

CPP 29: Poster: Crystallization, Nucleation, Self Assembly

Time: Tuesday 18:15–21:00

Location: Poster B2

CPP 29.1 Tue 18:15 Poster B2

Non-classical crystallization in the presence of multivalent ions — ●BENEDIKT SOHMEN, ANDREA SAUTER, FAJUN ZHANG, and FRANK SCHREIBER — Institut für Angewandte Physik - Universität Tübingen, Tübingen, Deutschland

Progress in the understanding of non-classical crystallization pathways of proteins was reported only recently [1]. Here, we present a real-time study of non-classical crystallization of bovine β -lactoglobulin in the presence of ZnCl_2 with respect to salt concentration c_s , protein concentration c_p and temperature by optical microscopy. The investigated c_s - c_p -phase diagram can be used as a guide to control and tune the behavior of proteins in solutions. Slightly below a certain salt concentration c^* crystals grow in a classical one-step pathway from clear solution. Increasing c_s above c^* , up to a certain salt concentration, referred to as pseudo- c^{**} , the crystallization follows a non-classical pathway with a dense phase as intermediate state. The crystals nucleate at the interface between dense and dilute phase. With progressing crystal growth, the dense phase dissolves. Above c^{**} , big aggregates are formed and no crystal growth is observed. The real-time microscopy and x-ray study provides detailed insight into the characteristics of non-classical growth and elucidates the role of the intermediate state.

[1] Sauter et al. J. Am. Chem. Soc. 137,1485-1491, (2015)

CPP 29.2 Tue 18:15 Poster B2

Study on the Crystallization Behavior of Nucleated Polypropylene under Shear at Isothermal Conditions — ●SABINE STOCKENHUBER and GERHARD EDER — Institute of Polymer Science, Johannes Kepler Universität, Linz

Thermoplastic Polymers show big changes in their solidification behavior, orientation and crystallization when they are processed under different conditions. These also alter the mechanical properties of the polymer. An experimental study was performed to show the effect of shear stress, total shear, additive concentration and temperature on crystallinity, orientation and solidification time. The solidification process and therefore the solidification time of the samples without additives was traced by measuring the transmission of light through the sample by an optical system containing a laser, an analyzer and a photodiode detector. The solidification was supposed to be completed when the transmittance was approximately zero. The total shear was controlled manually and obtained by a displacement transducer. The samples from the shear experiments were cut with a microtome perpendicular and parallel to the shear direction. Subsequently, the morphology and orientations were analyzed using polarization microscopy.

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Isothermal and non-isothermal crystallization of polyethylene at large undercooling — ●EVGENY ZHURAVLEV¹, VADLAMUDI MADHAVI², RENÉ ANDROSCH³, and CHRISTOPH SCHICK¹ — ¹University of Rostock, Institute of Physics, Wismarsche Str. 43-45, 18051 Rostock, Germany — ²ExxonMobil Research & Engineering Company, 1545 Route 22 East, LD 152, Annandale, New Jersey 08801, USA — ³Martin-Luther-University Halle-Wittenberg, Center for Engineering Sciences, 06099 Halle/S., Germany

The crystallization kinetics of high-density polyethylene and random copolymers of ethylene with up to 16 mol% 1-octene was studied by ultra-fast scanning calorimetry. In order to account for the inherently high crystallization rate of polyethylenes, in non-isothermal and isothermal crystallization experiments cooling rates up to 1,000,000 K/s and crystallization times as short as 10^{-6} s, respectively, were employed. It was possible to supercool the melt of high-density polyethylene down to 57 °C, and the melt of a copolymer with 16 mol% 1-octene down to -33 °C, without prior crystallization. At these temperatures, the characteristic time of the primary crystallization process is of the order of magnitude of 100^{-6} s. Complete vitrification of the liquid would require cooling even faster than 1,000,000 K/s. Compared to the homopolymer, the cooling-rate dependence of the crystallization temperatures and the temperature dependence of the characteristic time of primary crystallization of copolymers both are essentially parallel shifted to lower temperatures, which is suggested being caused by the depression of the equilibrium melting temperature.

CPP 29.4 Tue 18:15 Poster B2

Crystallization of furan-based polyesters — ●ANDREAS WURM¹, VASILIOS TSANAKTIS², DIMITRIOS BIKIARIS², and CHRISTOPH SCHICK¹ — ¹University of Rostock, Inst. of Physics, Germany — ²Aristotle University of Thessaloniki, Dept. of Chemistry, Greece

Isothermal and non-isothermal crystallization behavior of polymers can be investigated with traditional calorimeters often in a limited temperature region only. This results from the fast crystallization processes on optimal conditions, which appears in most polymers in a few seconds or less. The chip-based fast scanning DSCs allow applying heating and cooling rates of several 1000 K/s, which enables for many polymers to follow crystallization in the whole temperature range between glass transition and melting temperature.

We applied the Mettler Toledo Flash DSC 1 chip calorimeter for investigation of the non-isothermal and isothermal crystallization behavior of different furan-based polyesters from renewable resources (poly(ethylene furanoate) to poly(dodecylene furanoate)). For poly(butylene furanoate) the influence of different nanofillers on the crystallization process is discussed.

