network structure (Figure 1A on the left), we systematically introduce 2-arm PEG segments to reduce the number of crosslinks and increase the mesh size. Using this procedure, we were able to design soft tetraPEG hydrogels that mimic the structure and rheology of mucus. These soft hydrogels were then comprehensively characterized using oscillatory shear rheology and scattering techniques to obtain detailed information about their structure and dynamics, which are also instructive about mucus.

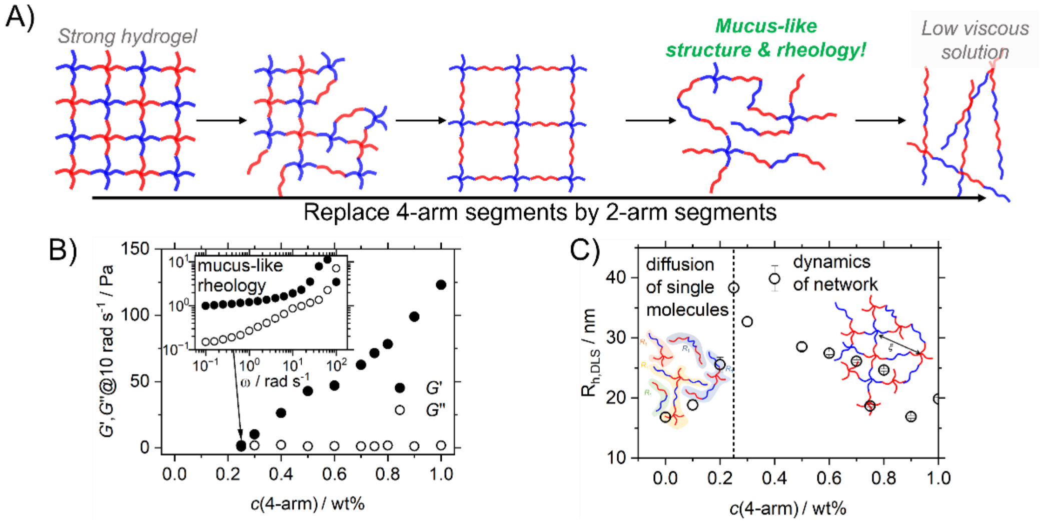

Figure 1. *A) Proposed hydrogel structures obtained by introducing 2-arm segments into a tetraPEG hydrogel. B) At a specific composition, mucus-like rheology can be achieved. C) Dynamic light scattering reveals two regimes: below a critical 4-arm concentration, diffusion of single molecular fragments is seen while above we see the dynamics of the network.*

Acknowledgements: We thank the *Deutsche Forschungsgemeinschaft* for funding this work as part of SFB 1449. We thank the *Deutscher Akademischer Austauschdienst* for funding a research stay in the Sakai lab at the University of Tokyo, where large parts of this research were conducted.

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Polyphotoacids – multi-stimuli-responsive polymers for the drug delivery applications

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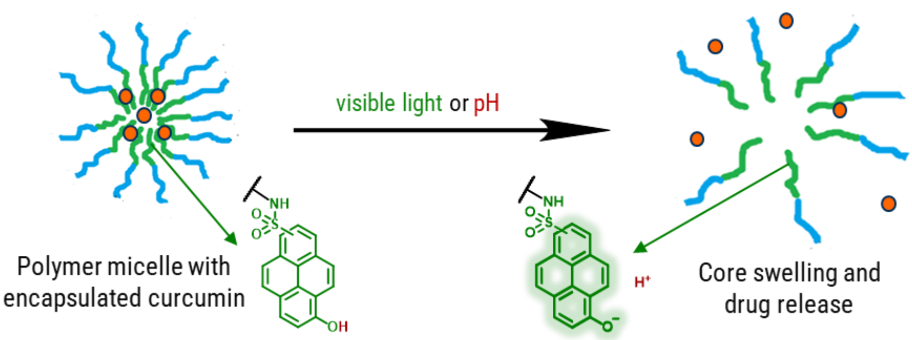
Keywords: photoacid, light-responsive, self-assembly, poly(2-oxazoline)

Here, we report on the synthesis and investigation of novel macromolecular photoacids containing 1-pyrenol. The concept of photoacid is based on a significant drop of the pK_a value of such molecules upon irradiation by light of appropriate wavelength – so-called excited-state proton transfer (ESPT). The pK_a drop of 1-pyrenol photoacids can be achieved by visible light irradiation, making them appropriate for application on living tissues.

We have formed a library of amphiphilic multi-stimuli-responsive (temperature, pH, light) polymers of different structures using subsequent polymerization and post-polymerization modification. The obtained polymers form nanoparticles in water that are able to encapsulate a hydrophobic drug – curcumin. The obtained results show the potential of polymeric photoacids in controlled drug delivery.

Figure 1. *Schematic representation of the drug release from the polyphotoacid micelles.*



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A versatile method for facile and reliable synthesis of gradient colloidal particles

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Keywords: gradient size distribution, chemical gradient, intrinsic glass transition temperature gradient, silica particle gradient

Colloidal particles are widely used in a large field of applications. Many of these require a well-tailored particle size and size distribution.[1] Seeded growth reactions are well reported approaches to target these demands. However, mainly batch-wise syntheses return discrete particle sizes.[2] Since gradient structures coming into the focus of current research, novel versatile methods to produce well controlled continuous gradient colloidal particles are needed. With the controlled emulsion extraction process (CrEEP), Schöttle *et al.* presented the first method to cope with that.[3] We introduce the next iteration of the setup, providing a higher degree of reliability and versatility. We achieved particles with a time-resolved size gradient, which can be adjusted to exclude specific particle sizes. Further, we demonstrate the level of versatility by additional variation of the monomer feed composition leading to gradual change in size and glass transition temperature. Beyond polymer particles, CrEEP can be also applied to sol-gel methods, such as silica Stöber synthesis. The controlled Stöber extraction process (CrESP) also results into a size gradient.

