Leibniz-Institut
für Polymerforschung
Dresden e. V.

TECHNISCHE
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15TH DRESDEN POLYMER DISCUSSION

Meißen, Germany, April 17 to 20, 2016

Polymer Materials in the Transition from Responsiveness to Interactivity and Adaptivity

BOOK OF ABSTRACTS

The 15th Dresden Polymer Discussion is supported by

DFG Deutsche Forschungsgemeinschaft

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PREFACE

Responsiveness towards environmental stimuli is a classical feature of polymeric materials. However in many cases, not just passive responsiveness, but rather interaction with the environment often resulting in complex adaptation of materials properties is desired. Natural systems show many examples of these features, such as bone remodeling upon load, healing and regeneration processes or chemotaxis. Modern polymer science starts to provide the tools necessary to translate principles of adaptivity and interactivity to artificial systems, thus providing new options for controlling interactions with biosystems, but as well giving access to the next generation of smart materials, which have no biological blueprints, but only share generic concepts. In this conference, we focus the role of synthetic polymer and polymer composite systems in this development.

TOPICS

- Synthesis and assembly of interactive coatings
- Healing and regeneration in biomimetic and artificial systems
- Polymeric building blocks
- Composite materials
- Use of responsiveness for actuation and sensing
- Experimental methods for studying dynamics of structure/property changes on multiple length scales
- Multi-scale modelling of self-healing and adaptive systems

GENERAL INFORMATION

VENUE AND REGISTRATION/CONFERENCE OFFICE

Evangelische Akademie Meißen
Freiheit 16, 01662 Meißen
Phone: +49 (0) 3521 47060

The conference office is located in the foyer of the main entrance.
Phone of the conference office: 0160/97216924

The lecture hall is called “Propsteisaal” (2nd floor).

Opening hours:

Sun, April 17, 2016:	from 17:00 to 22:00
Mon, April 18 to Wed, April 20, 2016:	from 8:30 throughout all sessions

COFFEE AND LUNCH BREAKS

Drinks and snacks during the breaks will be available at buffets close to the lecture hall (2nd floor) and the poster displays in the room “Katharina” (1st floor). Lunch is served at the dining hall “Tonne” in the ground floor (accessible from the foyer of the main entrance).

INTERNET

WLAN/WiFi access is provided for the participants during the meeting and is free of charge. It is available in the lecture hall “Propsteisaal” and in the cafeteria.
Access data can be obtained in the conference office with one ticket for all conference days.

PRESENTATIONS

UPLOAD OF PRESENTATIONS

Please contact one of our student helpers in the lecture hall to upload your presentation in the break before your presentation at the latest.

POSTERS

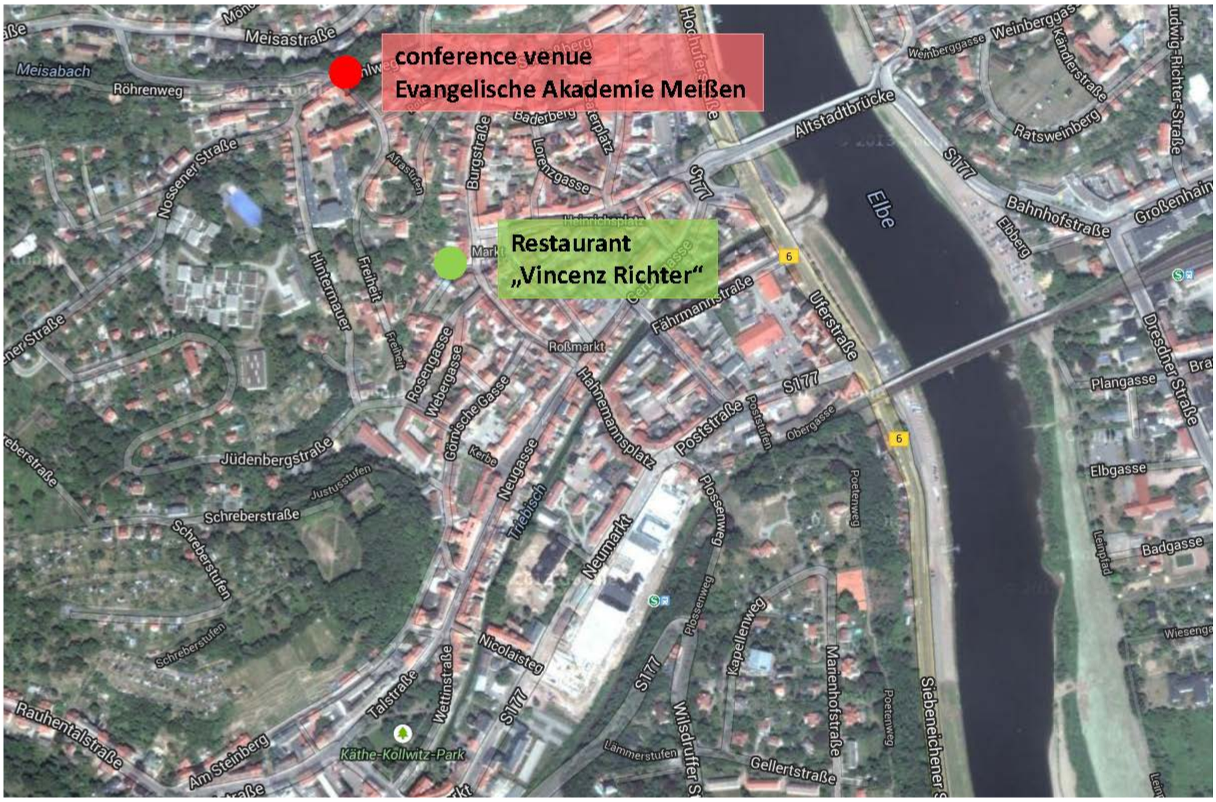
Posters should be mounted by the end of the lunch break on Monday and will be up during the entire duration of the meeting.

SOCIAL EVENTS

SIGHTSEEING AND CONFERENCE DINNER

Tuesday, April 19, 2016, 17:15 to 18:45 Sightseeing in Meissen
After enjoying the sightseeing we get up to the historic restaurant "Vincenz Richter" which is located at the market square of Meißen – You may expect dinner in an informal and relaxing atmosphere in one of the oldest houses in the historic centre.

No special dressing code. Registration is required (no extra charge for active participants, EUR 55 for accompanying persons).



conference venue
Evangelische Akademie Meißen

Restaurant
„Vincenz Richter“

Program

Sunday, April 17

17:00	Arrival Start of registration	
19:30	*Supper/Get-together*	
	Discussions	

Monday, April 18

8:15	*Breakfast*	
9:00	Opening	
9:15	**Christopher Barner-Kowollik** Karlsruhe, Germany	Photochemical macromolecular material design
9:45	**Volkmar Stenzel** Bremen, Germany	Self-repairing surfaces via supramolecular interactions - a realistic perspective?
10:15	*Break*	
10:45	**Andrij Pich** Aachen, Germany	Functional microgels as building blocks for interactive materials
11:15	**Sjoerd Postma** Nijmegen, The Netherlands	Enzymatic reaction networks controlling metamorphosis and mechanical properties of hydrogels
11:45	**Lukas Arens** Karlsruhe, Germany	Desalination of salt water via polyelectrolyte hydrogels and osmotic motors
12:15	*Lunch*	
13:15	**Sergiy Minko** Athens, USA	Remote control of soft stimuli-responsive materials
13:45	**Igor Luzinov** Clemson, USA	Operational nanoscale polymer layers
14:15	**Marcus Müller** Göttingen, Germany	Structure formation in multicomponent polymer systems: A computer simulation study
14:45	*Break*	
15:15	**Oleg Borisov** Pau, France	Responsive brushes: The impact of polymer architecture
15:45	**Karsten Hinrichs** Berlin, Germany	Correlation of IR spectra with thin-film structure at solid water interfaces
16:15	**Alexander Revzin** Davis, USA	Microsystems for cultivation and analysis of cells
16:45	**Martina Stenzel** Sydney, Australia	Design of functional micelles for enhanced cellular uptake and their movement in cancer spheroids
17:15	*Break*	
17:30	Poster Discussion	
18:30	*Supper*	

15th Dresden Polymer Discussion

last update: April 7, 2016

Tuesday, April 19

8:15	*Breakfast*	
09:00	**Peter Fratzl** Potsdam, Germany	Structure and mechanical response of natural interactive and adaptive materials
09:30	**Jörg Lahann** Ann Arbor, USA	Stimuli-responsive polymer materials enabled by compartmentalization
10:00	**Aranzazu del Campo** Saarbrücken, Germany	Light-tuning morphology and composition in biomaterias and the consequences for embedded cells
10:30	*Break*	
11:00	**Leonid Ionov** Athens, USA	Programmable materials from shape-changing polymers
11:30	**Rudolf Zentel** Mainz, Germany	LC-elastomers as responsive and interactive materials
12:00	**Marlen Kamperman** Wageningen, The Netherlands	Silk-inspired protein polymers
12:30	*Lunch*	
13:30	**Martin Möller** Aachen, Germany	Self-assembled silica hybrid materials - Water based chemical transformation for hierarchical structure formation from silicasomes to bicontinuous membranes
14:00	**Molly Stevens** London, UK	New polymer based approaches for biosensing and regenerative medicine
14:30	**Georg Oenbrink** Essen, Germany	Polymeric drug release systems
15:00	*Break*	
15:30	**Edmondo Benetti** Zürich, Switzerland	Designed polymer assemblies at interfaces: Imitation of nature and synthetic improvisation
16:00	**Stefan Schmidt** Düsseldorf, Germany	Probing specific surface interactions of ligand functionalized hydrogels
17:15	*Sightseeing walk*	
19:00	*Dinner*	*Historical Restaurant Vincenz Richter*

Wednesday, April 20

8:15	*Breakfast*	
09:00	**Elena Kramarenko** Moscow, Russia	Hysteresis of the viscoelastic properties and the normal force in magnetorheological elastomers
09:30	**Katja Loos** Groningen, The Netherlands	From metallic gyroid structures to piezoelectric nanoporous networks
10:00	**Joris Sprakel** Wageningen, The Netherlands	Mechanochromic chains as molecular force sensors
10:30	*Break*	
11:00	**Andreas Dahlin** Göteborg, Sweden	Macromolecular gates: Polymer brushes on nanopores
11:30	**Matthias Pauly** Strasbourg, France	Oriented self-assembled thin films of anisotropic nanoparticles for (chiral) plasmonics
12:00	Concluding remarks	
12:20	*Lunch*	

List of posters

nr.	*name*	*surname*	*title*	*affiliation*	*abstract title*
1	Appelhans	Dietmar	Dr.	IPF Dresden	Polymersomes as multifunctional and -responsive platform for biomedical applications
2	Bauer	Anna		IPF Dresden	Crosslinked and pH-responsive polymersomes: Functionalization and post-modification by host-guest-interactions
3	Ye	Chunhong	Dr.	IPF Dresden	Programmed “micro-bubble” constructions within patterned silk film for encapsulation
4	Krause	Andreas		IPF Dresden	Swelling characteristics of bisensitive hydrogels for microfluidics
5	Bludau	Herdis		TU Dresden	Investigation of poxylated tobacco mosaic virus based drug delivery systems for cancer therapy
6	Holz	Lisa		TU Dresden	Side selective conjugation of folic acid with poly(2-oxazoline)s for active targeting drug delivery systems
7	Jordan	Rainer	Prof.	TU Dresden	Poly(2-oxazoline) based nanoformulation of paclitaxel with superior safety and efficacy in vivo
8	Müller	Martin	Dr.	IPF Dresden	Cell responsive adhesive drug loaded coatings of polyelectrolyte complex nanoparticles for bone healing
9	Rüb	Jannick		TU Dresden	Tailored and biodegradable poly(2-oxazoline) microbeads as 3D matrices for stem cell culture
10	Rühs	Patrick		ETH Zurich	Adaptive bio-inspired composites with tailored microcapsules
11	Schubel	René		TU Dresden	Chemical doping and functionalization of SWNTs
12	Rosenthal	Alice		IPF Dresden	Biofunctionalization of polymer brushes using click chemistry
13	Marschelke	Claudia		IPF Dresden	Stimuli-responsive hairy particles for enzymatic reactions in bulk and at interfaces
14	Synytska	Alla	Dr.	IPF Dresden	Hybrid hairy Janus particles as novel building blocks for active surfaces and interfaces
15	Kirillova	Alina		IPF Dresden	Hybrid hairy Janus particles: Controlled design and assembly
16	Müller	Madeleine		IPF Dresden	Anti-icing and de-icing surfaces based on core-shell particles as building blocks
17	Münch	Alexander	Dr.	IPF Dresden	Polymer brushes on thin celulose layers with non-fouling properties
18	Che	Yunjiao		TU Dresden	Waterborne SI-CuCRP: Decablock monopolymer brushes
19	Du	Yunhao		TU Dresden	Polymer bottle brush brushes (BBBS) and gradients by surface initiated CU(0) mediated controlled radical polymerization (SI-CUCRP)
20	Förster	Paul		TU Dresden	Poly(3-hexythiophene) brushes on graphene
21	Gieseler	Dan		TU Dresden	Molecular brushes of poly(2-oxazoline)s via controlled radical polymerization and grafting through
22	Nawroth	Jonas		TU Dresden	Nanopatterned polymer brushes by reactive writing and positioning of DNA origami on stimuli-responsive surface features
23	Hafner	Daniel		TU Dresden	Bioinspired polymer carpets
24	Keßler	Christian	Prof.	TU Dresden	Magnetic functionalization of poly(N-isopropylacryl-amide) hydrogels for sensor applications
25	Rohn	Mathias		TU Dresden	Defined photo crosslinked tetra-PEG networks

26	Zhang	Tao		TU Dresden	Lights on! A significant photoenhancement effect on ATRP by ambient laboratory light
27	Newland	Bend	Dr.	IPF Dresden	Synthesis of polymer nanotubes via photopolymerization of crosslinking units
28	Höhne	Susanne	Dr.	IPF Dresden	GMA-Blockcopolymers for covalent linkage to hybrid surfaces obtained by twin polymerization
29	Boye	Susanne	Dr.	IPF Dresden	In-situ characterization of stimuli-responsive polymeric vesicles by AF4
30	Brandt	Josef		IPF Dresden	Temperature dependent size exclusion chromatography
31	Lesnichii	Vasilii		University of Freiburg	The bifurcation of dye diffusion coefficient in bulk polymer film below glass transition
32	Guskova	Olga	Dr.	IPF Dresden	Hydrogen-bonded supramolecular bis-urea-based polymers on solid support: Computational insights into
33	Romeis	Dirk	Dr.	IPF Dresden	Microstructure versus shape effect in magneto-sensitive elastomers
34	Ivaneiko	Dmytro		IPF Dresden	Dynamic moduli of magneto-sensitive elastomers
35	Neubauer	Jens		IPF Dresden	Visualization of contact stress distributions from mechano-responsive polyelectrolyte brushes
36	Goncalves-Schmidt	Diana		IPF Dresden	Selective Glioblsatoma multiforme-cancer stem cell targeting by gold nanorods in MMP-cleavable 3D hydrogels
37	Suckow	Marcus		IPF Dresden	Self-healing concepts for Bromobutylrubber – Supramolecular bond formation by ionic interactions and hydrogen bonds
38	Seuß	Maximilian		IPF Dresden	Switchable elasticity of novel core-shell microgels with constant adhesion properties - A micro-mechanical study
39	Tsurkan	Mikhail	Dr.	IPF Dresden	Two photon synthesis of biohybride hydrogels
40	Hahn	Dominik		IPF Dresden	Cell-instructive biohybrid hydrogels with adaptable physicochemical properties
41	Kuttner	Christian	Dr.	IPF Dresden	Self-assembled plasmonic core/satellite nanoclusters
42	Mehner	Philipp		TU Dresden	Modeling of a concentration-triggered micro-valve
43	Braun	Hans Georg	Dr.	IPF Dresden	Magnetoresponsive bioreactors from self assembled oligopeptide
44	Sievers	Jana		IPF Dresden	Thermoresponsive biohybrid interpenetrating polymer networks based on poly(N-isopropylacrylamide)
45	Maitz	Manfred	Dr.	IPF Dresden	Improvement of a feedback controlled anticoagulant release system by different release-triggers

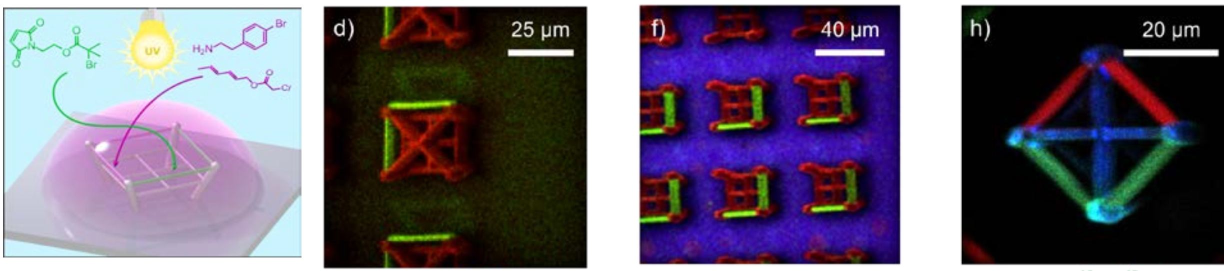
Abstracts of the lectures

L1

PHOTOCHEMICAL MACROMOLECULAR MATERIAL DESIGN

Ch. Barner-Kowollik[1,2,3]
[1] *Karlsruhe Institute of Technology (KIT), Institut für Technische Chemie und Polymerchemie, Preparative Macromolecular Chemistry, Engesserstr. 18, 76128 Karlsruhe, Germany*
[2] *Karlsruhe Institute of Technology (KIT), Institut für Biologische Grenzflächen, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[3] *Queensland University of Technology (QUT), Physics and Mechanical Engineering, School of Chemistry, Brisbane, QLD 4000, Australia*

Installing chemical functionality at precise locations within complex macromolecules as well as onto three dimensional direct laser written constructs in the mildest possible fashion (visible light) and without any catalyst becomes possible with powerful light driven, quantitative ligation protocols.[1-6] Advanced light induced processes enable the parallel encoding of multiple molecules onto predefined locations on surfaces[7] as well as the wavelength dependent addressing of specific parts of a macromolecule for its highly orthogonal functionalization (λ-orthogonal photochemistry).[8] In addition to exploring the above technologies, the lecture will highlight how polymer functionalization can be directed in its selectivity with light by exploiting light controlled reaction manifolds[9] as well as explore if diffraction unlimited laser lithography is possible based on photo-click chemistry concepts.[10]



Sum of $^{35}Cl^-$, $^{37}Cl^-$, PEG fragments and SiO_2

Sum of $^{79}Br^-$, $^{81}Br^-$, PEG fragments and SiO_2

Sum of $^{35}Cl^-$, $^{37}Cl^-$, $^{79}Br^-$, $^{81}Br^-$ and PEG fragments

Figure 1: Encoding three dimensional direct laser written scaffolds in specific pre-defined positions with chemical functionality via a self-directed light induced molecular sorting process.[7] The site-specific functionalization is evidenced via high resolution ToF-SIMS.

[1] G. Delaittre, A. S. Goldmann, J. O. Mueller, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2015) *54*, 11388–11403.
[2] J. O. Mueller, F. G. Schmidt, J. P. Blinco, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2015) *54*, 10284–10288.
[3] O. Altintas, M. Glassner, C. Rodriguez-Emmenegger, A. Welle, V. Trouillet, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2015) *54*, 5777–5783.
[4] T. Pauloehrl, A. Welle, M. Bruns, K. Linkert, H. G. Börner, M. Bastmeyer, G. Delaittre, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2013) *52*, 9714–9718.
[5] E. Frick, A. Anastasaki, D. M. Haddleton, C. Barner-Kowollik: *J. Am. Chem. Soc*. (2015) *137*, 6889–6896.
[6] T. Pauloehrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H. G. Börner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2012) *51*, 1071–1074.
[7] T. K. Claus, B. Richter, V. Hahn, A. Welle, S. Kayser, M. Wegener, M. Bastmeyer, G. Delaittre, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2016) DOI: 10.1002/anie.201509937.
[8] K. Hiltebrandt, T. Pauloehrl, J. P. Blinco, K. Linkert, H. G. Börner, C. Barner-Kowollik: *Angew. Chem. Int. Ed.* (2015), *54*, 2838–2843.
[9] K. Hiltebrandt, K. Elies, J. Blinco, C. Barner-Kowollik: (2016) submitted.
[10] P. Müller, C. Barner-Kowollik, M. Wegener: (2016) unpublished results.

L2

SELF-REPAIRING SURFACES VIA SUPRAMOLECULAR INTERACTIONS – A REALISTIC PERSPECTIVE?

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Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Wiener Straße 12,
28359 Bremen, Germany

Self-healing polymers offer the ability to heal damages automatically with an external stimulus (heat, pressure or UV-irradiation) or autonomously. As a consequence cracks of microscopic scale in materials that are caused by mechanical stress and/ or thermal fatigue which can lead to material failures and indispensability can be self-healed to maintain and prolong the lifetime of the material.

Inspired by nature a huge number of self-healing concepts were proposed in recent years.[1] The self-healing concepts can be divided into two categories: (i) extrinsic, which offers self-healing through an separated (e.g. microencapsulated) self-healing agent and (ii) intrinsic, which can realize self-repair by a special molecular architecture with reversible covalent or non-covalent bonds. The latter concept describes a supramolecular polymeric system that interacts through weak physical bonds like hydrogen bonds. Those molecules are able to build supramolecular networks and show polymer-like similarities in rheological and mechanical properties.[2,3,4,5] After cracks occur the supramolecular polymeric network is able to self-heal through the formation of reversible breaking and reforming of non-covalent bonds. Figure 1 shows for instance the self-healing of cracks in a hard epoxy clearcoat on a steel plate. The cracks were prepared by Erichsen cupping.

