CPP 4: Crystallization, Nucleation and Self-Assembly I

Time: Monday 11:30–13:00 Location: H34

CPP 4.1 Mon 11:30 H34

Confined crystallization for studying kinetics and crystal orientation of interface-induced polymer crystallization — •Marthinus van Niekerk, Thomas Thurn-Albrecht, and Oleksandr Dolynchuk — Experimental Polymer Physics, Martin Luther University Halle-Wittenberg, Germany

Understanding interfacial interactions is essential to understanding the mechanisms and kinetics of interface-induced crystallization (IIC), namely heterogeneous nucleation or prefreezing, and resultant material properties. While heterogeneous nucleation is an activated process occurring below T_m, prefreezing is an equilibrium process producing a stable crystalline layer above T_m that thickens upon cooling. Quantifying the influence of interfacial interactions on the kinetics of IIC and crystal morphology has long been elusive and is addressed in this work. We present a systematic study of confined crystallization in micrometer-sized dewetted droplets of poly(ϵ-caprolactone) (PCL) on a range of substrates, allowing numerical analysis of isolated nucleation events and kinetics. Our results show that prefreezing significantly enhances crystallization kinetics compared to nucleation, resulting in simultaneous crystallization of PCL droplets close to T_m. X-ray scattering reveals the preferred crystal orientation in PCL droplets crystallized by IIC, which is strongest for prefreezing and is supported by striking differences in lamellar morphologies observed in AFM. Thus, we present both quantified nucleation kinetics and crystal orientation for different cases of IIC and show that prefreezing enhances crystallization kinetics and anisotropic crystal orientation most effectively.

CPP 4.2 Mon 11:45 H34

Liquid crystalline ordering of conjugated polymers at the vacuum interface — Anton Sinner, Alexander Johannes Much, and •Oleksandr Dolynchuk — Experimental Polymer Physics, Martin Luther University Halle-Wittenberg, Germany

Structure formation in films of conjugated polymers (CPs) strongly affects their optoelectronic properties and is of fundamental interest in the context of sanidic liquid crystalline (SLC) phases discovered in board-like polymers. Recent experimental results on films of the model CP poly(3-hexylthiophene) (P3HT) revealed the edge-on crystal orientation in the top film layer and suggested that the vacuum interface induces it. Here, we use grazing-incidence wide-angle X-ray scattering to study in situ the crystallization and melting in films of P3HT and polydiketopyrrolopyrrole (PDPP), another board-like CP, at the vacuum interface. Upon cooling from the melt, the ordering of both P3HT and PDPP indeed starts at the vacuum interface as an edge-on oriented disordered SLC phase and undergoes multiple SLC transitions with decreasing temperature. The same thermal hierarchy of SLC phases is observed for both CPs during melting, demonstrating that the vacuum interface stabilizes the edge-on disordered SLC phase above its bulk transition temperature, similar to the surface freezing of short alkanes. Notably, the observed effects are much stronger for PDPP, also resulting in a thicker edge-on oriented layer of more than 100 nm. Thus, we show that surface-induced SLC ordering is a general phenomenon of CPs, presumably due to their board-like architecture, and it significantly influences the molecular orientation in CP films.

CPP 4.3 Mon 12:00 H34

How Aqueous Solutions of Low-end Mono-alcohols Crystallize? — •Vasileios Moschos[1] and George Floudas[1,2] — [1]Department of Physics, University of Ioannina, 45110 Ioannina, Greece — [2]Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Aqueous solutions of low-end aliphatic mono-alcohols, such as ethanol and 1-propanol, display several peculiar features originating from hydrogen bonding, and in particular, antagonistic hydrophilic/hydrophobic interactions of the head/tail that give rise to local nano-heterogeneity. By combining structural (XRD), thermodynamic (Differential Scanning Calorimetry, DSC) and dynamical (Dielectric Spectroscopy, DS) probes, the pertinent phase diagrams of the two binary mixtures are established, comprising of liquid 1-propanol/ethanol, liquid water, hexagonal ice and different hydrates. The two phase diagrams are discussed in terms of up to five different Regimes (Regime I-V), all sharing a droplet arrangement of the minority component, with the exception of Regime I in ethanol/water binary system, where molecular mixing of the two components occurs. By probing the dynamics of the mixtures over an extended frequency and temperature range, different relaxation processes are identified, either associated with with the dynamics of pure alcohol (Debye-like and α-process) or alcohol/water mixtures.

