

## CPP 40: Polymer Crystallization and Semicrystalline Polymers

Time: Thursday 10:30–13:00

Location: ZEU 160

**Topical Talk**

CPP 40.1 Thu 10:30 ZEU 160

**Crystallization in block copolymer thin films** — ●CHRISTINE M. PAPADAKIS<sup>1</sup>, CHARLES DARKO<sup>1</sup>, and GÜNTER REITER<sup>2</sup> — <sup>1</sup>TU München, Physikdepartment, Physik weicher Materie, Garching — <sup>2</sup>Universität Freiburg, Fakultät für Physik

Polymer crystallization in microphase-separated block copolymers proceeds in thermodynamic confinement. To characterize the crystalline structure, e.g. the crystal orientation, macroscopic alignment of the domains is required. Numerous experiments have been carried out on bulk samples which were macroscopically oriented by high amplitude shear. The thin film geometry has the advantage that the domains orient macroscopically, and imaging methods can be used to characterize the surface texture of crystallized films. Grazing-incidence X-ray diffraction and small-angle scattering allow a detailed characterization of the crystalline structure in a wide range of length scales.

Two examples will be presented. In thin films of lamellae-forming poly(styrene-*b*-(ethylene oxide)), we have found that the resulting crystalline structure – the orientation of the chain stems, their orientational distribution and the size of the crystallites – strongly depends on the degree of supercooling. In thin films of cylinder-forming poly(isoprene-*b*-(ethylene oxide)), crystallization can only proceed very slowly and only at the film surface which is due to a mismatch in crystalline layer thickness and cylinder radius.

CPP 40.2 Thu 11:00 ZEU 160

**Growth Pathway and Precursor States in Single Lamellar Crystallization: MD Simulations** — ●CHUANFU LUO and JENS-UWE SOMMER — Leibniz Institute of Polymer Research Dresden, Dresden, Germany

Molecular dynamics (MD) simulations are carried out to study the growth pathway of a single polymer crystal from a highly entangled dense melt via self-seeding[1]. Linear lateral growth, lamellar thickening and slipping of monomers along the chain direction are directly observed. We have introduced a measure of orientational-temporal persistence to characterize the state of monomer sequences out of equilibrium. This analysis allows us to define a birth-time for each stem and accordingly, folding kinetics of individual chains is analyzed as a function of their lifetime. Two stages can be identified for the growth of stem length with lifetime: The stem length increases linearly with lifetime at the precursor stage while it increases logarithmically at the thickening stage. Folds are created at the precursor stage and refolding events are statistically irrelevant. Precursor states can be identified as an early stage of a stem formed by semi-flexible segments. The semi-flexible segments are possessing orientational-temporal persistence which can potentially crystallize, and can be thus considered as unstable short stems. The classical Lauritzen-Hoffman (LH) or Sadler-Gilmer (SG) models are not consistent with our results which correspond to a time scale of about  $\lesssim 45$  ns. We thank DFG(SO 277/6-1) for financial support and ZIH of TU-Dresden for computing time. [1]C. Luo and J.-U. Sommer, Phys. Rev. Lett. 102, 147801 (2009)

CPP 40.3 Thu 11:15 ZEU 160

**Melt dynamics and semi-crystalline structure of polyethyleneoxide** — ●ALBRECHT PETZOLD and THOMAS THURN-ALBRECHT — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle (Saale)

During crystallization polymers form a crystalline-amorphous superstructure consisting of lamellar crystals with a typical thickness of about 10nm. This non-equilibrium structure is often explained by the kinetics of crystallization during which the crystals which form fastest, are selected. The thickness  $d_a$  of the amorphous layers separating adjacent crystals is in most cases not considered. To find out which parameters and physical processes determine  $d_a$ , we undertook a systematic study of the corresponding structural parameters by small angle x-ray scattering using a series of polyethyleneoxide (PEO) with different molecular weight as a model system. We show that for this system the thickness of the amorphous layers is a well defined quantity which depends only on molecular weight and temperature, and not on the conditions of crystallization, while the thickness of the crystalline layers is strongly influenced by the kinetics of crystallization and lamellar thickening and in general is much less uniform. The semi-crystalline

morphology is related to the structure of the chains in the amorphous melt before crystallization. For fast crystallization the coiled structure remains almost unchanged during crystallization and frozen topological defects limits the crystal size. When there is enough time for reorganization the crystal thickness exceeds the size of the coil in the melt and the crystal thickness is maximised.