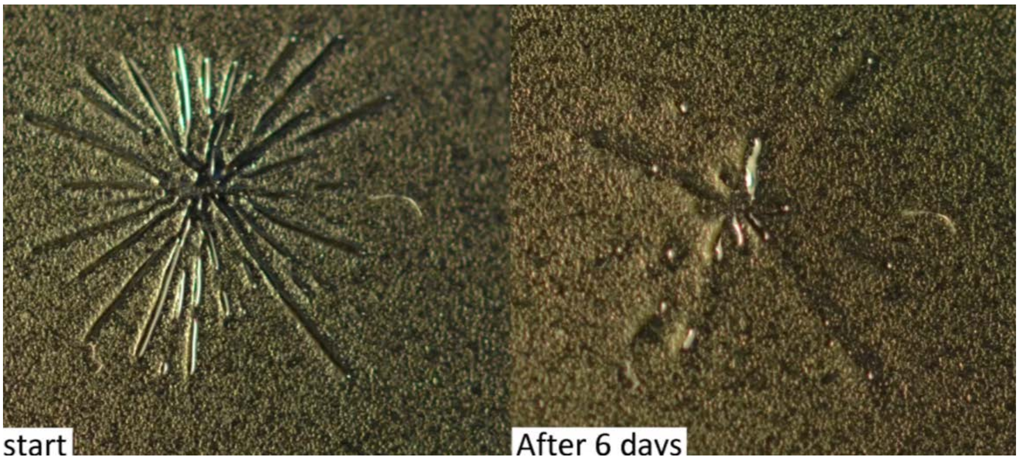

Figure 1: Self-healing of cracks in epoxy-coating (Picture: IFAM)

The intrinsic self-healing mechanism via weak hydrogen bonds is a delicate procedure which is influenced by external factors like temperature, humidity and others. These influences define the possible parameter-window for technical applications of such coatings.

[1] S. van der Zwaag: Self Healing Materials. Netherlands: Springer (2007).
[2] L. Bouteiller: Advances in Polymer Science 207 (2007) p. 79–112.
[3] J. M. Lehn: Polymer International 51 (2002) p. 825–839.
[4] M. Weck: Polymer International 56 (2007) p. 453–460.
[5] L. S. Shimizu: Polymer International 56 (2007) p. 444–452.

L3

FUNCTIONAL MICROGELS AS BUILDING BLOCKS FOR INTERACTIVE MATERIALS

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[1] *Leibniz Institute for Interactive Materials e. V., 52056 Aachen, Germany*
[2] *RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, 52056 Aachen, Germany*

Aqueous microgels are crosslinked finite macromolecular networks swollen in water. Due to their unique architecture microgels exhibit extraordinary properties like softness, reversible deformability, surface activity, and stimuli-responsiveness. Microgels can display sensitivity to temperature, pH, light, ionic strength etc. and adapt to the environment by changing their size and shape. In addition, synthesis of aqueous microgels can be performed in controlled way to tune particle size and size distribution, chemical functionality, surface charge, swelling degree, and colloidal stability. Therefore microgels can be used as building blocks for the design of interactive materials of different dimensions and complexity.[1]

One of the important attributes of microgels are crosslinks that are responsible for the regulation of swelling degree, control of diffusion processes inside microgels and adjustment of mechanical properties.[2] Along with permanent crosslinks cleavable (non-reversible) or dynamic (reversible) crosslinks can be integrated into microgels leading to new properties and functions.[3]

Present paper will consider synthesis, characterization and application of microgels containing permanent and dynamic ionic crosslinks formed by zwitterionic side groups. We used different synthesis methods (precipitation polymerization, polymerization in W/O emulsions) that allow application of different reactive building blocks and control the amount and distribution of zwitterionic groups in microgels.[4] Microgels were synthesized by copolymerization of *N*-vinyllactams with (methacryloyloxy)ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide in presence of a crosslinking agent (bisacrylamide) in water-in-oil emulsions. Monodisperse colloidally stable microgels with a high amount (> 30 mol-%) of zwitterionic groups were synthesized. High contents of zwitterionic groups in microgels led to the formation of dynamic reversible ionic crosslinks along with permanent covalent crosslinks generated by bisacrylamide. Obtained microgels exhibit interesting temperature-triggered swelling/deswelling behavior in aqueous solution. With increase of the temperature above 10°C microgels swell due to the destruction of the ionic crosslinks. Above lower critical solution temperature of poly(*N*-vinyllactam) chains at $T>32$ °C microgels shrink due to the destruction of the hydrogen bonds and enhanced hydrophobic interactions. The variation of zwitterionic groups and crosslinker concentrations influenced the extent of swelling/ deswelling at different temperatures. New doubly thermo-responsive microgels were synthesized using three homologues: *N*-vinylcaprolactam (VCL), *N*-vinylpiperidine (VPi) and *N*-vinylpyrrolidone (VPy). It was shown that the temperature-triggered deswelling of microgels is strongly dependent on the size of the lactam ring.

The behavior of zwitterionic microgels in aqueous solutions was investigated to understand their properties like swelling/deswelling, charge modulation and colloidal stability. Zwitterionic microgels are interesting colloidal templates for the biomineralisation and controlled growth of the $CaCO_3$ nanocrystals as well as building blocks for design of protein-repellent coatings.

[1] G. Agrawal, X. Zhu, M. Möller, A. Pich. Chem Mater. (2014); 26, 5882–5891.
[2] F. Schneider, A. Balaceanu, A. Feoktystov, V. Pipich, W. Pyckhout-Hintzen, A. Pich, G. J. Schneider, Langmuir (2014); 30(50), 15317–15326.
[3] G. Agrawal, B. Brüster, X. Zhu, M. Möller, A. Pich. Soft Matter (2013); 9(22), 5380–5390.
[4] A. Schmid, R. Schröder, T. Eckert, A. Radulescu, A. Pich, W. Richtering. Colloid Polymer Sci. (2015); 293, 3305–3318.

L4

ENZYMATIC REACTION NETWORKS CONTROLLING METAMORPHOSIS AND MECHANICAL PROPERTIES OF HYDROGELS

S. G. J. Postma[*], *I. N. Vialshin, W.T.S. Huck*
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The Netherlands

Nowadays, materials are often static and have only a single purpose. In contrast, a living cell is dynamic and adaptive because of its ability to sense and respond to changes in its environment. Inspired by these features of living systems, we designed a polyacrylamide hydrogel which responds in three different ways depending on the amount of enzyme applied. This property emerges from a dormant enzymatic reaction network in the hydrogel that is activated by the applied enzyme. The enzymatic reaction network can (1) inhibit the enzyme and does not change at all, (2) form new crosslinks faster than the initial ones are broken down, changing the gel at a molecular level while retaining its shape, (3) degrade the initial crosslinks faster than the new ones are formed, leading to a gel-sol-gel transition that ultimately changes the shape and molecular make-up of the hydrogel. Since the initial and newly formed crosslinks are completely independent, we achieve control over the mechanical properties of the system as well. For example, we can start with a soft gel, but end up with a much stiffer one.

We believe that this new approach to combine enzymatic reaction networks and hydrogels paves the way towards creating new materials with adaptive, life-like properties.

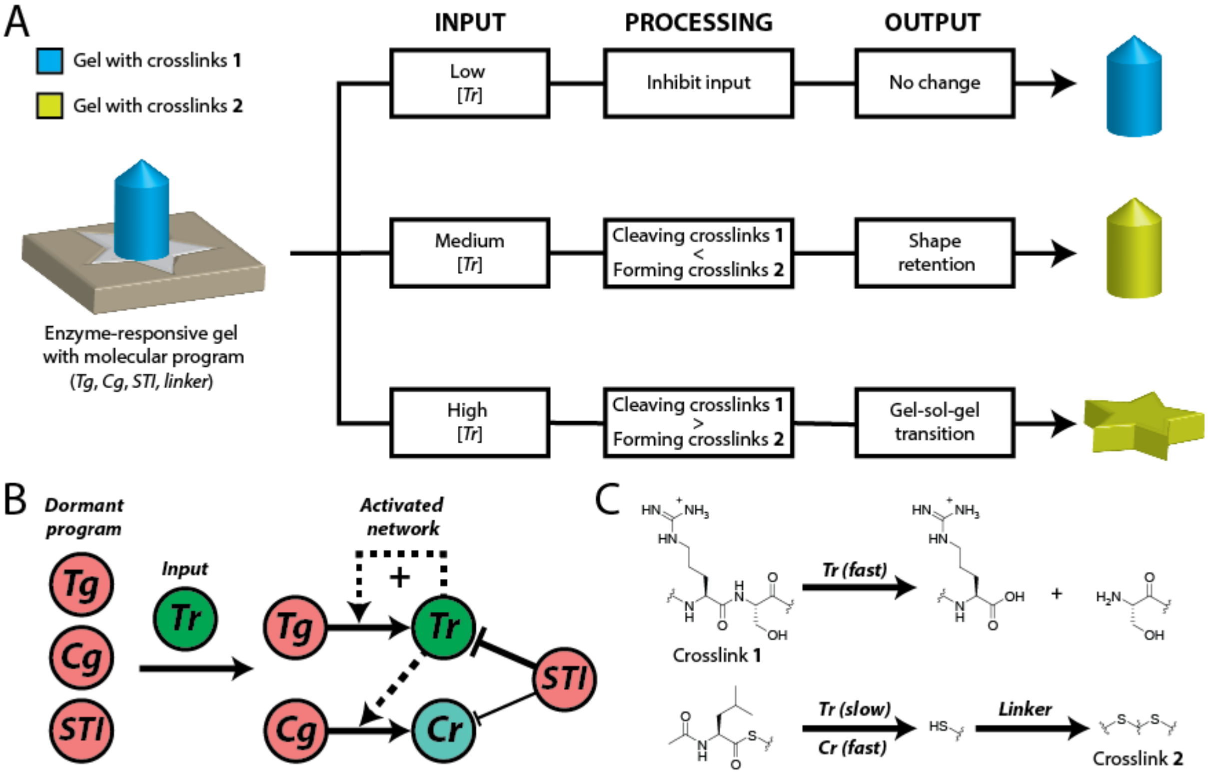

Figure 1: Dose-dependent metamorphosis of hydrogels a) Flow chart showing the three possible outputs depending on the amount of enzyme added (Tr = trypsin). b) The enzymatic reaction network controlling metamorphosis (Tg = trypsinogen, Cg = chymotrypsinogen, STI = Soybean Trypsin Inhibitor, Cr = chymotrypsin). c) The initial crosslinks **1** are degraded fast by the enzyme trypsin, while chymotrypsin quickly produces crosslink **2** (formation of crosslink **2** by trypsin occurs at a much slower rate).

L5

DESALINATION OF SALT WATER VIA POLYELECTROLYTE HYDROGELS AND OSMOTIC MOTORS

*J. Höpfner, L. Arens, K. Schlag, C. Pfeifer, M. Wilhelm**
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Engesserstr. 18/20, 76131 Karlsruhe, Germany

Charged hydrogels are a class of materials with a high affinity for water. On a microscopic scale, they are composed of cross-linked polyelectrolyte polymer chains that incorporate a large amount of water or aqueous solution. Due to the large water uptake of such networks, often 1000 times more than their own weight, the term "superabsorber" is used. Superabsorber have different applications, whereby the largest market is personal hygiene products (like diapers) with a production of more than 8 x 10^6 tons in 2011 worldwide.

We investigated and described a novel approach for water desalination using such charged hydrogels under externally applied mechanical forces. The desalination mechanism is based on the unequal distribution of an added salt between gel and surrounding solution phase. We synthesized acrylic acid-based hydrogels of various compositions and investigated their desalination properties with a specially designed experimental press setup that allowed us to control online the force exerted on the gel and to measure the water elution from the gel bed as well as the salt concentration of the eluate.[1,2,3]

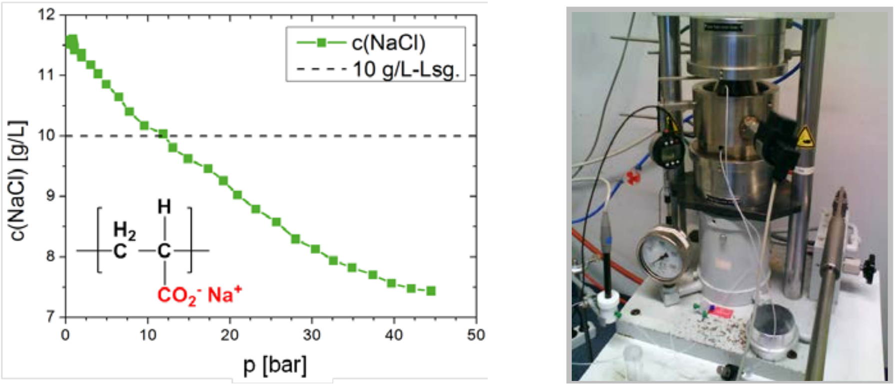

Figure 1: Effective desalination of a brine solution (10 g/L NaCl) by applying pressure on swollen hydrogel beads (left), self-constructed experimental setup to measure the desalination performance online (right).

Furthermore, we were looking at an inverse approach - using a salt gradient in water solution to obtain mechanical force: The electrostatic interaction of polymers in solution depends on the ionic strength, hence additional salt in the medium will reduce interactions between the polymer chains. By adding additional charges to the water, the electrostatic repulsion of the crosslinked polymer chains will decrease, resulting in a less swollen hydrogel. As a consequence of the screened electrostatic interaction and the rubber elasticity, a polymeric hydrogel and the concentration gradient between seawater and fresh water can be used to propel a mechanical motor.[4]

[1] J. Höpfner, C. Klein, M. Wilhelm: Macromol. Rapid Commun. (2010) 31, p. 1337–1342.
[2] J. Höpfner, T. Richter,P. Kosovan, C. Holm, M. Wilhelm: Prog. Coll. Poly. Sci. (2013) 140, p. 247–263.
[3] J. Höpfner, G. Guthausen, K. Saalwächter, M. Wilhelm: Macromolecules (2014) 47, p. 4251–4265.
[4] Video of the osmose motor in operation: http://www.itcp.kit.edu/wilhelm/osmosemotor.php.

L6

REMOTE CONTROL OF SOFT STIMULI-RESPONSIVE MATERIALS

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Recent achievements in the synthesis and study of stimuli-responsive particulates open avenues for the developments in the area of remotely controlled materials when electric and magnetic fields are used to trigger changes and responses in colloidal systems. This presentation is to discuss our recent research projects on remotely controlled materials.[1,2,3,4,5,6,7] Such materials promise plentiful applications, specifically at microscopic scale when a precise positioning of building blocks is substantially challenging due to thermal fluctuations. Homogeneous external fields provide energy sources that are sufficient to overcome thermal fluctuations and align building blocks in a broad range of dimensions from a few nanometers to micrometers. This area of field-directed assembly is receiving increasing attention owing to the possibilities for the generation of anisotropic structures at different length scales.

Not less diverse opportunities can be developed using non-uniform fields. In this case transport of particulates towards the greatest field gradient is used for generation of structures with complex architecture. Building blocks can be assembled into secondary structures which then are transported and assembled yielding hierarchically structured materials. Special attention is attracted by remotely controlled interfaces. Very intriguing opportunity to regulate remotely wetting/nonwetting, adhesive/non-adhesive, catalytic/inert transitions could stimulate a number of new applications and technologies.

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L7

OPERATIONAL NANOSCALE POLYMER LAYERS

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Controlled operation of nanoscale polymer layers/films is an important element of practical nanotechnology. To this end, deposition of ultrathin grafted polymer layer can provide a powerful synthetic route to designing the operational nanoscale layers/films with necessary performance. In our work, we demonstrated that grafting technique developed by us can be readily applied to surface modification of various objects leading to generation of hydrophobic, hydrophilic, switchable, mechanically/optically/magnetically active, and sensing materials.[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16]

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L8

STRUCTURE FORMATION IN MULTICOMPONENT POLYMER SYSTEMS: A COMPUTER SIMULATION STUDY

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Development and processing of functional materials is an important topic in micro- or nano-technologies. By virtue of their stability and versatility as surface coatings and their ability to change their conformation in response to external-stimuli, polymer brushes have found ample applications for designing of "functionalized" smart interfaces and surfaces.

The description of these systems by theory and computer simulation poses challenges:
(i) Can minimal models that only capture the relevant interactions like e.g., chain connectivity and pairwise interactions accurately describe the rich behaviour? How can one incorporate detailed characteristics of the different chemical constituents?
(ii) How to design simulation models that are able to describe the high degree of polymerization and the concomitant, large overlap between macromolecules that characterize experimental systems and that are important to accurately describe fluctuation effects.
(iii) How can computer simulation reach the protracted time scales of structure formation?
No single computational model can simultaneously address all three issues and different approaches will be discussed in the talk.

In the first part, we employ molecular dynamics simulation of a soft, coarse-grained model to study the temperature and pH-sensitive response of mixed brushes composed of poly(N isopropylacryl-amide) [PNIPAM] and poly(acrylic acid) [PAA] polymers. This description captures the interactions via an effective virial expansion of the equation of state. Additionally, the behavior of nanoparticles that preferentially interact with functional blocks in the PAA-portion of the mixed brush is investigated as a function of their radius and the number of functional blocks.

In the second part of the presentation, weak polyelectrolyte brushes are studied by particle-based simulations. Using a semi-grandcanonical partition function in the framework of the Single-Chain-in-Mean-Field (SCMF) algorithm, the weak polyelectrolyte is conceived as a supramolecular mixture of polymers in different dissociation states, which are explicitly treated in the partition function and sampled by the SCMF procedure. One obtains a local expression for the equilibrium acid-base reaction responsible of the charge regulation of the charged groups that is also incorporated into the SCMF sampling. Coupled to a simultaneous treatment of the electrostatics, the approach is shown to capture the main features of weak polyelectrolyte brushes as a function of the bulk *pH*-value in the solution, the salt concentration, and the grafting density. Results are compared to experimental and theoretical works from the literature using coarse-grained representations of poly(acrylic) acid (PAA) and a poly(2-vynil pyridine) (P2VP) polymer-based brushes. As the Born self-energy of ions can be straightforwardly included into the numerical scheme, we also study its effect on the local charge regulation mechanism of the brush. We find that its effect becomes significant when the brush is dense and under high (typically physiological) salt concentrations. The numerical methodology is then applied *(i)* to the study of the kinetics of collapse/swelling of a P2VP brush, *(ii)* to the ability of an applied voltage to induce collapse/swelling of a PAA brush in a *pH* range close to the pK_a value of the polymer and *(iii)*, to the *pH*- and salt-induced swelling of a mixed brush composed of oppositely charged polymers like P2VP and PAA.

L9

RESPONSIVE BRUSHES: THE IMPACT OF POLYMER ARCHITECTURE

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We overview recent advances in theory of responsive brushes formed by non-ionic or charged (ionic) macromolecules of various architectures and complement them by insights from self-consistent field numerical modelling. In particular we are interested in dendron brushes which are built up of dendritically branched macromolecules grafted by a root segment to a planar surfaces or to colloidal particles. The main focus is on specific effects arising due to branched topology of the brush-forming macromolecules and its interplay with solvophilic/solvophobic and long range electrostatic interactions.

A scaling approach for describing large-scale properties of dendron brushes in the linear (Gaussian) elasticity regime involves inevitably assumptions about intra-molecular strain distribution. A more refined self-consistent field (SCF) analytical theory enables us to justify these assumptions and to get a better insight into intrinsic structure of brushes formed by branched macromolecules of arbitrary topology. This approach is further coupled to the Poisson-Boltzmann approximation for analysis of structural properties of brushes formed by ionic branched macromolecules.

The SCF method enables us to analyse structure of mixed brushes formed by macromolecules which differ in their degree of branching and even topology. We demonstrate that branched and linear macromolecules with selected molecular weights and architectures can distribute their free ends all over the volume of a mixed brush and produce unified polymer density profiles which results in equal availability of terminal functional groups. This property is controlled solely by architecture of the brush-forming chains irrespectively of the specific nature of intermolecular interactions.

This universality, however, breaks down when the brush-forming dendrons approach the limit of extensibility. An inherent property of the dendron brushes in the non-linear stretching regime is vertical stratification manifested in segregation of dendrons in weaker and stronger stretched populations. We demonstrate how this stratification is developed upon an increase in gradating density or/and interactions strength.

Compared to brushes of linear chains, the dendron brushes provide a sharper increase in the repulsive force when the brushes pushed to overlap. The dendron brushes decorating apposing surfaces exhibit weaker interpenetration than brushes of linear chains. We discuss the impact of branching on the tribological properties of the brush-decorated surface and colloidal stability of dispersions.

L10

CORRELATION OF IR SPECTRA WITH THIN-FILM STRUCTURE AT SOLID WATER INTERFACES

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An important issue in the infrared characterization of solid-liquid interfaces in electrochemistry, polymer sciences and bio-analytics is the understanding of the correlations between spectra and structure of the thin film. For interpretation optical calculations are required particularly in order to interpret the spectral range overlapping with water vibrational bands. For in situ infrared measurements flow cells of different types were coupled with an infrared ellipsometer.[1] Recent progress shows the applicability for microfluidic applications.[2] Exemplarily the properties of stimuli responsive polymer brushes, the swelling behavior, dissociation and molecular interactions as well as the pH- and temperature dependent adsorption of proteins are discussed.[1,2,3,4,5]

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L11

MICROSYSTEMS FOR CULTIVATION AND ANALYSIS OF CELLS

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Traditionally, cells are analyzed by collecting media for off-dish functional assays such as ELISA. Our lab has been interested in developing assays that may be miniaturized and placed at the site of small groups of cells for on-dish detection of cell function. In developing these assays or biosensors we strive to achieve local and continuous detection of molecules appearing in extracellular space. Three categories of biosensors for cell secreted molecules under development in our lab will be discussed: aptamer-based sensors for protein detection, peptide-based sensors for protease activity monitoring and enzyme-based biosensors for small metabolite analysis. Applications of these technologies to diagnosis of infectious diseases and monitoring cellular responses to injury will be discussed.

L12

DESIGN OF FUNCTIONAL MICELLES FOR ENHANCED CELLULAR UPTAKE AND THEIR MOVEMENT IN CANCER SPHEROIDS

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Micelles and vesicles have long been proposed as carriers for low molecular weight molecules including drugs. Especially micelles are found to be useful for the encapsulation of hydrophobic drugs in the core while maintaining the water solubility of the system with the hydrophilic shell. Polymer chemist have designed a variety of different micelles and tested their ability to deliver drugs using a tradition assay of cell in 2D.

However, the uptake of nanoparticles in vitro does not take the actual structure of tumors into account, which requires the movement of particles into the tissue. Multicellular tumor spheroids (MCTS) can act as a 3D tumor model to investigate the biological responses to polymeric micelles as nanocarriers for therapeutic applications. However, to the best of our knowledge, the micelle penetration pathways in MCTS are yet unknown. Therefore, a range of nanoparticles were prepared to study the correlation between nanoparticle type and spheroid penetration. It was found that stable micelles, which were stabilized by crosslinking, penetrated deeper and delivered more drugs into MCTS than the diffusion of the free drug. It was found that the micellar penetration depended more on transcellular transport than on diffusion through extracellular matrices between the cell (Figure 1).

