

CPP 20: Focus: Functional Polymer Hybrids I

Organizers: Marina Grenzer (Leibniz-Institut für Polymerforschung Dresden e.V.), Thomas Hellweg (Universität Bielefeld), Svetlana Santer (Universität Potsdam)

Functional polymer hybrids represent a combination of synthetic polymer with organic/inorganic additives which render material a new function. So, addition of iron particles provides the hybrid material with a strong sensitivity against magnetic fields. A vast research field includes polymers with light-sensitive moieties and plasmonic hybrids converting the light energy into heat. The session aims to bring together representatives from leading groups to discuss in a congenial atmosphere recent advances and new challenges in this exciting field.

Time: Tuesday 9:30–12:45

Location: H51

Invited Talk CPP 20.1 Tue 9:30 H51
Photoinduced Surface Patterning in Azo-Polymers: How Can Supramolecular Functionalization Strategies Serve Us? — ●ARRI PRIIMÄGI — Department of Chemistry and Bioengineering, Tampere University of Technology, Finland

The light-induced surface patterning in azobenzene-containing materials is a good example of the photomechanical power of azobenzene, the isomerization of which can actuate macroscopic motions into the material system it is incorporated into. The surface deformation can be very pronounced, and a great deal of research effort is being put into gaining fundamental understanding on the light-induced motions as well as into the use of the photoinduced surface patterns in applications in photonics and nanofabrication.

Supramolecular functionalization strategies, i.e., the use of non-covalent intermolecular interactions to attach azobenzenes into passive host matrices, are pertinent from both fundamental and applied perspectives. In particular, supramolecular interactions provide a platform to experimentally study the structure-function relationships that govern the surface patterning and the limits beyond which the process does not occur anymore. Even weak interactions make a large difference, and not only the strength but also the directionality of the non-covalent interaction must be considered when designing supramolecular materials that move efficiently in response to light.

CPP 20.2 Tue 10:00 H51
Cooperative Photo-Switching in Nanofibers of Azobenzene Oligomers — ●STEFAN KOWARIK¹, CHRISTOPHER WEBER¹, MANUEL GENSLE¹, TOBIAS LIEBIG¹, ANTON ZYKOV¹, LINUS PITHAN¹, JÜRGEN P. RABE^{1,3}, STEFAN HECHT^{2,3}, and DAVID BLÉGER² — ¹Department of Physics & — ²Department of Chemistry & — ³IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

The integration of molecular switches into hierarchical assemblies makes it possible to amplify a single-molecule mechanical photoreponse to macro-scale events involving many molecules. Here, we demonstrate that multi-azobenzene oligomers can assemble to form robust supramolecular nanofibers in which they can be photo-switched repeatedly between the E- and Z-configuration. While in isolated oligomers the azobenzene units undergo reversible photoisomerization independently, in the nanofibers they are coupled via mechanical and electronic interactions and switch cooperatively as evidenced by unusual thermal and kinetic behavior. Depending on the fraction of Z-azobenzene in the nanofibers the photoisomerization rate from the Z-isomer to the E-isomer is increased by more than a factor of 4. This demonstrates the great potential of coupling individual photochromic units for increasing their quantum efficiency and amplifying molecular switching events with potential relevance for actuation and sensing.

CPP 20.3 Tue 10:15 H51
Optically controlled shape of soft nano-objects — ●SELINA SCHIMKA^{1,2} and SVETLANA SANTER¹ — ¹University of Potsdam, 14476 Potsdam, Germany — ²Max Plank Institute of Colloids and Interfaces, 14424 Potsdam, Germany

What have acid-group containing microgels and DNA in common? Right, both of them are negatively charged polymers, drawing attention of research because of possible applications in biological and biomedical application.

But beside this, both are soft nano-objects, that can be reversibly and non-invasively changed in their shape by light, with assistance of an azobenzene containing agent [1,2]. Although the mechanisms behind this process differs if microgel or DNA is used, and apparently even with the used azobenzene containing agent, the effect is quite simi-

lar - from a widely expanded state (swollen microgel or decompacted for DNA) with a high water content, they undergo a transition to a compacter, smaller state (shrunken microgel or compacted DNA), and back to the expanded state, depending on the illumination conditions. This behavior is in any case related to the trans cis isomerization of the azobenzene containing agent, which can be switched between a hydrophilic trans (visible light) and a hydrophobic cis (UV light) state, which alters its interaction with the microgel/DNA. Regarding previous works, we consider questions of toxicity and systematic behavior by the help of a set of new azobenzene containing agents.

[1] A.L.M. Le Ny, *JACS* **2006**, 128, 6400.

[2] Y. Zakrevsky, *Adv Funct Mater* **2012**, 22, 5000.

