

CPP 35: Focus: Polymer Crystallization - from Model Systems to New Materials I

Organisers: Jens-Uwe Sommer (IPF Dresden), Thomas Thurn-Albrecht (Martin-Luther-Universität Halle)

Polymers with special semicrystalline morphologies play a key role in current research as e.g. in polymeric semiconductors, in the crystallization in polymer networks or in crystalline biopolymers. Notably, the physics of polymer crystallization itself is a topic of ongoing debate. This focus session aims at highlighting selected fundamental and applied aspects of polymer crystallization and at bringing together contributions from different fields to enable common discussions and exchange.

Time: Wednesday 10:15–13:00

Location: ZEU 222

CPP 35.1 Wed 10:15 ZEU 222

Characterization of polymer crystallization in conducting thin films using grazing incidence x-ray scattering — STEPHAN PRÖLLER¹, JENNY LEBERT¹, MIHAEL CORIG¹, PETER MÜLLER-BUSCHBAUM², ALEXANDER HEXEMER³, and ●EVA M. HERZIG¹ — ¹TU München, Munich School of Engineering, Herzig Group, 85748 Garching, Germany — ²TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ³Lawrence Berkeley National Laboratory, Advanced Light Source, Berkeley, USA

The material properties of conducting thin films are - like for many other material systems - closely linked to the nanoscale order and disorder of the involved polymers. Therefore it is important to have adequate experimental methods allowing the characterization of crystallization and aggregation of polymers in thin films, and ideally also during thin film formation. Grazing incidence wide angle x-ray scattering is more and more frequently used to examine the nanoscale order in thin films. Using examples of model systems and novel materials studied in our group the capabilities and limitations of this method are demonstrated.

CPP 35.2 Wed 10:30 ZEU 222

Controlled Crystallization of n-type Semiconducting Polymer Thin Films — ●SABINE LUDWIGS — Institute of Polymer Chemistry, University of Stuttgart

This contribution will focus on current activities in my group on thin films of n-type semiconducting poly[N,N*-bis(2-octyldecyl)-1,4,5,8-naphthalene-dicarboximide-2,6-diyl]-alt-5,5*-(2,2*-bithiophene) (PNDI2OD-T2) and its regioirregular analogues. The assignment of these donor-acceptor copolymers as conjugated redox polymers will be discussed based on electrochemical and field effect transistor measurements. (1,2) Solvent vapor annealing proves to be an excellent tool to obtain spherulitic structures with controlled nucleation density and crystalline order over large areas in thin films. (3) The role of post-annealing procedures to tailor textures and polymorphism will be further highlighted. (1) D. Trefz et al. J. Phys. Chem. C 2015, 119, 22760. (2) Y. Gross et al. Tuning aggregation by regioirregularity in n-type P(NDI2OD-T2) donor-acceptor copolymers, 2017, to be submitted. (3) G. Schulz, S. Ludwigs Adv.Funct.Mater. 2016 DOI: 10.1002/adfm.201603083.

CPP 35.3 Wed 10:45 ZEU 222

In-operando study of changes in the crystalline parts of P3HT:PCBM solar cells — DANIEL MOSEGUÍ GONZÁLEZ¹, CHRISTOPH J. SCHAFER¹, STEPHAN PRÖLLER², JOHANNES SCHLIPP¹, LIN SONG¹, SIGRID BERNSTORFF³, EVA M. HERZIG², and ●PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ²TU München, MSE, Lichtenbergstr. 4, 85748 Garching — ³Elettra-Sincrotrone Trieste, 34149 Basovizza, Italy

Organic solar cells based on poly(3-hexylthiophen-2,5-diyl):phenyl-C60-butyric acid methyl ester (P3HT:PCBM) have developed into a well-controlled model system for studying fundamental questions, although device efficiencies of other blends using low band gap polymers demonstrated significantly higher device efficiencies. Based on an in-operando investigation of a P3HT:PCBM-based solar cell we address for the first time the correlation between the crystalline state of the materials in the organic solar cell and the open circuit voltage probed in the IV-characteristics. We use in-operando grazing incidence wide angle x-ray scattering to probe changes in the crystalline parts of the active layer. The findings give a better understanding of aging of organic solar cells during operation.

CPP 35.4 Wed 11:00 ZEU 222

Impact of Molecular Dynamics on Structure Formation of Donor-Acceptor Block Copolymers — ●MATTHIAS FISCHER¹, CHRISTIAN DAVID HEINRICH², MUKUNDAN THELAKKAT², and THOMAS THURN-ALBRECHT¹ — ¹Martin Luther University Halle-Wittenberg — ²University of Bayreuth

Donor-Acceptor block copolymers (BCP) are attractive materials for organic photovoltaics due to their intrinsic property to form an equilibrium nanostructure on the length scale of exciton diffusion. As usually semiconducting polymers are crystalline or liquid crystalline structure formation is complex in these BCPs. We here present a study of the interplay between phase separation, crystallization and glass transition in two donor-acceptor BCPs of poly(3-hexylthiophene)-block-poly perylene bisimide (P3HT-b-PPBI) incorporating P3HT as donor and polystyrene with two different pendant perylene bisimides as acceptor. In order to study the effect of backbone glass transition on side chain crystallization in the acceptor block low molecular weight model compounds, homopolymers and BCPs were compared using differential scanning calorimetry and temperature dependent wide- and small-angle x-ray scattering as central methods. While microphase separation in the liquid state led to a cylindrical morphology in both cases the crystallization of the side chains depended strongly on the backbone glass transition temperature as compared to the ordering temperature of the PBI units. Surprisingly, a strong π - π -interaction was found even in the absence of lateral ordering of the side chains possibly explaining the relatively high electron mobility of these disordered materials.