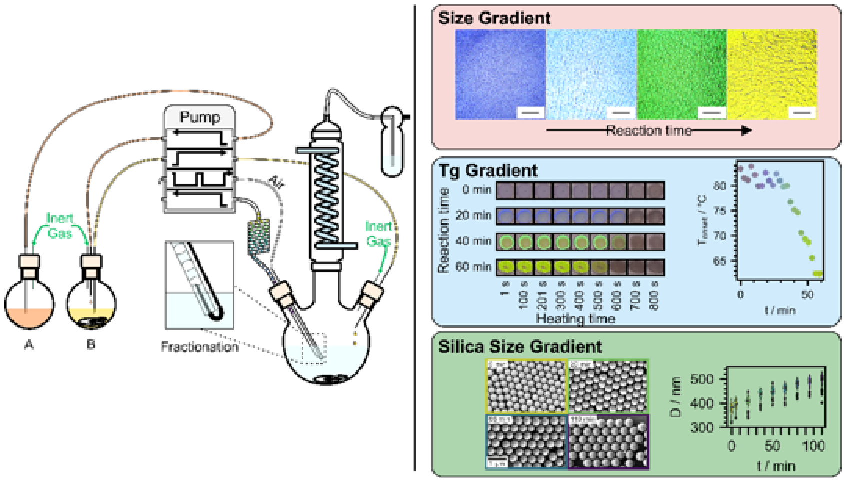

Figure 1. *Setup of the CrEEP and CrESP methods. With those, we are able to synthesize a size gradient, as well as a gradient in glass transition temperature. Further, we adapted the concept and transferred it to silica Stöber synthesis.*

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Stabilization of Apolar Nanoparticle Dispersions by Molecular Additives

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Keywords: dispersion, non-polar nanoparticles, colloidal stability, molecular additive, SAXS, MD simulations

Ligand-stabilized inorganic nanoparticles (AuNPs) are promising building blocks for materials with well-defined structures and properties. Their colloidal stability is limited, and uncontrolled agglomeration causes undefined microstructures that impede functionality. Previous work has shown that the temperature-dependent agglomeration of AuNPs is governed by the disorder-to-order transition of the ligand shell and affected by ligand-ligand and ligand-solvent interactions [1]. For example, the addition of cyclohexane promotes disordered shells and improves the colloidal stability. Excess ligand molecules destabilize dispersions by an entropic mechanism [2]. Here, we study how cyclical amines and thiols stabilize the disordered state of the ligands and improve the colloidal stability of the dispersion.

Small angle X-ray scattering was used to determine the agglomeration temperature, T_{agglo}, of hexadecanethiol-coated AuNP in the presence of small concentrations of pyrrolidine, azonane, tetrahydrothiophene and thionane. Amine-based additives lowered T_{agglo} by not more than 2 K, while sulfide-based additives lowered T_{agglo} up to 28 K, where smaller molecule showed a stronger stabilizing effect. MD simulations indicated, that physisorption cannot account for this decrease; chemisorption and replacement of hexadecanethiol by cyclical sulfides on AuNP surfaces was shown to strongly hinder ligand ordering, thereby reducing T_{agglo}. Surprisingly, higher additive concentrations increased T_{agglo}, possibly due to a clustering transition on the AuNP surface.

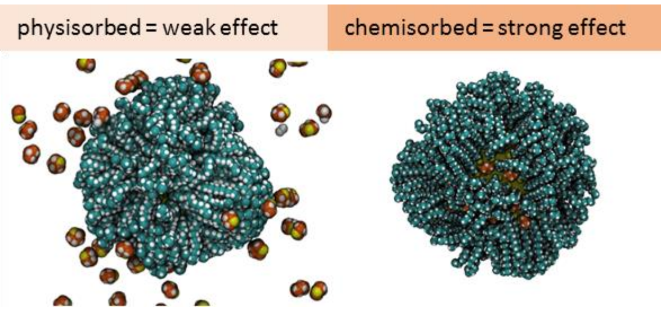

Figure 1: *Overview of the possible interaction mechanism of the additives with an AuNP and the resulting stabilizing effect. Left: physisorption with a weak stabilizing effect, right: chemisorption with a strong effect.*

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The impact of film thickness on the piezoresistive effect of carbon black/polydimethylsiloxane composites

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Keywords: carbon black, stretchable conductors, piezoresistive effect, film thickness

Fully soft robots will open new possibilities and applications [1]. Many such robots are powered by dielectric actuators and controlled by dielectric elastomer switches. Both require electrodes with well-defined piezoresistivity. They are usually based on composites of carbon black (CB) in soft matrices. The agglomeration state and distribution of CB affect the composites' electrical response to deformation, but the colloidal and structural background is poorly understood.

In this study, we examined the electro-mechanical characteristics and stability of CB-filled polydimethylsiloxane (PDMS) elastomers at different layer thicknesses. Composites with filling ratios of 8 vol% CB particles (from Thermo Scientific Chemicals) in liquid silicone (Sylgard 184, Dow Corning) and organic solvents were blended at 2350 rpm for 3 minutes using a speedmixer. The material was then spin-coated onto a circular silicone film (Wacker) with a thickness of 50 µm at spin speeds ranging from 1000 rpm to 8000 rpm for 1 minute, resulting in layer thickness between 1 to 20 µm. Subsequently, all the films were cured at 80 °C for 3 hours.

We assessed the electro-mechanical properties and the durability of the composites under cyclic loading using a tensile testing machine coupled with a 2-point electrical measurement. Composites of different thicknesses were subjected to 10% strain for at least 300 cycles. The results, presented in Figure 1, show an initial rapid increase in resistivity, which then plateaued at higher cycle counts. We observed that as the thickness of the film decreases, its piezoresistivity changes more significantly under the same strain due to the geometric restriction of the film. This effect will be discussed in terms of edge effects.

