

CPP 3: Crystallization, Nucleation and Self-Assembly I

Time: Monday 9:30–12:45

Location: H 0110

Invited Talk

CPP 3.1 Mon 9:30 H 0110

Flexibility, connectivity, and topological constraints in polymer crystallization — ●TOSHIKAZU MIYOSHI — The University of Akron, School of Polymer Science and Polymer Engineering, Akron, OH, United States

Since Keller's finding of single crystals in 1957, numerous research has been conducted in experimental, theoretical, and computational aspects in polymer crystallization. The accumulated experimental results have been used to develop polymer crystallization theories as well as have gradually shifts researchers' primary interest from the crystalline structure itself to the crystal-amorphous interface and amorphous structure. Connectivity, flexibility, and topological constraint are important structures to distinguish the uniqueness of long polymer chains from small organic molecules as well as large biomacromolecules, proteins. Chain-folding structure of semicrystalline polymer is one of key structures to reflect flexibility, connectivity, and topological constraint during crystallization. In this talk, the PI will present the impacts of flexibility, connectivity, and topological constraint on the chain-folding structure of semicrystalline polymers during crystallization. The molecular level structure is used to understand the crystallization mechanisms in a dilute solution as well as in a highly condensed melt.

CPP 3.2 Mon 10:00 H 0110

Crystallizability of free and tethered chains in nanometer-sized droplets — ●WING KIT OR, ALAA HASSAN, and MARTIN TRESS — Peter Debye Institute for Soft Matter Physics, Leipzig University, Leipzig, Germany

Although the crystallization of polymers has been investigated for decades, it is not yet fully understood. One way to gain more insight is to study the differences between bulk and confined polymer, focusing on how crystallization characteristics change depending on the size and type of confinement. Until now, most studies have used confinement in thin films, small droplets, or nanopores. We prepared separated aggregates as small as ten chains on average each to characterize their individualized crystallization by probing the change in orientational polarization using a nanostructured electrode arrangement. For that, a regular pattern of well separated gold nanodots was deposited on a silicon substrate to chemically graft end-functionalized polymer chains to these nanodots. In contrast to nanometer-sized spin-cast polymer droplets (prepared as reference), the grafted aggregates exhibit no signs of crystallization. This may be attributed to several constraints like restricted chain configuration, limited chain motion, too wide chain spacing, or altered interfacial energy due to the presence of the gold surface. Preliminary results suggest that spatial constraints which prevent crystalline conformations are dominating. In principle, this approach will enable to study aggregates of fewer chains down to individual ones, which until now was accessible only to computer simulations.

CPP 3.3 Mon 10:15 H 0110

Crystallization kinetics of polyamide 10.12 from Ultra-Fast Scanning Calorimetry — ●RENE SÄTTLER and MARIO BEINER — Fraunhofer IMWS, Walter-Hülse-Str. 1, 06120 Halle (Saale)

This report is focusing on the influence of isothermal and non-isothermal crystallization conditions on the crystalline states of polyamide 10.12 occurring in different polymorphic states. Results from Ultra-Fast Scanning Calorimetry (UFSC) are reported. *Isothermal* crystallization experiments at temperatures $T_{c,iso}$ below the Brill transition temperature ($T_B = 90$ °C, known from previous X-Ray Diffraction studies¹) show two distinct melting peaks while a single melting peak is found after isothermal crystallization at temperatures $T_{c,iso} \geq T_B$. Two-step isothermal measurements at selected temperatures provide further evidence for the formation of two distinct phases below and above T_B . Indications for melting of the non-stable α phase above T_B in UFSC heating scans are discussed. *Non-isothermal* crystallization experiments with various combinations of cooling and heating rates show that (i) crystal growth and (ii) nucleation can be suppressed completely. The critical cooling rate $q_{cool,crit}$, at which crystallization during cooling is prevented, is about 1,500 K/s. Interestingly, cold crystallization during heating can be also suppressed if $q_{cool} \geq q_{cool,crit}$ and a sufficiently fast heating rate

is subsequently used. The results will be discussed considering thermodynamics and relevant crystal nucleation and growth rates.

(1) R. Sättler, V. Danke, M. Beiner, *Macromol. Chem. Phys.* 224, (2023), 2200433.

CPP 3.4 Mon 10:30 H 0110

New in situ X-ray experiments to investigate shear-induced crystallization effects in thermoplastics — ●ANNA KATHARINA SAMBALE¹, ERIC EUCHLER¹, KAI UHLIG¹, REGINE BOLDT¹, MATTHIAS SCHWARTZKOPF², STEPHAN ROTH^{2,3}, and MARKUS STOMMEL^{1,4} — ¹Leibniz-Institut fuer Polymerforschung, Dresden, Germany — ²Deutsches Elektronen Synchrotron DESY, Hamburg, Germany — ³KTH Royal Institute of Technology, Stockholm, Sweden — ⁴Technical University Dresden, Dresden, Germany

The thermo-rheological conditions during the processing of semi-crystalline thermoplastics have a significant influence on their microstructure and, therefore, on the performance of the final product. During processing, inhomogeneous flow fields affect the polymer melt with different shear conditions, which significantly influence the crystallization behavior during cooling and solidification. Although studies have already been conducted on the crystallization behavior of polymer melts under shear, some interactions are still unknown, for example, the influence of (local) process conditions in commercial technologies, such as melt extrusion, on the crystallization behavior of polymorphic thermoplastics. To investigate such kind of interactions, a new experimental setup has been realized to investigate the structure formation of polymer melts in situ by synchrotron X-ray scattering. In this contribution, the first results are presented on the structure formation of iPP. Owing to the high temporal and spatial resolution, new insights into the shear-induced crystallization behavior of iPP under variations of the process parameters have been achieved.

