

CPP 48: Poster: Polymer Crystallization, Nucleation and Selfassembly

Time: Wednesday 18:30–21:00

Location: P2-OG1

CPP 48.1 Wed 18:30 P2-OG1

On the controversy close folds versus coils in polyethylene and the weight of evidence. — ●HEINZ H.W. PREUSS — Hameln

The highest weight of evidence in the field of morphology belongs to direct visualization and photography. Results of direct visualization and photography of entangled and coiled or looped chains of polymeric molecules in melts and of close folds of chains in solid polymers are not yet found to be published. But separated lamellae of HDPE could be visualized and photographed by H. Preuss (1) with a TEM after tearing them off from the surface of a specimen solidified from melt by slow cooling. The thickness of the lamellae (120 nm) was estimated from the shadow length in the fracture surface after evaporation of carbon under a 30° angle, and the orientation of the chains perpendicular to the plane of the lamellae was confirmed by electron diffraction. Thus the fold model of A. Keller could be confirmed as sure as for polyethylene crystals from dilute solution. *When the lamellae are isolated single entities, as in solution crystallization then given that the chains are perpendicular, or at a large angle to the basal plane, folding is a straightforward necessity as the chains have nowhere else to go.”(2) Entangled and coiled molecules remain a fiction until they would be observed directly. 1 - H.H.W.Preuss, physica status solidi, vol. 3, 1963, K 109 ff.; Plaste und Kautschuk, 22.Jg. Heft 12, 1975, 958-959 2 - A. Keller, Faraday Discussion 1979 p. 149

CPP 48.2 Wed 18:30 P2-OG1

NMR investigations of dynamics in the different phases of semicrystalline polymers — ●MAREEN SCHÄFER, RICARDO KURZ, MARTHA SCHULZ, ANNE SEIDLITZ, THOMAS THURN-ALBRECHT, and KAY SAALWÄCHTER — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle (Saale), Germany

The melt-crystallized morphology of semicrystalline polymers strongly depends on the diverse dynamics in the amorphous and crystalline region. The connections between structure formation and dynamics of polymer chains are investigated with SAXS and NMR spectroscopy, respectively, and polymers with and without intracrystalline dynamics (crystal-mobile and crystal-fixed) are compared. Proton time-domain techniques enable the analysis of the phase components, the intracrystalline and the amorphous phase dynamics. The intracrystalline motion displays only a weak dependence on morphology. SAXS results show that the morphology of the crystal-fixed polymer, poly-ε-caprolactone (PCL), and the crystal-mobile polymer, polyethylene oxide (PEO), are qualitatively different. The crystal thicknesses in PCL are well-defined whereas in PEO a crystal reorganization process caused by the intracrystalline dynamics leads to a uniform amorphous region. To investigate the impact of the crystalline growth and reorganization process on the morphology separately, polymers with slower intracrystalline mobility, e.g. polyoxymethylene (POM), will be investigated. Further investigations address the relationship between morphology and entangled dynamics in the amorphous phase.

CPP 48.3 Wed 18:30 P2-OG1

Molecular Dynamics simulations of deformation induced solubility of poly(ethylene oxide) in water — ●SERGIJ DONETS¹, OLGA GUSKOVA¹, and JENS-UWE SOMMER^{1,2} — ¹Institute Theory of Polymers, Leibniz-Institute of Polymer Research, D-01069 Dresden, Germany — ²Technische Universität Dresden, Institute for Theoretical Physics, D-01069 Dresden, Germany

Metastability of hydrated polymer solutions can lead to a spontaneous solidification via H-bonding in response to the stress fields, e.g. under flow conditions. This could potentially help to overcome the problem of high energy input at each stage of the processing path and provide us with low energy, wet-processing techniques for producing sustainable polymeric materials. Water solution of poly(ethylene oxide) is considered as a potential candidate capable of undergoing the phase transition as a result of loss of the hydrated structure. We have performed classical molecular dynamics simulations to study thermodynamic and structural properties of poly(ethylene oxide) under deformation in water.