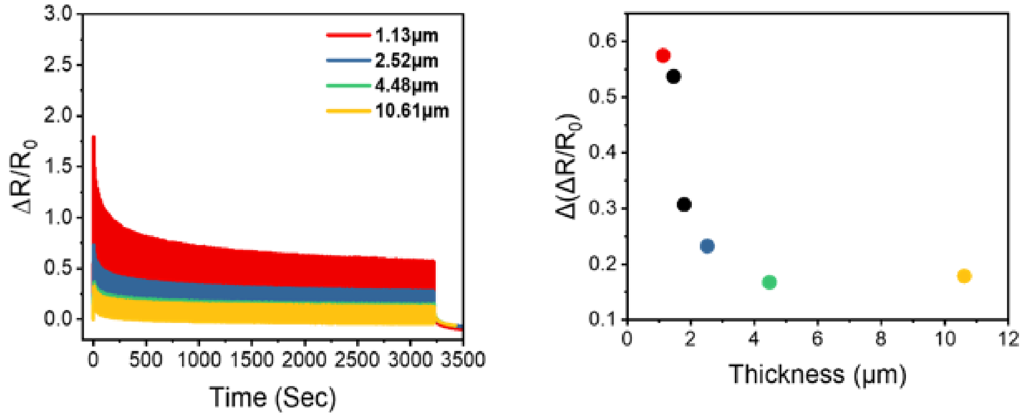

Figure 1. *Change in electrical resistances of 8 vol% carbon black/PDMS composite films under cyclical loading to 10% strain during 300 cycles (left). The maximal changes in piezoresistivity are shown as a function of film thickness (right).*

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Polymer-brush Assisted Microcontact Printing for Precise Surface Patterning (14pt, Arial, Bold)

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Keywords: Surface patterning, Microcontact printing, Polymer brushes.

Achieving precise transfer of functional molecules within the micrometer dimension on diverse substrates poses a significant challenge. [1] A solid-phase transfer of functional molecules as ink in such range through direct contact between an inked stamp and the substrate is possible *via* microcontact printing (µCP). [2,3] This technique can be used to pattern various substrates. However, the inherent difficulty lies in the accurate patterning of substrates, attributed to the molecular diffusion and mobility, particularly, if reactive small molecules are used as ink.

We, therefore, present an accurate surface patterning technique which involves grafting polymer-brushes directly from the stamp's surface efficiently restricting ink diffusion. [2,3] This approach allows for the covalent attachment of functional ink molecules to polymer chains, ensuring a stable bond upon transfer to the substrate and interaction with surface-active groups. Precise patterning of various rough-capillary active surfaces was successfully carried out employing the polymer-brush assisted method showcasing its versatility and efficacy in accurate surface patterning.

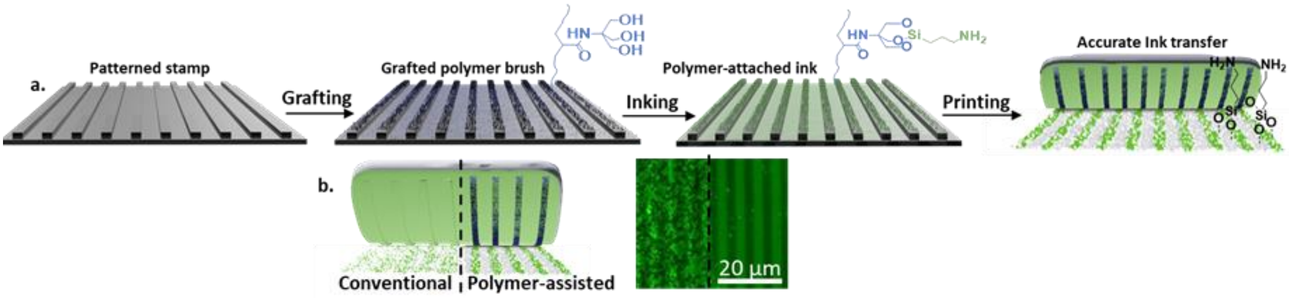

Figure 1 a. Schematic representation of Polymer-assisted µCP (alkoxysilane ink transfer to oxide surface). b. Comparison between the fluorescence microscopy images of patterned substrate using conventional and polymer-assisted µCP.

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Growing Micrometer-Thick Films of Low-Molecular Weight Hydrogelators by Electrogelation

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Keywords: Hydrogelation, Atomic Force Microscopy, Soft Matter, Potentiostatic Control

Electrogelation allows the growth of hydrogel films on a conductive surface with high temporal and spatial control in the formation process. Inducing a local change in pH by electrolysis of water at the electrode interface triggers the hydrogelation of a pH-responsive gelator molecule. In this study, we use gold electrodes to assemble hydrogel films of *N,N′,N″*-tris(4-carboxyphenylene)-1,3,5-benzenetricarboxamide (BTA) (cf. ***Fig.*** 1a) [1] by potentiostatic control. Protonation of BTA in the vicinity of electrodes triggers self-assembly into supramolecular fibers, which build a hydrogel network (cf. ***Fig. 1***).[2,3] We demonstrated the growth of BTA hydrogel films in the micrometer regime with an accuracy of a few tens of nanometers in thickness. Such films form at moderate potentials within a few seconds, making them interesting for biomedical coatings.

The thickness of these hydrogel films has been determined by two atomic force microscopy-based techniques: (a) dried films are imaged ex-situ (***Fig. 1c***) and (a) in-situ nanoindentation is employed to investigate the hydrated state (***Fig. 1c***). Further, we show how the gelation process depends on the gelation time, applied potential, and gelator concentration.[3] The here-introduced approach for electrogelation of BTA provides easy access to controlled hydrogel film formation in the low micrometer regime. Furthermore, the hydrogelation concept and analytical methods are easily transferable to other pH-responsive or reversibly forming hydrogel systems on a large variety of conductive surfaces.

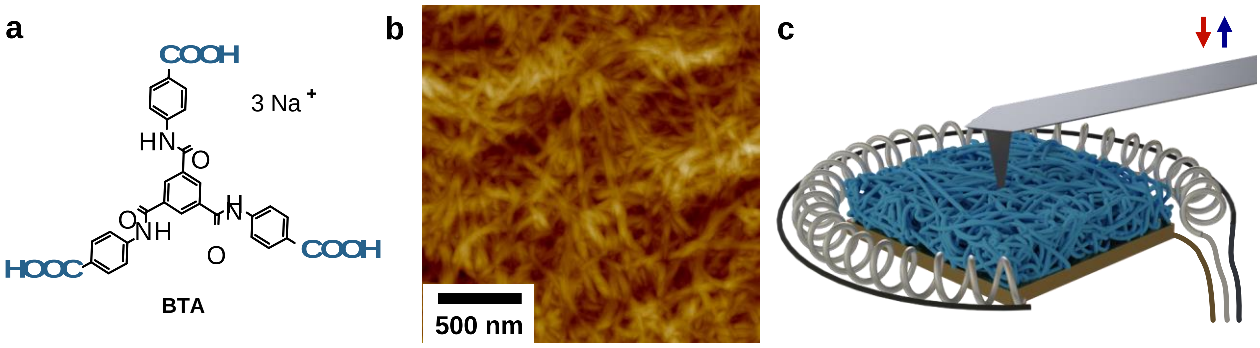

Figure 1. *BTA Electrogelation:* ***a)*** *Molecular structure of BTA****;*** ***b)*** *Fibrous structure of a dried BTA hydrogel by AFM;* ***b)*** *In-situ thickness determination of electrogelated hydrogel films by AFM nanoindentation.*

Acknowledgments: N. Raßmann thanks the VCI for granting the Kekulé Fellowship and support from the University of Bayreuth Graduate School and the Elite Network of Bavaria.

