CPP 59: Crystallization

Time: Friday 11:30–13:00 Location: ZEU/0260

CPP 59.1 Fri 11:30 ZEU/0260

Structure formation in Polyamide 6 under process-relevant conditions: In situ SAXS/WAXS study using a modular FlowCell setup — •Anna Katharina Sambale[1], Eric Euchler[1], Moritz Kurkowski[1], Enno Henn[1], Regine Boldt[1], Matthias Schwartzkopf[2], Sarathlal Koyiloth Vayalil[2,3], and Markus Stommel[1,4] — [1]Leibniz-Institut fuer Polymerforschung Dresden e.V., Dresden, Germany — [2]Deutsches Elektronen Synchrotron DESY, Hamburg, Germany — [3]Applied Science Cluster, UPES, Dehradun, India — [4]TUD Dresden University of Technology, Dresden, Germany

The microstructural evolution of semi-crystalline thermoplastics during melt processing is governed by local thermo-rheological conditions, which strongly influence crystallization kinetics and consequently, the final material properties. To analyze these interdependencies under process-relevant conditions, a modular FlowCell setup was developed for time-resolved in situ SAXS/WAXS experiments at the synchrotron beamline P03 at DESY, Hamburg. The setup combines a commercial single-screw extruder with customized temperature-controlled slit capillary that enables measurements during controlled cooling from the melt to solid state, with synchronized acquisition of IR-thermography data and, in extended configurations, Raman spectroscopy. Recent experiments on polyamide 6 demonstrate the impact of different cooling strategies and nucleation conditions on the resulting structure. The results highlight the relevance of spatially and temporally resolved analysis techniques for understanding structure formation towards industrial polymer processing.

CPP 59.2 Fri 11:45 ZEU/0260

Influence of Composition on Sanidic Liquid Crystalline Mesophases in Statistical Copolythiophenes — •Alexander Much[1], Jakob Danziger[1], Qian Wang[2], Michael Sommer[2], and Oleksandr Dolynchuk[1] — [1]Martin-Luther-Universität Halle-Wittenberg — [2]Technische Universität Chemnitz

Liquid-crystalline (LC) materials exhibit a variety of structural forms depending on the degree of order, allowing for the novel combination of their anisotropic properties. Board-like conjugated polymers with stiff backbones and short side chains, such as poly-(3-hexylthiophene) (P3HT), are of particular interest because they exhibit weakly explored sanidic LC mesophases.

Here, we study the influence of chemical side-chain modification on the LC phase transitions in statistical copolymers poly-(3-hexylthiophene)-stat-poly-[3-(6-cyanohexyl)thiophene] using differential scanning calorimetry (DSC) and temperature-resolved wide angle X-ray scattering. We find that the copolythiophenes go trough a cascade of sanidic LC mesophases during heating, similar to those in P3HT. Remarkably, the temperature range where sanidic mesophases exists follows the melting range from DSC as a function of comonomer composition and increases towards the intermediate composition with an apparent minimum in values of melting temperature and enthalpy. This suggest that energetic contributions reduce the thermal stability of sanidic LC phases in copolythiophenes, and that LC transition temperatures can be tuned through statistical copolymerization without negating their existence.

CPP 59.3 Fri 12:00 ZEU/0260

In-situ structure and morphology investigations of slot-die coated perovskite nanocrystal films — •Thomas Baier[1], Altantulga Buyan-Arivjikh[1], Lixing Li[1], Xiaojing Ci[1], Markus Döblinger[2], Matthias Schwartzkopf[3], Thomas Bein[2], Sarathlal Koyiloth Vayalil[3,4], and Peter Müller-Buschbaum[1] — [1]TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — [2]Department of Chemistry, LMU, Munich — [3]DESY, Hamburg — [4]UPES, Dehradun

Colloidal perovskite nanocrystals (PNCs) are promising in contributing to next-generation optoelectronic and energy conversion technologies. In this work, mixed-cation cesium-formamidinium lead-iodide (Cs(1-x)FAxPbI3) PNCs were synthesized via a colloidal hot-injection route and subsequently processed into thin-film active layers using slot-die coating for scalable manufacturing. The evolution of structural order during deposition was probed in-situ using grazing-incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS), providing direct insights into nanocrystal packing, ordering, and defect formation. Simultaneous optical characterization via photoluminescence (PL) provided complementary information on the evolution of optical properties during deposition, while transmission electron microscopy (TEM) enabled correlation with nanoscale information. By combining colloidal synthesis, in-situ structural probes, and optical characterization, this work directly links nanoscale assembly, defect states, and the optoelectronic performance of perovskite nanocrystal thin films.