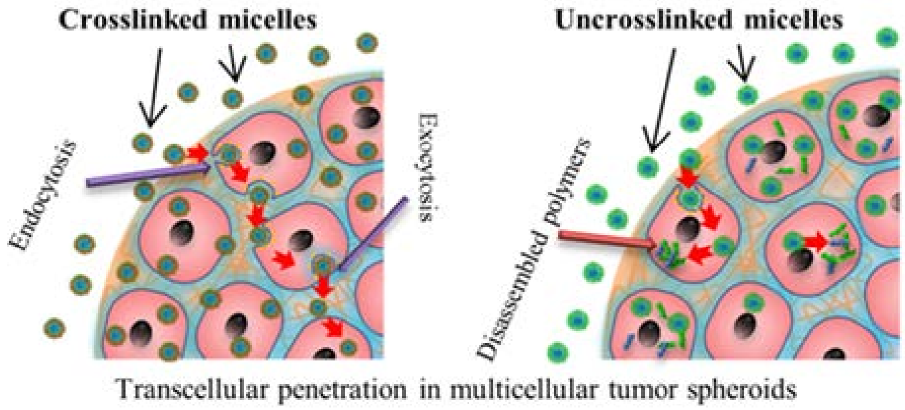

Figure 1: Penetration pathway of crosslinked micelles and uncrosslinked micelles into pancreatic spheroids

L13

STRUCTURE AND MECHANICAL RESPONSE OF NATURAL INTERACTIVE AND ADAPTIVE MATERIALS

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Biological tissues are naturally interactive and adaptive. In general, these features are due to the action of cells that provide sensing, actuation as well as tissue remodelling. In this context, it is interesting to compare the adaptation of materials where cells are able to remove and replace materials, such as in bone for example, to organisms where material cannot be removed and the adaption occurs by growth only, such as in wood.[1] It has to be stressed that an active metabolism is required in those cases where adaptation depends on the action of cells, providing mechanosensing, material formation and resorption. There are, however, examples of interactive materials synthesized by living organisms but which function without active metabolism as mechanosensors and actuators,[2] a situation which seems easier to be mimicked in the context of polymer science. The lecture will describe some structural principles leading to passive movement in seed capsules triggered by ambient humidity.[3,4] It will also briefly address the potential of the combination of weak and strong bonds in natural polymer structures to achieve self-healing properties,[5] as well as discuss the influence of internal architecture on the overall mechanical behaviour of materials and on their adaptive potential.

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L14

STIMULI-RESPONSIVE POLYMER MATERIALS ENABLED BY COMPARTMENTALIZATION

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Multicompartmental particles can be designed to feature substantially dissimilar materials in proximate regions.[1] The ability to co-locate materials with orthogonal properties into the close proximity enables a broad design space for engineering of multifunctional particles.[2,3] If these polymers are appropriately selected to undergo distinct responses to environmental cues, such as pH, temperature, or solvent composition. In this presentation, multicompartmental particles, fibers, and microcylinders with selective responses of individual compartments will be discussed. These anisotropic architectures can result in reversible switching, actuation, and even selective shape shifting.

Over the last decade, we have developed a synthesis method for bicompartmental nano-objects that we refer to as "*Electrohydrodynamic Co-Jetting*", because multiple fluid streams can be extruded in parallel to create particles and fibers with multiple distinct compartments.[3] More recently, our group has extended this concept to a range of different bi- and multicompartmental NP. The co-jetting technology lends itself to fabrication of diverse compartment geometries. For instance, bicompartmental particles with equally-sized compartments can be prepared from a range of different polymers including biodegradable PLGA, or PEO. Similarly, particles with more than two compartments can be fabricated with this technology for independently controlled release. Compartments can be made of different base polymers, which enable independent surface modification, decoupled release rates, responsiveness, or differential color.

Thus, electrohydrodynamic co-jetting is a simple, scalable, yet flexible fabrication method that can lead to multicompartmental particles. Using a biomimetic approach, we have designed actively responding microparticles that sense changes in their local chemical environment and respond in form of bending movement.[4] These microactuators are an example of responsive materials that are enabled by compartmentalization.[5,6]

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L15

LIGHT-TUNING MORPHOLOGY AND COMPOSITION IN BIOMATERIAS AND THE CONSEQUENCES FOR EMBEDDED CELLS

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The changes in the design and properties of the extracellular matrix (ECM) during development and during pathological states provide potent signals to embedded cells and drive relevant cellular transitions (i.e. EMT). Biomaterials able to recapitulate the dynamic character of the natural scaffold and reproduce it *in vitro* highlight the multiple roles of the ECM in regeneration and disease progression, and provide functional replacements for tissue engineering or novel targets for therapeutics.[1,2,3,4]

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L16

PROGRAMMABLE MATERIALS FROM SHAPE-CHANGING POLYMERS

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Nature offers an enormous arsenal of ideas for the design of novel materials with superior properties and interesting behaviours. In particular, self-assembly and self-organization, which are fundamental to structure formation in nature, attract significant interest as promising concepts for the design of intelligent materials. Shape-changing stimuli-responsive hydrogels are exemplary biomimetic materials and can be viewed as model systems for bioinspired actuation. Hydrogels in the form of films and fibres, on one hand, mimic movement mechanisms in certain plant organs and, on the other hand, are able to self-organize and form complex 3D structures. Complex actuation of such systems is achieved when two or more polymers with different swelling properties are combined together either in the form of a fibre or film.

In this contribution, we demonstrate different approaches for design of polymer films and fibers, which are able to actuate leading to formation of highly complex 3D shapes. In particular, films can undergo sequential steps of folding by forming various 3D shapes with sharp hinges. By analyzing the folding patterns we elucidated empirical rules, which allow programming of folding and the design of specific 3D shapes.

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L17

LC-ELASTOMERS AS RESPONSIVE AND INTERACTIVE MATERIALS

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Liquid crystalline elastomers (LCEs) are a class of materials, which combines the entropy elasticity of polymer networks (elastomers) with the ability of liquid crystals to self-organize into ordered liquid crystalline phases.[1] This combination of polymeric and liquid crystalline properties induces anisotropy into the polymer chain conformation. Thus by inducing a phase transition between the isotropic and liquid crystalline phases, the polymer chain conformation can be switched from a spherical to an anisotropic conformation. Consequently, LCEs are stimuli responsive polymers, which change their macroscopic shape reversibly during phase transition.

The improvement in the applicability of these systems as mechanical actuators will depend mostly on two points. On one hand it would be attractive to induce complex director pattern into the sample to allow complex deformation and secondly it gets important to control the deformation at the transition quantitatively to allow a controlled gradual and not just a mechanical on-off transition. This requires a local control of the temperature.

Here two examples will be presented. By aligning the monomeric LC-precursor in a radial magnetic field, LC-elastomers which act like an artificial iris can be prepared.[2] The incorporation of heating wires into the material allows it to preset a very controlled actuation.[2,3]

If a multitude of small actuating samples is the goal microfluidics is the method of choice. Here the flowing conditions in micrometer-sized channels can be used to induce an ordered director field in the liquid crystalline material. This concept could be demonstrated in previous publications.[1,4] Thereby it gets possible to prepare micrometer-sized actuators with different shapes, ranging from spheres to disks to highly shape anisotropic fibers. All samples show a reversible shape change, at the phase transition from the liquid crystalline to the isotropic phase.

Concerning more complex actuators, we succeeded recently in the fabrication of one-piece micropumps from liquid crystalline core-shell elastomers via a microfluidic double-emulsion process.[5] For this purpose the LCE elastomer particles are filled with a liquid core, which can be reversibly pumped into and out of the particle by actuation of the liquid crystalline shell in a jellyfish-like motion.[5]

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L18

SILK-INSPIRED PROTEIN POLYMERS

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To achieve control over cell response, regenerative medicine could benefit from biomaterials with a tunable content of different biofunctional groups. Genetic engineering allows the production of protein-based polymers containing any desired number of functional domains, at any desired position within the polymer chain. In this presentation I will describe the design, production, and testing of functionalized variants of a silk-inspired protein. These variants feature N-terminal extensions containing either integrin-binding (RGD) or proteoglycan-binding (KRSR) cell-adhesive motifs. The polymers were efficiently produced as secreted proteins using the yeast Pichia pastoris, and were essentially monodisperse. By mixing the three proteins in different ratios, self-assembled scaffolds with the same protein concentration but varying content of the functional domains were readily obtained. The scaffolds were used for the culture of MG-63 osteoblastic cells. RGD domains had a slightly stronger effect on adhesion, activity, and spreading than KRSR domains. Scaffolds featuring both functional domains revealed a clear synergistic effect on cell metabolic activity and spreading, as well as the highest final degree of cell confluency. The mixed scaffolds presented here allow to tailor cell response independently of the material's mechanical properties.

L19

SELF-ASSEMBLED SILICA HYBRID MATERIALS– WATER BASED CHEMICAL TRANSFORMATION FOR HIERARCHICAL STRUCTURE FORMATION FROM SILICASOMES TO BICONTINUOUS MEMBRANES

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Oragnosilicon Polymers present a rather unique class of materials comprising polysilylenes , polysiloxanes and poly(alkoxysilane)s with specific application properties, e.g., such as photoconductivity, ultra-low glass transition temperatures, low surface energy and surface activity as well as biocompatible chemical properties. Besides inertness und thermal stability, the later comprises also the facile hydrolytic transformation from a soft hydrophobic organosilicon polymer to inorganic silicates or inorganic/organic hybrid structures.

This presentation concerns the formation of self-assembled hierarchical structures from specially engineered silicon prepolymers to stratified multiilayer films, thin wall nanocapsules and silicasomes, high refractive index coatings, Janus-type particles for coatings with switchable surface properties and functional nanoparticles. While in the well-established sol-gel technology, the conversion of the organo-silicon precursor to solid and solvent resistant silica yields a porous and and irregular structure, our concepts are directed towards the formation of highly ordered nano- and microstructures.

L20

NEW POLYMER BASED APPROACHES FOR BIOSENSING AND REGENERATIVE MEDICINE

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Bio-responsive nanomaterials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering.[1,2,3] A disagreeable side effect of longer life-spans is the failure of one part of the body – the knees, for example – before the body as a whole is ready to surrender. The search for replacement body parts has fuelled the highly interdisciplinary field of tissue engineering and regenerative medicine. This talk will describe our research on the design of new materials to direct stem cell differentiation for regenerative medicine. This talk will also provide an overview of our recent developments in the design of materials for ultrasensitive biosensing. We are applying these biosensing approaches both in high throughput drug screening and to diagnose diseases ranging from cancer to global health applications.

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L21

POLYMERIC DRUG RELEASE SYSTEMS

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Novel polymers have been used in oral drug delivery since decades very successfully in protective formulations as well as in sustained and delayed release formulations. In this lecture, the actual status of polymethacrylate-based copolymers in drug delivery systems will be presented. EUDRAGITE is the brand name for a diverse range of anionic, cationic and neutral copolymers based on methacrylic acid and methacrylic/acrylic esters or their derivatives. The physicochemical characteristics and applications of different grades of EUDRAGIT in colon-specific, enteric-coated and sustained release delivery and taste masking applications will be addressed.

L22

DESIGNED POLYMER ASSEMBLIES AT INTERFACES: IMITATION OF NATURE AND SYNTHETIC IMPROVISATION

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Surface functionalization by polymer grafting is a key strategy in materials science, not only to protect surfaces, but also to provide function and activity to multidimensional materials, especially when these are intended to be applied in biology and medicine. Within biological or physiological environments, polymer grafts are employed to convey biopassivity, biocompatibility and/or stealth properties to flat surfaces and drug carriers. Alternatively, solid supports of various chemical natures can be modified with functionalizable polymeric layers to regulate the settlement of surface-interacting, seeded cells and direct their behavior. In my research, designed polymer architectures forming surface grafted layers are synthesized, characterized and applied to form polymeric biointerfaces that can respond to a variety of biological environments, including protein and bacterial suspensions, as well as adhering cells. Linear and crosslinked polymer brushes synthesized via "grafting-from" methods, and graft-copolymer brush films fabricated by "grafting-to" approaches are applied to diverse organic and inorganic biomaterials, to yield polymeric biointerfaces with tunable physico-chemical properties. The polymer-architecture-dependent morphological, mechanical and tribological characteristics are especially studied by advanced scanning probe methods, and they can be precisely modulated to ultimately tune the surface interactions of biological objects. By means of these multidisciplinary synthetic, surface-modification and characterization strategies, designed polymer assemblies have been demonstrated as high-performance anti-fouling layers, bio-lubricants for cartilage repair and coatings on scaffolds for tissue engineering. Whether their outstanding properties as biointerfaces are determined by structural imitation of their natural counterparts, or by the synthetic optimization of their physico-chemical character, the designed polymer grafts that are presented in this work can pave the way for the next-generation biomaterial coatings.

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L23

PROBING SPECIFIC SURFACE INTERACTIONS OF LIGAND FUNCTIONALIZED HYDROGELS

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Many biological processes are dictated by specific interactions of mechanically soft ligand- and receptor-functionalized scaffolds like the glycocalyx or the cellular membrane. Deciphering how the involved biomolecules associate and how their association is modulated by stiffness or ligand presentation of the soft scaffolds is crucial to further understanding basic biological functions but also for addressing biomedical questions. However, classic analytic biosensors lack the biological context of ligand - receptor association between soft hydrogel-like scaffolds and sufficient sensitivity. We set out to study surface interactions by constructing colloidal sensor particles composed of ligand decorated hydrogels that represent mechanical mimicries of soft biological materials. With these soft colloidal probes (SCPs) biomolecular interactions can be determined with high sensitivity by measuring the specific adhesion on receptor decorated planar surfaces via a JKR-type technique. As proof of this concept we studied various biomolecular interactions including cell adhesion proteins[1], acid-base interactions[2] or mussel peptides[3].

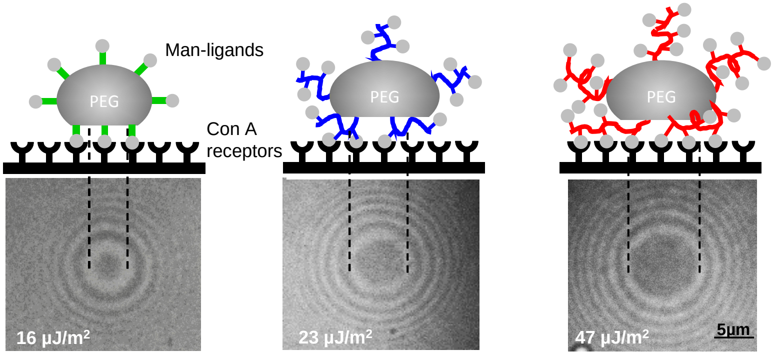

Figure: Schematics of the JKR-type adhesion assays with SCPs. Ligand density and grafting type affect specific adhesion of ligand functionalized hydrogels as signified by the increased adhesion areas[6] (central area of the concentric interference fringes).

Our current focus is to investigate sugar based interactions that constitute a central part of cell-surface interactions. A hallmark of protein receptor - carbohydrate interaction is their low affinity which is overcome by a multivalent binding. We mimicked the multiple presentation of ligands and receptors at surfaces with the SCP method (see Figure).[4] The results so far showed that SCPs functionalized with low affinity carbohydrate ligands exhibit enhanced binding with increasing ligand functionalization but no cooperative binding events.[5] We recently expanded the SCP method by means of AFM to elucidate carbohydrate ligand interactions directly on cells. Here we addressed the specific adhesion between CD44 receptors and their ligand hyaluronic acid as key players in inflammation processes and tumor development.[6] Overall, the measurement of specific adhesion energies via SCPs is a robust method to quantify specific interactions of biomimetic hydrogels.

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L24

HYSTERESIS OF THE VISCOELASTIC PROPERTIES AND THE NORMAL FORCE IN MAGNETORHEOLOGICAL ELASTOMERS

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The dynamic modulus, the loss factor and the normal force of magnetorheological elastomers (MREs) of various compositions are studied by dynamic torsion oscillations performed in the absence and in the presence of an external magnetic field. The emphasis is on the Payne effect, i.e. the dependence of the storage and loss moduli on the strain amplitude, and hysteresis of elastomer magnetorheological properties. MREs under study are based on silicone matrices differing in storage modulus (soft, $G' \sim 10^3$ Pa, and hard, $G' \sim 10^4$ Pa, matrices). Carbonyl iron particles are used as magnetic filler. The concentration of carbonyl iron particles with diameters of 3–5 µm was equal to 70 and 82 mass% in the composite material. Samples for each filler content, isotropic and aligned-particles, are investigated. Besides, MREs comprising various proportions of small (3-5 µm) and large (50-60 µm) carbonyl iron particles are obtained and the effect of the large particle content was elucidated.

It is found that the Payne effect significantly increases in the presence of an external magnetic field and varies with the cyclical loading which reaches saturation after several cycles. The results are interpreted as the processes of formation–destruction–reformation of the internal filler structure under the simultaneously applied mechanical force and magnetic field. Impacts of matrix elasticity and magnetic interactions on the filler alignment are elucidated.

It is shown that hysteresis is a characteristic feature of MREs observed both under increasing/decreasing magnetic field strength and increasing/decreasing strain amplitude. This hysteresis is attributed to the specific rearrangement of the magnetic filler network under simultaneously applied magnetic field and shear deformation. Rheological properties of the magnetic filler network formed in the magnetic field and, therefore, the rheological properties of MREs depend strongly on the filler composition and the magnetic field magnitude. Larger magnetic particles and higher magnetic fields provide stronger magnetic networks. Both factors result in the extension of the linear viscoelastic regime to larger strain amplitudes and lead to higher values of shear storage and loss moduli. It is found that the hysteresis width maximises at an intermediate magnetic field where it is attributed to the balance between elastic and magnetic particle interactions. This is apparently where the most significant restructuring of the magnetic network occurs.

The research presented provides an insight into the processes of structuring of the magnetic filler under simultaneously applied stress and magnetic field and is very important for further design of devices based on MREs.

L25

FROM METALLIC GYROID STRUCTURES TO PIEZOELECTRIC NANOPOROUS NETWORKS

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In this study we present two approaches to obtain nanoporous materials from block copolymer precursors. The first example is schematically depicted in Figure 1. A supramolecular complex of PS-*b*-P4VP diblock copolymer and amphiphilic PDP was used as a precursor for the nanoporous template for subsequent metal plating. PDP molecules interact *via* hydrogen bonds with the pyridine rings to form a PS-*b*-P4VP(PDP)$_x$ complex (Figure 1a). The block lengths of the block copolymer and the amount of PDP were selected in such a way that the self-assembly gave rise to a bicontinuous gyroid morphology with a PS network in a matrix of P4VP(PDP)$_x$ (Figure 1b). The PDP side chains were selectively removed in ethanol (Figure 1c), after which the P4VP chains collapsed onto the PS, thus forming a polar corona around the PS network struts. Subsequently, electroless deposition was performed such that the metal was distributed uniformly throughout the macroscopic thickness of the template (50 − 100 µm, Figure 1d). The metal nanofoam, obtained after the removal of polymer template, preserved the well-defined gyroid structure with long range order (Figure 1e and Figure 2).

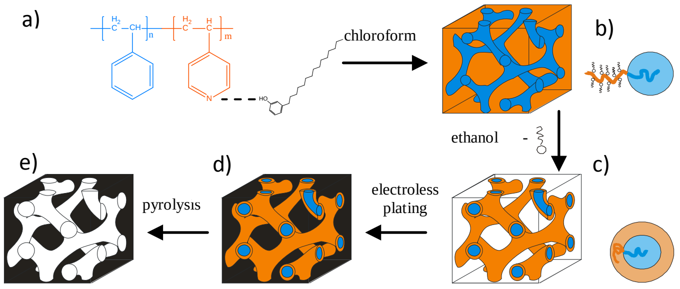

Figure 1: Schematic representation of the preparation of gyroid metallic nanofoams.

Nanoporous metal foams represent a new, very promising class of materials that combine the properties of metals, such as catalytic activity, thermal and electrical conductivity, and the properties of nano-porous materials: low relative density and high specific surface area. These unique properties allow nano-porous metal foams to be used for a large number of possible applications as, for example: high power-density batteries, substitutes for platinum-group catalysts, hydrogen storage materials, actuators etc.

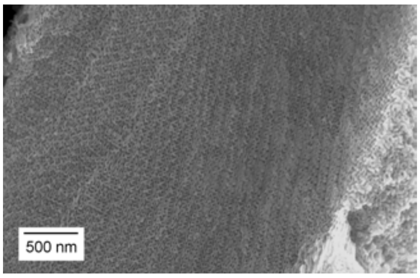

Figure 2: SEM image of an inverse gyroid Ni replica obtained after the polymer template removal by pyrolysis.

As a second example, we present the use of poly(vinylidene fluoride) containing block copolymers as precursors for nanoporous networks. PVDF is well-known for its excellent piezoelectric behavior, and therefore an interesting material to apply in nanofabrication.