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Tailoring the inert properties of zwitterionic coatings

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Keywords: coatings, protein resistance, zwitterion, amphiphilic, low fouling

Manmade materials in contact with aqueous environments become rapidly colonized by living matter like proteins, macromolecules, bacteria, diatoms, or other fouling species. Frequently failure of devices and substantial maintenance costs are among the penalties associated with fouling processes. As the use of biocides is heavily restricted in many applications, environmentally friendly low-fouling materials are intensively explored [1]. While several hydrophilic and hydrophobic materials show promising properties, their combination into amphiphilic coatings unites the best of the two worlds [2]. As hydrophilic compound, zwitterionic materials with different molecular architectures were developed and their structure-function relationship against different fouling organisms have been studied [3]. Amphiphilic coatings based on zwitterionic polymers have been designed and their anti-polyelectrolyte properties have been characterized by several methods including AFM and SPR. Their antifouling properties against a range of fouling species, in short term field exposures in the ocean, and in biomedical assays have been assessed and will be discussed [4,5,6]. Based on the obtained data, fundamental structure-property correlations and the implications for inert zwitterionic coatings will be discussed.

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Macromolecular Rapid Communications 2021, 43(12), 2100589

Functional Cubosomes: Exploiting Mesoporous Colloids

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Keywords: catalysis, drug delivery, energy storage, inverse morphologies, self-assembly

Block copolymer cubosomes are a novel and rapidly evolving class of mesoporous colloidal nanomaterials. They can be synthesized in a scalable manner by bottom-up self-assembly using block copolymers.[1] Cubosomes exhibit bicontinuous pore systems which permeate the entire structure. Therefore, they possess high surface areas, which is of great interest for many applications (see Figure 1).[2] Currently, almost all cubosomes consist of the chemically inert polystyrene (PS), which does not impart any function beyond mechanical stability. In this work, multiple alternatives to the inert PS are synthesized to yield functional polymer cubosomes:

Firstly, poly(4-vinylpyridine) (P4VP) has an addressable nitrogen atom. It can coordinate to various metals such as Pt for catalysis applications. Furthermore, organic substances like drugs can also be loaded and released in a controlled manner by adjusting the pH.

Secondly, mesoporous carbon is one of the most interesting materials in energy storage and conversion. However, most synthesis paths require hard templating, HF etching or further toxic and wasteful steps. Here, a direct synthesis was developed *via* poly(acrylonitrile) (PAN) cubosomes.

Finally, organic batteries often suffer from poor performance due to the low porosity of the cathode. By utilizing poly(TEMPO methacrylate) (PTMA) – a common cathode material in organic batteries – a cubosome-based cathode system was developed.

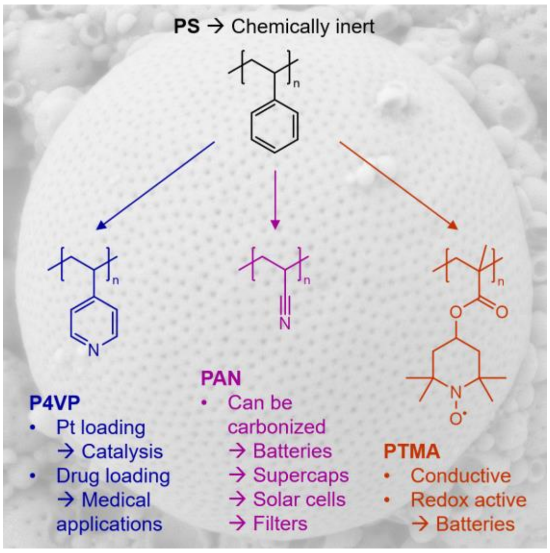

Figure 1. *Chemically inert PS and functional polymer alternatives from this work, which can form functional cubosomes. The background is an example of an SEM image of a cubosome.*

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Platinum Atomic Layer Deposition on Spray-dried SiO2/Iron oxide Supraparticles: Tuning the Activity by Scaffold Texture and Intrinsic Heating Properties

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Keywords: atomic layer deposition, supraparticles, structure control, catalysis, hydrogenation

In the development of new emerging materials, one field of interest is the forced assembly of nanoparticles through spray-drying, creating supraparticles. By adjusting the spray-drying parameters, supraparticles provide adjustable pore sizes and surface areas, along with the combination of multiple nanoparticle functionalities. These highly porous supraparticles have a large variety of applications e.g., as temperature recorders, magnetic sensors, and hydrogen indicators.[1,2] To fabricate even more advanced materials, further functionalization of supraparticles can be accomplished via the atomic layer deposition (ALD) process.[3]

ALD provides monolayer-by-monolayer material deposition, with platinum being a commonly used material for ALD. However, the combination of platinum with supraparticles through ALD is yet unprecedented. The synthesis of such new materials is shown in **Figure 1**. Supraparticles are spray-dried to generate systems with different pore sizes and surface areas. They are subsequently subjected to various Pt-ALD cycles and then tested for their catalytic activity in the reduction of 4-Nitrophenol. An increase in the pore sizes of the supraparticles is highly favored even though the active surface area and the amount of platinum are drastically reduced. This shows that diffusion and mass transport are highly important for such mesoporous supraparticle systems. Iron oxide nanoparticles are subsequently introduced to the supraparticles, allowing for additional magnetic separation and inductive heating capabilities.

