# CPP 26: Nanostructures, Nanostructuring and Nanosized Soft Matter I

Time: Wednesday 11:30–13:00 Location: H34

**Invited Talk** CPP 26.1 Wed 11:30 H34

**Polyelectrolytes in the confined space of mesopores for transport regulation** — •Annette Andrieu-Brunsen — Technische Universität Darmstadt, Macromolecular Chemistry - Smart Membranes, Germany

Nanopores are a key component in various technologies from oil production, separation and sensing, to drug delivery or catalysis and energy conversion. In contrast to technological pores, biological pores and channels demonstrate highly precise transport being directed, highly selective, and gated. A key factor to this performance is their nanoscale structure, and their local control on charge regulation and polarity in confined space. Inspired by this performance and precision we are interested in understanding the relation between the design of polymers in nanoscale space and its resulting properties to for example understand and advance transport performance of technological pores.

This talk will give insights into the interplay of polymer functionalization of mesoporous layers and resulting ionic mesopore accessibility. Among others, the effect of increasing polyelectrolyte amount and thus increasing charge density as well as the influence of polymer chain composition and the observation of confinement-induced pKa shifts will be discussed. Furthermore, ionic transport regulation by gradually adjusting the wettability of mesopores will be demonstrated including the influence of nanoscale wettability step-gradients in mesoporous silica layers. To indicate next steps our activities towards increasing precision in polymer functionalization of mesoporous silica materials will be outlined.

CPP 26.2 Wed 12:00 H34

**Infrared Scanning Near-Field Spectroscopic Insights into Self-Assembled Block Copolymer Nanostructures** — •Nadine von Coelln[1], Britta Weidinger[2], Christian Huck[1], Irene Wacker[3], Ronald Curticean[3], Rasmus R. Schröder[3], Eva Blasco[2], and Petra Tegeder[1] — [1]Institute for Physical Chemistry — [2]IMSEAM — [3]BioQuant, Heidelberg University, Germany

Block copolymers (BCPs) are known for their ability to self-assemble into a variety of morphologies on the nanometer scale. While the self-assembly of 2D thin films has been extensively investigated, less attention has been paid to 3D bulk morphologies. In this work, the internal nanostructure of long-range ordered 3D bulk morphologies of a well-defined diblock copolymer consisting of polystyrene and a methacrylate-based copolymer is studied by means of infrared scanning near-field optical microscopy (IR-SNOM). We demonstrate that by irradiation at an absorption band specific to one polymer block, it is possible to chemically image the blocks nano-ordered spatial arrangement [1]. Representative images were successfully correlated with scanning electron microscopy (SEM) data. By altering the molar fraction of polymer blocks, a variety of nanostructures was imaged. For some polymer compositions, the nanostructure formed was observed to change upon post-functionalization. Additionally, nanotomography of the bulk material is approached by imaging and volume reconstruction of serial sections.

[1] B. Weidinger, N. von Coelln et al., Polym. Chem., **15** (2024) 4093-4100.

CPP 26.3 Wed 12:15 H34

**Star-like molecular brushes with poly(2-oxazoline)-based amphiphilic diblock copolymer side arms** — •Wenqi Xu[1], Laura Fietzke[2], Rustam A. Gumerov[3], Feifei Zheng[1], Peiran Zhang[1], Cy M. Jeffries[4], Dmytro Soloviov[4], Rainer Jordan[2], and Christine M. Papadakis[1] — [1]TUM School of Natural Sciences, Technical University of Munich, Garching, Germany — [2]Faculty of Chemistry and Food Chemistry, Technical University of Dresden, Dresden, Germany — [3]DWI Leibniz Institute for Interactive Materials, RWTH Aachen University, Aachen, Germany — [4]EMBL at DESY, Hamburg, Germany

Poly(2-oxazoline)s (POx) are synthetic, non-toxic, and biocompatible polymers developed to replace the increasingly immunogenic poly(ethylene glycol) in biomedicine. Among many architectural variants of POx, studies on POx-based star brushes are still scarce. In the present work, we investigate molecular brushes, in which diblock copolymers from hydrophilic poly(2-methyl-2-oxazoline) and hydrophobic poly(2-*n*-butyl-2-oxazoline) are grafted onto star-shaped poly(methyl methacrylate) backbones with the stars having functionalities ranging from 2 to 5. The size and shape of the star brushes were investigated in dilute aqueous solutions using computer simulation, dynamic light scattering, and synchrotron small-angle X-ray scattering. Our results show that these star brushes form ellipsoids with different degrees of elongation. Moreover, a size growth is found for the star brushes at high temperatures, which is attributed to the aggregation of the amphiphilic side arms.

CPP 26.4 Wed 12:30 H34

**STED-inspired optical lithography beyond acrylates** — Sourav Islam, Georgii Gvindzhiliia, and •Thomas A. Klar — Institut für Angewandte Physik, Johannes Kepler Universität Linz, Austria

STED-inspired[1], and hence sub-diffractional, nanolithography was so far restricted to free radical polymerizations, predominantly of (meth)acrylates.[2] We now expand the STED-inspired toolkit to cationic[3, 4] and oxidative polymerizations,[5] comprising the technologically important classes of epoxides and pi-conjugated polymers. In both cases, we achieved structure sizes below 100 nm using transient-state absorption depletion (TAD) in systems comprising depletable photosensitizers, optionally combined with onium salts. The pi-conjugated nanostructures are particularly intriguing, because they potentially will allow for sub-diffractional organic electronic devices.

[1] Klar, Hell, Opt. Lett. 24, 954 (1999). [2] Fischer, Wegener, Las. Phot. Rev. 7, 22 (2013). [3] Islam, et al., J. Phys. Chem. C 127, 1873 (2023). [4] Islam, Klar, ACS Omega 9, 19203 (2024). [5] Islam, et al., Proc. SPIE 1299503(2024).

CPP 26.5 Wed 12:45 H34

**In-situ investigation of the lateral and vertical structure of PNIPAM-microgels at the air-liquid and solid-liquid interfaces** — Olaf Soltwedel, Joanne Zimmer, •Hayden Robertson, and Regine von Klitzing — Institut für Physik Kondensierter Materie, Technische Universität Darmstadt, D-64289 Darmstadt, Germany

The novel surface characterisation approaches presented here highlight, for the first time, the use of both specular and off-specular X-ray reflectivity (XRR) to probe the vertical and lateral structure of adsorbed polymer microgels particles at various interfaces, offering *in situ*, non-invasive insights without the need for doping or transfer-induced artefacts. In particular, we demonstrate the complementarity of two readily accessible laboratory techniques on characterising the structure of adsorbed microgels: atomic force microscopy (AFM) and XRR. Initial *ex situ* AFM scans of Langmuir-Blodgett deposited microgels at the solid interface revealed strong lateral 2D hexagonal ordering across a broad range of surface pressures. However, for the first time, these results are confirmed by off-specular XRR, demonstrating the existence of the hexagonal long-range ordering at low and intermediate surface pressures for *in situ* conditions at the air-water interface. Upon uniaxial compression of the interface, the microgel lattice constants decrease monotonically, indicating tighter packing. At these higher surface pressures, both AFM and off-specular XRR also reveal the formation of microgel domains; hexagonal short-range ordering is maintained whereas long-range ordering is diminished.