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L26

MECHANOCHROMIC CHAINS AS MOLECULAR FORCE SENSORS

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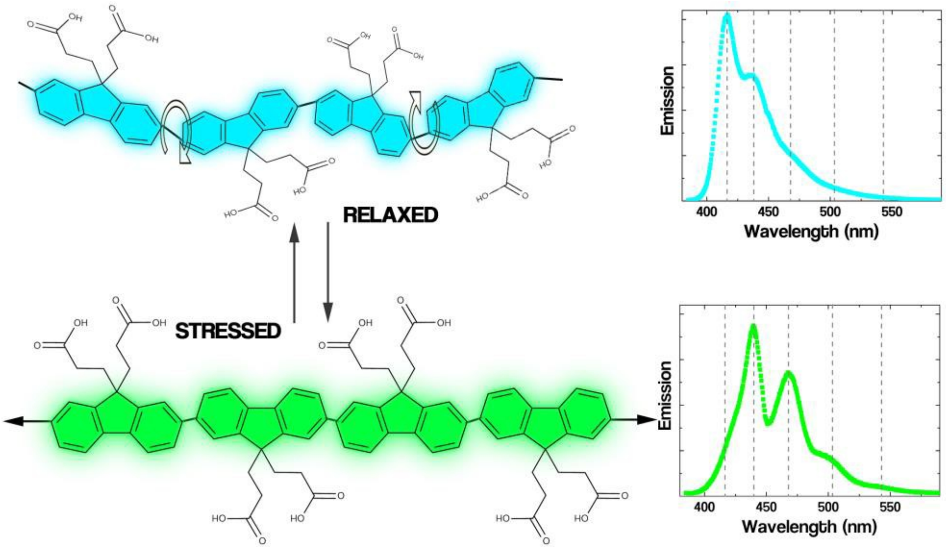
Conjugated polymers derive their optoelectronic properties from a delocalised electronic structure along the macromolecular backbone. As a result, the spectral response of most semiconducting chains is uniquely sensitive to the spatial conformation of the polymer chain. This provides a distinct coupling between mechanical stresses and optical properties, known as mechanochromism. In this talk I will highlight recent work from our group where we use macromolecular mechanochromism to probe nanoscopic forces in self-assembling systems.[1,2] I will first show how we can probe sub-piconewton forces with vibronic spectroscopy of conjugated chains that are forced into a stretched and planarised conformation. We then apply these molecular force sensors to illuminate two complex self- assembly scenarios: i) the to-date elusive condensation transition predicted to occur during charge-drive polyelectrolyte complexation and ii) the strongly cooperative self-assembly of artificial viruses from designer proteins. Our results show how mechanochromic polymers can be effectively exploited as a sensitive greyscale force reporters to shed light on even very complex self-assembly phenomena.



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L27

MACROMOLECULAR GATES: POLYMER BRUSHES ON NANOPORES

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In the living cell one finds remarkable supramolecular gating systems which enable selective biomolecular transport, the most famous example being the nuclear pore complex which controls molecular translocation to the nucleus. This makes it possible to uphold high concentration gradients across membranes and separated chemical environments. Many transporters are entirely passive and operate by facilitated diffusion. One can also find examples in biology of active gates that switch between an open or closed state by chemical binding events that induce structural changes (e.g. ion channels), in some cases enabling unidirectional transport. In many ways the organelles inside a living cell can be viewed as nanoscale reaction chambers.

Inspired by biology, we are developing so called “macromolecular gates” based on the combination of solid state nanopores and polymer brushes.[1] By choosing the right type of polymers and unique types of nanopores we can tune and measure the permeability of the gates to larger molecules such as proteins. In brief, our nanopores are prepared in thin metal films which makes it possible to perform plasmonic sensing[2] and to implement electrical control.[3] The plasmonic sensing verifies polymer grafting and detects changes in brush morphology. The electrical control can be used to locally heat the surface or to modify the pH by water hydrolysis.

So far we have developed two types of polymer brushes which we have started to implement with our nanopores. One is poly(ethylene glycol) brushes prepared by grafting-to.[4] These brushes are highly resistant to protein adsorption and form a basis for making “passive” gates. By introducing receptors together with the polymers we hope to make the gates highly selective so that, for instance, a specific protein can be separated from a complex sample.

The other type of polymer brush is poly(N-isopropylacrylamide) prepared by grafting-from.[5] This thermo-responsive polymer makes it possible to prepare “active” gates that switch between an extended (coil) or closed (globule) state by crossing the lower critical solution temperature of 32 degrees C. This is achieved by resistive heating of the thin metal film. If the heating can be localized such that polymer brushes collapse on one side of the nanpores only, the combination with liquid flow could enable entrapment of molecules in an entirely non-invasive manner.

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L28

ORIENTED SELF-ASSEMBLED THIN FILMS OF ANISOTROPIC NANOPARTICLES FOR (CHIRAL) PLASMONICS

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Recently there has been great interest in developing materials that could control the flow of electromagnetic waves in unprecedented ways. In particular, metal nanoparticles are particularly interesting due to their surface plasmon resonance. Metallic self-assembled nanoparticle arrays have numerous potential applications such as Surface-Enhanced Raman Spectroscopy (SERS), plasmon-enhanced fluorescence or on-chip waveguiding. In particular, significant progress has been made in the area of nanowire and nanorods synthesis and device application in the past several years.[1] A big challenge, however, still resides in the hierarchical organization of these nanoscale building blocks into functional assemblies and ultimately a useful system. Discovering new bottom-up methods to assemble one-dimensional nanomaterials into two- or three-dimensional structures with well-controlled location, orientation, and spacing across multiple length scales has attracted lots of attention, owing to the potential applications in electronic and optical devices.[2]

I will present a novel technique we have developed for the self-assembly of anisotropic nanoparticles as mono- and multilayer thin films. It allows aligning anisotropic nano-objects on large areas with tunable particle density and orientation. Furthermore, the Layer-by-Layer assembly technique[3] is used to build multilayer thin films in which the architecture and orientation can be controlled independently in each layer. With this, helical assemblies of metallic nanorods and nanowires can be prepared. The optical properties as function of the thin film geometry will be detailed, with a special emphasis on oriented mono- and multilayers and on helical plasmonic superstructures, which display very high chiroptical activity.

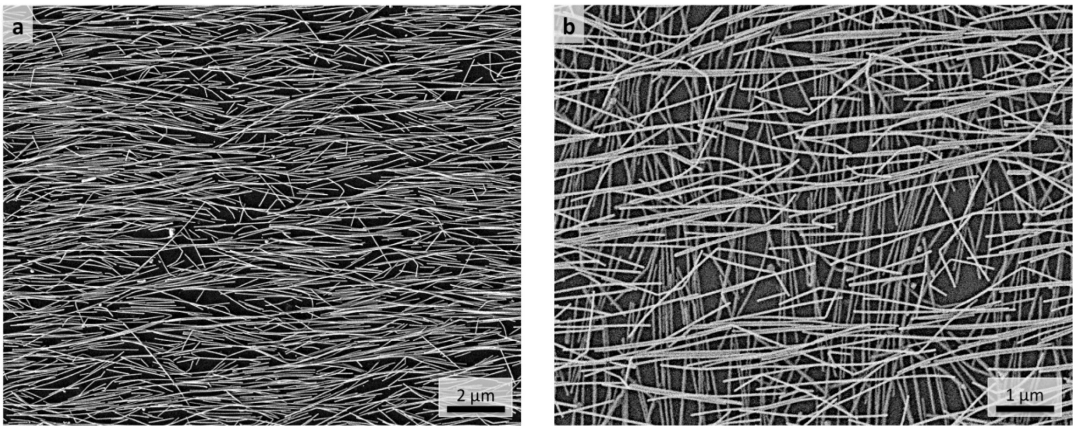

Figure: SEM pictures of aligned silver nanowires a) in a dense monolayer and b) in a bilayer in which the second layer is aligned perpendicular to the first one.

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Abstracts of the posters

P1

POLYMERSOMES AS PLATFORM FOR CONTROLLABLE (MULTI)ENZYMATIC REACTIONS

D. Appelhans[1,*], *H. Gumz*[1,2], *V. Krönert*[3], *D. Gräfe*[1,2], *B. Voit*[1,2]
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Over the last years, huge efforts have been undertaken to develop feasible polymer-based systems for biomedical applications and synthetic biology.[1] Polymeric capsules and polymersomes among other have been proven to be promising candidates for such purposes. Compared to their biological counterpart, the liposomes, the membrane from polymersomes is considerably thicker and shows increased mechanical and chemical strength.[2] In this context, our efforts were directed to establish pH-stable polymersomes over a broad pH range by the incorporation of two different photo-crosslinkable moieties in the membrane. This allows us for undergoing reversible switching of polymersome´s membrane to trigger the uptake and release of small molecules under various pH values und to squeeze out dendritic glycopolymers under shear forces.[3,4]
For developing even more complex polymeric vesicles usable in biomedical applications and synthetic biology, where post-non-covalent conjugation steps and/or de-conjugation/displacement steps are required, we report further progress on pH- and size-controlled diffusion processes. Results are presented and discussed in respect to pH-dependent (multi-)enzymatic conversion steps[3,5,6] as well as enhanced folic acid-enhanced uptake of doxorubicin-loaded polymersomes by folic acid-sensitive cells.[7] Furthermore, one example is presented, where polymersomes are considered as permeable supramolecular cages. The encapsulated enzyme esterase remains fully active, but is not able to escape from the polymersomes’ lumen even when the membrane is kept in a steadily open state for 2 days. This new development will give the possibility to fabricate new types of multicompartmentalized capsules for synthetic biology.

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P2

CROSSLINKED AND PH-RESPONSIVE POLYMERSOMES: FUNCTIONALIZATION AND POST-MODIFICATION BY HOST-GUEST-INTERACTIONS

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For a large number of biological processes in cells vesicles, also known as liposomes, are important compartments. Artificial analogues to these vesicles are called polymersomes and formed by self-assembly of amphiphilic block copolymers with a defined block ratio and narrow molecular weight distribution. They exhibit several advantages over the well-known liposomes such as enhanced mechanical and chemical stability with the aid of a thicker bilayer as well as the flexible chemical design. This enables us additionally to incorporate various functional groups into these polymer bilayers.[1] The inclusion of pH-responsive units into the block copolymers leads to polymersome disassembly upon trigger of the stimulus and subsequent cargo release. The disassembly can be avoided by photocrosslinking of UV-responsive moieties in the polymersome membrane. This results in reversible swelling and shrinking as a response to changing pH values between 4 and 8. These specific polymersomes can be applied as nanoreactors and drug delivery systems.[2,3]

Furthermore, the usage of synthetic block copolymers allows the introduction of specific functional end groups. If the desired functionality is bound to the hydrophilic block of the block copolymer, the resulting polymersome will display these groups on its membrane surface outside and inside. This approach has been exploited for the incorporation of fluorescent dyes and targeting moieties[3] as well as for surface immobilization of the particles onto substrates[4] and to initiate sequential post-conjugation[5,6]. In particular, controlled post-modification of the inner and outer polymersome surface using non-covalent approaches offers new possibilities for innovative biomedical applications. To achieve this goal, pH-controlled host-guest interaction and purification steps were smoothly carried out. This approach is only available by synthesizing adamantane functionalized block copolymers for utilization of the strong adamantane – β-cyclodextrin host-guest interactions.

In this manner we demonstrate the possibility of simple, but extremely versatile non-covalent post-modification to the polymersomes' surface. Utilizing the pH-responsive behaviour of the vesicles, the post-modification is not only limited to the outer surface, but can also be applied to the polymersome's lumen.

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P3

PROGRAMMED “MICRO-BUBBLE” CONSTRUCTIONS WITHIN PATTERNED SILK FILM FOR ENCAPSULATION

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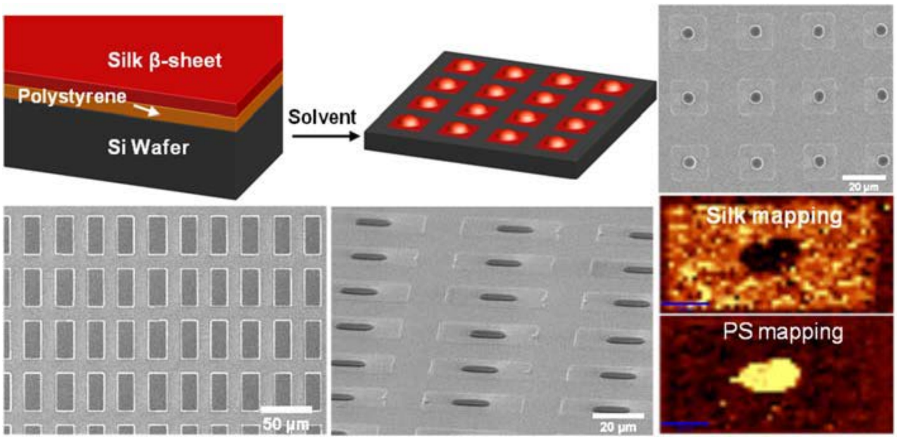
We demonstrated a novel method to fabricate individually addressable “micro-bubble” constructions by confining dissolution of a polystyrene prelayer in the polystyrene-silk fibroin multilayer thin film which was patterned to specific shape and dimension by photolithography. Raman spectra revealed that the polystyrene only presented in the self-formed “micro-bubble” region, indicating the successfully “self-encapsulation” property of the “micro-bubble” structures. The count and shape of “micro-bubbles” on each silk fibroin pattern can be well controlled by the pattern thickness and geometry. Furthermore, the silk fibroin pattern with “micro-bubble” constructions also indicated the capability for “self-encapsulation” for various materials, such as hydrophobic and hydrophilic polymers, nanoparticles, which provided a novel method for the application in the field of solid-state delivery system, drug delivery and bioengineering.



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P4

SWELLING CHARACTERISTICS OF BISENSITIVE HYDROGELS FOR MICROFLUIDICS

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Stimuli-sensitive polymeric hydrogel networks provide the basis for various advanced applications such as microelectromechanical sensors (MEMS), continuous health monitoring, on-line control and sensors and actuators for microfluidics. The combination of two different stimuli into one hydrogel remarkably extends possible applications. Combining the continuous and discontinuous swelling characteristics of different stimuli-sensitive monomers allows performing enhanced switching and sensing operations with hydrogel-based devices. Overall this leads to the opportunity of chemical transistors (chemostats).

Interpenetrating polymeric networks (IPNs) and semi-IPNs provide the opportunity to combine different stimuli. Therefore, it also enhanced the mechanical stability of the resulting hydrogel due to their structure. For our study temperature- and pH-sensitive hydrogels net-PNiPAAm-ipn-net-P(AA-co-AAm), net-PNiPAAm-ipn-net-PAA and net-PNiPAAm-sipn-PAA were intensively investigated and optimized to achieve suitable swelling properties for their use in microfluidic actuators and sensing.

The swelling kinetics based on Tanaka et al.[1] has been modified to characterize and predict the size- and shape-dependent swelling of complex hydrogel systems. For this cylindrical samples with different aspect ratios have been used to compare the common cooperative diffusion coefficient Dcoop for the molecular mobility of subchains in the networks. The results show after applying the shape correction a convincingly small standard deviation. The gained shape-corrected cooperative diffusion coefficients were verified with dynamic light scattering. Dcoop can also be used to predict the swelling time of hydrogels at any size. This allows for the estimation of the switched off/on time of hydrogel-based valves in microfluidics in advance. Only macroscopic hydrogel samples have to be investigated for this purpose. Furthermore, the developed swelling kinetics can be used to easily detect crack formation within the sample.

Additionally, the investigation of the structure-property relationships for those networks allows to synthesize bisensitive hydrogels networks with tailored properties, like accurate stimulus, reduced swelling time, optimized intensity of the property change due to the applied stimulus, balanced stimuli-related swelling ratio and stiffness.

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P5

INVESTIGATION OF POXYLATED TOBACCO MOSAIC VIRUS BASED DRUG DELIVERY SYSTEMS FOR CANCER THERAPY

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Nanoparticles accumulate preferentially in solid tumours compared to healthy tissue, increasing chemotherapeutic efficacy and reducing toxic side effects compared to free drugs. Thus a broad platform of nanoscale drug delivery systems are currently under investigation to develop effective carriers for toxic drugs for cancer therapy.[1] Each nanocarrier comes with advantages and limitations. Non-infectious viral nanoparticles (VNPs), derived from plants, are protein-based, biodegradable and biocompatible, self-assembling materials which form highly symmetrical and monodisperse structures. VNPs production in plants is highly scalable; viruses are available in wide range of shape including rods and spherical icosahedrons and can be further tailored using genetic and chemical modifications [2]. By selecting a preferred viral shape and modifying the surface, *in* vivo properties of VNPs can be adjusted. For example, several studies indicates that spherical materials are cleared more rapidly compared to rod-shaped systems[3,4] and circulation half-life can be prolonged by the attachment of stealth layer generating polymers[3]. The most commonly used, well-defined polymer for biomedical applications, is polyethylene glycol (PEG).[2,5] According to the general accepted assumption, PEG is also known to reduce bio specific interactions and immunogenicity.[2] However, recent studies revealed that 22-25% of healthy, human blood donors developed antibodies against pegylated nanomaterials.[6] Poly(2- oxazoline), a polymer with almost identical properties is an interesting alternative to PEG.[5] In this work we combine the advantages of each material. Tobacco mosaic virus (TMV) is a rod-shaped plant virus (300nm length, 18 nm diameter and a 4 nm-wide interior channel) which consist of 2130 coat proteins.[3] We modified the exterior phenol groups of tyrosine residues (TYR139) to obtain a polymer coated dye labelled TMV particle using a two-step diazonium coupling followed by the covalent attachment of two azide functionalized Poly(2-methyl-2-oxazoline) or azide functionalized PEG by copper catalyzed azide alkyne cycloaddition (CuAAC). Both well-defined Poly-(2-oxazoline)s were synthesized via cationic ring opening polymerization with a very low dispersity ($M_n/M_w < 1,1$). We determined that approximately 900-1000 tyrosine residues were modified with POx and 400-500 with PEG. To understand the biological behaviour and differences between both systems, we will also present results of cell uptake studies with macrophages (RAW 264.7) and pharmacokinetic studies.

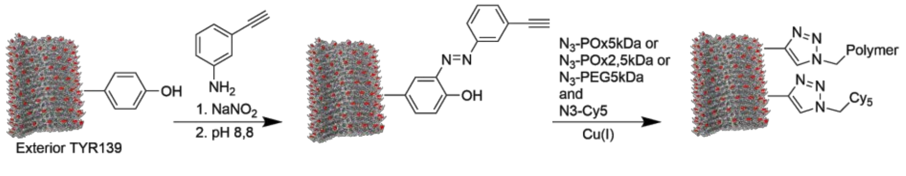

Figure 1: Modification of exterior phenol groups of tyrosine residues using CuAAc.

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P6

SIDE SELECTIVE CONJUGATION OF FOLIC ACID WITH POLY(2-OXAZOLINE)S FOR ACTIVE TARGETING DRUG DELIVERY SYSTEMS

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In numerous cancer types, cancer cells significantly overexpress the folate receptor (FR) which can be used for targeted drug delivery of drugs using folic acid (FA).[1] However, conjugation of FA to the drug delivery system (DDS) is normally performed via the α- and the γ- carboxylic group and their different binding affinities to the FR target are extensively discussed.[2] This work presents the first site selective synthesis of α- and γ-FA conjugates with various poly(2-oxazoline)s (POx) as a first step towards active drug targeting with the POx DDS platform. They were obtained by the reaction of glutamate terminated POx with pteroyl azide[3] (Fig. 1).

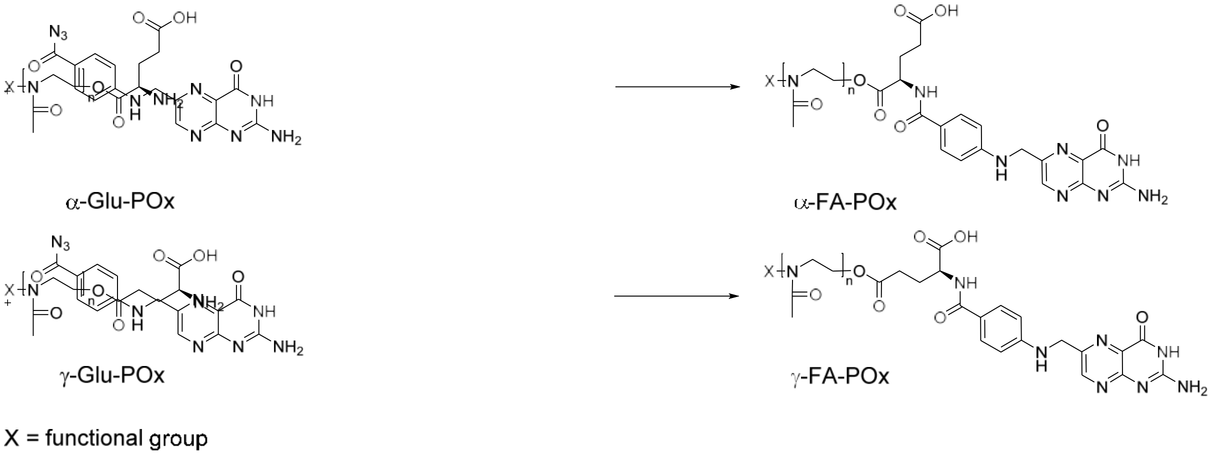

Figure 1: Synthetic route for either folate(α)-POx or folate(γ)-POx.

For both, α-FA-POx and γ-FA-POx, high functionalization of POx with folic acid were obtained [4]. Further investigations were performed with amphiphilic block copolymers and proximal functionalized POx to yield α,ω-functionalized POx.

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P7

POLY(2-OXAZOLINE) BASED NANOFORMULATION OF PACLITAXEL WITH SUPERIOR SAFETY AND EFFICACY *IN VIVO*

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The poor solubility of paclitaxel (PTX), the commercially most successful anticancer drug, has long been hampering the development of suitable formulations. Here, we report on a nanoformulation of PTX with a poly(2-oxazoline) triblock copolymer (POx), which is characterized by a facile preparation, extraordinary high drug loading of 50 % wt. and PTX solubility of up to 45 g/L that calculates to a solubility increase by a factor of 50.000. The formulation shows excellent shelf stability and defined, sub-100 nm size spherical micelles. We observe favorable *in vitro* and *in vivo* safety profiles and a higher maximum tolerated dose as compared to PTX formulations currently used in chemotherapy. Pharmacokinetic analysis reveals that the higher dose administered leads to a higher exposure of the tumor to PTX. As a result, we observed improved therapeutic outcome in orthotopic tumor models including the very aggressive “T11” mouse claudin-low breast cancer orthotopic, syngeneic transplants which is considered as a clinical faithful cancer model. The very promising preclinical data for the POx/PTX nanoformulation demonstrate the need to investigate new polymer excipients. The significant anti-tumor efficacy and superior safety renders nanoformulations with amphiphilic POx triblock as candidates for clinical trials.

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P8

CELL RESPONSIVE ADHESIVE DRUG LOADED COATINGS OF POLYELECTROLYTE COMPLEX NANOPARTICLES FOR BONE HEALING

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The therapy of fractures and defects in the systemically diseased hard tissue is one of the great challenges in medicine. Artificial allogenic bone substituting materials (BSM) are used for bone remodelling and tissue regeneration, but have problems or fail in the case of systemic bone diseases osteoporosis (OP) and multiple myeloma (MM). This work aims at the development of an adhesive nanoscaled carrier system for bone therapeutic drugs usable for the functionalization and improvement of BSM. We have chosen biocompatible polyelectrolyte complex (PEC) nanoparticles (NP) loaded by relevant therapeutics.