CPP 3.5 Mon 10:45 H 0110

Infrared Scanning Near-Field Spectroscopic Studies of Self-Assembled Nanostructures Based on Photo-Crosslinkable Block Copolymers — ●NADINE VON COELLEN¹, BRITTA WEIDINGER², CHRISTIAN HUCK¹, IRENE WACKER³, RONALD CURTICEAN³, RASMUS R. SCHRÖDER³, EVA BLASCO², and PETRA TEGEDER¹ — ¹Institute for Physical Chemistry, Heidelberg University, Germany — ²IMSEAM, Heidelberg University, Germany — ³BioQuant, Heidelberg University, Germany

Block copolymers, are materials known for their ability to self-assemble into a variety of morphologies on the nanometer scale. The self-assembly of block copolymers has been extensively investigated for 2D thin films, however, less attention has been paid to 3D bulk morphologies. In this work, long-range ordered 3D bulk morphologies of a well-defined diblock copolymer consisting of polystyrene and a methacrylate-based copolymer decorated with photo-crosslinkable units were prepared via solvent annealing. The internal lamellar or cylindrical nanostructures are studied based on infrared scanning near-field optical microscopy (IR-SNOM), which offers the unique possibility of infrared chemical imaging and spectroscopy with a spatial resolution down to around 20 nm. We demonstrate that by irradiation at an independently addressable absorption band of a polymer block, it is possible to chemically image the blocks' nano-ordered spatial arrangement. By changing which polymer block is excited, a switch of the relative optical phase, related to the local absorption, is observed, revealing a strong phase segregation via spectroscopic contrast.

CPP 3.6 Mon 11:00 H 0110

Strong light-matter interaction to control intermolecular interaction and correlation — MATTEO CASTAGNOLA², TOR HAUGLAND², ENRICO RONCA³, HENRIK KOCH², and ●CHRISTIAN SCHÄFER¹ — ¹Department of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden. — ²Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway. — ³Istituto per i Processi Chimico Fisici del CNR (IPCF-CNR), Via G. Moruzzi, 1, 56124, Pisa, Italy.

Chemistry is the realm of atomic and molecular interactions, acting according to rules that we often perceive as set in stone. Optical environments, in particular the strong coupling of molecules with them, are capable to modify those interactions [1,2,3] which provides means to

control chemistry itself. We provide a brief overview of the fascinating experimental accomplishments that include control over crystallization, ionic conductivity, and the reaction rate. Furthermore, we discuss how strong coupling is able to alter correlation between molecules and influences solvation and aggregation structures [4].

[1] PNAS, 116 (11), 4883, (2019). [2] J. Chem. Phys. 154, 094113 (2021). [3] arXiv:2311.09739v1. [4] M. Castagnola, T. Haugland, E. Ronca, H. Koch, C. Schäfer, to be submitted (2024).

15 min. break

CPP 3.7 Mon 11:30 H 0110

X-ray scattering techniques to study the nucleation and growth of anisotropic perovskite nanoparticles and 2D-phases — ●BERT NICKEL, KILIAN FRANK, NINA HENKE, and ALEXANDER URBAN — Fakultät für Physik, Ludwig-Maximilians-Universität München

Lead halide perovskites are an emerging materials class for optoelectronic applications. Due to the ionic character of this semiconductor material, nucleation and growth processes differ profoundly from covalent semiconductor materials such as Si or GaAs. Successful solution based synthesis schemes provide shape and orientation control which is difficult to rationalize. We employ in-situ x-ray studies, especially small angle x-ray scattering (SAXS) and Bragg diffraction to study such non-classical nucleation pathways. Within this approach, we identify the water air interface [1] and internal interfaces in colloidal mesophases as driving forces for nucleation and growth.

[1] Elucidating the Origins of High Preferential Crystal Orientation in Quasi-2D Perovskite Solar Cells Lehner, L. E., Demchyshyn, S., Frank, K., Minenkov, A., Kubicki, D. J., Sun, H., Hailegnaw, B., Putz, C., Mayr, F., Cobet, M., Hesser, G., Schöffberger, W., Sariciftci, N. S., Scharber, M. C., Nickel, B., Kaltenbrunner, M. *Advanced Materials* 35 (5) 2208061 (2023)