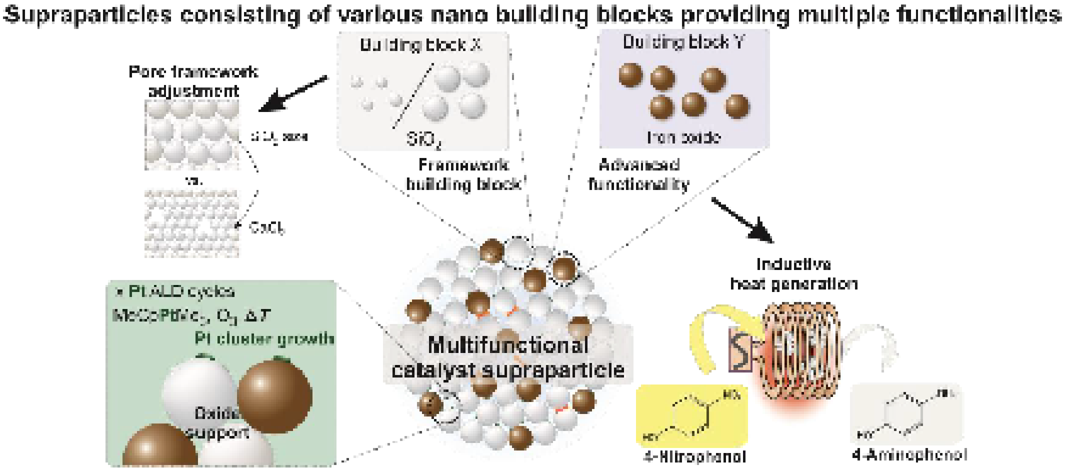

***Figure 1.** Scheme of the synthesis of supraparticles from different nanoparticle building blocks and their further functionalization with platinum via atomic layer deposition (ALD) towards catalytically active supraparticles.*

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Investigation of Model Hydrogels of Increasing Complexity that Approach the Structural Features of Mucin

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Keywords: Mucus, Rheology, PMAA, PEO, Viscoelasticity, Hydrophobicity

Mucus, a complex biological hydrogel, which consists of Mucus glycoproteins (mucins), lipids, ions, proteins, cells, cellular debris, and water as components [1], surrounds the surfaces of the human body, including the respiratory organs and digestive tract. It fulfills important functions, such as acting as a protective barrier against foreign bodies [2]. Apart from that, it is well known that this kind of slime forms a three-dimensional viscoelastic network structure which is stabilized by diverse molecular interactions for instance hydrogen bonding, hydrophobic and electrostatic interactions [3]. Our goal is to comprehend how the dynamic properties of native mucus are related to its mesoscopic structure. This project is related to the collaborative research centre (CRC) 1449 which is financed by the German Research Foundation and tends to investigate the protective functions of hydrogels at biological interfaces. For this purpose we try to mimic the viscoelastic properties of this biological hydrogel by synthesizing a non-toxic one which consists of poly(ethylene oxide) (PEO) as well as hydrophobically modified poly(methacrylic acid) (HM-PMAA). The modification of PMAA with C_{12} or C_{16} – side chains leads to hydrophobic interactions besides the already existing hydrogen bonds between PMAA and PEO, which forms a hydrogel after blending both polymers in a certain ratio and a certain pH-range. After the establishment of this model-system a non-ionic surfactant, Brij O10, was additionally added to strengthen the hydrophobic interactions and to understand the self-assemblance of the side chains acting as crosslinking points in the hydrogel network. Macrorheology is the key method for hydrogel characterization.

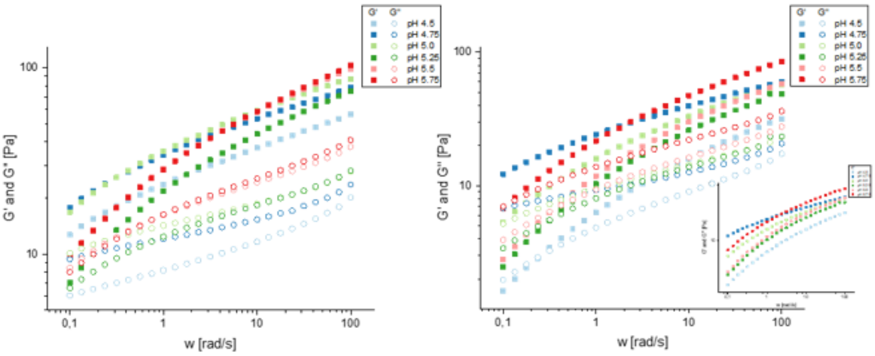

Figure 1. *Macrorheology data (G' and G") of the hydrogel which consists of HM-PMAA and PEO at various pH [left] and the same hydrogel in the presence of 2 mol% Brij O 10 [right]. PMAA was modified with 5mol% Hexadecylamine (C16).*

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The effect of pH on the formation of gold-polythiophene nanoparticles for hybrid electrochemical sensors

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Keywords: polythiophenes, gold sulfur bond, hybrid gold nanoparticles

A series of customisable and portable sensors have been developed since Clark and Lyons developed the first oxygen biosensor in 1962 [1]. Conventional fabrication of electronic biomedical sensors requires multi-step fabrication processes involving thermal sintering and the use of environmentally harmful chemicals to achieve sufficient electrical conductivity. [2] A novel approach that avoids multi-step fabrication involves the use of electrically conductive, sinter-free inks for direct printing. The nanoparticles' surface is modified with a conductive polymer to increase conductivity and enable direct attachment of specific sites.[3] We study how the formation and structure of this shell depends on the pH-dependant dispersion state and conformation of the conductive polymer.

We investigated the pH-dependent ligand exchange of cetyltrimethylammonium bromide (CTAB) on gold nanoparticles (AuNPs@CTAB) with a diameter of 74 nm by the conductive polythiophene poly(3-hexylthiophene-2,5-diyl) (P3KHT). The pH-dependent dispersibility of P3KHT in water that we find in Static Light Scattering (SLS) and UV-Vis (**Figure 1A**) implies improved dispersibility of the polymer at higher pH and coiling at lower pH. Ligand exchange at pH values between 8 and 12 led to hybrid nanoparticle dispersions that we characterized with Raman spectroscopy. **Figure 1B** shows that higher pH levels lead to relatively more pronounces Au-P3KHT bond fingerprint peaks and a decrease in Au-CTAB bonds. Both indicate a pH-dependant efficiency of the ligand exchange process.

The results show that the pH value during the ligand exchange with polymers can affect its efficiency and affect the functionality of the dispersions.