PEC NP can be prepared by mixing aqueous solutions of oppositely charged biorelated polyelectrolytes (PEL) optionally in the presence of further charged compounds.[1] Herein, charged drugs like antibiotics, bisphosphonates, statins and proteinogenic growth factors relevant for bone healing were loaded.[2,3,4,5,6] Casting and drying loaded PEC NP dispersions onto material substrates results in coatings, from which drugs and functional proteins can be released upon contact to relevant buffered media under local and kinetic control. Model substrates like germanium[2,3,5] and relevant BSM substrates like planar Ti40Nb alloy plates[4] and porous calcium phosphate disks[6] were coated. Results on the adhesiveness and drug release properties of PEC NP coatings under variation of PEL, drug and charge composition are presented using in-situ-ATR-FTIR-, UV/VIS- and circular dichroism spectroscopy.[2,3,4,5,6] The cell interaction of PEC NP was studied based on relevant human mesenchymal stem cells (hMSC) as well as human peripheral blood monocytes (hPBMC) using microscopic techniques and cell biological assays related to viability, differentiation and (bone mineral) pit formation.[4,5,7]

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P9

TAILORED AND BIODEGRADABLE POLY(2-OXAZOLINE) MICROBEADS AS 3D MATRICES FOR STEM CELL CULTURE

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We present the synthesis of hydrogel microbeads based on telechelic poly(2-oxazoline) (POx) crosslinkers and the methacrylate monomers (HEMA, METAC, SPMA) by inverse emulsion polymerization. While in batch experiments only irregular and ill-defined beads were obtained, the preparation in a microfluidic (MF) device resulted in highly defined hydrogel microbeads. Variation of the MF parameters allowed to control the microbead diameter from 50-500 µm. Microbead elasticity could be tuned from 2 to 20 kPa by the POx:monomer composition, the POx chain length, net charge of the hydrogel introduced via the monomer as well as by the organic content of the aqueous phase. The adhesion and initial proliferation of human mesenchymal stem cells (hMSCs) on the microbeads were studied. While neutral, hydrophilic POx-PHEMA beads were bioinert, excessive colonization of hMSCs on charged POx-PMETAC and POx-PSPMA was observed. The number of adhered cells scaled roughly linear with the METAC or SPMA content. Additional collagen I coating further improved the stem cell adhesion and proliferation. Finally, a first POx-based system for the preparation of biodegradable hydrogel microcarriers is described and evaluated for stem cell culturing.[1]

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P10

ADAPTIVE BIO-INSPIRED COMPOSITES WITH TAILORED MICROCAPSULES

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Biological materials self-heal and adapt to stresses by the coordinated action of living cells. Bone is a prominent example of a biological material in which the dynamic functionality of cells is used to enable adaptive reinforcement in response to heterogeneous local stresses. Despite the unparalleled complexity of biological systems, major efforts have been made to generate engineered microcompartments and capsules that partly replicate just a few key features of the fascinating dynamic response of living cells. We present our recent efforts to create mechanically-responsive microcompartments that can be incorporated into polymer matrices to generate a composite material that locally self-reinforces in response to non-uniform mechanical loading. We obtain polymer-based capsules with predictable size, shell thickness, tunable mechanical behavior, and shell microstructure through a microfluidic approach. Such level of control over the structure and properties of capsules is achieved by using microfluidic double emulsions as soft templates for the microcompartments. We show how the mechanics of microcapsules incorporated in a composite can be tuned to enable local rupture without significant damage of the host polymer matrix. The local release of reactive species upon capsule rupture eventually allows for cross-linking of the polymer matrix only at sites that are subjected to high mechanical stresses. While the adaptive behavior of the capsule-loaded composites remain very far from reaching the responsiveness of truly dynamic biological systems, our ability to create materials that can adjust their mechanical properties according to the demands of the environment represent a paradigm shift in the design and fabrication of materials for structural applications.

P11

CHEMICAL DOPING AND FUNCTIONALIZATION OF SWNTS

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Carbon nanotubes are one of the most promising materials for post silicon electronics.[1] Especially single-walled carbon nanotubes (SWNT), as a one-dimensional sp^2 - carbon based material, have potentials in advancing electronics,[2] e.g. in field effect transistors (FET) and amplifiers. Nevertheless it is necessary to improve the properties of integrated SWNTs by modifying their electrical characteristics.[3] To achieve this we show different approaches of modification and strategies to prevent bundle formation.[4] These techniques allow an adjustment of the properties by grafting density and functional groups of the polymer or self-assembled monolayer (SAM). The functionalization of wafer is achieved by SAMs and polymer brushes to minimize the differences of free surface energy between SWNT and SiO_2.[5] The polymerization of SWNTs is done by self-initiated photografting and photopolymerization (SIPGP). The grafting and polymerization process of monomer works only with the help of UV light and is suitable from SAMs as well as from SWNTs.

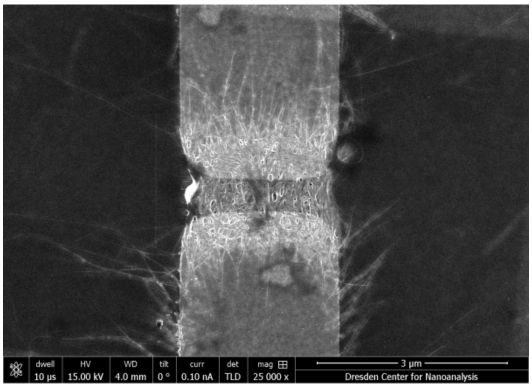

Figure 1: SEM image of enwrapped carbon nanotubes within a field effect transistor with homogeneous polymer layer.

Analysis of polymerized SWNTs displays enwrapped CNTs (Fig.1) with a homogeneous polymer layer. SIPGP and polymers offers a versatile and fast method for a covalent modification as well as high doping of SWNTs, without the need of an additional initiator or any pre-treatment.

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P12

BIOFUNCTIONALIZATION OF POLYMER BRUSHES USING CLICK CHEMISTRY

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Smart Surfaces based on polymer brushes play an important role in a wide range of biological and medical applications. The creation of such systems can be achieved by grafting stimuli-responsive polymers by one end to a solid surface.[1] The polymer chains are capable of responding to external stimuli such as temperature, pH and solvent polarity, generally showing a reversible swelling-deswelling behavior. Moreover, accessible functional groups at the outer extremity of polymer brushes enable the immobilization of active ligands like enzymes.[2]

We report on the immobilization of the model enzyme horseradish peroxidase (HRP) to temperature-responsive Poly (N-isopropylacrylamide) (PNIPAAm) brushes with alkyne functionality at the chain ends. Click Chemistry (Copper-catalyzed Alkyne-Azide Cycloadditon) was used to covalently bind azide-functionalized biotin to the chain ends of the polymer brushes. In a second step, streptavidin-conjugated horseradish peroxidase was bound to the surface via the biotin-streptavidin affinity reaction. In-situ spectroscopic ellipsometry investigations have been used to characterize the biofunctionalized polymer brushes concerning temperature-responsive swelling behavior. The amount of immobilized enzyme on the brushes was determined for biotinylated PNIPAAm brushes with different biotin spacer arm lengths at immobilization temperatures below and above the lower critical solution temperature (LCST) of the PNIPAAm brushes. The catalytic activity of the enzyme on the brush surface was confirmed with a colorimetric assay. The influence of the immobilization conditions on enzyme activity and immobilized enzyme amount will be discussed.

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P13

STIMULI-RESPONSIVE HAIRY PARTICLES FOR ENZYMATIC REACTIONS IN BULK AND AT INTERFACES

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Enzymes are versatile but highly specific and selective biocatalysts which act under mild conditions. Enzyme-based processes are more environmentally friendly, cost-effective and sustainable than conventional catalytic methods. Therefore, enzymatic reactions are of great interest for the textile and food industry as well as for pharmaceutical transformations.

The effective immobilization of enzymes aims at improving their solubility, stability, and re-use by preserving or increasing their catalytic properties. However, separation and reusability still remains a challenging task.

Herein, we propose a stimuli-responsive carrier system for efficient immobilization, effective catalytic capability and reusability of laccase from *Trametes versicolor*. For this, we synthesized a series of stimuli-responsive core-shell particles, which consist of an inorganic core and hairy polymeric shells, thus offering complex systems with controlled and tunable chemical functionality, surface charge and grafting density.[1,2] We systematically investigated and discussed these positively, negatively and uncharged hairy core-shell particles with respect to the efficiency of immobilization and effectiveness of the catalytic performance of laccase.[2]

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P14

HYBRID HAIRY JANUS PARTICLES AS NOVEL BUILDING BLOCKS FOR ACTIVE SURFACES AND INTERFACES

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Janus particles represent a class of multifunctional anisotropic building blocks, combining two distinct functions at their opposite sides.[1,4] The unique asymmetry of the Janus particles allows them to target complex self-assembled architectures and materials inaccessible for homogeneous building blocks.[2,3] Despite the numerous reported synthetic strategies for the preparation of Janus particles, their truly large-scale synthesis and technological applications are still highly challenging tasks.

Herein, we report on the synthesis of hybrid hairy Janus particles with controllable size, geometry, chemical functionality, Janus balance, and responsiveness/adaptability.[1,4] Such Janus particles can be prepared on a large scale, thus opening new perspectives for their applications. Furthermore, we propose two application directions that would benefit from the unique properties and architecture of the Janus particles: active surfaces and interfaces.[2,3,5,6,7]

In the first approach, we exploit the superior interfacial activity of the Janus particles and apply them for interfacial catalysis through a selective modification of one of their sides with metallic nanoparticles.[5] In this way, functional active interfaces loaded with hybrid hairy Janus particles are created in an emulsion, resulting in successful catalysed reactions in the water phase and the subsequent easy recovery of the hybrid catalyst.

In the second approach, we use the hybrid hairy Janus particles as building blocks to create robust active structured surfaces.[6,7] We apply the fabricated surfaces in different environments and test their anti-icing as well as anti-fouling performance. The designed Janus particle-based surfaces offer the possibility to construct composite materials and advanced coatings with controllable adhesiveness.

[1] S. Berger, A. Synytska, L. Ionov, K.-J. Eichhorn, M. Stamm. Macromolecules (2008) 41, 9669–9676.
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[7] A. Kirillova, C. Marschelke, J. Friedrichs, C. Werner, A. Synytska. submitted.

P15

HYBRID HAIRY JANUS PARTICLES: CONTROLLED DESIGN AND ASSEMBLY

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Colloidal self-assembly may be considered as a very powerful tool for the development of materials with tunable properties based on the rich functionality of the individual particles. The assembly of isotropic building blocks typically leads to symmetric structures, whereas asymmetric or anisotropic building blocks can assemble into more complex structures with significantly different macroscopic properties.

Janus particles represent a unique class of multifunctional anisotropic particles, comprising two different functions at their opposite sides.[1,2] Taking advantage of their asymmetric structure, the assembly of Janus particles has gained tremendous attention in the recent years, leading to a variety of sophisticated structures inaccessible to their homogeneous counterparts.[3] Moreover, apart from the Janus-Janus particle assembly, which is typically in focus of the investigations, the combination of homogeneous-Janus particles could also be very interesting.[4]

Hence, we report on the synthesis of hairy core-shell Janus particles, which consist of an inorganic core and hairy polymer shells, and possess controllable size, geometry, surface chemical functionality, and Janus balance.[1,2] Furthermore, we pursued two different routes for the assembly investigations of the fabricated Janus particles. In the first route, we developed an easy and scalable bottom-up approach for the programmed assembly of oppositely charged colloidal particles, both homogeneous and Janus, into specially designed target structures: raspberry-like and dumbbell-like micro-clusters.[4] The assembly was based on electrostatic interactions mediated by polyelectrolytes on the surface of the particles. The resulting micro-cluster architectures may further be treated as “colloidal molecules” to assemble even more complex hierarchical materials.

In the second route, we investigated the self-assembly/disassembly of various kinds of functional Janus particles in dispersions depending on their nature and the surrounding media conditions.[3] The Janus particles were decorated with different functional polymers: hydrophobic and hydrophilic, charged and uncharged, positively and negatively charged ones. It was found that, under specific conditions, the Janus particles formed hierarchical chain-like structures in solutions, which were not observed in the case of the homogeneous particle mixtures.

[1] S. Berger, A. Synytska, L. Ionov, K.-J. Eichhorn, M. Stamm. Macromolecules (2008) 41, 9669-9676.
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P16

ANTI-ICING AND DE-ICING SURFACES BASED ON CORE-SHELL PARTICLES AS BUILDING BLOCKS

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Icing is a common phenomenon in nature and technology that influences our daily lives. In most cases, icing causes severe problems such as, for example, increase in the energy consumption of transport vehicles (aircrafts, cars), or alternative energy sources (wind turbines), which eventually leads to failures.

To solve these problems, the design of multifunctional polymeric anti-icing composite materials with controlled wetting and adhesion properties are needed. The concept used for the fabrication of such surfaces is based either on the reduction of ice adhesion, or the inhibition of ice growth. One approach is the design of superhydrophobic surfaces, where the contact area between the ice and the surface is very low, and the formed ice can easily be removed. However, there is a substantial need for simple and scalable approaches for the design of robust anti-icing materials.

Therefore, we suggest two approaches for the design of robust ice-phobic surfaces. The first approach is based on the use of polymer-modified diatomaceous earth particles. In this way, robust surfaces with excellent anti-icing and de-icing capability can be prepared on a large scale.[1]

The second approach is based on the desing of ice-phobic surfaces using polymeric modified raspberry-like core-shell particles as building blocks with controlled and tunable chemical composition and final surface topography.[2]

[1] N. Puretskiy, J. Chanda, G. Stoychev, A. Synytska, L. Ionov. Adv. Mater. Interfaces (2015) p. 1500124.
[2] J. Chanda, L. Ionov, A. Kirillova, A. Synytska. Soft Matter (2015) p. 9126–9134.

P17

POLYMER BRUSHES ON THIN CELLULOSE LAYERS WITH NON-FOULING PROPERTIES

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Cellulose is the most abundant biopolymer in the world and finds applications in different areas because of its attractive properties such as biocompatibility, biodegradability, and renewability. The most important application of cellulose is the use as raw material for paper. Due to its low cost, flexibility, disposability, non-toxicity, and the adaptability to large-scale manufacturing paper has become increasingly popular as a material for the construction of various high-tech devices like sensor systems, smart membranes, micro fluidic devices, and cell-based assays. For many of these applications non-fouling is a prerequisite. A promising method to create functional surfaces is the grafting of polymers having a terminal functional group with sufficient grafting density in such a way that they form a so called "polymer brush".[1,2] The properties of this very thin functional coating can be tailored by using polymers which deliver at one hand the desired physico-chemical properties and on the other hand the option for a processability in a technological coating process. Additionally polymer brushes offer the possibility to create smart surfaces which are able to respond dynamically, due to structural and physical changes of their properties, to changes of environmental stimuli, which may be an option to improve non-fouling.

Herein, we present a simple way to create ultrathin films of cellulose on silica samples by coating of the soluble trimethylsilyl derivate followed by a conversion to pure cellulose by an acidic hydrolysis.[3] These samples represent model substrates for technical papers and are used to investigate the formation of various polymer brushes using the "grafting-to" approach.[4] This technique is one intensively investigated method creating polymer brushes by applying pre-formed terminal functionalized polymers from solution resulting in a covalently attached layer at the cellulose film. For this purpose comb like polymers were synthesized which have functionalities for the covalent attachment in the backbone and highly hydrophilic side chains. These polymers could be grafted in a one-step procedure to cellulose. For studying the polymer brush formation on cellulose, we investigated the layers by IR-spectroscopy, contact angle measurements, AFM, and XPS. Furthermore, for the investigation of the desired non-fouling behavior swelling and protein repellent behavior was analyzed in-situ by spectroscopic ellipsometry.

In this contribution we will demonstrate a simple and versatile way to modulate the properties of thin cellulose layers modified by functional polymer brushes as a model system for the implementation of tailored properties, like non-fouling, on paper surfaces.

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P18

WATERBORNE SI-CUCRP: DECABLOCK MONOPOLYMER BRUSHES

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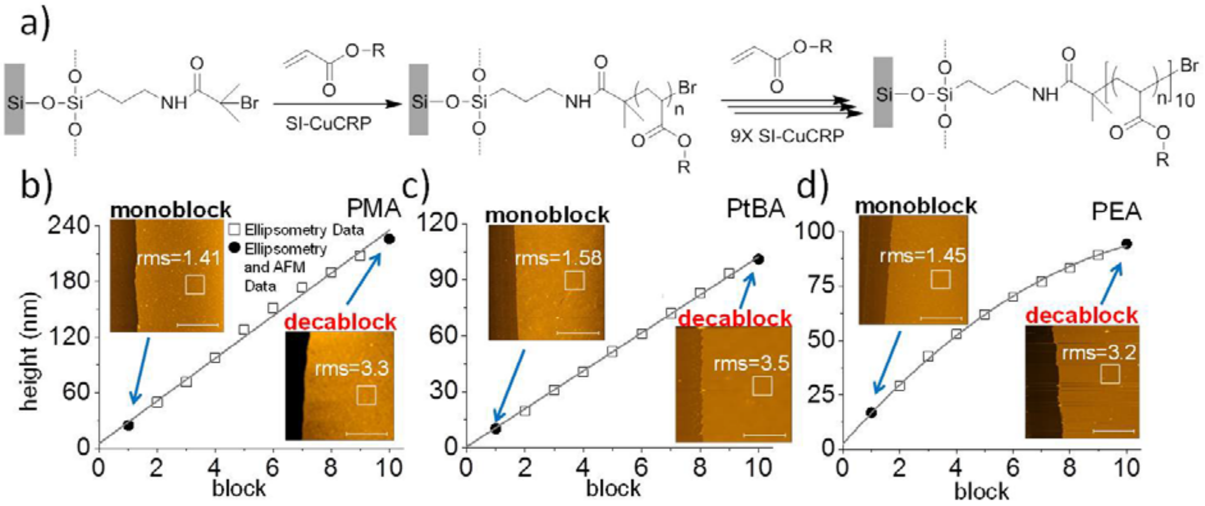
The synthesis of hydrophobic polyacrylates brush with extremely low monomer molarity at ambient condition is reported via surface-initiated Cu(0) mediated controlled radical polymerization (SI-CuCRP) using a copper plate as catalyst in aqueous Media.[1,2,3] Optimal reaction conditions for high thickness polymer brush formation were determined, indicating that 120 nm layer with an area of 60 mm^2 can be rapidly polymerized by only 1,37 micromoles monomer without standard degassing procedures and the thickness can also be modulated by changing molar concentration. Homopolymer decablock was also well controlled and characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), including methyl acrylate (MA), ethyl acrylate (EA), and tert-butyl acrylate (tBA).[4] This simple, fast, low-cost method offers a possibility to fabricate a variety of homo- and blockpolymer brushes and provides an excellent application prospect in scale-up process.



[1] T. Zhang, Y. Du, F. Müller, I. Amin, R. Jordan. Polym. Chem. (2015) 6, 2726–2733.

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P19

POLYMER BOTTLE BRUSH BRUSHES (BBBS) AND GRADIENTS BY SURFACE INITIATED CU(0) MEDIATED CONTROLLED RADICAL POLYMERIZATION (SI-CUCRP)

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[2] *ETH Zürich, Laboratory for Surface Science and Technology, Department of Materials, 8093 Zürich, Switzerland*

The so called polymer bottle-brush brushes (BBB)s haven been used in many biomedical applications such as recognition sites for cells, non-fouling surface preventing undesirable adhesions, biomedical devices and sensors.[1,2]

In this work the well-defined BBBs and gradients based on poly(ethylene-glycol) methyl-ether-methacrylate (POEGMA) and poly(2-oxazoline)s (POx)s on silicon oxide were successfully prepared through two strategies: “grafting from” by the combination of surface initiated cu(0)-mediated controlled radical polymerization (SI-CuCRP) catalyzed by a cooper plate[3] and living cationic ring opening polymerization (LCROP) (Fig. 1, a); “grafting through” by SI-CuCRP from pre prepared macromonomers (Fig. 1, b). The mechanical properties, layer height, surface morphology, wettability, polymer structures and protein adsorption were studied. The accesses to functionalities have been tested by fluorescence labelling.

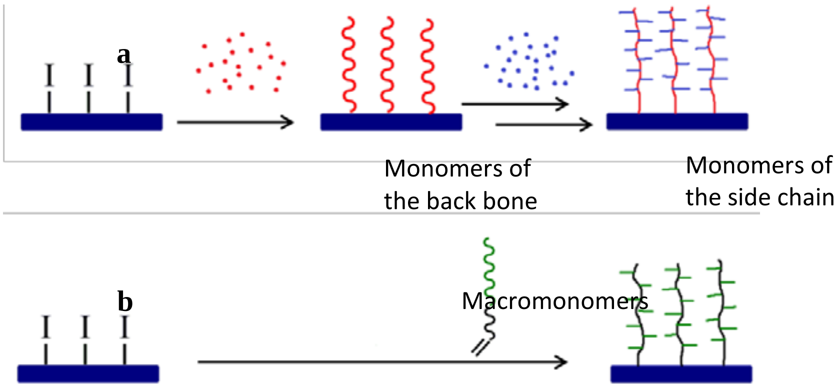

Figure 1: a, “grafting from” synthesis route of the polymer BBBs; **b**, “grafting through” synthesis route of the polymer BBBs. (I=initiator system)

[1] H. I. Lee, J. Pietrasik, S. S. Sheiko, K. Matyjaszewski: Prog. Polym. Sci. (2010) 35; p. 24–44.
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P20

POLY(3-HEXYTHIOPHENE) BRUSHES ON GRAPHENE

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When the exceptional properties of graphene and the broad variety of functionalities that can be introduced with polymer brushes are combined, new potential applications can be possible. Consequently, numerous publications appeared towards the functionalization of graphene.[1,2] For example, functionalized graphene can possibly be used as gas sensors,[3] flexible organic solar cells[4] or organic light emitting diodes (OLEDs).[5] Here we show a method to graft conducting and photoactive polymer brushes on large-area single layer graphene. Therefore, CVD-graphene is functionalized with three different initiator systems, a diazonium salt, a thin polymer layer of poly (4-bromo styrene) and small aromatic molecules (anthracenes and pyrenes). Subsequently, poly (3-hexylthiophene) (P3HT) is grafted via surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP). Each step is characterized by atomic force microscopy and Raman spectroscopy.