CPP 40.4 Thu 11:30 ZEU 160

**Influence of Alkyl Side Chain Length on the Crystallite Orientation of Low-temperature and RT Cast Poly(3-alkylthiophene) Thin Films** — ●SHABI THANKARAJ SALAMMAL<sup>1</sup>, SOUREN GRIGORIAN<sup>1</sup>, ULLRICH PIETSCH<sup>1</sup>, MARTIN BRINKMANN<sup>2</sup>, NILS KOENEN<sup>3</sup>, and ULLRICH SCHERF<sup>3</sup> — <sup>1</sup>University of Siegen — <sup>2</sup>CNRS, Strasbourg — <sup>3</sup>University of Wuppertal

The effect of alkyl side chain length on the orientation of polymer crystallites was studied for a series of poly(3-alkylthiophene)s (P3ATs) like poly(3-pentylthiophene) (P3PT), poly(3-hexylthiophene), poly(3-heptylthiophene) (P3HeptT), and poly(3-octylthiophene) (P3OT). Thin films were cast on the Si/SiO<sub>2</sub> substrate at RT and -30°C. The orientation of the crystallites was studied using x-ray and electron diffraction techniques. The 2D diffraction pattern of -30°C cast P3PT film shows the presence of well in-plane stacked edge-on oriented crystallites which are favor for the charge transport. The scattered intensity of -30°C as-cast films are 5 times higher than the RT cast one and it increase to 8 by treating the substrate with OTS. Surprisingly, the -30°C cast P3OT film has few face-on oriented crystallites. But, the mixed edge- and face-on oriented crystallites were observed in RT cast films and showing the powder like distribution of crystallites. Those face-on oriented crystallite was able to resolve through HRTEM. Such an enhancement in ordering of the crystallites with decreasing the growth temperature and side chain length can be explained by the controlled supersaturation ratio as well as the decrease in flexibility of side chain length which may induce the surface nucleation.

CPP 40.5 Thu 11:45 ZEU 160

**Confined dynamics and crystallization in self assembled alkyl nanodomains** — ●SHIREESH PANKAJ<sup>1</sup> and MARIO BEINER<sup>1,2</sup> — <sup>1</sup>Naturwissenschaftliche Fakultät II, Martin-Luther Universität Halle-Wittenberg, 06099 Halle (Saale), Germany — <sup>2</sup>Fraunhofer-Institut für Werkstoffmechanik, Walter-Hülse-Str. 1, 06120 Halle (Saale), Germany

Long alkyl groups are often used to improve the performance of functional polymers. The methylene sequences in such systems usually show a strong tendency to aggregate to form small alkyl nanodomains which can be either completely amorphous or partly crystalline. The influence of main chain packing, domain size and density on the properties of self-assembled alkyl nanodomains is studied based on a comparison of regio-random and regio-regular poly(3-alkyl thiophenes) (P3ATs) with different side chain length as model systems. We show that the dynamics of the CH<sub>2</sub> units in amorphous alkyl nanodomains is mainly independent on the packing and microstructure of the main chains. Relaxation spectra show a similar CH<sub>2</sub> dynamics despite of the fact that the thiophene main chains are crystalline in regio-regular but amorphous in the regio-random P3ATs. Reasons for the systematic dependence of the CH<sub>2</sub> dynamics on the length of the alkyl groups are considered. The influences of average volume per CH<sub>2</sub> unit and geometrical confinement are studied. A competition of main and side chain crystallization mechanisms is discussed which should be considered if higher P3ATs are optimized for optoelectronic applications.

CPP 40.6 Thu 12:00 ZEU 160

**Self-assembling in solution of crystalline-amorphous olefin block-copolymers investigated by wide-Q SANS and microscopy** — ●AUREL RADULESCU<sup>1</sup>, GÜNTER GOERIGK<sup>1</sup>, LEWIS FETTERS<sup>2</sup>, and DIETER RICHTER<sup>3</sup> — <sup>1</sup>Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science, 85747 Garching, Germany — <sup>2</sup>School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853-5021, USA — <sup>3</sup>Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, 52425 Jülich, Germany

Self-assemblies formed in solution by olefin block-copolymers (OBC) that consist of crystallizable ethylene-octene blocks (hard) with very low co-monomer content and high melting temperature alternating

with amorphous ethylene-octene blocks (soft) with high co-monomer content and low glass transition temperature were characterized within a wide temperature range over a wide length scale (between 1nm and 10  $\mu\text{m}$ ) by combining optical microscopy with crossed polarizers and pinhole- and mirror-focusing-SANS techniques at the KWS-2 and KWS-3 small- and very-small-angle diffractometers set up at the FRM II reactor in Garching. Complex aggregates revealing multiple size levels and hierarchical structural organization were fully characterized with respect to the morphology and the geometrical and density parameters.