CPP 20.4 Tue 10:30 H51
Photoisomerization kinetics in azobenzene-containing polymers — ●TATIANA PETROVA^{1,2}, JAROSLAV ILNYTSKYI^{1,3}, VLADIMIR TOSHCHEVIKOV¹, and MARINA SAPHIANNIKOVA¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Cherepovets State University, Russia — ³Institute for Condensed Matter Physics, Lviv, Ukraine

Azobenzene-containing polymers belong to a class of smart materials, which are able to transform the light energy into mechanical stress [1, 2]. We study the photoisomerization kinetics in azobenzene-containing polymers using the coarse-grained simulations and a theoretical model for the kinetic processes. The reorientation of azobenzene chromophores under trans-cis and cis-trans isomerization processes are taken explicitly into account. It is shown that the population kinetics of trans- and cis-isomers and their stationary orientation states depend on the ratio between characteristic times which characterize the rotation diffusion of the isomers, the frequency of photoisomerization of trans-isomers and the time of cis-trans relaxation. The form of the reorientation potential of the mean force acting on the isomers is analyzed and its use is validated.

[1] T. Petrova et al. *Soft Matter* 11 (2015) 3412

[2] J. Ilnytskyi et al. *ChemPhysChem* 16 (2015) 3180

CPP 20.5 Tue 10:45 H51
Approach to macroscopic functional colloidal optical metamaterials — ●TOBIAS A.F. KÖNIG¹, SVETLANA SANTER², and ANDREAS FERY¹ — ¹Institute of Physical Chemistry and Polymer Physics, Leibniz Institute of Polymer Research (IPF), Dresden — ²Department of Experimental Physics, Potsdam

We are interested in optical and mechanical interactions between functionalized nanoparticles and functionalized surfaces to assemble nanoparticles on the macroscopic area. Two assembly approaches will be discussed in this contribution: First, using the prevailing surface forces to move nanoobjects and second, using lithography free templates to assemble plasmonic nanoparticles. In the first approach, we use a plasmonically induced azobenzene mass transport to move nanoparticles. This allows us to analyse the underlying plasmonic effects by changing polarization or wavelength observed at a fixed position. In the second approach, we present ensembles of surface-ordered nanoparticle arrangements, which are formed by template assisted self-assembly of monodisperse, functionalized gold nanoparticles in wrinkle-templates. Both methods are confirmed with electromagnetic simulations (FDTD) to analyse the responsible forces of the nanoimprints and to discuss the collective optical response of the assembled nanoparticles. We discuss the expansion of these approaches towards colloidal optical metamaterials and light management concepts.

15 min. break

Invited Talk

CPP 20.6 Tue 11:15 H51

Plasmon coupling in self-assembled colloidal monolayers — ●MATTHIAS KARG — Physical Chemistry I, University of Bayreuth, Universitätsstr. 30, 95440 Bayreuth, Germany

Organized nanoscale structures which can guide or manipulate the propagation of electromagnetic fields at optical frequencies are of great importance for applications in sensing, all-optical computing and photovoltaics. While such structures are typically created by lithographic approaches, the realization of optically functional superstructures through bottom-up assembly of colloidal building blocks remains challenging. In this contribution I will report on our latest results of using wet-chemically synthesized plasmonic colloids, their assembly into highly periodic superstructures as well as their optical performance. Structural control is achieved by using polymer encapsulation strategies which allow us to tune inter-particle interactions[1]. Different methods for 2D assembly will be presented yielding isotropic as well as anisotropic particle arrays of high order[2]. Long-range dipolar plasmon resonance coupling is observed for assemblies with extraordinarily high degrees of order[3]. The enhanced Q-factors of these coupled arrays are promising for low-threshold plasmonic lasing.

[1] A. Rauh, T. Honold, M. Karg, *Colloid Polym Sci* 2015, DOI: 10.1007/s00396-015-3782-6 [2] T. Honold, K. Volk, A. Rauh, J.P.S. Fitzgerald, M. Karg, J. Mater. Chem. C 2015, 3, 11449-11457 [3] K. Volk, J.P.S. Fitzgerald, M. Retsch, M. Karg, *Adv. Mater.* 2015, DOI: 10.1002/adma.201503672

CPP 20.7 Tue 11:45 H51

Thermoelectric thin films based on a polymer/nanoparticle nanocomposite — ●NITIN SAXENA^{1,2}, ANTON GREPPMAIR³, MICHAEL CORIC⁴, JAN WERNECKE⁵, STEFANIE LANGNER⁵, MICHAEL KRUMREY⁵, EVA M. HERZIG⁴, MARTIN S. BRANDT³, and PETER MÜLLER-BUSCHBAUM^{1,2} — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ²Center for NanoScience, LMU München, 80539 München, Germany — ³TU München, Walter-Schottky-Institut and Physik-Department, 85748 Garching, Germany — ⁴TU München, Munich School of Engineering, 85748 Garching, Germany — ⁵PTB, BESSY II Helmholtz-Zentrum Berlin, 12489 Berlin, Germany