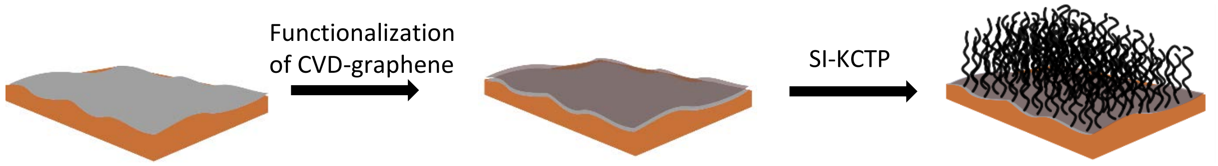

Figure1: Functionalization of single layer CVD-graphene and subsequent surface-initiated Kumada catalyst transfer polycondensation of 3-hexylthiophene.

[1] S. H. Lee, D. R. Dreyer, J. An, A. Velamakanni, R. D. Piner, S. Park, Y. Zhu, S. O. Kim, C. W. Bielawski, R. S. Ruoff. Macromol. Rapid Commun. (2010) 31 (3), 281–288.
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P21

MOLECULAR BRUSHES OF POLY(2-OXAZOLINE)S VIA CONTROLLED RADICAL POLYMERIZATION AND GRAFTING THROUGH

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Molecular brushes of poly(2-oxazoline)s (POx) are an interesting class of polymers, as they combine a unique macromolecular architecture with the promising properties of POx-based biomaterials.[1,2,3] We present a new synthetic pathway to such molecular brushes by using controlled radical polymerization of respective macromonomers, with the focus on aqueous ATRP at room temperature (Fig. 1).

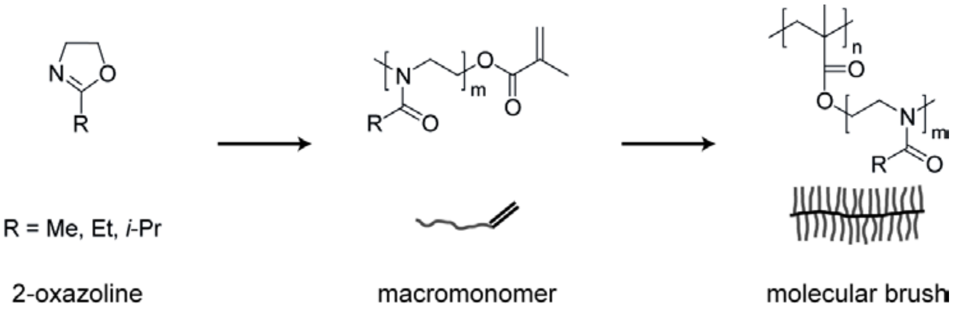

Figure 1: Synthesis of molecular brushes based on poly(2-oxazoline)s by *grafting through*.

Analysis of the synthesized brushes with ^{1}H-NMR, SEC and SEC-MALLS revealed maximum grafting densities, narrow molar mass distributions ($Đ \leq 1.16$) and molar masses, which were adjustable by different macromonomer-initiator ratios. Although kinetic studies imply slight deviation from ideal first order behavior, possible chain extension indicates living chain ends up to high conversions. Moreover, several of the molecular brushes show thermoresponsive behavior with a sharp and reversible phase transition. This new developed approach for the synthesis of molecular brushes based on POx is fast, controlled, robust, environmentally benign and efficient.

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P22

NANOPATTERNED POLYMER BRUSHES BY REACTIVE WRITING AND POSITIONING OF DNA ORIGAMI ON STIMULI-RESPONSIVE SURFACE FEATURES

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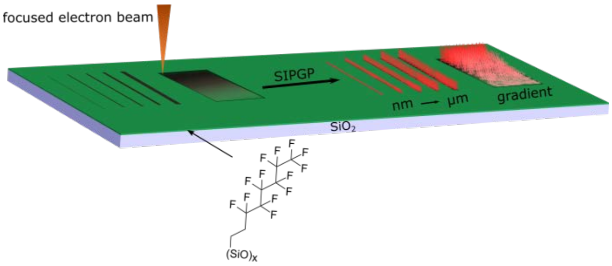
The fabrication capacity of electronic or photonic devices by conventional semiconductor based methods is limited. Self-assembled building blocks from DNA origami and nano-objects (hybrid structures) allow pushing the fabrication limitations by several orders of magnitude. However, the positioning of these hybrid structures into integrated circuits is a key challenge. Here we use stimuli-responsive polymer brushes for the controlled deposition of DNA hybrid structures.

Polymer brush patterns were prepared by a combination of electron beam induced damage in self-assembled monolayers (SAMs), creating a stable carbonaceous deposit, and consecutive self-initiated photografting and photopolymerization (SIPGP). This newly applied technique, reactive writing (RW), is investigated with *1H,1H,2H,2H*-perfluorooctyltriethoxysilane SAM (PF-SAM) on silicon oxide, which, when modified by RW, can be selectively functionalized by SIPGP.[1] With the monomer *N,N*-dimethylaminoethyl methacrylate (DMAEMA) we demonstrate the straightforward formation of polymer brush gradients and single polymer lines of sub-100 nm lateral dimensions, with high contrast to the PF-SAM background. This new technique expands the range of the already reported technique of Carbon Templating by giving the opportunity to not only vary the chemistry of the created polymer patterns with monomer choice but also vary the chemistry of the surrounding substrate.



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P23

BIOINSPIRED POLYMER CARPETS

D. Hafner[1], L. Ziegler[1], M. Ichwan[3], I. Amin[1,2], K. Hinrich[4], R. Jordan[1,2,*]*
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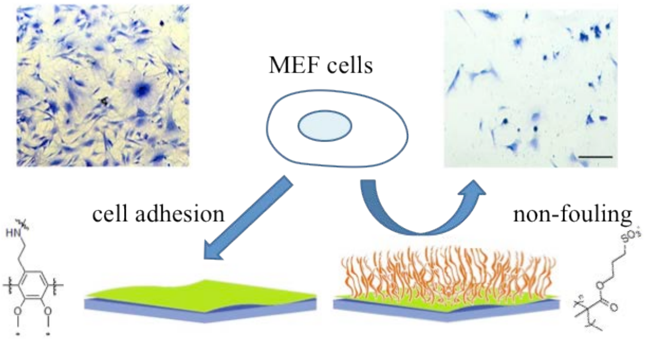
Two-dimensional (2D) mussel-inspired polydopamine (PDA) nanosheets, with thicknesses of tens of nanometers and a lateral size up to centimeters, are utilized as a functional substrate for grafting diverse polymer brushes via a simple self-initiated photografting and photopolymerization (SIPGP) method, leading to freestanding bioinspired polymer carpets[1]. The thickness of the carpets can be tuned by simply varying the photopolymerization time. The carpets are robust and stable against harsh conditions, not only during the detachment from its substrate, but also against many solvents after detachment. Furthermore, cell adhesion tests showed that PDA nanosheets promote cells growth and attachment whilst by simply grafting of 3-Sulfopropyl methacrylate (SPMA) on PDA nanosheets, the composite layers exhibit antibiofouling properties.



[1] D. Hafner, L. Ziegler, M. Ichwan, T. Zhang, M. Schneider, M. Schiffmann, C. Thomas, K. Hinrichs, R. Jordan, I. Amin. Advanced Materials 28 (2016) p. 1489–1494.

P24

MAGNETIC FUNCTIONALIZATION OF POLY(*N*-ISOPROPYLACRYLAMIDE) HYDROGELS FOR SENSOR APPLICATIONS

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To develop a universally applicable hydrogel sensor system suited for measuring the degree of swelling in real time, nanocomposite poly(*N*-isopropylacrylamide) (PNIPAM) hydrogels[1] were modified with Fe_3O_4 and CrO_2 nanoparticles (NPs). The sensor uses the Hall effect to depict the degree of swelling as an electrical signal.[2]

The hydrogel modification was first carried out with pristine NPs which resulted in gels with up to 50 w% NP content but went hand in hand with a decrease of the mechanical stability. This is the result of a decreasing network density which also leads to a higher degree of swelling. To counter these problems the particles were coated with 3-(trimethoxysilyl) propylmethacrylate to allow for a covalent bonding to the network structure.[3]

The effects on the network density and chain length of both coated and uncoated NPs were investigated via compression measurements und compared with one another. Furthermore the magnetic properties of the particles and the resulting hydrogels were characterized through vibrating sample magnetometer measurements.

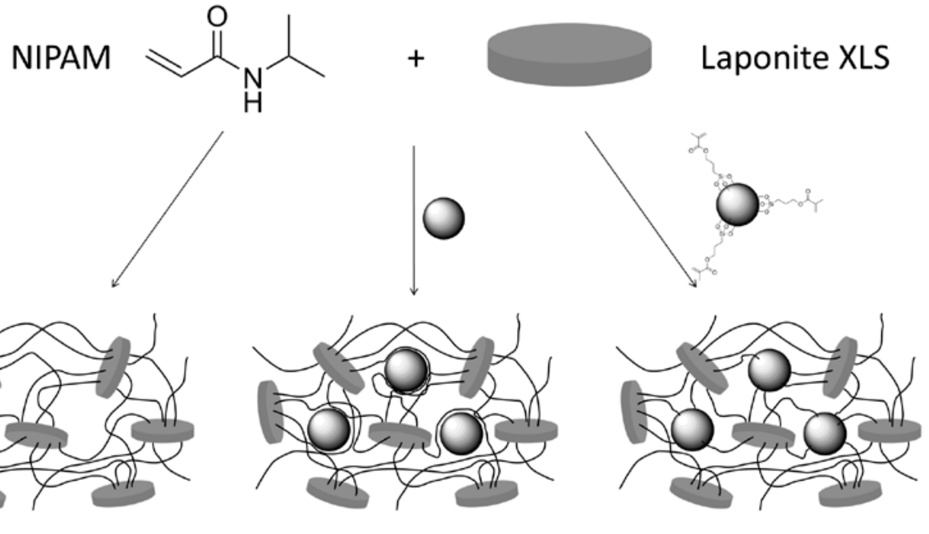

Figure 1: Synthesis of nanocomposite PNIPAM hydrogels with coated and uncoated magnetic nanoparticles

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P25

DEFINED PHOTO CROSSLINKED TETRA-PEG NETWORKS

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[2] *Technische Universität Dresden, Professur für Magnetofluiddynamik, 01069 Dresden, Germany*

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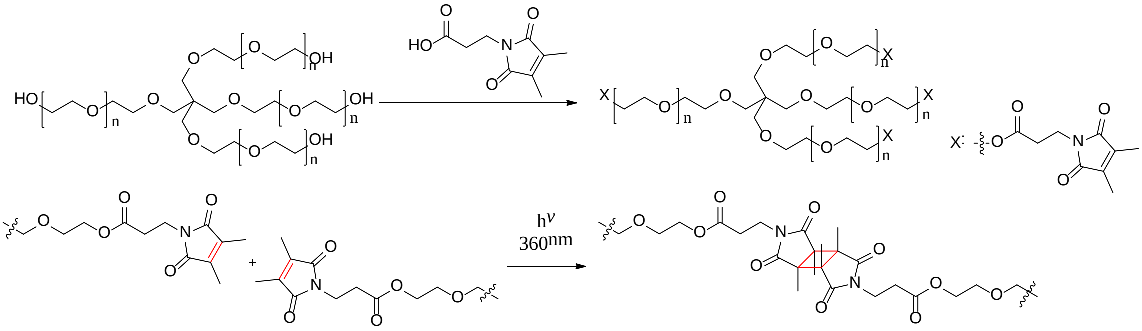
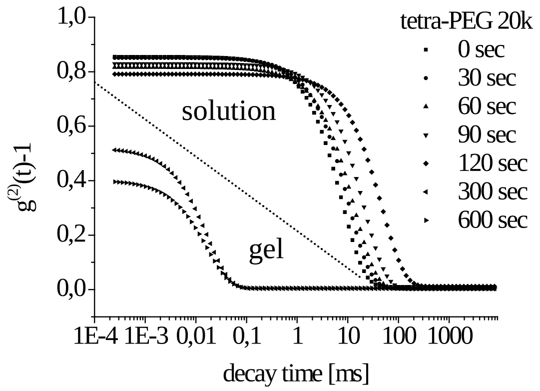
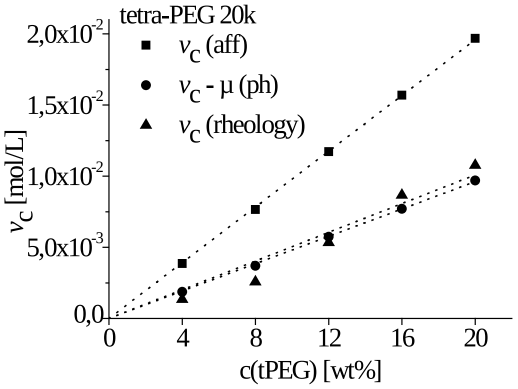
Tetra-PEG hydrogels, based on poly(ethylene glycol)-macromolecules with 4 arms of near the same length, were synthesized by photo-crosslinking reactions through UV-irridation. The Tetra-PEG's are terminated with maleimide anhydride groups. Light irridation induce a [2+2] cycloaddition through the maleimide doublebonds.[1]



In dependence of the molecular weight and concentration of the Tetra-PEG macromers investigations for conversion and swelling behavior were carried out. Dynamic light scattering was performed to get information about the gelation mechanism of the polymer networks.[2] Rheology measurements were done to get information about the mechanical properties of the gels. From the storage modulus G', the concentration of effective cains v_c was calculated and compared with the values determined from the conversion. This was done considering the affine and free fluctuating (phantom) network model.[3]





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P26

LIGHTS ON! A SIGNIFICANT PHOTOENHANCEMENT EFFECT ON ATRP BY AMBIENT LABORATORY LIGHT

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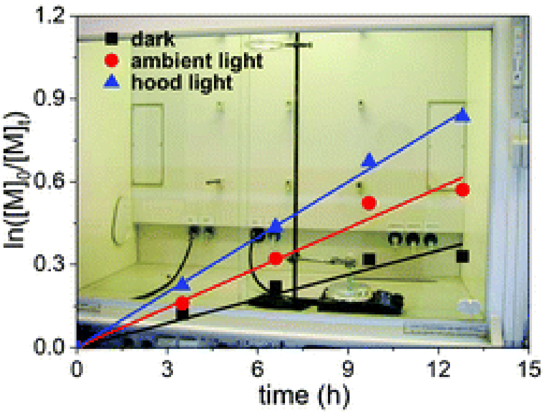
Recently we reported on photoinduced ATRP using a household fluorescent lamp as the light source (T. Zhang, et al., Polym. Chem., 2014, 5, 4790).[1] Results implied that typical laboratory light might have a considerable impact on the ATRP reaction as fluorescent lamps are commonly used for ceiling and fume hood illumination. This initiated a recent concern on the contribution of photochemistry in activator regeneration in ATRP.[2,3] Here, we show the influence of ambient laboratory light on AGET, ARGET, and classical ATRP reactions. Except for ARGET ATRP, for all other ATRP types a significant photoenhancement effect by light originating only from fluorescent lamps was observed. A standard fume hood illumination caused the strongest influence.[4]



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P27

SYNTHESIS OF POLYMER NANOTUBES VIA PHOTOPOLYMERIZATION OF CROSSLINKING UNITS

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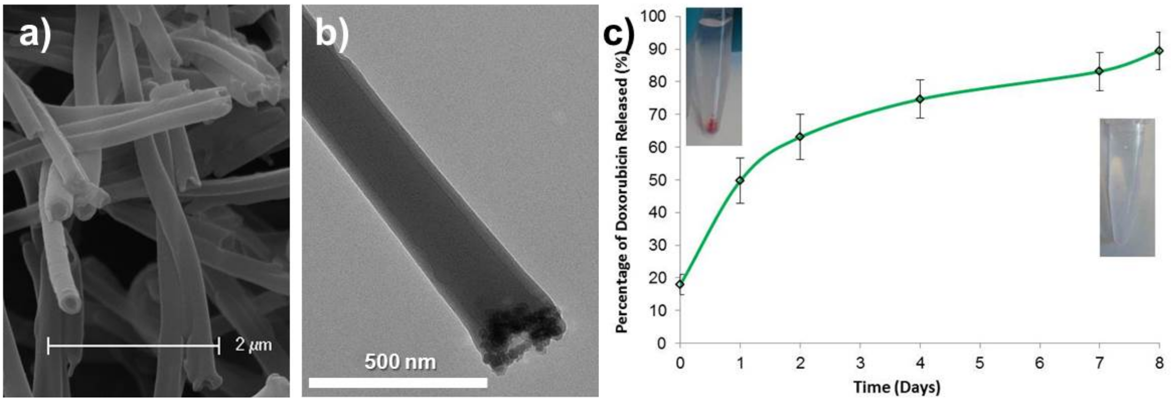
This work represents a simple route to flexible, polymer nanotubes that can be functionalized in situ for applications in drug delivery. Whilst the vast majority of research into high aspect ratio nanoscale drug delivery systems has focused on carbon nanotubes (CNTs), there are certain drawbacks associated with the use of CNTs. The intrinsic toxicity and lack of biodegradation are two of such factors which must be addressed for eventual use in the body, while the high strength displayed by CNTs is not necessarily required for drug delivery.

In contrast, from a range of crosslinkers we have produced polymer nanotubes which are less toxic than multi-walled carbon nanotubes (MWCNTs) of comparable dimensions. A cyclized homopolymer of ethylene glycol dimethacrylate was used,[1] and photocrosslinked within a sacrificial template to yield nanotubes of controlled diameter, but varied length (Fig **a**).

Furthermore, these nanotubes show the ability to be functionalized in situ with iron oxide nanoparticles (Fig **b**) to yield magnetic sensitivity. Another benefit over the MWCNTs is that they uptake both fluorescent dyes and the drug doxorubicin (Fig **c**). This turns the white nanotubes pink, which slowly fades over the course of a week as the doxorubicin is released over a sustained period (quite remarkable for such small, high surface area structures).

This is a work in progress[2] and we are currently investigating methods of synthesizing nanotubes with defined lengths and also ways to produce nanotubes with various surface charges.



Scanning electron microscope image **(a)** of polymer nanotubes synthesized via a sacrificial aluminium template showing the open pore ends and controlled diameter. Transmission electron microscope image **(b)** of an *in situ* functionalized nanotube to give magnetic sensitivity at one end. These nanotubes can be loaded with doxorubicin **(c)** which is released over a period of one week.

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P28

GMA-BLOCKCOPOLYMERS FOR COVALENT LINKAGE TO HYBRID SURFACES OBTAINED BY TWIN POLYMERIZATION

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The freezing of technical surfaces is a widespread problem that involves high costs and impairs safety and functionality. There exist some approaches to prevent the icing on surfaces using passive operating coatings. They base on different mainly biomimetic concepts and include hydrophobic and/or hydrophilic layers.[1] One approach uses thin hydrophilic covalently bonded polyethylene glycol (PEG) containing layers, which reduce the ice adhesion on the surfaces.[2]
The (simultaneous) twin polymerization (STP) is a one-step method for producing nanostructured, organic-inorganic, stable hybrid material of composition and morphology on demand.[3] The introduction of functional groups (e.g. NH$_2$-groups) within one of the twin monomers leads to hybrid materials, which bear these functionalities and offer new perspectives regarding their application as adhesion promoter between technical surfaces and functional polymers.
In this work a number of block copolymers containing PEG side groups in the first block (A) and anchor groups for bonding onto surfaces in a second block (B) were synthesized. Figure 1 shows the concept of synthesis and anchoring on surfaces of these polymers.

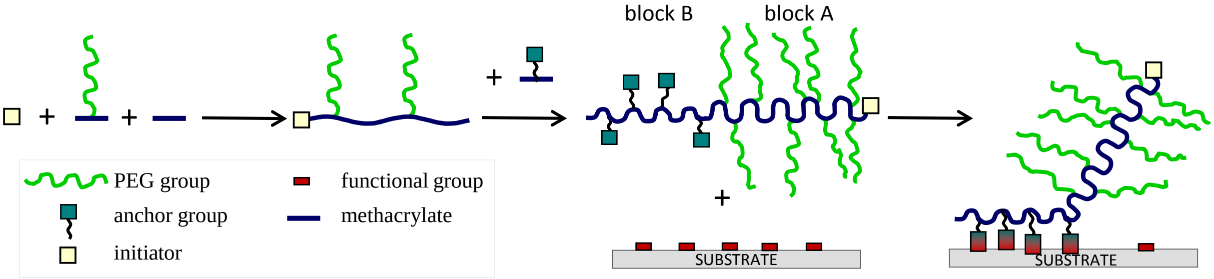

Figure 1: Principle of the synthesis of the functional block copolymers based on methacrylates and their bonding onto surfaces with reactive groups.

The polymerization of the block copolymers was realized by ATRP in a one pot procedure. Several polymers with varying ratios of the components incorporated in block A were synthesized. Two lengths of PEG were used and as additional groups *t*-butyl methacrylate units were incorporated, which can be acidolyzed after production of layers. For block B glycidyl methacrylate units were used as anchor groups, which are able to react with surface amino groups of the hybrid materials obtained by STP. The polymers were characterized by NMR spectroscopy, GPC and DSC.
The attachment of the polymers onto STP hybrid particles with amino functionalities was proofed by ^{13}C-{1H}-CP-MAS-NMR spectroscopy and FTIR investigations. Furthermore amino functional layers resulting from STP were used as substrate for these polymers. The STP layers and polymer coated STP layers were investigated by X-ray photoelectron spectroscopy (XPS).

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P29

IN-SITU CHARACTERIZATION OF STIMULI-RESPONSIVE POLYMERIC VESICLES BY AF4

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In (bio-)medicine, polymersomes are a class of self-assembled macromolecules in artificial vesicles with bilayer morphology similar to liposomes. Polymersomes are made using amphiphilic synthetic block copolymers to form the vesicle membrane, and have radii ranging from 50 nm up to a few micrometers.[1,2] Usually polymersomes contain an aqueous solution in their core and are useful for encapsulating and protecting sensitive molecules, such as drugs, enzymes, or other proteins.[3,4] The stimuli-responsive polymersomes‘ membrane provides a physical barrier that isolates the encapsulated material from external media, such as those found in biological systems.

