

CPP 41: Crystallization, Nucleation and Self-Assembly

Time: Thursday 15:00–17:30

Location: H39

Invited Talk

CPP 41.1 Thu 15:00 H39

Interface-induced crystallization in polymers: From model systems to applications for semiconducting polymers —MUHAMMAD TARIQ¹, ROBERT KAHL¹, MUKUNDAN THELAKKAT², THOMAS THURN-ALBRECHT¹, and ●OLEKSANDR DOLYNCHUK¹ — ¹Experimental Polymer Physics, Martin Luther University Halle-Wittenberg — ²Applied Functional Polymers, University of Bayreuth

Crystallization is usually initiated at interfaces. Understanding the physical process underlying interface-induced crystallization (IIC) is of fundamental interest and is relevant for material applications. IIC of liquids can occur either by heterogeneous nucleation (HN) or by the equilibrium phenomenon of prefreezing. First, we present a combined theoretical and experimental study of the effect of the substrate-material interactions on the thermodynamics of prefreezing and on the kinetics of HN in model polymers on various substrates. Second, the acquired knowledge about IIC elucidates the role of interfaces for crystal orientation in films of conjugated polymers, which is important for device performance. Using polythiophenes as model conjugated polymers, we show that different crystal orientations can be formed at the interfaces to a substrate and vacuum as a result of two competing interfacial interactions. Our results demonstrate that increasing the polarity of polythiophene side chains influences the interactions at the interfaces, resulting in a change of crystal orientations. Thus, we disclose the crucial role of the interfacial interactions for crystallization kinetics, thin film morphology, and control of molecular orientation in films of model and semiconducting polymers.

CPP 41.2 Thu 15:30 H39

Determination of Morphologically Tailored Chirality in Supramolecular Nanostructures by X-ray Scattering —●ASENA CERHAN HAINK¹, FELIX WENZEL², KLAUS KREGER², HANS-WERNER SCHMIDT², RICHARD HILDNER³, and EVA M. HERZIG¹ — ¹Dynamik und Strukturbildung-Herzig Group, Universität Bayreuth, Universitätsstr.30, 95447 Bayreuth, Germany — ²Makromolekulare Chemie I, Universität Bayreuth, Universitätsstr.30, 95447 Bayreuth, Germany — ³Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Designed supramolecular nanostructures allow control over their optical and electronic properties which make them promising candidates for light-harvesting applications. Recently, we presented long-range (μm) transport of excitation energy in supramolecular nanofibres based on a carbonyl-bridged triarylamine (CBT). Here, we study supramolecular CBT building blocks with chiral side groups, which result in a distinct circular dichroism (CD) signal from self-assembled nanofibres. For bundles of supramolecular nanofibres, we observe an inversion in the CD signal as a function of temperature. To understand the origin of this effect, we performed morphological characterisation using temperature-dependent Wide Angle X-ray Scattering on the CBT-based bundles. We demonstrate systematic temperature-dependent variations in the π - π stacking and the column-column distances, which indicates that the CBT-based bundles have thermoelastic behaviour and change chirality at the critical temperature.

CPP 41.3 Thu 15:45 H39

Learning the Crystallisation Behaviour of Bidisperse Branched Model Polymers using Coarse-Grained Molecular Dynamics Simulations —●WILLIAM FALL¹, JOERG BASCHNAGEL¹, OLIVIER LHOST², and HENDRIK MEYER¹ — ¹Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg Cedex, France. — ²TotalEnergies One Tech Belgium, Zone Industrielle C, 7181 Feluy, Belgium

Model polymer systems allow fundamental questions about polymer crystallisation to be tackled precisely. Molecular dynamics (MD) simulations can provide insights but studying large lamellar structures is challenging. Meyer and Muller-Plathe set the stage for molecular dynamics (MD) simulations of large lamella structures, by demonstrating that reproducing local crystalline structures is unimportant when large crystalline and amorphous regions dominate properties. Here, the role of short chain branches (SCBs) (C4) on the melt and crystalline properties of monodisperse polyethylene systems (C400) is investigated, using CGMD simulations. SCBs are grown into the melt to minimise computational expense, providing access to large systems. Cooling

and heating cycles reveal the crystalline morphology depends strongly on both cooling rate and number of branches. Bidisperse mixtures of ultra-long C4000 and C400 are also studied, with different branch distributions, which mimic industrial PE morphologies. Via self-seeding, well aligned lamella are grown and morphological features, i.e. tie chains analysed. We begin to address how these features influence crystalline structure and material properties. We thank TotalEnergies for funding and GENCI/IDRIS (Orsay) and CAIUS/HPC centre.

CPP 41.4 Thu 16:00 H39

Aggregation and ordering in small alkane systems — ●TIMUR SHAKIROV and WOLFGANG PAUL — University of Halle, Halle, Germany

Ordering of small alkanes differs drastically from the bulk one. The difference is not only quantitative but also qualitative: short-chain single alkanes fold at low temperatures into non-trivial structures [1] in contrast to fully-stretched-chain lamellae in bulk. For the few chain systems we demonstrate the leading role of torsional stiffness in the ordered structure formation and investigate the corresponding conformations, which vary from spirals to tilted lamellae. For the fully stretched chain lamellae we find a two-step ordering, the indications of which remain at least up to 16 chain aggregates. In contrast to the low-temperature ordering, the aggregation or liquid-vapor transition leads to similarly disordered structures for all system sizes, which allows correction of size effects and extrapolation of the estimated aggregation temperatures to the thermodynamic limit. Our calculations of aggregation/boiling temperatures at normal pressure are in good agreement with experimental data. The presented equilibrium results are based on Wang-Landau-type Monte Carlo simulations [2,3] of a chemically realistic united atom model [4].