CPP 59.4 Fri 12:15 ZEU/0260

Interplay of heterogeneous nucleation and prefreezing in PBS droplets on graphene — •Marthinus van Niekerk, Moritz Hartelt, and Oleksandr Dolynchuk — Experimental Polymer Physics, Martin-Luther-University Halle-Wittenberg, Germany

The dominant crystallization mechanism depends on the kinetics of formation and crystal growth. Heterogeneous nucleation, leading to spherulitic morphology, and prefreezing, leading to epitaxial morphology, are two mechanisms of interface-induced crystallization in polymers. However, research on prefreezing is in a seminal phase, and its possible competition with nucleation during cooling remains unexplored. Here, we study the crystallization behavior of dewetted poly(butylene succinate) (PBS) droplets on graphene, a known prefreezing substrate for PE and PCL, during cooling from the melt at different rates using optical- and atomic force microscopy and wide-angle X-ray scattering. Across a large range of cooling rates, nucleation was found to be dominant, resulting in spherulitic morphology in large droplets. However, indications of prefreezing were observed in very small droplets exhibiting epitaxial morphology. Subsequent annealing close to T_m resulted in significant reordering and enhancement of out-of-plane orientation, causing a change in morphology from spherulitic to epitaxial for all droplets up to several hundred nanometers. Theoretical analysis revealed a significant lattice mismatch between graphene and PBS, suggesting it is a plausible reason for the absence of rapid prefrozen layer growth during initial cooling from the melt.

CPP 59.5 Fri 12:30 ZEU/0260

Crystallization of polymer networks in the constant-strain and constant-stress ensembles — Atmika Bhardwaj[1], Huzaifa Shabbir[1], Jens-Uwe Sommer[1,2], and •Marco Werner[1] — [1]Bereich Theorie der Polymere, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — [2]Institut für Theoretische Physik, Technische Universität Dresden, Germany

We investigate how deformation and cross-links affect the crystallization of polymer networks using molecular dynamics simulations. A cooling- and heating cycle are simulated both under constant-strain and constant-stress conditions, monitoring specific volume, crystallinity, and orientational order as functions of temperature. In both ensembles, deformation induces chain pre-alignment along the loading direction, driving crystallization at higher transition temperatures. Under constant stress, the pre-alignment promotes crystal growth along the mechanically induced director resulting in a substantial increase of deformation in favor of that direction. These results show how mechanical ensemble, deformation, and cross-linking can be combined to tailor the shape response of polymer networks upon phase transition.

CPP 59.6 Fri 12:45 ZEU/0260

Surface-induced ordering and continuous breaking of translational symmetry in conjugated polymers — Anton Sinner, Alexander Much, and •Oleksandr Dolynchuk — Martin Luther University Halle-Wittenberg, Germany

Surface-induced liquid crystalline (LC) phase transitions elicit fundamental interest and hold potential for leveraging the accompanying anisotropic order at the surface. Board-like conjugated polymers are of particular interest due to the novel sanidic LC phases they exhibit, which have remained largely unexplored. Specifically, although preferential molecular orientation near the free surface has been observed in films of conjugated polymers, the mechanism of its formation is not yet fully understood. In this study, grazing-incidence X-ray scattering is employed to monitor the formation and breaking of positional order in situ in thin films of two conjugated polymers representative of two classes: polythiophenes and polydiketopyrrolopyrroles. Our findings demonstrate that the surface induces positional order in films of both conjugated polymers via the formation of a highly oriented, sanidic disordered LC phase. The ordering process continues upon cooling and undergoes multiple LC transitions into more ordered phases, both at the surface and in the bulk, which can compete with each other. The positional smectic-like order parameter displays continuous temperature dependence in the vicinity of the transition, signifying a continuous breaking of translational symmetry by the surface. Theoretical analysis enables accurate description of the order parameter when critical behavior is considered.