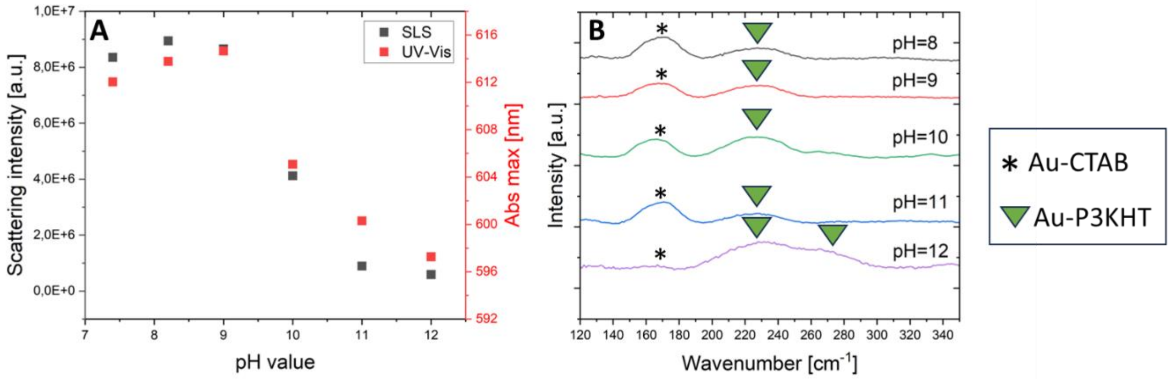

Figure 1. *(A) Static light scattering (150°) and UV-vis absorption maxima of aqueous P3KHT solutions as a function of pH. The change in dispersion state affects ligand exchange of AuNPs@CTAB as visible in (B) Raman spectra after treatment with P3KHT solutions at different pH.*

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AI-Aided Pattern Recognition as an Efficient Tool to Analyze Micrographs of Complex Nanoparticles

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Keywords: nanoparticle analysis, image processing, electron microscopy, artificial intelligence

Complex structures can be deconstructed into smaller, more elemental subunits, with their characterization involving an examination of both subunits and their spatial arrangement. These structures manifest across a wide array of systems, spanning from cells and living tissues to alloys, galaxies, and colloids. Particularly in the field of colloids, multi-lobed particles and particle-based materials stand out prominently. Despite the significance of micrograph analysis, its application to complex particles remains restricted. In this study, polymer model colloid particles undergo comprehensive morphological investigation. Herein, we present an endeavor showcasing the morphological characterization of subdivided particles using a generalist artificial intelligence model. Our approach employs pre-trained neural networks, specifically the Segment Anything algorithm, for automated segmentation between particle subdivisions. Subsequently, these subdivisions are organized into sets representing individual particles, marking a novel advancement in this field. This methodological innovation enhances the insights obtained from microscopy analysis by organizing subdivisions into sets to characterize complex nanoparticles. The efficacy of the proposed approach is validated through comparison with previously published results (Figure 1), showing its ability to avoid systemic errors and human biases. By applying this novel method, we ensure a more accurate and reliable characterization of model colloids, thereby advancing the frontier of nanoparticle analysis.

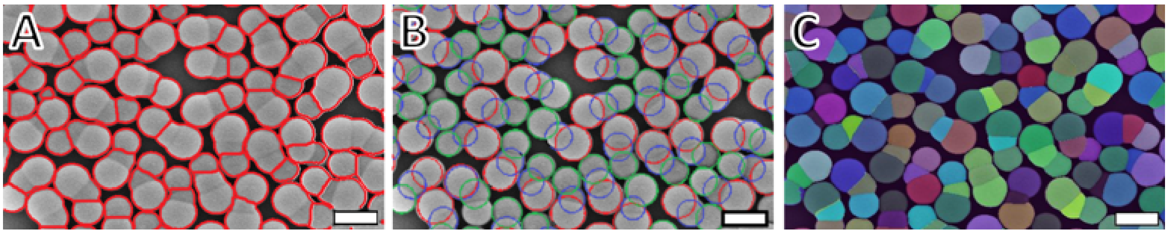

Figure 1. *Image segmentation between the lobes of trimer nanoparticles using the (A) Euclidean-based* watershed *algorithm, (B) manual fitting of ellipses, and (C) the Segment Anything Model (SAM). SAM was shown to provide accurate data with respect to the morphology of multi-lobed particles. The scale bars represent 250 nm.*

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Light-Driven Charge Regulation at Oil/Water Interfaces in Nanoemulsions

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Keywords: Nanoemulsions, Responsive Interfaces, Second-Harmonic Scattering

Emulsions are indispensable in everyday life and industrial applications, and the demand for emulsions' diversity and control of properties is therefore substantial. As emulsions possess a high internal surface area, understanding of oil/water (o/w) interfaces on the molecular level is fundamental, but is often impaired by experimental limitations on the probing of internal o/w interfaces in emulsions in situ.

In order to study and to tune o/w interfaces in nanoemulsions we utilize photoswitchable surfactants and a multi-length scale and multi-method approach. We therefore investigated the adsorption of an arylazopyrazole sulfonate (AAP) surfactant, which can be photoisomerized between *E* and *Z* isomers by visible and UV light irradiation.[1] The configurational changes cause massive changes in the interface tension at the extended o/w interface and a drastic shift in the surfactants' critical micelle concentration, which we have applied to control both the stability and phase separation in macroemulsions through UV irradiation.

Different from macroemulsions, nanoemulsions with a hydrodynamic radius of 90 nm were not susceptible to *E*/*Z* photoisomerization in terms of changes in the droplet size or the ζ-potential. However, in situ second-harmonic scattering experiments show dramatic and reversible changes in SHS intensity driven by *E*/*Z* isomerization, which is directly linked to surface potential at the nanoscopic interfaces.

The apparent differences in ζ-potentials and surface excess provide evidence for a fixed charge to particle size ratio and the need for counter ion condensation to renormalize the particle charge to a critical charge, which is markedly different compared to the behavior of very large particles in macroemulsions.[2] Our results indicate that we not only can control the surface coverage of the light-responsive AAP at extended and nanoscopic o/w interfaces but also the degree of counter ion condensation within the same system without further additives and exclusively by light irradiation.

Thus, our findings may have broader implications as the electrostatic stabilization of nanoparticles require much lower surfactant concentrations, allowing for a more sustainable use of surfactants.