CPP 4.4 Mon 12:15 H34

Intra-crystalline chain diffusion, semicrystalline morphology and mechanical modulus of selected aliphatic polyesters — •Qiang Yu, Albrecht Pezold, and Thomas Thurn-Albrecht — Martin-Luther-University Halle-Wittenberg

Aliphatic polyesters are good candidates to replace commodity plastics in many applications due to their similar mechanical and thermal properties, and superior degradability. However, their intra-crystalline chain diffusion (ICD, the mobility of polymer chains in the crystalline phase) and semicrystalline morphology have not been widely studied. From our recent studies, based on model polymers, semicrystalline polymers exhibit different morphological features depending on the timescale of ICD ($\langle\tau_c\rangle$) relative to the kinetics of crystal growth (τ_{lc}). To check the generality of the findings, our study is expanded into a series of A-B aliphatic polyesters. $\langle\tau_c\rangle$ and τ_{lc} of the polyesters were investigated by nuclear magnetic resonance (NMR) and polarized optical microscope, respectively. The semicrystalline morphology was monitored by small angle X-ray scattering (SAXS) during isothermal crystallization. Long $\langle\tau_c\rangle$ (not measurable by NMR) was qualitatively differentiated by different crystal thickening slopes (SAXS measurement). The results show that our findings are also valid for the investigated polyesters. The different crystal thickening slopes show that the ICD of polymers slows down due to the formation of layers of ester groups in the crystal. At last, we report on the exponential dependence of shear modulus of the polyesters with long $\langle\tau_c\rangle$ on their crystallinity.

CPP 4.5 Mon 12:30 H34

Self-assembled Peptides Structure Mediated by Solid Interfaces — •Leila Sahebmohammadi[1], Pol Besenius[2], Markus Mezger[3], and Regine von Klitzing[1] — [1]Soft Matter at Interfaces, Department of Physics, Technical University of Darmstadt, Germany — [2]Department of Chemistry, Johannes Gutenberg-Universität Mainz, Germany — [3]Faculty of Physics, Universität Wien, Austria

The self-assembly of amphiphilic, C3-symmetric dendritic peptides is driven by non-covalent interactions and steric limitations. This study focuses on peptides with a thermosensitive moiety. In phosphate buffer, oppositely charged peptide amphiphiles form 1D nanorod-like patterns, confirmed by circular dichroism spectroscopy to follow a ß-sheet structure. Atomic Force Microscopy (AFM) revealed temperature-dependent helical filaments, where higher temperatures increased filament length and pitch due to the hydrophobic thermosensitive moiety, while reducing filament height. Quartz Crystal Microbalance with Dissipation (QCM-D) showed a temperature-responsive, layer-by-layer adsorption process forming stable multilayers. Lysine-based cationic comonomers improved adsorption and coating uniformity on gold (Au) and silicon (Si) surfaces. Extreme pH conditions (2 or 12) caused multilayer removal, revealing a pH-responsive mechanism from weakened electrostatic interactions. This study demonstrates how self-assembly and surface confinement adapt peptide assembly, offering insights for modifying surface properties for diverse applications.

CPP 4.6 Mon 12:45 H34

Crystallization and Pseudo-Isodimorphism in Statistical Co-Polythiophenes — •Alexander Johannes Much[1], Jakob Boris Günther Danziger[1], Qian Wang[2], Michael Sommer[2], and Oleksandr Dolynchuk[1] — [1]Martin-Luther-Universität Halle-Wittenberg — [2]Technische Universität Chemnitz

Statistical copolymerization is a powerful and widely used way to tailor material properties like solubility or mechanical properties. The copolymer properties depend largely on their co-crystallization and the crystal structure formed, which has been studied for polyesters, polyamides, and polycarbonates. The results suggest three co-crystallization scenarios: (1) total exclusion of comonomers, (2) total inclusion of comonomers (isomorphism), and (3) partial inclusion of comonomers into two crystal lattices (isodimorphism).

Here we study the co-crystallization and crystal structure of poly-(3-hexylthiophene)-stat-poly-[3-(6-cyanohexyl)thiophene] statistical copolymers using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). The composition-dependent melting temperatures and enthalpies obtained from DSC show minima, which is typical of isodimorphic co-crystallization. However, WAXS clearly indicates single crystal lattices in all copolymers, with a monotonic dependence of lattice constants on composition. This finding is inconsistent with isodimorphism, making the co-crystallization of these statistical copolythiophenes only pseudo-isodimorphic. Hence, our results suggest that the current classification of statistical copolymer crystallization is incomplete and needs to be extended.