

## CPP 44: P9: Crystallization, Nucleation and Self Assembly

Time: Wednesday 10:00–13:00

Location: Poster A

CPP 44.1 Wed 10:00 Poster A

**Experimentelles zum zum Beleg der Kettenfaltung in Lamellen bei massivem HDPE** — ●HEINZ PREUSS — 31785 Hameln

Es werden die experimentellen Verfahrensschritte dargestellt, die zum elektronenmikroskopischen Nachweis der Existenz von Lamellen als relativ selbständige Strukturformen in massivem Niederdruckpolyethylen (HDPE) geführt und Belege für die Realität des Kettenfaltungsmodells gebracht haben. Dabei handelt es sich um einen Oberflächenabriss mit einer Metallmatrize aus aufgedampftem Gold mit galvanischer Verstärkung durch Kupfer und Schrägbedampfung (30 Grad) mit Kohlenstoff aus einem Lichtbogen. Ein weiterer Beleg ergibt sich mit der im TEM direkt beobachteten faktisch übergangslosen Umwandlung von Lamellen in Fasern beim Zerreißen einer dünnen PE-Haut die beim Kristallisieren aus einer Lösung mit Xylol auf heißem Wasser entstanden ist. (H.H.W.Preuß, Dissertation. Leipzig 1963; Plaste und Kautschuk 22. Jg. Heft 12/1975, S. 958 ff.)

CPP 44.2 Wed 10:00 Poster A

**Crystallization of nearly hard spheres under shear** — ●DAVID RICHARD and THOMAS SPECK — Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany

Rare events are an outstanding challenge in modern computational science: protein folding, chemical reactions, nucleation during phase transitions. During the last decades, advanced numerical schemes have been developed to study the transition between two states A and B. In liquid and colloidal systems, Umbrella Sampling and Forward Flux Sampling have been shown to be in good agreement with 'brute force' Molecular Dynamics simulations for crystallization rates [1][2]. However, the nucleation process under external forces like electric fields or flow remains poorly understood. Therefore, rare event sampling techniques have to be extended for systems driven out of equilibrium. We present results for crystallization rates in a liquid of nearly hard spheres under a weak linear shear flow using straightforward Molecular Dynamics and Forward Flux Sampling.

[1] Crystal nucleation of hard spheres using molecular dynamics, umbrella sampling, and forward flux sampling: A comparison of simulation techniques. L.Filion, M. Hermes. R. Ni, and M. Dijkstra. The Journal of Chemical Physics 133 (2010)

[2] Simulation of nucleation in almost hard-spheres colloids: The discrepancy between experiment and simulation persists. L.Filion, R.Ni, D.Frenkel, and M.Dijkstra. The Journal of Chemical Physics 134 (2011).

CPP 44.3 Wed 10:00 Poster A

**Direct Observation of Crystallization through Surface Wrinkling in Polymer Thin Film** — ●PENG ZHANG<sup>1</sup>, GONZALO SANTORO<sup>1</sup>, SARATHLAL K. VAYALIL<sup>1</sup>, EZZELDIN METWALI<sup>2</sup>, PETER MÜLLER-BUSCHBAUM<sup>2</sup>, TIANBAI HE<sup>3</sup>, and STEPHAN V. ROTH<sup>1</sup> — <sup>1</sup>Deutsches Elektronen Synchrotron, Notkestr. 85, 22607 Hamburg, Germany — <sup>2</sup>Technische Universität München, Physik-Department, LS E13, James-Franck-Str.1, 85747 Garching, Germany — <sup>3</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Polymer crystallization is a well concerned and yet unclear phase transition from amorphous coils to well organized nanoscale lamellae. Among the research areas of interest are fundamental issues relating to the early stages of polymer crystallization. Here we explore the structural transition at the early stages of ordering towards crystallization in diblock copolymer thin films. The structure change at early stages of crystallization is unraveled from a perspective of cooling induced density change. The diblock copolymer thin film offers a well confined crystallization case where the density change can be linked with the lateral molecular diffusion. Moreover, the cooling induced surface wrinkling promotes the nucleation and crystal growth in polymer. These findings provide us a new perspective to understand the whole scenario of polymer crystallization. [1] Strobl, G. Eur. Phys. J. E 3, 165 (2000); [2] Cheng, S. Phase Transitions in Polymers: The Role of Metastable States; Elsevier Science: Amsterdam, 2008.