Acknowledgements: We gratefully acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for our projects with Collaborative Research Center CRC 1459 Intelligent Matter (Project-ID 433682494) as well as for funding the DFG project ID 409537869.

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Numerical insights in the uptake behavior of cationic oligopeptides in pH-responsive anionic polyelectrolyte microgels

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Keywords: pH-responsive microgels, oligopeptides, polyelectrolytes, drug delivery, simulations

Microgels exhibit tunable uptake and release of guest molecules under external stimuli, particularly pH variations, rendering them promising candidates for drug delivery systems. However, predicting the electrostatically driven uptake of pH-responsive microgels and guest molecules poses challenges due to the dependence on multiple parameters. This study employs Metropolis Monte Carlo simulations to systematically investigate the uptake of weak cationic oligomers, mimicking oligopeptides, into weak anionic polyelectrolyte microgels.

By varying parameters such as monomer p*K* values, microgel and guest molecule concentrations, and oligomer chain lengths, we elucidate the complex interplay governing uptake phenomena. Our findings reveal that polyelectrolyte networks efficiently uptake oligomers when both species are charged, leading to mutual enhancement of their ionization and subsequent complex formation. Longer oligomers intensify network ionization and complexation, while higher microgel concentrations enhance uptake near the isoelectric point but hinder it at higher pH due to decreased entropy gain from counterion release. These insights advance our understanding of cationic oligomer uptake into oppositely charged polyelectrolyte microgels and offer design guidelines for anionic microgels as carriers, particularly for molecules such as antimicrobial peptides.

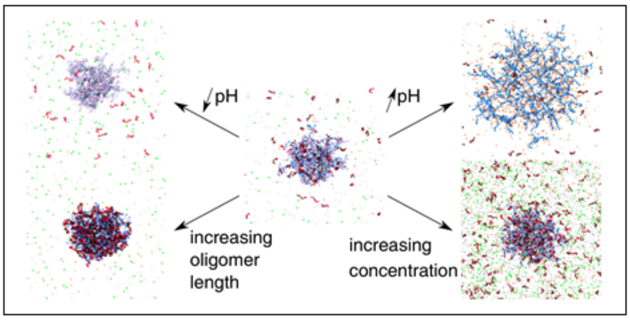

Figure 1. Snapshots reveal the impact of pH variation, oligomer length, and concentration on microgel/oligomer systems.

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Plasmonic core-shell microgels: The role of the core size

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Keywords: core-shell microgels, *in situ* core overgrowth, small-angle scattering, form factor analysis

Hybrid colloids that combine polymers and plasmonic nanoparticles, e.g. gold and silver, gained increasing interest over the last years.[1] Gold-poly-*N*-isopropylacrylamide (Au-PNIPAM) core-shell microgels were used for periodic coatings due to the localized surface plasmon resonance (LSPR) of the cores leading to surface lattice resonance (SLR).[2] The position of the resonance strongly depends on the size of the cores.[3] Compared to other core-shell microgels, Au cores can be precisely overgrown in the shell *in situ*.[2] Although the cores grow in size, the overall hydrodynamic diameter of the microgels does not change. It is not known how the structure of the shell changes during the overgrowth.

Here, we are analyzing Au-PNIPAM microgels with two crosslinker densities of 8 mol% and 16.5 mol%. The cores are overgrown from 14 nm in diameter to 100 nm (see Figure 1a, 1b). We perform dynamic and static light scattering (DLS/SLS) and small-angle X-ray and neutron scattering (SAXS/SANS) to study the respective form factors (Figure 1c, 1d). SAXS provides information about the gold cores, LS about the shell and the cores and SANS about the shell. We investigate the changes at different temperatures around the volume phase transition of the PNIPAM shell. Thus, we can compare swollen and collapsed state of each microgel batch. Additionally, extinction spectra are recorded to study the optical properties. We also perform Monte Carlo simulations of the different microgels to get information on the internal structure of the shell and the polymer distribution.

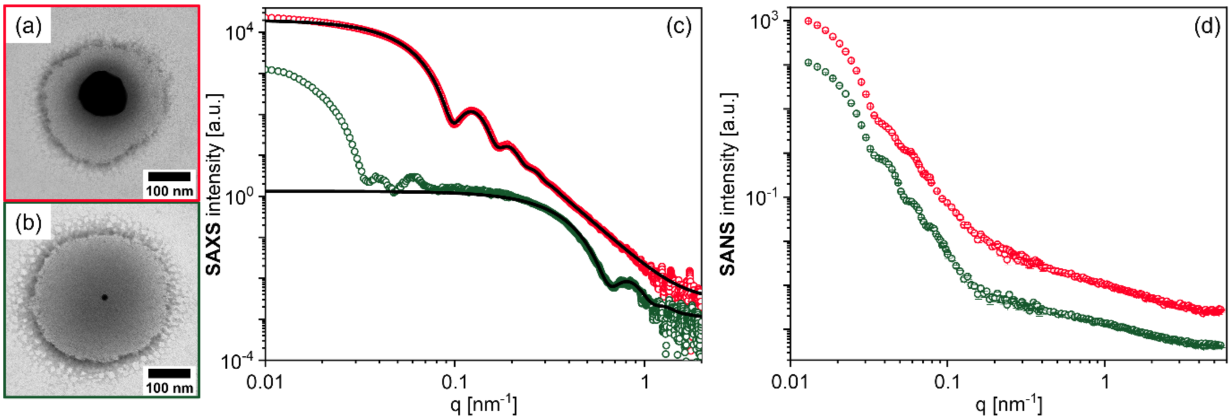

Figure 1. *TEM images of Au-PNIPAM microgels with core sizes of 100 nm (a) and 14 nm (b) in diameter. Corresponding SAXS (c) and SANS (d) curves of the Au-PNIPAM microgels. Fits are shown in black.*

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NIPMAMol: a high VPTT Microgel

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Keywords: Microgels, Acrylamides, high VPTT

Microgels are spherical, soft, colloidal particles comprising a cross-linked polymer network internally. Their size ranges from 100 nanometers to some micrometers. So-called smart microgels do undergo a change of conformation due to external stimuli such as pH and temperature. Due to their smart behavior, microgels are promising candidates for e.g. drug delivery or switchable filtration membranes. The LCST of a monomer can be tuned by the hydrophilicity of the end group.[1]

Fuel cells are a critical part of the transformation of the energy sector and an integral part of e.g. the German hydrogen strategy. Low-temperature fuel cells operate around 80-90°C and a key component is the membrane for the charge separation. If such membrane is self-regulating the safety of fuel cells could be further improved.