CPP 35.5 Wed 11:15 ZEU 222

Structural in-operando investigations on PEDOT:PSS electrodes under high humidity conditions — ●LORENZ BIESSMANN¹, MARKUS TRUNK¹, BO SU¹, HONG XU¹, SIGRID BERNSTORFF², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ²Elettra-Sincrotrone Trieste, 34149 Basovizza, Italy

Towards flexible substrates for organic light emitting diodes and organic photovoltaics it is of significant interest to get rid of brittle, costly electrodes like ITO or FTO as well. PEDOT:PSS offers with its good conductivity, easy processibility, and inherent flexibility a suitable alternative to its rigid and transparent conducting oxide counterparts. The crystallinity as well as orientation of crystals in PEDOT:PSS films is known to have a significant influence on the film conductivity. In particular, the appearance of water in air can cause oxidation and thus decrease the device efficiency or cause device failures. Therefore, we investigate changes of the crystal structure of spray-deposited PEDOT:PSS films under high humidity conditions. We monitor changes in crystallinity and orientation of crystals with in-operando grazing incidence wide angle x-ray scattering (GIWAXS). The variation of conductivity of PEDOT:PSS is linked to the GIWAXS findings. Furthermore, reversibility is studied.

15 min break

Invited Talk CPP 35.6 Wed 11:45 ZEU 222
Density functional theory of crystallization: from anisotropic particles to polymers — ●HARTMUT LOEWEN — Universitaetsstrasse 1, 40225 Duesseldorf

Classical density functional theory for freezing is used to predict the equilibrium bulk phase diagram of anisotropic particles. Explicit results are obtained for orientable hard rectangles in 2 spatial dimensions where isotropic, nematic and smectic phases do occur as a function of particle aspect ratio and number density. Then the density functional theory is applied to the smectic phase on a nontrivial curved manifold like a cone. Confinement-induced phase transition are calculated.

Last, ideas to extend the theory towards polymer crystallization are described.

CPP 35.7 Wed 12:15 ZEU 222

Real-time observation of non-classical protein crystallization — •BENEDIKT SOHMEN¹, MARCUS MIKORSKI¹, ANDREA SAUTER¹, FELIX ROOSEN-RUNGE², RALF SCHWEINS², FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany — ²Institut Laue-Langevin, Grenoble, France

In order to approach a better understanding of non-classical crystallization a huge diversity of mechanisms has been discussed recently [1,2]. Here, we present a combined SAXS and SANS real-time study of the crystallization pathways of β -lactoglobulin in the presence of CdCl₂ with respect to protein concentrations c_p and salt concentrations c_s . Depending on the location in the c_p - c_s phase diagram, different crystallization pathways are observed. For $c_s < c^*$, the solutions are clear and crystallization follows a classical one-step pathway. For $c^* > c_s > c^{**}$, the system enters a condensed regime where an intermediate phase prior to crystallization is observed. By investigating the structure and the temporal evolution of the intermediate phase we clarify its role with respect to crystallization. Based on our studies, we suggest that β -lactoglobulin can follow different non-classical crystallization pathways. The intermediate phase can act as both, a material reservoir and a crystal precursor. [1] De Yoreo et al., *Science*, **349**, 2015, 6760 [2] Sauter et al., *J. Am. Chem. Soc.*, **137**, 2015, 1485-1491

CPP 35.8 Wed 12:30 ZEU 222

Lattice free energy functional for anisotropic particles with pure hard-core interaction and with short-ranged attractions — •MOSTAFA MORTAZAVIFAR and MARTIN OETTEL — Institut für Angewandte Physik, Eberhard Karls Universität Tübingen, Tübingen, Germany

By using a free energy functional of fundamental measure type, the equilibrium properties of a pure hard-rod mixture and hard rods with short-ranged attractions are investigated in a lattice model where the position and the orientation of rods are restricted to discrete values.

Attractions are incorporated via one or more species of polymeric lattice particles in the spirit of the Asakura-Oosawa model. By changing size and shape of these particles, effective attractions of different strength and range can be generated.

We have investigated phase diagrams of 2- and 3-dimensional bulk systems and of monolayers formed with 3-dimensional rods. Bulk 3-dimensional systems exhibit liquid-vapor and isotropic-nematic transitions similar to the systems with rods in continuum. For the monolayers, the continuous nematic transition remains present above a critical temperature and is superseded by a gas-liquid transition below the critical temperature.

CPP 35.9 Wed 12:45 ZEU 222

Small polyethylene systems: On the ground state of single chains and few chain aggregates — •TIMUR SHAKIROV and WOLFGANG PAUL — Institute of Physics, University of Halle, Halle, Germany

The phase behavior of polyethylene has been under investigation for the last six decades. Investigation of single-chain crystallization in solution is a technically difficult problem, because in molecular dynamics simulations as well as in experiments, it is not so easy to distinguish kinetic and thermodynamic effects on chain folding. The general picture, however, is, that single polyethylene chains in solution fold into lamellar crystals. We present results of a Stochastic Approximation Monte Carlo (SAMC) simulation, which gives a possibility to analyze thermodynamical equilibrium properties of a system. Our simulation study of relatively short polyethylene chains is based on a chemically realistic united atom model [1]. Simulational results for low-energy states of single chains of different lengths demonstrate a set of various ground-state configurations: from stretched and hairpin-like configurations of short chains to a helix-like structure reeled round one of the chain*s ends. Aggregates of a few short polyethylene chains exhibit another set of ground states, depending on chain length and number of aggregated chains. However, with increasing chain length, single chain and aggregate morphologies become more similar.

[1] W. Paul, D. Y. Yoon, and G. D. Smith, *J. Chem. Phys.* **103** (1995) 1702-1709.