CPP 48.4 Wed 18:30 P2-OG1

Effects of the α_c -relaxation for PEO and POM: Impact on Crystallization Process, Morphology and Reorganization Behavior**havior** — ●MARTHA SCHULZ, ANNE SEIDLITZ, and THOMAS THURN-ALBRECHT — Institute of Physics, MLU Halle-Wittenberg, Germany

Depending on the presence or absence of an α_c -relaxation it is possible to distinguish between crystal-mobile and crystal-fixed semi-crystalline polymers. Only crystal-mobile polymers own a certain chain mobility in the crystalline phase. In contrast to the crystal-fixed polymer Polycaprolactone (PCL), we analyze the impact of the α_c -relaxation for two representatives of α_c -mobile polymers, Polyethylenoxide (PEO) and Polyoxymethylene (POM), using different methods like SAXS and Flash-/DSC.

SAXS-measurements show that crystal-fixed polymers follow the expectations of classical crystallization theories. The crystal thickness is determined by the crystallization temperature T_c . In contrast the crystal-mobile polymers shows a thickening of the crystalline lamellae up to a minimal thickness of the amorphous regions, enabled through the α_c -relaxation. As a consequence, crystal-mobile and crystal-fixed polymers exhibit a different reorganization behavior during heating. The crystallization of PCL leads to the formation of marginally stable crystallites which constantly reorganize during heating, while in PEO and POM due to the presence of the α_c -relaxation, much more stable (thickened) lamellar crystals form, which melt only at much higher temperatures. Crystallization at low temperatures on the other hand seems to suppress the α_c -induced stabilization also in PEO.

CPP 48.5 Wed 18:30 P2-OG1

Separated lamellae of HDPE solidified from melt by slow cooling. — ●HEINZ H.W. PREUSS — Hameln

The poster shows a representative selection of TEM photographs of mechanically separated lamellae of HDPE by H. Preuss (1). The specimen was heated in an oven and held for 20 minutes at 200 degrees centigrade, cooled down to 100 degrees centigrade in 30 minutes (3 K/min). The free surface was covered with a thin layer of gold (20 nm) by evaporation in vacuum. The gold layer was thickened with Cu by galvanization (0,1 mm). The metal sheet was torn off and the surface covered with C by evaporation in vacuum under an angle of nearly 30°. Then the copper was resolved with nitric acid and the gold after addition of hydrochloric acid. The C layer was put in the TEM on a grid woven with bronze wire. In the TEM one could see lamellae of polyethylene attached at the C layer showing the relief of the fracture surface by shadowing. The orientation of the molecular chains perpendicular to the plane of lamellae could be confirmed by electron diffraction. Thus the chain folding model of A. Keller (2) could be confirmed for HDPE solidified from the melt. 1. H.H.W.Preuss, physica status solidi Nr. 3 1963, 109 K ff; Plaste und Kautschuk 22. Jg. Heft 12/1975, 258 f. 2. A. Keller, Kolloidzeitschrift, 165, 3 (1959)

CPP 48.6 Wed 18:30 P2-OG1

Crystallization of polymers studied by combining AFM and fast scanning calorimetry — ●RUI ZHANG, EVEGNY ZHURAVLEV, and CHRISTOPH SCHICK — Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany and Competence Centre CALOR, Faculty of Interdisciplinary Research, University of Rostock, Albert-Einstein-Str. 25, 18051 Rostock, Germany

Atomic force microscopy (AFM) can show morphology of polymers at the early stages of crystallization (structures on a 100 nanometer scale). In combination with fast scanning calorimetry (FSC), AFM can detect polymer crystallization after fast quenches and after short annealing (sub second). The calorimetric chip sensor is mounted on the AFM and the fast scanning calorimetric measurements are possible without touching the sensor. This way a repeated heat treatment of the sample is possible and the formed structures are accessible for the AFM at room temperature if the glass transition temperature of the polymer is above room temperature. The primary results show morphologies after deep quenches in the homogeneous nucleation domain and for low supercooling in the heterogeneous nucleation domain. The spherulitic growth rates at high temperatures have been determined, which are faster than POM's data given by others.

