CPP 40: Focus: Polymer Crystallization - from Model Systems to New Materials II

Time: Wednesday 15:00–18:15   Location: ZEU 222

Invited Talk   CPP 40.1   Wed 15:00   ZEU 222
Architectural Engineering of Semi-Crystalline Elastomers —
●Sergei Sheiko — University of North Carolina at Chapel Hill, USA

Molecular assembling, including polymer crystallization and hydrogen bonding, is an effective tool for creating moldable and dynamic networks with unique physical properties such as reversible and time-programmable shape memory. Unlike linear polymer melts, the crystallization process of polymer networks is guided by the network architecture described by the mesh dimensions and branching of the network strands. Synthetic control of architectural parameters allows for accurate variation of the degree of crystallinity, physical crosslink density, and crosslink functionality. We will discuss different examples of the architectural control of structure-property correlations for different types of polymer networks including super-soft and super-elastic brush-like elastomers and linear-chain elastomers that display reversible shapeshifting.

CPP 40.2   Wed 15:30   ZEU 222
Thermally induced shape-memory actuators on the basis of crosslinked poly(ϵ-caprolactone) — ●Oleksandr Dolynchuk[1], Igor Kolesov[2], Dieter Jehnichen[1], Hans-Joachim Radusch[2], and Jens-Uwe Sommer[1,3] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Germany — [2]Martin Luther University Halle-Wittenberg, Center of Engineering Sciences, Germany — [3]Technische Universität Dresden, Institute for Theoretical Physics, Germany

Polymer materials capable of active motion in response to external stimuli have an outstanding potential for numerous applications from space engineering to smart bioimplants, nanostructures etc. The evolution of the thermally induced invertible shape-memory effect (SME) under constant load was investigated in crosslinked linear poly(ϵ-caprolactone) (PCL). The viscoelastic and thermal properties as well as morphology, size, and orientation of crystals in PCL networks were analyzed as well. In addition, PCL with the highest achieved crosslink density revealed remarkable invertible actuation under stress-free conditions. The oriented growth of crystals was found to be the origin of the invertible SME under and without load. The mean field approach was used to calculate the free energy change during non-isothermal crystallization of PCL networks under load, whereby the possible morphology and orientation of crystals were analyzed. The analytical results on the nanocrystalline structure along with fitting curves of strain vs. temperature, which were got by modeling the SME in PCL under load, correspond well to the experimental outcomes.

CPP 40.3   Wed 15:45   ZEU 222
Molecular order in strain-recrystallized Poly-Caprolactone — ●Wilhelm Kossack[1], Anne Seidlitz[2], Thomas Thurn-Albrecht[2], and Friedrich Kremer[1] — [1]Universität Leipzig, Molecular Physics, 04103 Leipzig, Germany — [2]Universität Halle-Wittenberg, Experimentelle Polymerphysik, 06120 Halle/Saale, Germany

Biaxial order in free standing films of Poly-ϵ-Caprolactone is induced by plastic deformation and concomitant re-crystallization. The three-dimensional orientation distribution is studied by Infrared transition moment orientational analysis (IR-TMOA) and X-ray diffraction (pole figure) measurements. The former method senses the alignment of *amorphous moieties and crystal directions* (*eg.* [001]), whereas the latter technique reveals the order of the (200)- and (110)-crystal-planes. The main chains of the polymers are aligned with the stretching direction, leading to a strong uniaxial order with an order parameter (Hermans orientation function) of $S_{xx} \approx 0.9 \pm 0.1$ for the crystalline $\underline{c}$-axes ([001]). The amorphous polymer backbones exhibit a lower, $S_{xx} < 0.7$, slightly biaxial order. Furthermore, changes in the XRD-diffractograms and IR-spectra upon stretching indicate strained lamellar crystallites and a reduction of crystallinity upon stretching.

CPP 40.4   Wed 16:00   ZEU 222
Aligned crystallization within a single gyroid network of a semicrystalline triblock terpolymer — ●James A. Dolan[1], Raphael Dehmel[1], Bodo D. Wilts[2], Alessandro Sepe[2], Yibei Gu[3], Timothy D. Wilkinson[1], Jeremy J. Baumberg[1], Ulrich Wiesner[3], Ullrich Steiner[2], and Ilja Gunkel[2] — [1]University of Cambridge, Cambridge, UK — [2]Adolphe Merkle Institute, Fribourg,

CH — [3]Cornell University, Ithaca, NY, USA

Semicrystalline block copolymers are an interesting model system for studying the crystallization of polymers under nanoscale confinement. Confined crystallization takes place if the crystallization temperature of the semicrystalline block is lower than the glass transition temperature of the amorphous block. This confinement is often found to induce aligned crystallization. In this work, the crystallization of semicrystalline poly(ethylene oxide) (PEO) confined within a single gyroid morphology was studied in solvent-annealed polyisoprene-*b*-polystyrene-*b*-poly(ethylene oxide) (ISO) triblock terpolymer films by means of GISAXS, GIWAXS, SEM, and optical microscopy. PEO is shown to crystallize preferentially in the direction of the least tortuous pathways of the gyroid, leading to a preferential alignment of the PEO crystallites within the self-assembled morphology. Strikingly, this gives rise to an optical birefringence of individual gyroid domains that allows mapping of the grain structure in self-assembled ISO films by means of optical microscopy.