Asymmetric flow field flow fractionation (AF4) is a versatile separation method suitable especially for the gentle separation and characterization of these molecular assemblies under varied conditions. Due to the lack of a stationary phase, interactions and shear forces are minimized. In this contribution, we will present pH sensitive polymersomes for the triggered loading and release of cargo. AF4 coupled to static and dynamic light scattering detection enables a comprehensive characterization of molar mass, molecular size and scaling behaviour of different loading stages of polymersomes.

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P30

TEMPERATURE DEPENDENT SIZE EXCLUSION CHROMATOGRAPHY FOR THE IN SITU INVESTIGATION OF DYNAMIC BONDING/DEBONDING REACTIONS

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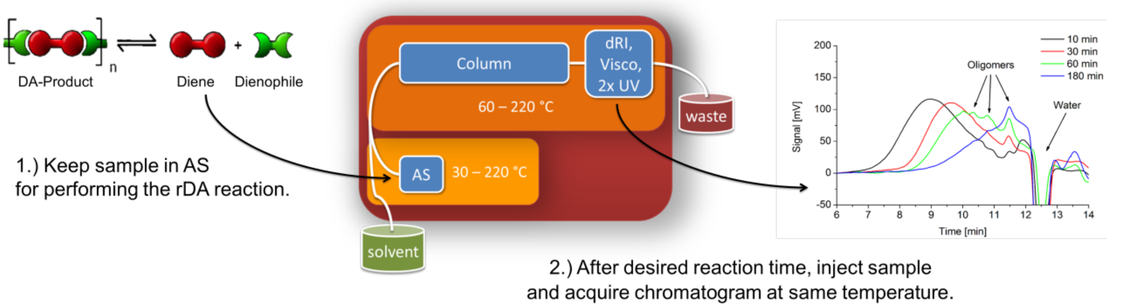
Polymers capable of thermally controlled reversible bonding reactions are promising candidates for stimuli responsive materials, as required for self-healing or drug delivery materials. Making a material ready for a particular application requires tailoring its performance to the exact needs of the desired application. Therefore the parameters that allow controlling the dynamic reactions behavior have to be deduced, which requires access to effective analytical tools. The analysis of reversibly bonding polymers is a particular challenge, as not only the polymers but can also the respective bonding reactions have to be investigated.[1] Herein, we employ size exclusion chromatography in a newly developed temperature dependent mode (TD SEC) for the *in situ* characterization of polymers that undergo retro Diels-Alder (rDA) reaction at temperatures higher than 60 °C. Monitoring the evolution of the molar mass distribution of the polymers during the rDA reaction and evaluating the data quantitatively gives detailed information about the extent of the reaction and allows elucidating structural parameters that can be used for controlling the polymers debonding behavior.[2,3,4,5]



In contrast to spectroscopic techniques, TD SEC analyzes only the size of the polymers and, hence, the polymers under investigation do not need to fulfill any particular requirements (e.g. presence of detectable functional groups) besides being soluble in a TD SEC. Therefore, TD SEC is applicable for a broad variety of different polymer systems. The analyses can be in a broad temperature range and in different solvents. An *in situ* image of the reaction is provided as analysis and reaction occur under identical conditions. Using multiple detectors (dRI, UV/Vis and Viscosity) enables conclusions about molar mass but also chemical composition and structural attributes (e.g. degree of branching).

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P31

THE BIFURCATION OF DYE DIFFUSION COEFFICIENT IN BULK POLYMER FILM BELOW GLASS TRANSITION

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In this study the dynamics of 9,10-phenanthrenequinone (PQ) molecules in the melt of short poly(4-methyl styrene) (PpMS) chains of 15 kg/mol molecular weight with polydispersity of 1.05, which was obtained by freeze drying its unentangled solution, was investigated below the glass transition temperature (T_g 106 °C) by means of Forced Rayleigh Scattering (FRS). The bifurcation behaviour of the diffusion coefficient dependency was revealed in this temperature region. Temperature and spatial scale dependencies of apparent diffusion coefficients (Fig. 1) have shown that the dynamics of the slower process obeys WLF law, while the faster one demonstrates activation mechanism of the dye movement. On the other hand, aging experiments below T_g have revealed changes in the ratio of both contributions. This gave rise to the explanation that at such temperatures there are dynamical ordered polymer structures with relatively short time of existence – dynamical heterogeneities, which govern dye's movement processes.

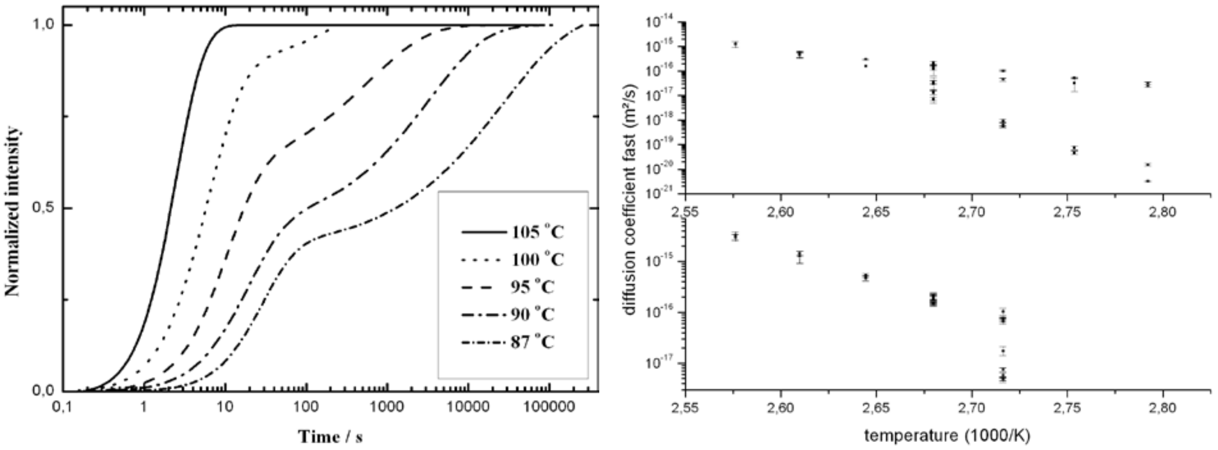

Figure 1: To the left: normalized diffracted light intensity vs. time (analogous to the intensity correlation function). Reflection gratings with 180 nm spacing were consequently recorded in different spots of the PQ-doped PpMS sample and read out at five different temperatures (consequentially downwards). To the right: a comparison of the apparent diffusion coefficient of the free dye for three different spatial scales: 170 and 190 nm (above, merged) and 430 nm (below).

Although these heterogeneities are commonly supposed to be of the order of few nanometres closely above T_g[1], some other studies for glass-forming liquids have shown the presence of domains up to hundreds of nanometres[2]. Also, the similar effect for translational diffusion was observed by H-FRAP in polystyrene.[3] This, as well as the reasonable expectation of heterogeneities to grow upon cooling below glass transition, explains our ability to sense them with FRS. Further investigations with model systems prepared from solutions with higher concentrations and higher molecular weights are in the focus of the ongoing work.

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P32

HYDROGEN-BONDED SUPRAMOLECULAR BIS-UREA-BASED POLYMERS ON SOLID SUPPORT: COMPUTATIONAL INSIGHTS INTO BOTTOM-UP SELF-ASSEMBLY

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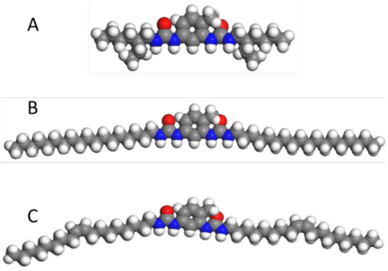
Supramolecular polymers, i.e. arrays of low-molecular-weight building blocks, usually held together by hydrogen bonding (HB) or other reversible noncovalent interactions. Bis-urea-based molecules with central bis-urea fragment exhibit the highest supramolecular polymerization ability, affording well-defined tape-like supramolecular nanofibers in a variety of organic solvents.[1]

In this poster presentation, two major points concerning the arrangement and properties of hydrogen-bonded bis-urea molecules EHUT, ODUT and OLUT (Scheme 1) on surfaces studied by combining density functional theory calculations and all-atom molecular dynamics simulations will be addressed.



Scheme 1: Corey-Pauling-Koltun representation of the objects of the study: A - *EHUT* (2-ethylhexyl-3-[3-(3-(2-ethylhexyl)ureido)-4-methylphenyl]urea), B – *ODUT* (2,4-bis(N,N’-octadecylureido)-toluene) and C – *OLUT* (2,4-bis(N,N’-oleylureido)-toluene) [2, 3].

The electronic properties of a single EHUT molecule, hydrogen-bonded dimers and tapes have explained the experimentally observed “mirage” effect, when some of the assembled molecules become invisible in STS images of molecules on gold surface. Calculations revealed that this effect is related to the energy splitting which can be explained by intermolecular HB interactions.

The ordering dynamics of both ODUT and OLUT molecules which differ only by a single cis-double bond in their side groups has been tested in all-atom molecular dynamics simulations. Modelling demonstrated that at early stages of self-assembly on graphite, the double bonds of OLUT favoured kinks at the level of individual molecules, which induced transient steric constraints hindering the spontaneous formation of long supramolecular polymers. In addition, due to these kinks, molecule–substrate interactions were weakened. At later stages, however, due to a progressively increasing number of directional intermolecular HBs between, the self-assembly process improved and thereby increased the length of the supramolecular polymers. ODUT molecules containing side chains with saturated bonds, owing to a better commensurability with the substrate lattice, formed ordered structures of supramolecular polymers. Observed difference in temporal stability can be attributed to a rapid alignment of molecules on the surface and thus rapid formation of supramolecular polymers. This faster alignment process translates into a higher nucleation rate for molecules with saturated side chains.

This work was done as a collaborative research between the Leibniz Institute of Polymer Research Dresden, the University of Freiburg, the Université Paris-Sorbonne and the Institut de Science des Materiaux de Mulhouse.[2,3]

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P33

MICROSTRUCTURE VERSUS SHAPE EFFECT IN MAGNETO-SENSITIVE ELASTOMERS

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Magneto-sensitive elastomers are composites that consist of magnetically permeable microparticles incorporated into an elastic polymer matrix. As a magnetic field is applied to such material a deformation and changes in the mechanical moduli take place. The sign and strength of the material response crucially depends on the actual distribution of the magnetizable particles and wether or not these particles can additionally rearrange with respect to the surrounding polymer network.
Based on a dipole approximation for the magnetic interactions we develop a mean-field approach for the description of magneto-sensitive elastomers. In accordance with experimental observations [1] we allow the formation of elongated microstructures in direction of the applied magnetic field. It turns out that the case of elongated structure formation can be solved very efficiently in the 3-dimensional thermodynamic limit. Therefore, we are able to systematically study the behavior of magneto-sensitive elastomers for a great range of the parameters. The results of our mean-field model are compared with the predictions of a microscopic contiuum model of similar composites proving our approach to work rather well.

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P34

DYNAMIC MODULI OF MAGNETO-SENSITIVE ELASTOMERS

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Magneto-sensitive elastomers (MSEs) establish a special class of smart materials, which are able to change their shape and mechanical behaviour under external magnetic field. Nowadays, MSEs are one of the most perspective smart materials, since they can be used for design of functionally integrated lightweight structures in sensors, robotics, actuators and damper applications.

MSEs typically consist of micron-sized magnetizable particles (e.g. carbonyl iron) dispersed within a non-magnetic elastomeric matrix. The spatial distribution of magnetic particles in MSEs can be either isotropic or anisotropic, depending on whether they have been aligned by an applied magnetic field before the cross-linking of the polymer. Depending on the magnetic properties of the particles, their shape, size and spatial distribution, the MSEs can exhibit different mechanical behaviour.

There are a lot of experimental works, theoretical studies[1,2] and computer simulations devoted to mechanical properties of MSEs in the equilibrium (static) state. On the other hand, very important topic is the dynamic-mechanical behavior of MSEs, since in various technical applications these materials can be influenced by the oscillating mechanical loading. There are a lot of experimental works which discuss the influence of the external magnetic field on the frequency dependences of the storage G' and loss G'' moduli. It was shown that the values of G' and G'' at a given frequency depend on the magnitude of the external magnetic field. For the shear geometry with the shear velocity perpendicular to the magnetic field vector **H** both G' and G'' are found to increase with the increase of the magnitude of external magnetic field at fixed frequency. Influence of structural parameters, such as the volume fraction of the magnetic particles and the degree of cross-linking of an elastomeric matrix, on the dynamic mechanical behavior of MSEs under magnetic field has been discussed in a number of experimental works.

In the present study the dynamic mechanical behaviour of magneto-sensitive elastomers (MSEs) with isotropic, chain-like or plane-like distributions of magnetic particles is investigated theoretically in a low-frequency regime under a uniform external magnetic field. We introduce a coarse-grained network model,[3] in which magnetic particles are distributed on the sites of a tetragonal lattice. The lattice anisotropy is defined by the ratio α of average distances between neighboring particles along and perpendicular to the symmetry axis of an MSE $\alpha = \langle r_{\parallel} \rangle / \langle r_{\perp} \rangle$: isotropic distribution ($\alpha = 1$), chain-like distribution ($\alpha < 1$) and plane-like distribution ($\alpha > 1$).

Equations of motion for magnetic particles take into account the influence of the elastic network and magnetic interactions between the particles under external magnetic field. It is shown that the relaxation spectrum depends on the anisotropy parameter α. The shear dynamic moduli G' and G'' of MSEs are calculated for different geometries of application of the oscillating shear strain with respect to the magnetic field **H**, which is directed along the symmetry axis of the MSE. It is shown that the application of the magnetic field leads to the anisotropy of the storage G' and loss G'' moduli. Moreover, G' and G'' can change up to one-two orders of magnitude in agreement with experiments.

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P35

VISUALIZATION OF CONTACT STRESS DISTRIBUTIONS FROM MECHANO-RESPONSIVE POLYELECTROLYTE BRUSHES

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In nature, animals and plants have developed hierarchically structured fibrils to adhere to different kinds of rough and smooth surfaces. By mimicking their contact geometry on pillar microstructures, the adhesion enhancement can be adapted. In particular, annular overhangs at the edges of the pillars (T-shapes) lead to a significant increase in adhesion compared to similar flat punch pillars.[1,2] Theoretical work predicted fundamentally different contact stress distributions for these geometries. Resulting in different failure modes, the detachment behavior of flat punch and T-shape micropillars has been investigated to approach experimental evidence.

We use a mechano-responsive polyelectrolyte brush to directly measure the contact stress distribution of flat punch and T-shaped micropillars. Therefore, a polycationic brush structure is polymerized grafting from surface and labeled with a fluorescent dye.[3] Dependent on the conformation of the brush structure, the dye can be quenched by the polyelectrolyte. Therefore, compression and tension can be distinguished locally from the fluorescence intensity. The fluorescence is read out spatially resolved with confocal laser scanning microscopy. The setup is combined with a micro-contact printer to control the approach and the retraction of the micropillar arrays. From the local fluorescence, compressive and tensile stresses could be resolved spatially in the contact area of the micropillars.[4]

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P36

SELECTIVE GLIOBLSATOMA MULTIFORME-CANCER STEM CELL TARGETING BY GOLD NANORODS IN MMP-CLEAVABLE 3D HYDROGELS

D. P. N. Gonçalves[1,*], *R. D.Rodriguez*[2], *L. J. Bray*[1], *M. Binner*[1], *C. Jungnickel*[1,3], *F. N. Gür*[4], *S. W. Poser*[5], *T. L. Schmidt*[4], *D. R. T. Zahn*[2], *A. Androutsellis-Theotokis*[5], *M. Schlierf*[3], *C. Werner*[1]

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Cancer stem cells (CSCs) are responsible for therapy resistance and tumor recurrence in Glioblastoma Multiforme (GBM).[1.2.3] Since nestin is a putative marker of the GBM-CSC phenotype,[4] gold nanorods (AuNRs) functionalized with a nestin binding peptide were developed for GBM-CSC selective targeting. Three-dimensional (3D) bioengineered tumor-microenvironments were developed as a test platform to assess the anti-tumor activity of AuNRs. We observed that GBM-CSCs were selectively and efficiently destroyed via plasmon-induced hyperthermia when irradiated with an 800 nm near infrared (NIR) laser.

[1] R. Stupp, W. P. Mason, M. J. van den Bent, M. Weller, et Al: N. Engl. J. Med. (2005) 352, p. 997–1003.
[2] S. Bao, Q. Wu, R. E. McLendon, Y. Hao, et al: Nature (2006) 444, p. 756–760.
[3] H. Brem, S. Piantadosi, P. C. Burger, M. Walker, et al: Lancet (1995) 345, p. 1008–1012.
[4] X. Jin, X Jin, J. E. Jung, S. Beck, H. Sim: Biochem. Biophys. Res. Commun. (2013) 433, p. 496–501.

P37

SELF-HEALING CONCEPTS FOR BROMOBUTYLRUBBER – SUPRAMOLEKULAR BOND FORMATION BY IONIC INTERACTIONS AND HYDROGEN BONDS

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Bromobutylrubber (BIIR) is a material of high practical importance e.g. as inner layer for rubber tires or in medicine as stoppers. Therefore, the implementation of self-healing properties utilizing dynamic reversible interactions is of great interest. Two different strategies were pursued to achieve self-healing properties.

The ionic modification of BIIR was recently published to achieve a physically well crosslinked self-healing elastomer.[1] The relatively small number of reactive bromine groups in BIIR (approx. 1 mole%) limits the amount of ionic bonds in this system. Therefore 1-chlorohexylimidazole was synthesized which is able to polymerize and graft to the rubber backbone simultaneously. By this way, longer side chains of a polyionic liquid can be attached to BIIR which allows to introduce more ionic groups whereby a covalent crosslinking is prevented. The ionic clusters which are formed by the ionic groups within the BIIR are responsible for the self-healing properties observed.

The second approach is based on hydrogen bonds between complementary functional groups covalently attached to the rubber and particular additives. The first step is the functionalization of the BIIR with hydrogen donor/acceptor groups to get potential linking points for self-healing interactions. These modification reactions are performed on the reactive bromine groups in BIIR. After blending of the grafted BIIR with a bifunctional cross-linker the formation of a reversible hydrogen bonded supramolecular network is assumed.

With both concepts it is possible to form a loose polymeric network which is assumed to heal damages by temperature or stress induced rearrangements. The thermo-mechanical behavior of the materials was characterized by different mechanical methods like dynamic mechanical analysis, stress-strain tests and curing tests.

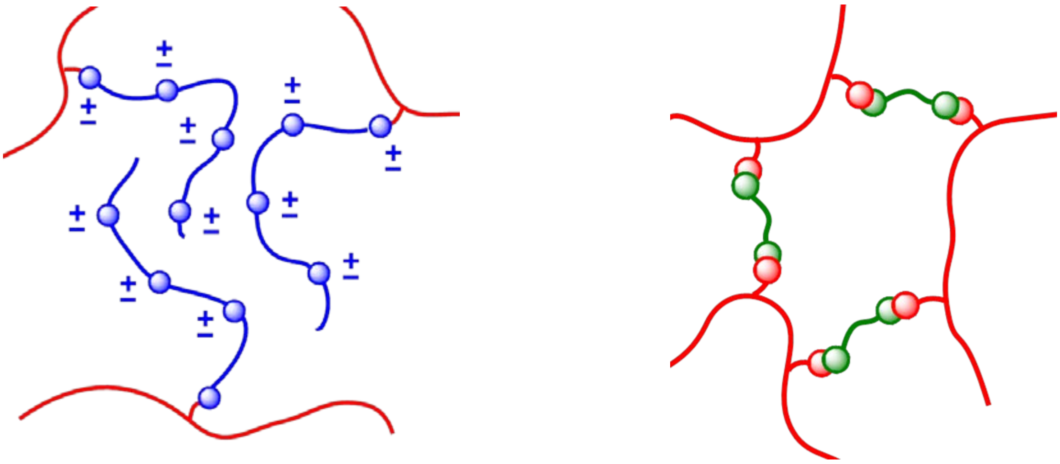

Figure 1: General concept of a supramolecular network via ionic interactions (left) and via self-complementary bifunctional linker with functionalized polymeric rubber chains (right)

[1] A. Das, A. Sallat, F. Böhme, M. Suckow, D. Basu, S. Wiessner, K. W. Stöckelhuber, B. Voit, and G. Heinrich, *ACS Appl. Mater. Interfaces*, vol. 7, no. 37, pp. 20623–30, Sep. 2015.

P38

SWITCHABLE ELASTICITY OF NOVEL CORE-SHELL MICROGELS WITH CONSTANT ADHESION PROPERTIES - A MICRO-MECHANICAL STUDY

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We present a novel class of thermo-responsive core-shell microgel particles. They allow to change their mechanical properties while their adhesive properties remain unaffected. The switching is introduced by a thermo-responsive hydrogel core exhibiting a volume phase transition, *e.g.* poly(N-isopropylacrylamide). Exceeding its lower critical solution temperature, the microgel deswells, densifies, and therefore becomes stiffer. Usually, this process is accompanied by a change in interfacial interaction forces since the microgel switches from hydrophilic to hydrophobic.[1] These effects can be decoupled from each other by encapsulating the microgel in a thermally non-responsive polyacrylamide shell in a droplet-based microfluidics approach.[2] Using colloidal probe AFM, we validated the constant adhesion properties of such core-shell particles between 28 and 40 °C. Further, we have proven that the elastic changes of the core material are preserved attenuatedly in the corresponding core-shell microgel particles.

[1] S. Seiffert, J. Thiele, A. R. Abate, D. A. Weitz, *J. Am. Chem. Soc.* (2010) *132*, 168.
[2] S. Schmidt, M. Zeiser, T. Hellweg, C. Duschl, A. Fery, H. Möhwald, *Adv. Funct. Mater.* (2010) *20*, 3235.

P39

TWO PHOTON SYNTHESIS OF BIOHYBRIDE HYDROGELS

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Polymeric biomaterials often aim at mimicking three-dimensional (3D) anatomical structures capable of supporting the regeneration of living tissues. Multi photon processes attract great attention in the 3D structuring of polymer-based materials as they can provide superior spatial control when compared to one-photon photochemistry. Such techniques are especially attractive for biological and medical applications as they can be applied within the “biocompatible” wavelength window (700-1200 nm). Research activities focusing on two photon applications in chemistry and material science have been increased over the last decade. The main limitation of two photon chemistry in biological applications is the low efficiency of the photoreactions which requires photo-initiators and chemically complex reactants as well as their conjugation to polymers. In the presented work we describe a previously unknown two photon catalyzed 2-2 cycloaddition reaction of maleimides. This reaction does not require any photo-initiators and can be applied to a great variety of readily available commercial maleimide containing polymers, fluorescent labels as well as bio-conjugates. The high efficiency of the explored approach is demonstrated for the formation of structured biohybrid polymer hydrogels in aqueous solutions and cell culture media.