CPP 48.7 Wed 18:30 P2-OG1

Formation of periodically modulated single crystals of isotactic polystyrene — ●PURUSHOTAM POUDEL, SUMIT MAJUMDER, and GÜNTER REITER — Physikalisches Institut, Albert-Ludwigs-Universität

sität Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg, Germany
 Polymer crystals are often composed of stacks of lamellae, separated by amorphous layers. The underlying mechanism of self-induced nucleation of secondary lamellae is at the origin of crystal growth in the direction of the surface normal of the lamellae, generating three-dimensional (3-D) stacks of lamellar crystal. In order to explore such growth of 3-D crystals consisting of correlated lamellae, we have chosen thin films of isotactic polystyrene. Interestingly, we observed the formation of periodically modulated crystalline structures consisting of stacks of correlated lamellae. The spacing between such stacks, i.e. the period, was found to increase with increasing crystallization temperature and film thickness. Detailed investigations via atomic force microscopy revealed that the periodically modulated structures resulted from the interplay between nucleation of stacks of secondary lamellae, growth of these lamellae and diffusion of polymer chains.

CPP 48.8 Wed 18:30 P2-OG1

Evidence for self-organized formation of logarithmic spirals during explosive crystallization of amorphous Ge:Mn layers — ●DANILO BÜRGER¹, STEFAN BAUNACK², JÜRGEN THOMAS³, STEFFEN OSWALD³, HORST WENDROCK³, LARS REBOHLE⁴, THOMAS SCHUMANN⁴, WOLFGANG SKORUPA⁴, DANIEL BLASCHKE⁴, THOMAS GEMMING³, OLIVER G. SCHMIDT^{1,2}, and HEIDEMARIE SCHMIDT¹ — ¹Material Systems for Nanoelectronics, Chemnitz University of Technology, Chemnitz 09126, Germany — ²Institute for Integrative Nanosciences, IFW Dresden, Helmholtzstraße 20, Dresden 01069, Germany — ³Institute for Complex Materials, IFW Dresden, Helmholtzstraße 20, Dresden 01069, Germany — ⁴Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, P.O. Box 510119, 01314 Dresden, Germany

Logarithmic spirals are found on different length scales in nature, e.g. in nautilus shells, cyclones, and galaxies. The underlying formation laws can be related with different growth mechanisms, pressure gradients, and density waves. Here we report on the self-organized formation of symmetric logarithmic crystallization spirals in a solid material on the micrometer length scale, namely in an amorphous Ge:Mn layer on a Ge substrate. After exposure to a single light pulse of a flashlamp array, the Ge:Mn layer is crystallized and reveals a partially rippled surface and logarithmic microspirals. Finally, we present a model describing the formation of the crystallization spirals by directional explosive crystallization of the amorphous Ge:Mn layer which is triggered by the flashlamp light pulse.

CPP 48.9 Wed 18:30 P2-OG1

Investigating crystal-liquid interface by using fundamental measurement theory — ●SHANGCHUN LIN and MARTIN OETTEL — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany

The crystal-liquid interface is important in material science. For the crystal-liquid interface, fundamental measure theory (FMT) within density functional theory (DFT) provides the almost accurate description of the hard-sphere system. In FMT, the equilibrium crystal-liquid interface has been evaluated within DFT, but has not been tackled within dynamic density functional theory (DDFT). The dynamics play a crucial role in non-equilibrium systems, such as nucleation. Thus, we developed a semi-empirical cut-off method to stabilize single crystals and the crystal-liquid interface. The results are in a good agreement with FMT within DDFT. The free energy difference is less than $10^{-4}k_B T$ for the crystal phase near crystal-liquid coexistence and surface tensions compare well with previous results from DFT. Also, preliminary results for crystals and interfaces in the Asakura-Oosawa model are presented.