15 min break

Invited Talk   CPP 40.5   Wed 16:30   ZEU 222
Chain Trajectory of Semicrystalline Polymers as Revealed by Solid-State NMR Spectroscopy — ●Toshikazu Miyoshi — The University of Akron, Department of Polymer Science, Akron OH, USA

Over the last half century, chain-folding structure of semicrystalline polymers has been debated in polymer science. Recently, 13C-13C double quantum (DQ) NMR spectroscopy combined with 13C selective isotope labeling has been developed to investigate re-entrance sites of the folded chains, mean values of adjacent re-entry number <n> and fraction <F> of semicrystalline polymers. This viewpoint highlights the versatile approaches using NMR and isotope labeling for revealing i) chain trajectory in melt- and solution-grown crystals, ii) conformation of the folded chains in single crystals, iii) self-folding in the early stage of crystallization, and iv) unfolding of the folded chains under stretching.

CPP 40.6   Wed 17:00   ZEU 222
Creating micrometer-high stacks of correlated lamellar crystals of precision polyethylene by self-induced nucleation — ●Sumit Majumder[1], Hanna Busch[2], Purushottam Poudel[1], Stefan Mecking[2], and Günter Reiter[1] — [1]Experimental Polymer Physics, University of Freiburg — [2]Chair of Chemistry, University of Konstanz

Crystallizable polymers often form stacks of correlated lamellar crystals. Formation of such stacks of lamellae requires a mechanism of self-induced nucleation at the fold surface (H. Zhang et. al. Phys. Rev. Lett. 112, 237801, (2014)). However, in polymer thin films, scarce availability of polymers on the fold surface and a low nucleation probability in general typically limit the formation of such stacks of lamellar crystals. Here, we investigate the possibility of enhancing stacking of lamellar crystals in thin films by introducing precisely spaced bulky methyl-phosphonate groups along the backbone of polyethylene. Presence of these bulky side groups impose constraints on folding and eliminate the possibility of lamellar thickening. We present experimental observations indicating that the stacking mechanism can be controlled by film thickness, crystallization temperature and molecular weight.

CPP 40.7   Wed 17:15   ZEU 222
Interface-induced crystallization via prefreezing: A first-order prewetting transition — ●Ann-Kristin Flieger, Martha Schulz, and Thomas Thurn-Albrecht — Experimental Polymer Physics, Institute of Physics, Martin Luther University Halle-Wittenberg, 06120 Halle, Germany

Prefreezing is a mechanism of surface-induced crystallization. In prefreezing a crystalline layer is formed at the interface of a solid substrate and the liquid phase already above the melting point. Wetting theory predicts a jump in thickness at the formation and a divergence upon approaching coexistence. However, the thickness of the prefreezing layer has not been experimentally measured so far.

We studied ultrathin films of Polycaprolactone during the crystallization on graphite. With AFM at high temperatures we observe prefreezing instead of heterogeneous nucleation. The corresponding crys-

talline layer is formed at a temperature above the bulk melting point. Similar observations were already made for polyethylene on graphite (A.-K. Löhmann et al., PNAS 49, 17368-17372 (2014)). In that case however, a direct measurement of the thickness of the prefreezing layer was not possible. Here, we show directly the finite thickness of the prefreezing layer for PCL. It forms with a thickness of a few nanometers which further increases during cooling. This observation demonstrates the transition is of first order, as expected for a prewetting transition.

The results prove that prefreezing can be described by common wetting theory. The studied system PCL-graphite is of importance for applications since graphitic materials are widely used as fillers for PCL.

CPP 40.8   Wed 17:30   ZEU 222

Interplay between the Relaxation of the Glass of Random L/D Lactide Copolymers and Homogeneous Crystal Nucleation: Evidence for Segregation of Chain Defects
— •Christoph Schick[1,2] and Rene Androsch[3] — [1]Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock — [2]Kazan Federal University, 18 Kremlyovskaya street, Kazan 420008, Russian Federation — [3]Center of Engineering Sciences, Martin Luther University Halle-Wittenberg, 06099 Halle/Saale

Random L isomer rich copolymers of poly(lactic acid) containing up to 4% D isomer co units have been cooled from the molten state to obtain glasses free of crystals and homogeneous crystal nuclei. The kinetics of enthalpy relaxation and the formation of homogeneous crystal nuclei have then been analyzed using fast scanning chip calorimetry. It has been found that the relaxation of the glass toward the structure/enthalpy of the supercooled liquid state is independent of the presence of D isomer co units in the chain. Formation of homogeneous crystal nuclei in the glassy state requires the completion of the relaxation of the glass. However, nucleation is increasingly delayed in the random copolymers with increasing D isomer chain defect concentration. The data show that the slower formation of homogeneous crystal nuclei in random L/D lactide copolymers, compared to the homopolymer, is not caused by different chain segment mobility in the glassy state but by the segregation of chain defects in this early stage of the crystallization process.

Invited Talk   CPP 40.9   Wed 17:45   ZEU 222

The Role of Entanglement in Polymer Crystallization — •Chuanfu Luo — Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1 OT Golm, 14476 Potsdam, Germany

Polymer crystallization is one of the fundamental topics in polymer science. A deeper understanding of it has a great industrial importance as about 70% industrial plastics are of semicrystalline states. We carried out large scale MD simulations of polymer crystallization by using a coarse-grained poly(vinyl alcohol) (CG-PVA) model. We simulated different situations for linear polymers such as of dense melts, of concentrated solutions, under confinement of two walls, and under steady shears. We analyzed the entanglement states before the crystallization by using primitive path analysis (PPA) and its geometric analogue, the Z1 method. We found that the crystallization behavior is strongly related to the initial entanglement states. The crystalline stem length (d) is directly controlled by the initial entanglement length (N_e). The slow relaxation of entanglement state can be a major reason for the thermal memory effect. We found a roughly linear relation of $d = N_e/f$ for most cases, where f means an effective folding number with a value about 2.5 for dense melts or slightly larger for concentrated solutions. We propose that thickness selection in polymer crystallization is mainly restricted by the initial entanglement length. Our simulations may provide a novel approach to understand polymer crystallization at different situations.