

DY 6: Crystallization, Nucleation and Self Assembly I (joint session CPP/ DY)

Time: Monday 9:30–11:30

Location: PC 203

DY 6.1 Mon 9:30 PC 203

Wang-Landau type Monte Carlo study of crystallization in melts of short semi-flexible polymers — ●TIMUR SHAKIROV and WOLFGANG PAUL — University of Halle, Halle, Germany

Phase transitions in polymer melts have been under intensive experimental as well as theoretical investigation during the last years. Wang-Landau type Monte Carlo simulations were successfully applied to investigate of single polymer chains, but they weren't used for simulations of dense polymer systems. We present results of Wang-Landau simulations of melts of short semi-flexible polymers. The estimated density of state functions cover more than 5000 orders of magnitude and describe thermodynamical properties at the full energy range of the system. An analysis of the density of states shows that our model system undergoes a first-order phase-transition upon increasing the chain stiffness at fixed density. The investigation of chain properties demonstrates crystallization of the model system into a rotator-like phase. Because inter-molecular interactions have a purely repulsive nature, the phase transition is driven by maximization of the system entropy. Ordering perpendicular to the director is governed by the effective thickness of the chains and this part of the ordering process is similar to the transition into a hexatic phase of 2d hard-disks systems. Due to the equal size of all beads and the purely repulsive inter-chain interaction the chains remain mobile along the nematic director. So that in contrast to the real rotator-phase systems (for instance stiff n-alkane chains) our system demonstrates only a weak tendency to produce lamellar positional ordering.

DY 6.2 Mon 9:45 PC 203

Double-Crystalline Diblock Copolymer Nanostructures by Crystal Thickening — ●ROBERT SCHULZE, TOBIAS N. 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

Semi-crystalline diblock copolymers (DBCP) can form defined nanostructures by crystal thickening. In double-crystalline DBCP, both blocks can crystallize and, thus, be used for crystal thickening, which was not investigated, so far.

Here, the hypothesis was tested, that an increase of the lamellar period can be achieved by controlled crystal thickening of both blocks of a linear poly(ethylene)-block-poly(ethylene oxide) DBCP.

In the bulk, we found annealing induced crystal thickening for both blocks using differential scanning calorimetry. Initially crystallized bulk samples were characterized by X-ray scattering and featured a lamellar long-period that corresponded to the extended chain length of the copolymer. Similarly crystallized thin films were characterized by atomic force microscopy and the lamellar long-period was found to be one-half of the extended chain length. Annealing these thin films at elevated temperatures caused crystal thickening and an increase of the lamellar long-period.

The controlled crystal thickening of double-crystalline DBCP can be used to fabricate tailorable nanopatterns which are interesting for applications requiring surface structures with different sizes, as e.g., in photonics or the biomedical field.

Invited Talk

DY 6.3 Mon 10:00 PC 203

Direct observation of prefreezing at the interface melt-solid in polymer crystallization — ANN-KRISTIN LÖHMANN, THOMAS HENZE, and ●THOMAS THURN-ALBRECHT — Institute of Physics, Martin-Luther-University Halle-Wittenberg, 06099 Halle, Germany

The microscopic ordering process that a liquid undergoes during crystallization is often initiated at an interface to a solid. This observation is classically explained by the assumption of a reduced barrier for crystal nucleation at the interface. However, an interface can also induce crystallization by prefreezing, i.e., the formation of a crystalline layer that is already stable above the bulk melting temperature. We present an atomic force microscopy (AFM)-based in situ observation of a prefreezing process at the interface of a polymeric model system and a crystalline solid, namely polyethylene on graphite. Explicitly, we show the existence of an interfacial ordered layer that forms well above the bulk melting temperature with thickness that increases on approaching melt-solid coexistence. Below the melting temperature, the ordered layer initiates crystal growth into the bulk, leading to an

oriented, homogeneous semicrystalline structure.