P40

CELL-INSTRUCTIVE BIOHYBRID HYDROGELS WITH ADAPTABLE PHYSICOCHEMICAL PROPERTIES

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The native extracellular matrix (ECM) consists of versatile types of supramolecular elements which define mechanical as well as chemical signals and therefore direct cell fate decisions. Compromising these signals is critically important for fully understanding cell–tissue interactions. For that purpose, a thoroughly studied hydrogel system consisting of the synthetic poly (ethylene glycol) (PEG)[1] and the bioactive, highly charged glycosaminoglycan heparin was modified to incorporate poly(oxazolines) (POX) –instead of PEG- as more versatile structural network building blocks. POX, synthesized by linear cationic ring opening polymerization (LCROP) of 2-substituted oxazolines[2], can be utilized to produce thermoresponsive gels with increased hydrophobicity at higher temperatures. Accordingly, the resulting hydrogel matrices should display tunable physico-chemical properties that are defined by the high anionic charge of the sulfated GAG and the partially hydrophobic side chains of the POX. The storage moduli and the swelling behavior of the resulting hydrogels were controlled by the polymer structure as well as the solution temperature. The so modified set of tunable materials will be exemplarily used to modulate growth factor release and enable cell sheet harvesting, referring to the requirements of cell transplantation approaches[3]. In sum, we demonstrate that POX-heparin hydrogels provide valuable new options for tissue engineering applications.

[1] U. Freudenberg, A. Hermann, P. Welzel, K. Stirl, S. Schwarz, M. Grimmer, A. Zieris, W. Panyanuwat, . S. Zschoche, D. Meinhold, A. Storch, C. Werner. Biomaterials (2009) 30; p. 5049-5060.
[2] R. Luxenhofer, Y. Han, A. Schulz, J. Tong, Z. He, A. Kabanov, R. Jordan. Macromol. Rapid Commun. (2012) 33; p. 1593-1719.
[3] J. Teichmann, M. Nitzschke, D. Pette, M. Valtink, S. Gramm, F. Härtel, T. Noll, R. Funk, K. Engelmann, C. Werner. Science and Technology of Advanced Materials (2015) 16; pp. 13.

P41

SELF-ASSEMBLED PLASMONIC CORE/SATELLITE NANOCLUSTERS

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We present the protein-assisted self-assembly of small spherical gold or silver NPs (as satellites) with a hydrophilic protein corona onto larger gold NPs (as cores) into three-dimensional nanoassemblies with core/satellite architecture (see Figure 1). The resulting dispersions exhibit high colloidal stability and allowed for the precise characterization of the core/satellite architecture in dispersion by small-angle X-ray scattering (SAXS). By combining the results from SAXS, UV/Vis spectroscopy, and electromagnetic simulations we were able to correlate the structural parameters with the plasmonic coupling within the core/satellite nanoclusters. [1] Strong near-field coupling between the building blocks results in distinct regimes of dominant satellite-to-satellite and core-to-satellite coupling. High robustness against satellite disorder was proved by UV/Vis diffuse reflectance (integrating sphere) measurements. Generalized multi particle Mie theory (GMMT) simulations were employed to describe the electromagnetic coupling within the nanoassemblies. The modularity in building block sizes and composition allows for tailoring of optical and structural characteristics - which opens new avenues for surface-enhanced spectroscopy applications *e.g.* SERS. [2]

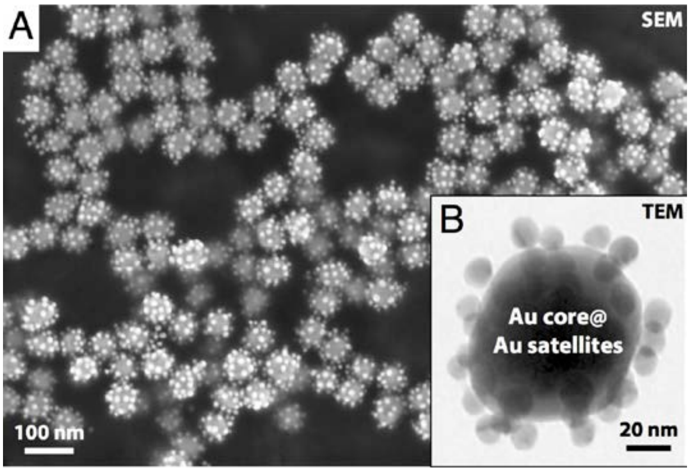

Figure 1: (A) Self-assembled corFLeibnize/satellite nanoclusters based on small gold NPs (16 nm) as satellites adsorbed onto larger gold NPs (84 nm) as cores. (B) The inset shows a single nanocluster indicating a high surface coverage of satellites close to the jamming limit.

[1] R. P. M. Höller, M. Dulle, S. Thomä, M. Mayer, A. M. Steiner, S. Förster, A. Fery, Ch. Kuttner, M. Chanana. *ACS Nano* (2016), DOI: 10.1021/acsnano.5b07533.
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P42

MODELING OF A CONCENTRATION-TRIGGERED MICRO-VALVE

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Stimuli-sensitive hydrogels are gaining more and more importance for highly dynamic microsystems. Their exceptional chemo-physical swelling behavior has found use especially in sensor-actuator systems of micro-fluidic applications (chemofluidic oscillator [1], pH-sensor [2] or self-folding scaffolds for cell alignment [3]). Hydrogels like Poly(N-isopropylacrylamide) (PNIPAAm) show enormous potential, but are difficult to fabricate and to control in their behavior. To better understand the nature and effects of stimuli-sensitive hydrogels, a computer-based model is created for a chemo-responsive hydrogel within a micro-valve.

We present a finite element model for a transistor-like microfluidic valve. In order to mathematically reproduce the chemical interaction within a finite element model, a thermal analogy for an alcohol-dependent phase-change of hydrogels is used. Hereby in ANSYS®, the thermal-mechanical solver describes hydrogel swelling (Fig. 1) and is coupled with the fluid solver to model the fluidic behavior of the valve (Fig. 2). The resulting behavior is implemented into a circuit model (Fig. 3) to more efficiently evaluate the performance of microfluidic chips.

These tools help to better understand, predict and visualize the behavior of hydrogels and support the development of modern micro-scaled applications.

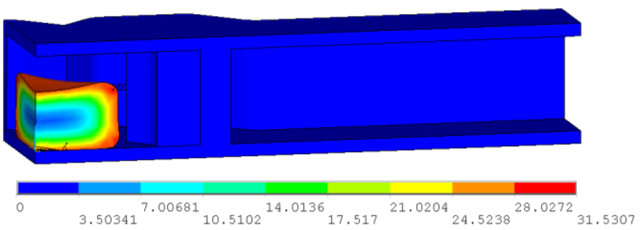

Figure 1: Hydrogel expansion of a quarter micro-valve caused by temperature diffusion after 13 % swelling, modeled in ASNYS.

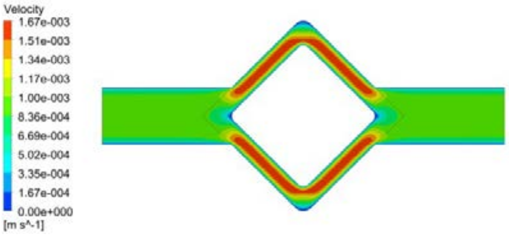

Figure 2: Fluid velocity plot for a 66% closed micro-valve modeled in ANSYS CFX.

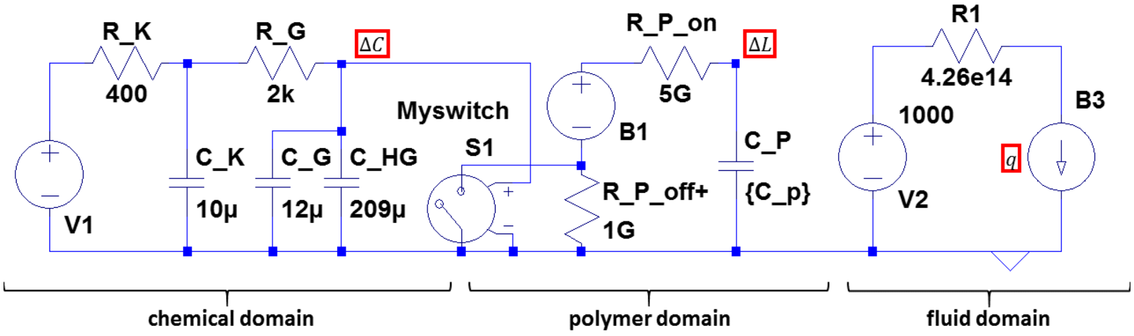

Figure 3: Circuit model of the micro-valve with chemical domain to replicate the concentration diffusion, polymer domain to determine the length change of the hydrogel and fluid domain for the volume flow of the micro-valve.

[1] G. Paschew et al. Advanced Materials Technologies (2016) DOI:10.1002/admt.201600005.
[2] G. Gerlach et al. Chemical (2005) p. 555-561.
[3] Ph. J. Mehner et al. Toward engineering biological tissues by directed assembly and origami folding. Origami6: II. Technology, Art, Education (2015) ISBN:978-1-4704-1876-2.

P43

MAGNETORESPONSIVE BIOREACTORS FROM SELF ASSEMBLED OLIGOPEPTIDE

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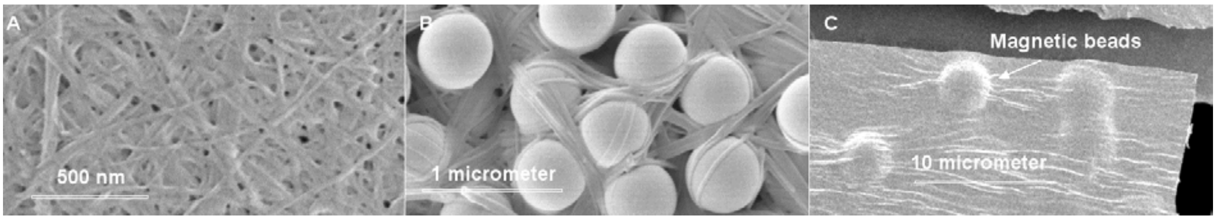
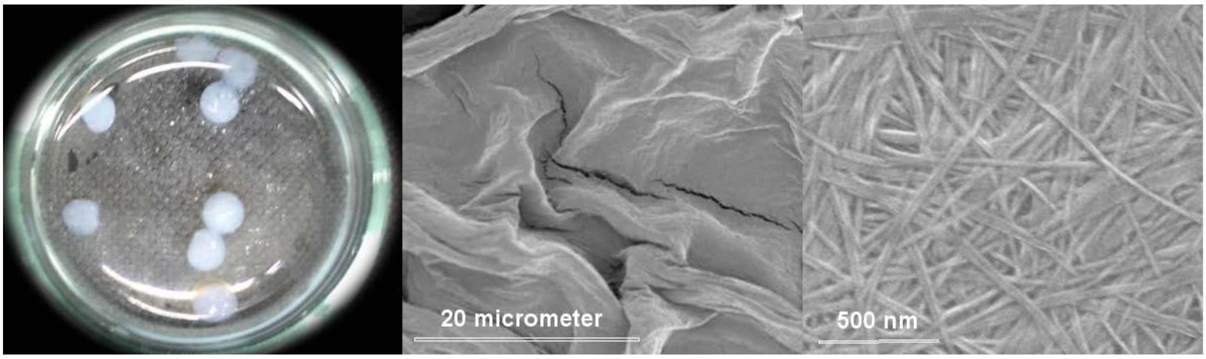


Oligopeptide molecules like Fmoc-diphenylalanine dipeptide (FmocFF) is well known to self-assemble in three-dimensional hydrogel bulk phase. This self-assembly (gelation) process is triggered either by solvent mixtures (DMSO/Water) or pH. It has been demonstrated [1] that pH change at the liquid gas interface creates thin membrane. Using this approach, we demonstrate the integration of colloidal objects like silica beads (B) and magnetic beads (C) into this self-organised membrane. The integration of magnetic particles of different sizes into the membrane could open the direction of interaction of external magnetic fields with the magnetic particles integrated into membrane.



Liquid phases can be encapsulated and stabilized by coating the liquid/gas interface with hydrophobic microparticles as for example PTFE powder. These so called “liquid marbles (LM)” [2] are prevented from wetting the underlying surface due to the rough interface originating from the hydrophobic powder particles. We demonstrate the pH triggered interfacial and bulk gelation of oligopeptide molecules (Fmoc-FF) to form stable mesoporous networks of ribbon like peptide assemblies [1]. Inclusion of magnetic particles into the membranes can offer an active mechanism to move the peptide containments in magnetic field or to change the shape of the oligopeptide containment. These high stable LMs can act as 3D scaffold for encapsulating cells, enzyme immobilization, gas sensors, etc. The shape, size, stability, limiting evaporation of material, controlling diffusion across the membrane and safe handling of the fragile LMs are some of the keys factors to be monitor in order to achieve high throughput micro-bioreactors.

[1] H.-G. Braun, A. Zamith Cardoso. Colloids and Surfaces B-Biointerfaces (2012) 97, 43-50.
[2] G. McHale, M. I. Newton. Soft Matter (2015) 11, 2530-2546.

P44

THERMORESPONSIVE BIOHYBRID INTERPENETRATING POLYMER NETWORKS BASED ON POLY(N-ISOPROPYLACRYLAMIDE)

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Various different hydrogel systems have been developed over the years that closely mimic key biophysical and biochemical aspects of the natural cellular environment. Despite their potential, conventional hydrogels are usually not able to recapitulate the highly dynamic nature of the cellular microenvironment. Therefore, the development of new, “smart” hydrogel systems based on the thermoresponsive polymer poly(N-isopropylacrylamide) (P(NIPAAm)) receive growing attention, due to their ability to respond to changes in temperature with a change in their physicochemical and mechanical properties. A general problem of conventional P(NIPAAm) based networks are often poor mechanical properties and the lack of sustained release capability. In this project, a biohybrid approach was applied to form interpenetrating polymer networks based on P(NIPAAm), poly-ethylenglycol, as well as an extracellular matrix derived bioactive glycosaminoglycan that allows the reversible binding and release of numerous mitogenic and morphogenic factors to the hydrogel matrix. The newly designed system showed thermoreversible swelling-deswelling responses that can be modulated depending on ambient temperature. Analysis of mechanical properties revealed a temperature-induced dramatic change in stiffness. Furthermore, cytokine release experiments showed promising temperature-dependent release profiles and first cell culture experiments using mesenchymal stem cells revealed a good cytocompatibility of the newly designed hydrogel system.

P45

IMPROVEMENT OF A FEEDBACK CONTROLLED ANTICOAGULANT RELEASE SYSTEM BY DIFFERENT RELEASE-TRIGGERS

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Background: Healthy vascular endothelium is considered the most effective anti-thrombogenic surface, which can adjust its anticoagulant properties to the actual requirements. Its transmembrane protein thrombomodulin has inherently responsive anticoagulant properties: Only in complex with the activated coagulation factor thrombin it converts Protein C to the anticoagulant Activated Protein C (APC). Activated coagulation thus triggers the formation and release of this anticoagulant. Once formed, the activity of APC is not restricted to the endothelial surface, but interrupts the coagulation process in the fluid phase.

A biohybrid hydrogel of 4-armed PEG (starPEG) crosslinked with heparin using thrombin-cleavable linker peptides presents a coagulation responsive anticoagulant system with similar behaviour [1]: Thrombin cleaves the linker peptides and releases heparin; this inhibits the thrombin activity and interrupts further degradation of the hydrogel (Figure 1). Since thrombin is a late enzyme in the coagulation cascade, the timing of the heparin release by this trigger may be suboptimal for thromboprotection. Faster degradation by thrombin or by more upstream coagulation factors may provide more efficient anticoagulant hydrogels.

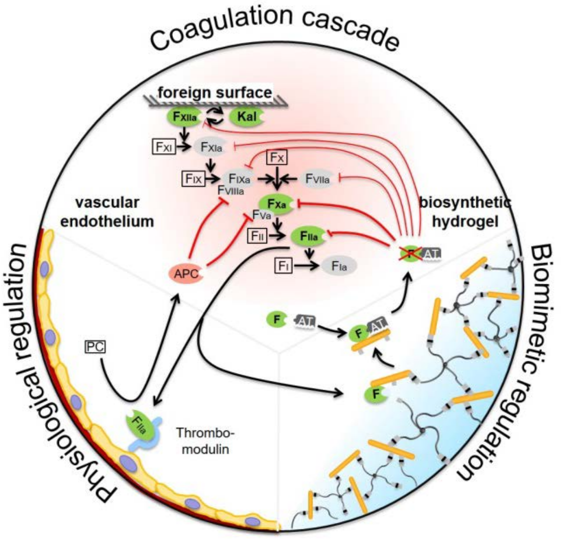

Figure 1: Scheme of feedback controlled coagulation regulation by physiological Thrombomodulin and by responsive starPEG-heparin hydrogels.

Method: In this study, starPEG-Heparin hydrogels were prepared using a previously described thrombin-cleavable peptide, a peptide with faster turn-over, a non-cleavable scrambled sequence of the peptide, a factor FXa cleavable, and a kallikrein/FXIIa cleavable peptide as responsive linkers. They were characterized for their general response behaviour and for the performance in whole blood.

Result: At equal concentration of the respective enzymes, the kallikrein responsive hydrogel was degraded fastest, followed by the FXa responsive gel and then the different thrombin responsive gels. In whole blood, the kallikrein-responsive gel also showed best anticoagulation, associated with highest heparin release, what is attributed to the low feedback effect of heparin on the contact phase system. The FXa- and the standard thrombin-responsive hydrogel had equal anticoagulant properties, but the FXa responsive system achieved this with lower heparin release due to the improved timing of the degradation.

Conclusion: Responsive anticoagulant hydrogels responding on FXa as trigger show a favourable profile of thromboresistance and inhibitor release.

[1] MF Maitz, U. Freudenberg, et al., Nat Commun (2013), DOI 10.1038/ncomms3168.

P46

HYDROGEL-BASED CHEMOFLUIDIC OSCILLATOR

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[2] *Technische Universität Dresden, Highly-parallel VLSI-Systems and Neuromorphic Circuits, Dresden, Germany*
[3] *Technische Universität Dresden, Center for Dynamics, Dresden, Germany*
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[5] *Technische Universität Dresden, Microsystems Technology, Dresden, Germany*
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[7] *Technische Universität Dresden, Center for Advancing Electronics Dresden, Dresden, Germany*
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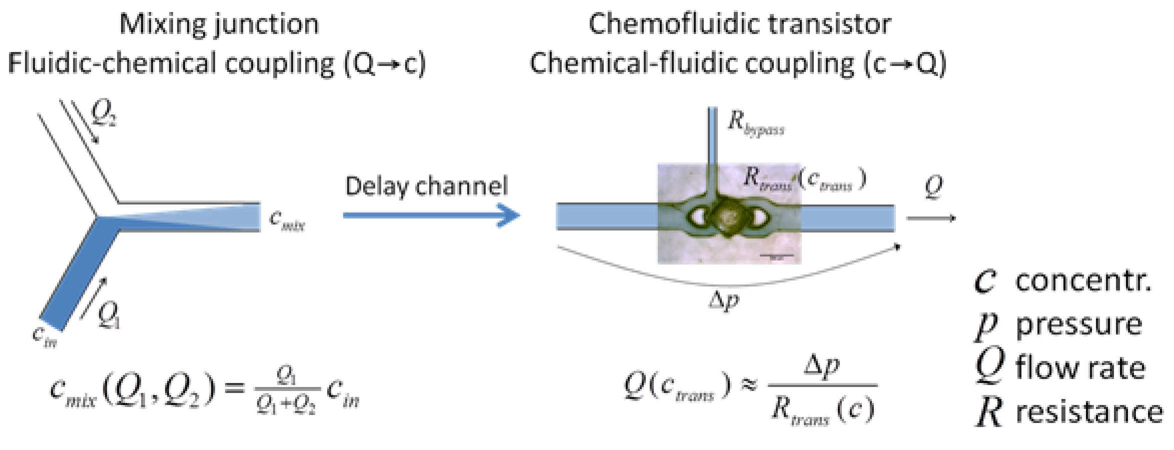
In the current state, flow control in microfluidic chips is based on the use of external sensing units (impedance-based or optical) and pneumatic valves actuated from outside the chip. Valves employing stimuli-responsive hydrogels (“chemofluidic transistors”) act as sensors/actuators that facilitate direct flow control depending on the state of the liquid without the need for external control. Here we present the use of a chemofluidic transistor in a microfluidic circuit that acts as an autonomous chemofluidic oscillator[1]. The swelling and shrinking of the PNIPAAm-Sodium-Acrylate hydrogel in the transistor depends on the concentration of 1-Propanol in the aqueous solution. The oscillator is based on employing negative feedback combined with a delay, a principle that is ubiquitous both in electronic circuits and in biological systems, e.g. in biochemical oscillations in cells. In a mixing junction (see figure) pure water is mixed with a solution containing 1-Propanol. A long microfluidic channel (“delay channel”) connects the junction with the transistor. Due to the dimensioning of the resistances and the flowrates/pressures of the pumps employed, a high concentration at the chemofluidic transistor (which makes the hydrogel shrink) will yield a low concentration after the mixing junction. This low concentration travels through the delay channel until it reaches the hydrogel, makes it swell and thus changes the mixing ratio after the mixing junction to a value of high concentration. This high concentration travels through the delay line until it reaches the transistor and starts the oscillation cycle anew. Driven by pumps with constant pressure or flowrate, the circuit generates oscillating flowrates, pressures and chemical concentrations. The chemofluidic oscillator is one of the key basic circuits necessary for a completely autonomous system for the processing of chemicals based on synchronized logic and storage units.



$$c_{mix}(Q_1, Q_2) = \frac{Q_1}{Q_1 + Q_2} c_{in}$$

$$Q(c_{trans}) \approx \frac{\Delta p}{R_{trans}(c)}$$

[1] G. Paschew, J. Schreiter, A. Voigt, C. Pini, J. P. Chávez, M. Allerdißen, U. Marschner, S. Siegmund, R. Schüffny, F. Jülicher, A. Richter. Adv. Mater. Technol. (2016), n/a.