Thermoelectric materials pose a compelling technology for power generation from renewable energies, since temperature gradients are transformed into voltages and thus electrical power. So far, highly efficient thermoelectrics comprise rare and/or toxic inorganic materials, and require cost- and energy-intensive fabrication. These points hinder the large-scale application of thermoelectrics. In order to overcome these limitations, we pursue a hybrid approach combining the semiconducting polymer blend PEDOT:PSS for its high electrical conductivity and inorganic nanoparticles in order to reduce thermal conductivity within the thin film. We investigate the influence of the nanoparticles on the morphology by GISAXS and correlate this with changes in the thermoelectric behavior. In addition, we also investigate the thermal conductivity of pristine PEDOT:PSS and of the hybrid film by IR thermography, in order to ultimately calculate the figure-of-merit ZT.

CPP 20.8 Tue 12:00 H51

Mesoscopic modeling of magnetic gels: reversibly switching elastic and superelastic stress-strain properties — PEET CREMER, GIORGIO PESSOT, HARTMUT LÖWEN, and ●ANDREAS M. MENZEL — Heinrich-Heine-Universität Düsseldorf, Düsseldorf, Germany

Magnetic gels are generated by embedding magnetic colloidal particles into a permanently crosslinked, possibly swollen elastic polymer matrix. Several of their material properties can be reversibly switched

from outside by applying external magnetic fields during operation. We model the switchability of such material properties on the mesoscopic level.

Previously, we had introduced simplified dipole-spring approaches to study the reversible tunability of linear elastic and dynamic properties. In contrast to that, we here mainly report on switchable nonlinear stress-strain properties. For this purpose, we focus on anisotropic magnetic gels that contain chain-like aggregates of magnetic colloidal particles. Continuum elasticity theory is now used to describe the elastic behavior of the surrounding polymer matrix. Upon stretching along the chain direction, we predict a pronounced plateau-like ("superelastic") regime on the stress-strain curves. Remarkably, applying external magnetic fields, this plateau can be shifted along the stress-strain curves or even be switched off. We identify two underlying mechanisms: a detachment of the embedded chain-like aggregates and a flipping of the magnetic moments. The origin of both mechanisms is explained. It should be possible to observe these effects on real experimental samples and to exploit them, e.g., for the construction of soft actuators.

CPP 20.9 Tue 12:15 H51

Self-assembly properties of magnetic filaments in supracolloidal brushes — ●PEDRO A. SÁNCHEZ¹, ELENA S. PYANZINA², EKATERINA V. NOVAK², JOAN J. CERDÀ³, TOMAS SINTES³, and SOFIA S. KANTOROVICH^{1,2} — ¹University of Vienna, 1090 Vienna, Austria — ²Ural Federal University, 620000, Ekaterinburg, Russia — ³IFISC (UIB-CSIC), 07122 Palma de Mallorca, Spain

Magnetic filaments are chains of magnetic colloids that have been crosslinked with polymers to form permanent polymer-like structures. Recently, we proposed the use of these filaments to create supracolloidal magnetoresponsive coatings with a broad potential for technological applications [Sánchez *et al.*, *Macromolecules* 2015, 48, 7658–7669; Sánchez *et al.*, *Faraday Discussions* 2015, DOI:10.1039/c5fd00133a]. The proposed system is obtained by densely grafting the filaments to the coated surface, forming a polymer brush-like arrangement. Our computer simulations show that this system experiences strong equilibrium structural changes as a response to two main external parameters: background temperature and applied magnetic fields. The overall structure of the brush is determined by the self-assembly of the magnetic beads from neighbouring filaments under the influence of such external parameters. Importantly, the presence of the constraints introduced by the grafting surface and the crosslinkers makes this self-assembly significantly different from the one inherent to non crosslinked magnetic colloids in bulk.

CPP 20.10 Tue 12:30 H51

The effect of particle rearrangement in magneto-sensitive elastomers — ●DIRK ROMEIS¹, PHILIPP METSCH², MARKUS KÄSTNER², and MARINA SAPHIANNIKOVA¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Technische Universität Dresden

Magnetorheological elastomers are composites that consist of magnetically permeable particles incorporated into an elastic polymer matrix. When the magnetic field is applied to such material, changes in the shape and the mechanical moduli occur. The response of the material crucially depends on the actual distribution of the magnetizable particles and whether or not these particles can additionally rearrange with respect to the surrounding polymer network. We present a mean-field approach for initially statistically distributed magnetic dipoles and allow the formation of elongated microstructures in direction of the applied field. The results of the mean-field approach are compared with the predictions of a microscopic continuum model of similar composites.