This work aims to utilize an alternative acrylamide monomer with a high LCST. To do that a terminal alcohol group is introduced to NIPMAM. The monomer N-(1-Hydroxy-2-propyl)methacrylamide is called NIPMAMol. Copolymer microgels with the conventional acrylamides NNPAM, NIPAM and NIPMAM are synthesized via radical precipitation polymerization to demonstrate the tunability of the VPTT. The microgels are characterized by photon correlation spectroscopy (PCS) and turbidity measurements. The VPTT of pNIPMAMol is extrapolated from a series of copolymer systems with a systematic variation of the copolymer ratio.

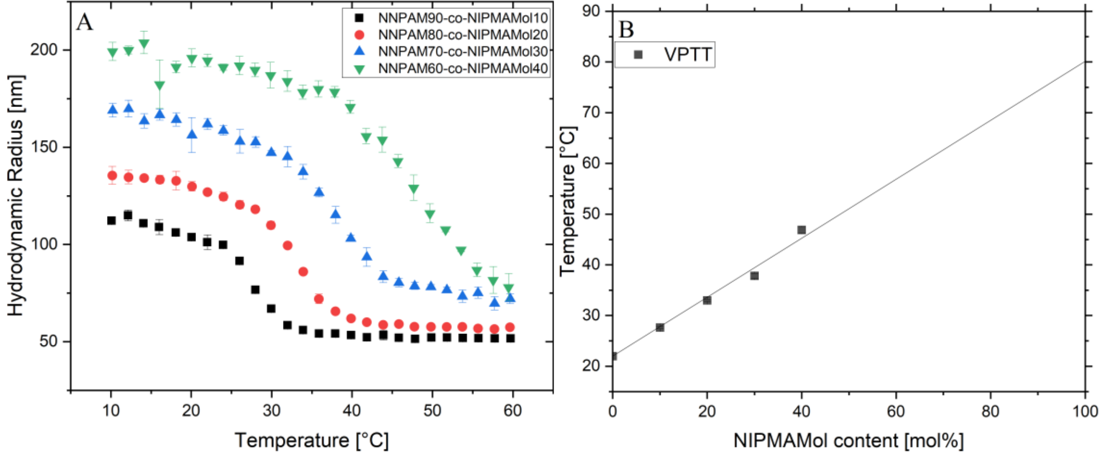

Figure 1. *A) Swelling curves of microgels with a systematic variation of the NNPAM and NIPMAMol ratio are shown. The size of the microgels in the swollen state and the VPTT of the systems increases with increasing NIPMAMol content. B) The obtained VPTTs of the microgel systems are extrapolated linearly to obtain a VPTT for pNIPMAMol.*

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Phase behavior of dipolar microgels from plastic crystals to “spin glasses”

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Keywords: composite microgels, magnetic nanoparticles, dense colloidal dispersions

Microgels display complex phase behavior and dynamics, which are heavily influenced by their chemical composition and inherent softness [1]. The degree of softness determines their ability to deform, interpenetrate, and contract at high-volume fractions. The phase behavior of microgels becomes increasingly intricate when considering anisotropic colloids, owing to the presence of directional dependencies in their interactions and dynamics. Employing magnetic core-shell microgels as a model system allows to study the phase diagrams of soft colloids.

In this study, we utilized core-shell microgels with a magnetic core comprising an anisotropic silica-coated maghemite nanoparticle and a crosslinked polymer network shell made of poly(isopropyl acrylamide). Under an external magnetic field, these microgels align with their long axis to the field, analogous to compasses. Used as colloidal analogs of “spins,” we investigated their phase behavior spanning the formation of plastic crystals in the presence of long-range electrostatic repulsion under deionized conditions to the formation of “spin glasses” above the colloidal glass transition at higher concentrations. Composite microgels featuring anisotropic cores offer several advantages. The orientation of the core can be monitored, serving as a valuable indicator of whether the system is jammed. Additionally, this system can be analyzed using cross-polarized microscopy, as the core can polarize light. This allows for a low-effort analysis of the dynamics of concentrated microgel dispersions and the jamming point. As microgel concentration increases, the magnetic nanoparticles exhibit decreased orientation under the influence of an external magnetic field due to their jamming within the microgel matrix. By analyzing the jamming behavior in relation to microgel concentration, we can gain valuable insights into these complex systems and evaluate the use of these microgels as tracers for less-scattering systems, such as ultra-low crosslinked microgels.

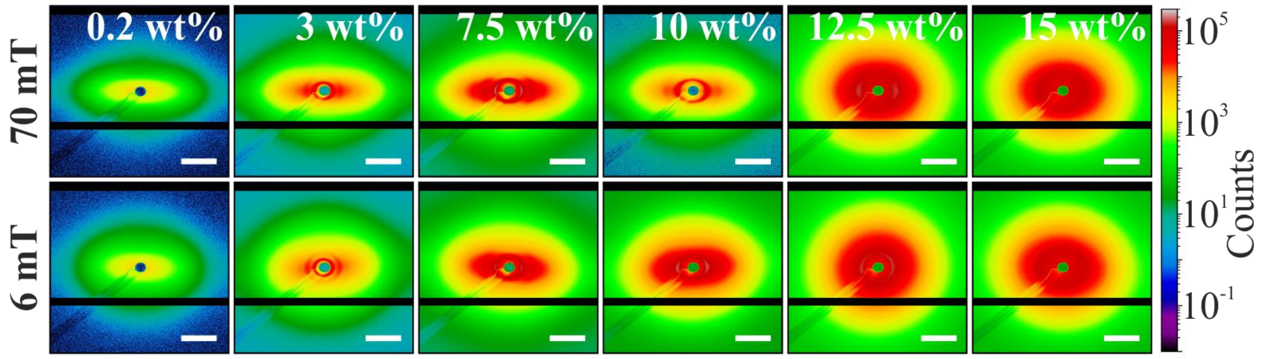

Figure 1. *SAXS patterns of concentrated microgel dispersions (0.2 – 15wt%) under static magnetic fields (6 - 70mT). Scale bars: 5.4 · 10^{-4} nm^{-1}.*

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