CPP 40.7 Thu 12:15 ZEU 160

**Application of Optical Coherence Tomography (OCT) for Monitoring the Crystallization of Polymers** — •PETER HIERZENBERGER<sup>1</sup>, GERHARD EDER<sup>1</sup>, ELISABETH LEISS-HOLZINGER<sup>2</sup>, and DAVID STIFTER<sup>1</sup> — <sup>1</sup>Johannes Kepler University, Linz, Austria — <sup>2</sup>Research Center for Non Destructive Testing GmbH, Linz, Austria

The use of Optical Coherence Tomography (OCT) as a novel non-destructive method for the investigation of structure development during polymer solidification is demonstrated. It is well known that the application of high shear gradients to crystallizable polymers produces highly oriented structures, whose development can be monitored by measuring the increasing optical retardation of the transmitted light. However, the increasing turbidity limits this method to conditions far from processing. By use of OCT - which measures reflected light in an interferometer arrangement - we are now able to go directly into that range and extend the experimental window to conditions more relevant to industrial polymer processing.

As a typical schedule molten isotactic poly(propylene) is extruded through a slit die, then quenched to a temperature slightly below the melting point, and after thermal equilibration sheared by resuming extrusion for a certain time. OCT enables on-line observation of structure development and gives depth-resolved images, which can be evaluated quantitatively afterwards and show the growth of the birefringent structures. Additionally, the cooled sample can be extracted and analyzed under the polarization microscope. Comparison of those ex-situ images with in-situ OCT images serves as validation of the method.

CPP 40.8 Thu 12:30 ZEU 160

**How Do Extended Chain Crystals Affect the Surface Morphology of Diblock Copolymers?** — •THOMAS F. KELLER, STEFAN WATZKE, ROBERT SCHULZE, and KLAUS D. JANDT — Institute of Materials Science and Technology (IMT), Friedrich-Schiller-University Jena, Germany

Recently, in short chain double-crystalline diblock copolymers several

temperature-dependent morphologies were reported, which are suppressed in similar high molecular weight copolymers. These morphologies were attributed to extended chain crystals with enhanced chain mobility at the interfacial boundary to neighboring domains.

The aim of the presented study was to test the hypothesis that these temperature-dependent morphologies form on the surface of thin films of such copolymers, and to investigate the phase separation as well as the nucleation and crystal growth behaviour.

By in-situ atomic force microscopy (AFM) we analyzed the temperature-dependent surface morphology of thin films of a short chain polyethylene-block-poly(ethylene oxide) copolymer. When cooling from the melt we observed a heterogeneous surface morphology. Needle-like plates formed. In between these needle-like plates a perpendicular lamellar morphology gradually built up.

A model to describe these observations is discussed, which bases on the formation of extended chain crystals. The current study shows how this formation of extended chain crystal induces new heterogeneous nanostructured copolymer surfaces for potential applications, such as in the biomedical field.

CPP 40.9 Thu 12:45 ZEU 160

**Single Molecule Studies of Stress Relaxation in Elastomeric Polypropylene** — •STEFAN KRAUSE<sup>1</sup>, MARTIN NEUMANN<sup>2</sup>, MELANIE BIBRACH<sup>2</sup>, HARALD GRAAF<sup>1</sup>, ROBERT MAGERLE<sup>2</sup> und CHRISTIAN VON BORCZYKOWSKI<sup>1</sup> — <sup>1</sup>Center for Nanostructured Materials and Analysis, Chemnitz University of Technology D-09107 Chemnitz, Germany — <sup>2</sup>Chemische Physik, Chemnitz University of Technology

Since the early 90s, single molecule (SM) spectroscopy studies provided a manifold of new information about systems with heterogeneities, such as biological systems, polymer melts and glasses. The fluorescence of a SM is a very sensitive probe and changes of the fluorescence lifetime, the emission wavelength, and the polarization can report spatial and temporal variations in the environment with high sensitivity[1]. Here we report on SM microscopy and spectroscopy studies of stress relaxation in thin films of elastomeric polypropylene, a semicrystalline polymer with a complex microstructure of crystalline and amorphous regions on the nanometer scale. The films are strained in-situ using a microtensile testing setup and the temporal evolution of mechanical stress is measured. Simultaneously, peryleneimide dyes embedded in the ePP film as isolated dye molecules or covalently linked to ePP molecules report their molecular dynamics and changes within their local environment via SM spectroscopy. This experiment allows for insights into the molecular dynamics within the amorphous regions of ePP which are not accessible with other microscopy techniques.

[1] S. Krause, P. F. Aramendia, D. Täuber and C. von Borczykowski, 2011, PCCP, accepted.