

CPP 10: Crystallization, Nucleation and Self-assembly I

Time: Monday 15:00–17:30

Location: H13

CPP 10.1 Mon 15:00 H13

The Underestimated Effect of Intracrystalline Chain Dynamics on the Morphology and Stability of Semicrystalline Polymers — ●MARTHA SCHULZ, ANNE SEIDLITZ, RICARDO KURZ, RUTH BÄRENWALD, ALBRECHT PETZOLD, KAY SAALWÄCHTER, and THOMAS THURN-ALBRECHT — Martin-Luther-Universität Halle-Wittenberg

Some polymers show translational motion of the chains in crystallites - the α_c -relaxation. Although it was recognized early by BOYD that α_c -mobile polymers have a higher crystallinity than crystal-fixed polymers, the relaxation process has been ignored in most crystallization models. We show that the α_c -relaxation has a strong influence on the crystallization process, changing morphology and stability of the semicrystalline structure. Using SAXS, we compare structural characteristics for PEO (α_c -mobile) and PCL (crystal-fixed) after isothermal crystallization and during heating. With NMR we can estimate the timescale of the α_c -relaxation depending on T_c . A direct comparison points out fundamental differences: PCL shows marginally stable lamellae with a narrow thickness distribution, starting to reorganize for $T > T_c$. In contrast, PEO shows a well-defined, narrowly distributed amorphous thickness d_a and a broad thickness distribution of the lamellae. For $T > T_c$, the lamellae are stable over a wide range. We hypothesize that due to the α_c -relaxation, the lamellae thicken directly behind the growth front up to a minimal d_a . This is supported by NMR-results: At high T_c the α_c -relaxation is fast enough to enable crystal reorganization to take place in a narrow zone directly behind the growth front.

Schulz, M.; *Macromolecules* 51, 8377 (2018)

CPP 10.2 Mon 15:15 H13

Combining Infrared Micro-Spectroscopy and Fast Scanning Chip Calorimetry to unravel homogeneous nucleation and crystallization in poly(amide-6-6) — WILHELM KOSSACK¹, EVGENY ZHURAVLEV², RUSTEM ANDRIANOV³, CHRISTOPH SCHICK^{2,3}, and ●FRIEDRICH KREMER¹ — ¹University Leipzig, molecular physics, Linnestr. 5, Leipzig, Germany — ²Institute of Physics and Competence Centre CALOR^o, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany — ³Institute of Chemistry, Kazan Federal University, 18 Kremlyovskaya Street, Kazan 420008, Russian Federation

A combination of Infrared micro-spectroscopy and Fast Scanning calorimetry is used for a simultaneous measurement of moiety specific IR-absorption and heat capacity in the super-cooled amorphous melt of poly(amide-6-6). The temporal evolution of both quantities is recorded depending on temperature and time to unravel the microscopic, moiety-specific mechanism of homogeneous nucleation. The IR results reveal a continuous increase of bands related to the crystalline phase on expense of the amorphous phase. In agreement with classical nucleation theory, first experiments do not reveal a moiety-specific interaction during homogeneous nucleation. Furthermore both, IR-signature and calorimetric crystallinity and nuclei densities follow similar kinetics. In summary, no evidence is found that homogeneous nuclei and early crystals differ qualitatively on the level of a unit cell from well grown lamellae. Based on these experiments an experimentally based estimate of the size of homogeneous nuclei is possible.