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Co-crystallization and Crystal Thickening in Blends of a Double-Crystalline Diblock Copolymer and Corresponding Homopolymers — ●ROBERT STÖSSEL, TOBIAS BÜTTNER, and KLAUS D. JANDT — Chair of Materials Science (CMS), Otto-Schott-Institute for Materials Research, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany

Size and shape of diblock copolymer (DBCP) nanostructures can be varied by blending with homopolymers and/or crystal thickening. In blends of double-crystalline diblock copolymers and crystalline homopolymers co-crystallization can occur. Targeted co-crystallization together with crystal thickening could further extend the range of double-crystalline DBCP nanostructures which was not investigated so far. The aim of the study was to test the hypothesis that the lamellar long period of a double-crystalline polyethylene-block-poly(ethylene oxide) (PE-b-PEO) can be increased by blending with PE and PEO homopolymers as well as by subsequent crystal thickening. Using differential scanning calorimetry, co-crystallization in blends was evaluated by the presence of a single melting endotherm. X-ray scattering experiments showed that co-crystallization can increase the lamellar long period compared to the native PE-b-PEO. Subsequent, annealing experiments revealed crystal thickening of the co-crystals and a further increase of the lamellar long period. Defined co-crystallization and subsequent crystal thickening of double-crystalline DBCP/homopolymer blends can be used to fabricate tailorable nanopatterns for materials science applications in photonics or the biomedical field.

CPP 29.6 Tue 18:15 Poster B2

Real-Time BAM Studies of Cardiolipin Monolayers — ●RENKO KENSBOCK, HEIKO AHRENS, and CHRISTIANE A. HELM — Institute of Physics, University of Greifswald, 17487 Greifswald, Germany

We investigate electrostatic interactions within negatively charged cardiolipin monolayers at the water-air interface with isotherms and real-time Brewster angle microscopy (BAM). A non-monotonic dependence for the LE/LC transition surface pressure on salt concentration (NaCl, KCl) is observed with a maximum at 0.1 mol/l. This is in accordance with calculations taking into account head-group interactions. The calculations consist of an electrostatic contribution (Grahame's equation) and counter-ion binding according to the law of mass action. For salt concentrations above 0.1 mol/l the electrostatic repulsion is predominantly screened, whereas for salt concentrations up to 0.1 mol/l the degree of dissociation increases. The electrostatic interaction also determines the surface area of domains as observed with BAM. Depending on line tension and long range electrostatic repulsion, domain nucleation and growth are differently affected by changes in ionic strength. The observed number of domains, compared at fixed molecular area in the LE/LC coexistence region, shows a similar behavior to that observed with the transition surface pressure - fewest observed domains for the pure water subphase, with an increase in number up to 0.1 mol/l NaCl and thereafter a decrease for 1 mol/l NaCl.

CPP 29.7 Tue 18:15 Poster B2

Modeling of metal cluster growth on hard surfaces — SVEN-

JANNIK WÖHNERT^{1,2}, •MATTHIAS SCHWARTZKOPF², STEPHAN V. ROTH², and CHRISTIAN SCHROER² — ¹Universität Hamburg — ²Deutsches Elektronen-Synchrotron (DESY)

Sputter deposition is one high-throughput method to install patterned nanostructures on surfaces with high deposition rates. Grazing incidence small-angle X-ray (GISAXS) scattering nowadays delivers a wealth of information during in-situ processes and real-time observations. The geometric model of [1] then allows to extract general cluster parameters to describe the growth of metal clusters on surfaces.

The geometric model of [1] then allows to substract general cluster parameters to describe the growth of metal clusters on surfaces. To gain insight into the specific evolution of cluster growth, we investigated cluster formation during sputter deposition at different temperatures on various hard surfaces in order to discover dependencies and relations on atomic level.

Therefore, we present a phenomenological Monte-Carlo simulation comparing cluster parameters with the results of the GISAXS measurements. We provide information about the dependencies of surface diffusion, nucleation and cluster interaction on the cluster evolution.

[1] Schwartzkopf et al., *Nanoscale* 5, 5053 (2013)

CPP 29.8 Tue 18:15 Poster B2

A tensor-based model for the interaction of charged Janus particles — •REINT HIERONIMUS and ANDREAS HEUER — Westfälische Wilhelms-Universität Münster, Institut für physikalische Chemie, Corrensstrasse 30, 48149 Münster, Germany

We analyse the interaction of charged Janus spheres, including screening effects. The explicit interaction is mapped via a least square method on a variable number n of systematically generated tensors that reflect the angular dependence of the potential. For $n = 2$ we show that the interaction is equivalent to a model previously described by Erdmann, Kröger and Hess[1]. Interestingly, this mapping is not able to capture the subtleties of the interaction for small screening lengths. Rather, a larger number of tensors has to be used. We obtained cluster structures up to the size of 13 particles for $n = 2, 36$ and screening lengths $\kappa^{-1} = 0.1, 1.0$ that we analysed to discuss the influence of the screening length. The cluster structures are also compared to results for an explicit electrostatic potential[2] and for the DLVO theory[3].

[1] T. Erdmann, M. Kröger, S. Hess, *Phys. Rev. E* 2003, 67, 041209

[2] L. Hong, A. Cacciuto, E. Luijten, S. Granick, *Nano Letters* 2006, 6, 2510–2514

[3] J. de Graaf, N. Boon, M. Dijkstra, R. van Roij, *J. Chem. Phys.*, 2012, 137, 104910