[1] T. Shakirov, and W. Paul, *J. Chem. Phys.* 2019, 150, 084903.[2] F. Liang et al, *J. Am. Stat. Assoc.* 2007, 102, 305-320.[3] T. Shakirov, *Comp. Phys. Commun.* 228 (2018), 38-43.[4] W. Paul, D. Y. Yoon, and G. D. Smith, *J. Chem. Phys.* 103 (1995) 1702-1709.

CPP 41.5 Thu 16:15 H39

How the competition between crystal growth and intracrystalline chain diffusion determines the lamellar thickness in semicrystalline polymers — MARTHA SCHULZ, MAREEN SCHÄFER, KAY SAALWÄCHTER, and ●THOMAS THURN-ALBRECHT — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle

The non-equilibrium thickness of lamellar crystals in semicrystalline polymers varies significantly between different polymer systems and depends on the crystallization temperature T_c . There is currently no consensus on the mechanism of thickness selection. Previous work has highlighted the decisive role of intracrystalline chain diffusion (ICD) in special cases, but a systematic dependence of lamellar thickness on relevant timescales such as that of ICD and stem attachment has not yet been established. Studying the morphology by small-angle X-ray scattering and the two timescales by NMR methods and polarization microscopy, we present data on poly(oxyethylene), a case with relatively slow ICD. It fills the gap between previously studied cases of absent and fast ICD, enabling us to establish a quantitative dependence of lamellar thickness on the competition between the noted timescales. *Ref. Nature Communications*, 13.1 (2022): 1-10.

15 min. break

CPP 41.6 Thu 16:45 H39

The Crucial Role of Solvation Forces in Inter-Nanoplatelet Interactions and Stack Formation — ●NANNING PETERSEN, MARTIN GIRARD, ANDREAS RIEDINGER, and OMAR VALSSON — Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz

Cadmium selenide nanoplatelets show the tendency to form stacks in apolar alkane solvents. This effect is very similar to the stack formation of micron-sized discs, which can be induced by depletion forces. However, the interplay of the various forces leading to stack formation of nanoplatelets remains unclear. Solvation forces are in their origin and behaviour very similar to depletion forces.

Here, we use coarse-grained molecular dynamics simulations of nanoplatelets in octane solvent to investigate the role of solvation

forces in nanoplatelet interactions. We demonstrate that solvation forces resulting from solvent layering are sufficiently strong to stabilize nanoplatelet stacks. We examine the dependence of solvation forces on the nanoplatelets' ligand shell, size, and other parameters. In particular, we demonstrate that for sufficiently large nanoplatelets, solvation forces are proportional to the interacting facet area, and their strength is intrinsically tied to the softness of the ligand shell. The solvation forces exhibit an oscillatory nature; increases in their strength leads to a stronger attraction between close nanoplatelet facets and in addition to an increase in the kinetic barriers.

[1] N. Petersen, M. Girard, A. Riedinger, and O. Valsson, ChemRxiv, doi:10.26434/chemrxiv-2022-mw1cs (2022)

CPP 41.7 Thu 17:00 H39

In situ small-angle X-ray scattering and total scattering to study CuPd nanoparticle growth and self-assembly — •KILIAN FRANK¹, DAVIDE DERELLI², DOROTA KOZIEJ², and BERT NICKEL¹ — ¹Faculty of Physics and Center for Nanoscience (CeNS), Ludwig-Maximilians-Universität, Geschwister-Scholl-Platz 1, 80539 München, Germany — ²University of Hamburg, Institute for Nanostructure and Solid-State Physics, Center for Hybrid Nanostructures, 22761, Hamburg, Germany

Combining noble metals with abundant materials is a promising design strategy for new catalytic nanomaterials, e.g. for CO₂ reduction. Reliable synthesis routes of nanoparticles with a low size dispersity are required, but often an understanding of the formation pathway is lacking. Therefore, we investigated the entire synthesis of CuPd alloy nanoparticles using simultaneous small-angle X-ray scattering (SAXS) and the atomic pair distribution function obtained from total scattering (TS) to establish the sequence of structures from the atomic level to the nanoscale. We use a dedicated reaction cell for heating

and stirring at the high-energy beamline P07 (PETRA III, DESY), extending our previous studies on cobalt oxide nanoparticle formation (<https://doi.org/10.1038/s41467-021-24557-z>). We characterize the transformation of precursors and early nucleation by TS, and the subsequent particle growth and assembly by SAXS in a model-based analysis. Upon cooling, we observe a rich temperature-dependent phase behavior of particle assemblies. These can serve as a potential templating strategy for efficient particle-based catalysts.

CPP 41.8 Thu 17:15 H39

Ligand-stabilized gold nanorods as an ideal model system for anisotropic colloids — •MARCEL KRÜSMANN and MATTHIAS KARG — Physikalische Chemie I: Kolloide und Nanooptik, Heinrich-Heine-Universität Düsseldorf, Düsseldorf, 40225, Germany

Anisotropic colloidal particles have interesting optical, electronic and self-assembly properties. Yet the investigation of their phase behavior is often difficult due to limitations in quantity, monodispersity and colloidal stability for many particles. An additional challenge is the precise determination of particle number concentrations.

The easily scalable synthesis of gold nanorods gives access to monodisperse anisotropic colloids with a broad range of aspect ratios. The functionalization of gold nanorods with a polymer ligand increases the colloidal stability and removes the large excess of surfactant that is most often used in particle synthesis.

These anisotropic particles can now be studied with various methods. One of this methods is small-angle X-ray scattering for which gold has an excellent contrast. In combination with the good colloidal stability it is now possible to not only study the form factor but also the structure factor at high concentrations and/or during induced aggregation. The addition of absolute intensity measurements gives access to the particle number concentration, that can be related to measured extinction from spectroscopy.