CPP 10.3 Mon 15:30 H13

Visualization of Polymer Crystallization by a Combination of Atomic Force Microscopy and Fast Scanning Calorimetry — ●RUI ZHANG^{1,2}, EVGENY ZHURAVLEV^{1,2}, and CHRISTOPH SCHICK^{1,2,3} — ¹Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany — ²Competence Centre CALOR, Faculty of Interdisciplinary Research, University of Rostock, Albert-Einstein-Str. 25, 18051 Rostock, Germany — ³Kazan Federal University, 18 Kremlyovskaya street, Kazan 420008, Russian Federation

Atomic force microscopy (AFM) can show the morphology of the crystal structures of semi-crystallized polymers with resolution from micrometers to nanometers scales. Meanwhile, fast scanning calorimetry (FSC) can treat the polymer sample heating and cooling until 1,000,000 K/s, which enables to achieve expected annealing temperature without re-crystallization processes. By combining with AFM and FSC (AFM-FSC), the scanner of AFM plays as the chip-sensor holder and enables the FSC to be directly measured on the AFM with-

out changes of the sensor. By this way, the polymer sample can be annealed at expected temperature and time and these formed crystals structures can be accessed to AFM after fast cooling to environmental temperature. Some results will be reported in presentation.

CPP 10.4 Mon 15:45 H13

Visualization of Dynamic Processes with Video-Rate Atomic Force Microscopy — ●TED LIMPOCO, MARIO VIANI, and MARTA KOCUN — Asylum Research, an Oxford Instruments company, 6310 Hollister Ave, Goleta, U.S.A.

Atomic Force Microscopy (AFM) is a unique and powerful tool for measuring structural, mechanical, and electrical properties of materials at the nanometer scale. A limitation of conventional AFM is that it is a slow technique, with image acquisition times on the order of minutes. The recent introduction of a practical video-rate AFM has improved imaging speeds and makes it now possible to capture movies with a temporal resolution better than a second. This presentation will cover some recent results taken via video-rate AFM, including the real-time self-assembly of collagen into fibrils and the migration of surfactant micelles on graphite. Additionally, we will discuss related results such as the melting/re-crystallization of polymers and consider future research opportunities that might be enabled by this technology.

15 min. break

CPP 10.5 Mon 16:15 H13

Polymorphism and crystal stability of syndiotactic polystyrene from multiscale simulations — ●CHAN LIU, KURT KREMER, and TRISTAN BEREAU — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Syndiotactic polystyrene (sPS) exhibits complex polymorphic behavior upon crystallization. Computational modeling of polymer crystallization has remained a challenging task because the relevant processes are slow on the molecular time scale. In previous work, we have found that our coarse-grained (CG) model of sPS significantly speed up the simulations, while stabilizing the main polymorphs α and β , observed experimentally. However, to study the stability of polymorphs, we require reasonably larger system and more advanced enhanced-sampling methods, such as Metadynamics. Furthermore, we rely on Markov state models to gain insight into the kinetics of interconversion between polymorphs and to verify the convergence of Metadynamics.

CPP 10.6 Mon 16:30 H13

Thermodynamic Principles of Prefreezing as a First-Order Transition — ●OLEKSANDR DOLYNCHUK, MUHAMMAD TARIQ, and THOMAS THURN-ALBRECHT — Experimental Polymer Physics, Institute of Physics, Martin Luther University Halle-Wittenberg, Germany

Crystallization of liquids on a solid surface can be initiated by either heterogeneous nucleation or prefreezing. The latter phenomenon is the crystalline layer formation at an interface to a solid substrate at a temperature higher than that of a bulk crystal. As it was recently determined, prefreezing is a first-order transition, since the formation of the crystalline phase is abrupt and reversible.

Here, we present a phenomenological theory of prefreezing and analyze such equilibrium properties as the temperature dependent thickness of the pre-frozen layer, the maximum temperature range of prefreezing T_{max} , and the mesoscopic jump of thickness during crystallization or melting. The theory provides a clear first-principles explanation of the first-order nature of prefreezing and defines the corresponding transition temperature T_{max} as a function of the interfacial free energies. As shown, it is the difference of the interfacial energies that controls T_{max} and serves as a driving force for prefreezing. The theoretical outcomes are applied to quantify the recent experimental results for poly(ϵ -caprolactone) crystallized on graphite via prefreezing.