CPP 44.4 Wed 10:00 Poster A

**Ultra-fast scanning calorimetry of polymers implying cooling up to 10,000,000 K/s** — ●EVGENY ZHURAVLEV<sup>1</sup>, SANDER VAN HERWAARDEN<sup>2</sup>, VADLAMUDI MADHAVI<sup>3</sup>, and CHRISTOPH SCHICK<sup>1</sup> — <sup>1</sup>University of Rostock, Rostock, Germany — <sup>2</sup>Sensor Integration, Delft, Netherlands — <sup>3</sup>ExxonMobil Research & Engineering Company, Annandale, NJ, USA

The complexity of polymer crystallization is often demonstrated on the example of simple polyethylene molecule. But its simplicity can become a disadvantage. The simple molecules can crystallize so fast, that few to none experimental technique is able to follow it. Especially in the region of homogeneous nucleation - approaching a glass transition temperature from the melt - a point of controversy in polymer science. Bypassing glass transition, avoiding crystallization, for the purpose of its further investigation at any desired temperature has been challenged by ultra-fast scanning calorimetry since years. Recent achievements has extended maximum possible cooling rate of nanogram sample up 10,000,000 K/s. Further reheating of this sample at 1,000,000 K/s, showing the glass transition, cold crystallization and melting of quenched polyethylene, is reported.

CPP 44.5 Wed 10:00 Poster A

**Neutron and X-ray Scattering Studies on Nanoconfined Liquids and Solids** — ●TOMMY HOFMANN<sup>1</sup>, DIRK WALLACHER<sup>1</sup>, and PATRICK HUBER<sup>2</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany — <sup>2</sup>Hamburg University of Technology, Eißendorfer Straße 42, 21073 Hamburg, Germany

Condensed matter confined on nanometer-sized length scales exhibits different structural and dynamical properties than its bulk counterparts. Surface interactions and pure confinement effects alter the characteristics of matter as the system size is reduced in an intriguing way. On this poster, we discuss how confinement in tubular, aligned channels a few nanometer across affects the mesoscopic arrangement of liquids and the crystal structure and texture of solidified condensates. We present x-ray as well as neutron scattering studies on pore-confined deuterium, nitrogen, oxygen and various n-alkanes.

CPP 44.6 Wed 10:00 Poster A

**Enhanced phase purity in sexithiophene thin films through laser illumination** — ●LINUS PITHAN<sup>1</sup>, CATERINA COCCHI<sup>1,2</sup>, HANNES ZSCHIESCHE<sup>1</sup>, CHRISTOPHER WEBER<sup>1</sup>, ANTON ZYKOV<sup>1</sup>, SEBASTIAN BOMMEL<sup>1,3</sup>, PETER SCHÄFER<sup>1</sup>, STEVEN LEAKE<sup>4</sup>, CLAUDIA DRAXL<sup>1,2</sup>, and STEFAN KOWARIK<sup>1</sup> — <sup>1</sup>Institut für Physik, Humboldt Universität zu Berlin — <sup>2</sup>IRIS Adlershof, HU Berlin — <sup>3</sup>DESY, Hamburg — <sup>4</sup>Swiss Light Source, PSI, present address: ESRF, France

We study the influence of light on the phase coexistence in  $\alpha$ -sexithiophene (6T) thin films. We focus on vacuum deposited films grown on potassium chloride (KCl) that exhibit a bimodal growth with two co-existing crystal phases, the low-temperature (LT) and high-temperature (HT) 6T polymorphs. We find that laser illumination (532 nm, 1.5 W/cm<sup>2</sup>) during growth suppresses the formation of HT crystallites, thus the phase purity is enhanced compared to the bimodal growth without light. To understand the mechanism behind this optical control, we use *in situ* x-ray diffraction, atomic force microscopy (AFM), optical absorption measurements, as well as first-principles calculations for the optical absorption spectra of the HT and LT phase. We deduce that the phase purification is due to optical heating of the molecular film and lower cohesive energy of the HT phase compared to the LT phase. This finding demonstrates that light can serve as an additional control parameter in molecular crystal growth to optimize the structural quality of molecular thin films.