CPP 48.10 Wed 18:30 P2-OG1

Investigating crystal-liquid interface by using fundamental measurement theory — ●SHANGCHUN LIN and MARTIN OETTEL — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany

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CPP 48.11 Wed 18:30 P2-OG1

The role of trivalent salts in protein nucleation and crystallization — ●MARCUS MIKORSKI¹, ANDREA SAUTER¹, FAJUN ZHANG¹, BENEDIKT SOHMEN¹, RALPH MAIER¹, GEORG ZOCHER², THILO STEHLE², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany — ²IFIB, Tübingen, Germany

Crystal structures of proteins are essential for understanding protein function. However, crystallography of proteins depends on high quality crystals for diffraction and is therefore often a challenging task. Using the negatively charged protein human serum albumin, we developed a model system to study nucleation and crystallization pathways via theoretical modelling and SAXS and SANS measurements. We found that in a reentrant condensation state diagram, for negatively charged globular proteins, there are two boundaries at which the probability for high quality crystals is high. Between these boundaries a phase separated regime occurs [1]. This interaction can be tuned by using different trivalent salts (YCl_3 , $LaCl_3$, $CeCl_3$, $GdCl_3$) and varying the solvent (D_2O , H_2O). Here, we present data on the influence of these salts on the effective protein-protein interactions and the phase behavior, the pathways of crystal growth and finally the location of metal ions in the crystal unit cell and their role in stabilizing the crystal structure. Crystals grown in different salt and solvent conditions have the same unit cell. Thereby we provide a toolbox for growth of high quality protein crystals for diffraction.

[1] Zhang et al. Pure & Appl. Chem. 2014, 86, 191-202

CPP 48.12 Wed 18:30 P2-OG1

Self-assembly of Partially Fluorinated Hexabenzocoronene Derivatives in the Solid State — ●TOBIAS BREUER¹, MICHAEL KLUES¹, PAULINE LIESFELD², ANDREAS VIERTEL², MATTHIAS CONRAD¹, STEFAN HECHT², and GREGOR WITTE¹ — ¹Philipps-Universität Marburg, Germany — ²Humboldt-Universität Berlin, Deutschland

Fluorination of polycyclic aromatic hydrocarbons (PAHs) is a well-established method to enhance the stability of organic semiconductors (OSCs) and render them n-type. For hexabenzocoronene (HBC) it has been observed that fluorination leads to a modification of the molecular packing motif from a herringbone arrangement to a parallel-packed motif. Here, we study whether this transformation of the molecular packing is also found for newly synthesized, partially fluorinated HBCs. Combining powder diffraction and NEXAFS dichroism measurements, we reveal that indeed all partially fluorinated compounds adopt a parallel molecular packing, hence maximizing the intermolecular contact area. We identify fluorine-hydrogen bonds as mediating driving force to stabilize this molecular arrangement. Furthermore, we show that the relative orientation of the HBCs on the underlying surface can be precisely controlled by varying substrate materials. Finally, the energetic states of the compounds are analyzed by photoelectron spectroscopy, optical spectroscopy and DFT to identify the effects of fluorination on these fundamental electronic characteristics.

[1] T. Breuer et al., PCCP, 2016, DOI: 10.1039/C6CP06126E

CPP 48.13 Wed 18:30 P2-OG1

Generating network structures with long-range order in triblock terpolymer films by controlled solvent vapor annealing — ●KAROLINA KORZEB¹, JAMES A. DOLAN², ULLRICH STEINER¹, and ILJA GUNKEL¹ — ¹Adolphe Merkle Institute, Fribourg, Switzerland — ²University of Cambridge, Cambridge, United Kingdom

Triblock terpolymers are an interesting class of polymers due to their potential to self-assemble into a variety of continuous network structures. Amongst these network structures the gyroid is of particular interest. Due to its unique geometry, a gyroid-structured plasmonic material exhibits interesting optical properties, e.g. linear dichroism. While triblock terpolymers were shown to serve as templates for the fabrication of a nanostructured gold gyroid, the anisotropic optical properties related to the gyroid morphology became only evident for samples showing large individual gyroid grains. However, the fabrication of polymer templates with long-range lateral order still remains a

challenge. In this work, we show that continuous network structures with long-range lateral order can be generated by means of controlled solvent vapor annealing of a PI-b-PS-b-PGMA (ISG) triblock terpolymer film. In-situ GISAXS was used to identify the regime where films swollen in THF vapor exhibit well-ordered morphologies. The degree

of order in these swollen films was maintained only after controlled solvent removal. In this way, grains of about $10\ \mu\text{m}$ in size were produced in dry ISG films as determined by AFM Moiré patterns. These films are therefore very promising candidates for the fabrication of gyroid-structured plasmonic materials.