CPP 10.7 Mon 16:45 H13

Small polyethylene systems: aggregation and low temperature configurations — ●TIMUR SHAKIROV and WOLFGANG PAUL — Institute of Physics, University of Halle, Halle, Germany

The phase behavior of dilute solutions of polyethylene chains has been under investigation for many decades. But investigation of the equilibrium structures of single alkane chains and their aggregation have been

addressed in far less detail. We present here results of a Wang-Landau-type Monte Carlo simulation [1,2], which give a possibility to analyze thermodynamic equilibrium properties of a system. Our simulation study of short polyethylene chains is based on a chemically realistic united atom model [3]. Simulation results for deep-energy (or equivalently low temperature) states demonstrate a set of various ground-state configurations: from stretched configurations of short chains to a helix-like structures reeled round one of the chains. Aggregates of a few chains demonstrate complex temperature behavior having disordered and ordered phases even for aggregates composed of a couple of chains. Corresponding low-energy configurations differ from configurations of single chains having the same number of monomers. However, with increasing chain length, single chain and aggregate morphologies become more similar.

[1] F. Liang, C. Liu, R. J. Carroll, *J. Am. Stat. Assoc.* 2007, 102, 305-320.

[2] T. Shakirov, *Comp. Phys. Commun.* 228 (2018): 38-43.

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

CPP 10.8 Mon 17:00 H13

Steric and Hydrophobic Interactions Determine Self-assembly of Supramolecular Nanorods — •SAIKAT CHAKRABORTY¹, CHRISTIAN BERAC², POL BESENIUS², and THOMAS SPECK¹ — ¹Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 7-9, 55128 Mainz, Germany. — ²Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, Germany.

C_3 -symmetric amphiphilic peptides have been successfully applied for the construction of supramolecular aggregates of defined size and shape. These compounds typically contain a hydrophobic core and three amphiphilic arms. In water, due to combined effects of hydrophobic interactions, hydrogen bonding and shielding effects of flexible hydrophilic chains, the monomers stack over one another to form one-dimensional nanorods. We present a minimal model for efficient sim-

ulations of such unidirectional self-assembly without the requirement of an explicit solvent. Composites of the monomers interact among themselves via simple pair potentials to invoke hydrophobic and steric effects. We show that these factors are sufficient to obtain self-assembly of the monomers into elongated, defect-free, rod-like structures from highly dilute, disordered initial state. This assembly kinetics have been linked to the microscopic processes governing the polymerization. The understanding thus obtained, has been used to draw comparison with the experiments. Further, study of the morphology of the nanorods reveals that beyond a threshold value of hydrophobic interactions among these achiral building blocks, there is a transition to helical structure.

CPP 10.9 Mon 17:15 H13

Fabrication of polymeric Janus nanoparticles and their behavior at liquid-liquid interfaces - a simulation study — •TATIANA MOROZOVA and ARASH NIKOUBASHMAN — Johannes Gutenberg University, Mainz, Germany

Polymeric nanoparticles (NPs) are promising candidates for a wide range of applications such as colloidal self-assembly and targeted therapeutics. Flash Nanoprecipitation (FNP) is a scalable technique for fabricating monodisperse polymeric NPs through rapid micromixing of a polymer solution with a miscible poor solvent. In this simulation work, we are studying the fabrication of Janus NPs with one solvophilic and one solvophobic hemisphere, and their behavior at liquid-liquid interfaces. We performed coarse-grained molecular dynamics simulations of the FNP process using two types of solvophobic homopolymers and one type of amphiphilic blockcopolymers (BCPs). We systematically investigated the influence of the composition and concentration of the BCPs on the resulting NP morphology. We determined the parameter space where amphiphilic Janus or core-shell NPs can be formed, and studied the conformation of BCPs at the NPs surface. Finally, in order to test the potential of these NPs as colloidal stabilizing agents, we placed them at the interface between two immiscible liquids. Indeed, we observed a significant reduction of the surface tension for both core-shell and Janus NPs.