CPP 44.7 Wed 10:00 Poster A

**A soft, bilayer phase in nanoparticle-doped n-CB homologues** — ●ALEXANDER LORENZ<sup>1</sup>, DENA M. AGRA-KOOIJMAN<sup>2</sup>, DEAN R. EVANS<sup>3</sup>, HEINZ-S. KITZEROW<sup>4</sup>, and SATYENDRA KUMAR<sup>2</sup> — <sup>1</sup>Stranski-Laboratorium, Sek. TC 9, Technische Universität Berlin, Str. des 17. Juni 124, 10623 Berlin, Germany — <sup>2</sup>Department of Physics, Kent State University, Kent, Ohio 44242, USA — <sup>3</sup>Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio 45433, USA — <sup>4</sup>Department of Chemistry, Universität Paderborn, Warburger Straße 100, 33098

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Several homologues of the n-alkyl-cyanobiphenyl series were doped with BaTiO<sub>3</sub> nanoparticles (dispersed in heptane) [1,2]. Synchrotron x-ray scattering experiments of the doped n-pentyl-cyanobiphenyl and n-octyl-cyanobiphenyl samples revealed nine orders of a primary Bragg reflection, respectively [2]. These scattering signals were caused by a soft, one-dimensional multilayer structure and were not present in the neat substances. The scattering signals were used to calculate the electron density profiles inside the multilayers by Fourier analysis; the multilayers were found to be one-dimensional, multilayered, smectic nanostructures in each case. In conclusion, doping clearly induced a novel, self-assembled nanostructure in which the rigid aromatic part, and not the overall length, of the molecules defined the layer spacing. A. Lorenz et al. *Physical Review E* 86, 051704 (2012). A. Lorenz et al., *Physical Review E* 88, 062505 (2013).

CPP 44.8 Wed 10:00 Poster A

**Reversible switching between self-assembled nanoribbons and nanotubes** — ●ASAD JAMAL<sup>1,2</sup>, PHILIPPE MESINI<sup>3</sup>, and GÜNTER REITER<sup>1,2</sup> — <sup>1</sup>Physikalisches Institut und — <sup>2</sup>Freiburger Materialforschungszentrum, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany — <sup>3</sup>Institut Charles Sadron, 23 rue du Loess BP 84047, 67034 Strasbourg Cedex 2, France

Depending on the quality of the solvent, achiral 3,5-bis(5-hexylcarbamoyl-pentyloxy)-benzoic acid decyl ester (BHPB-10) molecules were self-assembled into nanotubes of about 10 nanometer in width and nanoribbons with a diameter of ca. 40 nanometer, both having several micrometers in length. In solvents weakly interacting with BHPB-10 like cyclohexane nanotubes were formed while in solvents with comparatively strong molecule-solvent interactions like cyclohexanone nanoribbons were created. Interestingly, annealing nanoribbons in the vapor of cyclohexane allowed to switch them to nanotubes. Moreover, changing the solvent from cyclohexane to cyclohexanone switched nanotubes back into nanoribbons. Atomic force microscopy studies indicated that nanoribbons transitioned through helical twisted nanosheets into tubular structures. We relate the nanotube formation to hydrogen-bonds among the BHPB-10 molecules which are not possible in cyclohexanone.

CPP 44.9 Wed 10:00 Poster A

**Breath figure template: an effective fabrication technique for large area micro-lenses array** — ●FARID FARAJOLLAHI, OTHMAR MARTI, and MASOUD AMIRKHANI — Institute of Experimental Physics, University of Ulm, 89069 Ulm, Germany

Condensation of water on polymeric solution can produce a micro pattern by using of breath figure technique. The hexagonal arrangement of micro droplets of water does imprint pore structure on the surface of the polymer after evaporation of all liquid. The pore size and arrangement can be adjusted by changing the concentration of polymer and solution composition. The microstructure on polymer film is used as a template for fabricating micro-lens array by molding technique. Polydimethylsiloxane (PDMS) can be cast on the template to make a replica version of micro-pattern, which creates convex micro lenses with hexagonal arrangement. The shape, focal length and the filling factor of micro-lenses are measured by optical microscope and SEM. This method provides a fast and simple way to fabrication of hexagonal micro-lens structure.

CPP 44.10 Wed 10:00 Poster A

**Applying breath figure technique for the fabrication of porous film using various solvents** — ●MANDEEP SINGH, FARID FARAJOLLAHI, OTHMAR MARTI, and MASOUD AMIRKHANI — Institute of Experimental Physics, University of Ulm, 89069 Ulm, Germany

Elsewhere, has been shown that using the breath figure technique and adding the appropriate amount of alcohol to the solution of polymer/chloroform one can fabricate a well order honeycomb structure on the surface of polymer film. In this study, we show how different solvent may effect on the structure and size of pores on the surface. We employed several organic solvent from different solvent family and with various evaporation rates while the polymer (polystyrene) and alcohol (methanol) remain same for all samples. This study enables us to formulate underlying important parameter, which governs the formation of porous structure.