CPP 3.8 Mon 11:45 H 0110

Effect of Perovskite Nanocrystal Nucleation Seeds on Microstructure and Crystallization Pathways in Organic-Inorganic Halide Perovskite Thin Films — ●ALTANTULGA BUYAN-ARIVJIKH¹, MATTHIAS SCHWARTZKOPF², SARATHLAL KOYILOTH VAYALIL², STEPHAN V. ROTH², GUANGJIU PAN¹, JINSHENG ZHANG¹, ZHUIJUN XU¹, THOMAS BAIER¹, YANAN LI¹, and PETER MÜLLER-BUSCHBAUM^{1,3} — ¹TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — ²DESY, 22604 Hamburg, 22607, Germany — ³MLZ, TUM, 85748 Garching, Germany

Organic-inorganic halide perovskites have gained a huge interest in the scientific community owing to their favorable optoelectronic properties combined with their ease of production and abundance of raw materials. In many cases, polycrystalline thin films are fabricated for which thin film crystallinity and morphology are key factors affecting the perovskite properties. In this work, we present a novel approach for improving the thin film quality by employing external perovskite nanocrystals as seeds in slot-die coated formamidinium lead iodide thin films. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements show that the seed crystals improve the thin film texture by inducing a preferred crystallite orientation. Furthermore, we reveal a new crystallization pathway in seeded thin films with respect to unseeded ones via in-situ GIWAXS measurements.

CPP 3.9 Mon 12:00 H 0110

Electric-field effects on protein phase behavior — DEBES RAY¹, MAHNOUSH MADANI², JAN K. G. DHONT¹, ●FLORIAN PLATTEN^{1,2}, and KYONGOK KANG^{1,3} — ¹FZ Jülich, IBI-4, Jülich, Germany — ²HHU Düsseldorf, Faculty of Mathematics and Natural Sciences, Düsseldorf,

Germany

We experimentally study the state diagram of protein solutions in the presence of a weak external alternating-current electric field. The collective behavior of the protein solutions and their response to the electric field are followed in-situ by polarized optical microscopy. The crystallization boundary and the metastable liquid-liquid coexistence curve are affected by the electric field, such that the crystallization gap is widened. Both nucleation and growth of protein crystals can be modulated by the frequency and strength of the field.

CPP 3.10 Mon 12:15 H 0110

Self-assembled Peptides Structure Mediated by Solid Interfaces — ●LEILA SAHEBMOHAMMADI¹, REGINE VON KLITZING¹, MARKUS MEZGER², and POL BESENIUS³ — ¹Soft Matter at Interfaces, Department of Physics, Technical University of Darmstadt, Germany — ²Faculty of Physics, Universität Wien, Austria — ³Department of Chemistry, Johannes Gutenberg-Universität Mainz, Germany

This study investigates the self-assembly dynamics of thermosensitive amphiphilic dendritic C3-symmetric peptides containing lysine and glutamic acid, respectively. Using Quartz Crystal Microbalance with Dissipation (QCM-D) techniques, our observations reveal temperature-dependent layer-by-layer adsorption of the oppositely charged peptides, achieving the formation of multilayers. Atomic Force Microscopy (AFM) substantiates these findings, providing visual confirmation of the confinement distribution pattern on the surface. Simultaneously, a strategic combination of supramolecular assembly and surface confinement is explored using QCM techniques.

Lysine emerges as the optimal grafting layer, exhibiting heightened adsorption on gold (Au) and silicon (Si) surfaces. Further QCM-D investigations show the same growth increment for the oppositely charged peptides at pH 6.5. Notably, exposure to extreme pH conditions (2 or 12) induces the removal of multilayers, due to low charge density of one of the peptides. This results in a better understanding of peptide self-assembly and insights for customizing surface properties through combining self-assembly and surface confinement.

CPP 3.11 Mon 12:30 H 0110

Enhancing SERS Sensitivity and Uniformity through Directional Self-Assembly of Plasmonic Nanoparticle Lattices — ●SEZER SEÇKIN¹ and TOBIAS A. F. KÖNIG^{1,2} — ¹Leibniz-Institut für Polymerforschung e.V., Hohe Straße 6, 01069 Dresden — ²Center for Advancing Electronics Dresden, Technische Universität Dresden, 01062 Dresden

Despite recent developments, surface-enhanced Raman spectroscopy (SERS) applications face challenges in achieving high sensitivity and uniform signals over a large area. Using the directional self-assembly of plasmonic nanoparticles in lattice structures, we show how one can increase the SERS signal 43-fold over randomly aligned gold nanoparticles without relying on the photoluminescence of Rhodamine 6G [Seçkin et al., *ACS Appl. Mater. Interfaces* 2023, 15(36), 43124-43134]. We have chosen the lattice constant for an off-resonant case that matches the lattice resonance and super-radiant plasmon mode along the particle chain. Supported by electromagnetic simulations, we analyze the radiative components of the plasmon modes by varying the particle size while keeping the lattice periodicity constant. We perform polarization-dependent SERS measurements and compare them with other SERS excitation wavelengths. Using the self-assembled plasmonic particle lattice [Gupta et al., *Adv. Funct. Mater.* 2021, 31(36) 2105054], we have developed an effective SERS substrate that provides a significantly higher signal with 73% less surface coverage. This colloidal approach enables the cost-effective and scalable fabrication of sensitive, uniform, and polarization-dependent SERS substrates.