CPP 44.11 Wed 10:00 Poster A

**Optical waveguiding and anisotropic behavior of large single crystal of thiophene-based oligomers** — ●SAJEDEH MOTAMEN<sup>1</sup>, YINGYING WANG<sup>1</sup>, JEAN-PIERRE MALVAL<sup>2</sup>, THIBAUT JARROSSON<sup>3</sup>, FRANÇOISE SEREIN-SPIRAU<sup>3</sup>, LAURENT SIMON<sup>2</sup>, and GÜNTER REITER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Albert-Ludwigs-Universität, 79104 Freiburg, Germany — <sup>2</sup>Institut de Sciences des Matériaux de Mulhouse IS2M, 4 rue des freres Lumiere, 68093 Mulhouse, France — <sup>3</sup>Institut Charles Gerhardt de Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier cedex 05, France

Unique properties of conjugated organic molecules are responsible for their remarkable potential as active elements in optoelectronic devices such as field-effect transistors or solar cells. For achieving high performance, ordering of these conjugated molecules within the active layer of these devices has been considered as a promising pathway. Single crystals with unique molecular orientation represent ideal model systems for the corresponding systematic studies. Here, we report the formation of large single crystals of 2,5-dialkoxy-phenylene-thienylene-based oligomers (3TBT). Compared to disordered aggregates in spin-coated thin films, single crystals exhibited a pronounced red shift in absorption and photoluminescence spectra, indicating an increase of the conjugation length. As a consequence of high molecular order, an extremely high dichroic ratio was observed. Without any external stimulation, light could travel along the long axis of the crystal over few hundreds of micrometer. We relate structural properties to this observed optical waveguiding effect, which may be of relevance in applications.

CPP 44.12 Wed 10:00 Poster A

**Atomistic simulations of oriented attachment of hematite nanoparticles** — ●HENNING HÖRSTERMANN, THOMAS GRUHN, and HEIKE EMMERICH — University Bayreuth, Chair of Material and Process Simulations, Bayreuth, Germany

Interactions between two hematite nanoparticles with diameters of a few nanometers are studied via molecular statics and molecular dynamics methods. We try to identify favorable crystal faces for oriented attachment by calculating the contact energies of nanoparticles attached to each other via aligned contact areas of a defined structure. We present an approach to identify the time scales on which particles approach each other and their relative orientation changes towards perfect alignment by combining information about the interaction of the particles with direct observation of the attachment process. This information can be used to formulate criteria to decide if two particles with given initial relative position and orientation will combine or disperse and if the differences in alignment can be eliminated before attachment and to estimate probabilities and rates for aggregation and oriented attachment.

CPP 44.13 Wed 10:00 Poster A

**Photonic materials from hydrogel-coated gold nanocrystals: Effect of cross-linker density, temperature and volume fraction** — ●ASTRID RAUH and MATTHIAS KARG — Physical Chemistry I, University of Bayreuth, Germany

The self-assembly of soft polymer colloids allows the preparation of photonic materials with responsive bandgap behavior. To increase the refractive index of a polymer material and thus the diffraction, the implementation of inorganic cores can be useful. We synthesized a series of single gold nanoparticle cores encapsulated in a cross-linked poly-N-isopropylacrylamide (PNIPAM) shell. To investigate the influence of the thermoresponsive hydrogel shell morphology on the crystallization behavior, the shell thickness and cross-linker density were varied. The cross-linker density influences the softness and the swelling capacity of the polymer network.

The crystallization behavior was investigated in dependence of volume fraction and temperature. We found crystalline structures with diffraction in the visible for a broad range of concentrations. A lower crosslinking density supported the crystal formation. Increasing the temperature, the volume fraction of the core-shell particles is lowered.[1] Therefore, a melting of the crystals in a certain concentration range can be achieved. Upon cooling the crystalline structures exceed the critical volume fraction and form again colloidal crystals. This indicates the reversibility of the structure formation.

[1] M. Karg, T. Hellweg, P. Mulvaney, *Adv. Funct. Mater.* 2011, 21, 4668-4676