DY 6.4 Mon 10:30 PC 203

Experimental test of Tammann's nuclei development approach in crystallization of macromolecules — ●EVGENY ZHURAVLEV¹, JÜRGEN W.P. SCHMELZER¹, and ALEXANDER S. ABYZOV² — ¹University of Rostock, Rostock, Germany — ²Kharkov Institute of Physics and Technology, Kharkov, Ukraine

A first attempt to probe the size distribution of homogeneously formed nuclei in polymers was realized employing Tammann's two-stage crystal nuclei development method and fast scanning calorimetry. A transfer heating rate of 500,000 K/s prevents nuclei growth on heating in poly(ϵ -caprolactone). The employed temperature profile was adapted from Tammann's two-stage crystal nuclei development method implying formation of nuclei at large undercooling (low temperatures) and following their isothermal growth at higher temperatures. Fast scanning calorimetry allowed us to reach the deep supercooling of the melt at 100,000 K/s avoiding heterogeneous and homogeneous nuclei formation and growth. Then crystal nuclei were allowed to form isothermally at the temperature corresponding to the maximum of the steady-state nucleation rate for homogeneous nucleation (210 K for PCL, $T_g = 209$ K), where both the effect of heterogeneous nucleation and the growth rate are low. The presence of these crystal nuclei and its effect on crystallization was probed by heating the sample to higher temperatures and observation of the overall crystallization process, determining the crystallization half-time. A theoretical explanation of the observations was developed.

DY 6.5 Mon 10:45 PC 203

Morphological development of poly(butadiene)-block-poly(ethylene oxide) during annealing — ●TOBIAS N. BÜTTNER¹, STEFAN HÖLZER², ROBERT SCHULZE¹, and KLAUS D. JANDT¹ — ¹Chair of Materials Science (CMS), Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany — ²Laboratory of Organic Chemistry and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstraße 10, 07743 Jena, Germany

Nanostructures of semi-crystalline diblock copolymers (DBCP) can be tuned by controlled crystal thickening, whereby the knowledge of the mechanisms and kinetics is relevant for possible applications.

In the present study we tested the hypothesis that the morphological development of a poly(butadiene)-block-poly(ethylene oxide) depends on the kinetics of crystal thickening during annealing and can be described by combining time- and temperature-dependent X-ray scattering (SAXS) and differential scanning calorimetry (DSC).

Depending on the annealing temperature, three effects predominated: crystal thickening, thermal fractionation and complete melting. We investigated the absolute long period growth due to crystal thickening by SAXS measurements. In addition, DSC based crystal thickness distributions were used to explain the running processes during annealing. The combination of both methods enables the precise tailoring of DBCP nanostructures without changing the degree of polymerization.

Nanostructures with defined dimensions are interesting for nanotemplating applications, e.g. the biomedical field.

DY 6.6 Mon 11:00 PC 203

Crystallization of binary colloidal mixtures with polymer-induced attraction — ●NICOLE SCHAERTL^{1,2}, THOMAS PALBERG³, and ECKHARD BARTSCH^{1,2} — ¹Institut für Physikalische Chemie, Universität Freiburg, Deutschland — ²Institut für Makromolekulare Chemie, Universität Freiburg, Deutschland — ³Institut für Physik, Universität Mainz, Deutschland

Polystyrene (PS) microgel colloids serve as model system for hard spheres (HS). Binary mixtures of dispersed small (S) and large (L) PS particles with diameter ratios of S to L close to a value of $\Gamma = 0.8$ have been widely used to investigate glass formation as well as re-entrant melting introduced by short-ranged depletion attraction. Previously, we have shown that depletion attractions not only enhance particle mobility, leading to a melting of the glass, but also enforce crystallization of a colloidal eutectic which is kinetically suppressed in the corresponding HS system [1]. Here we show that a subtle change of the system parameters to slightly larger Γ leads to a completely different enforced

crystallization scenario. Using static light scattering to investigate structure and kinetics including crystal size growth and packing, we observe hexagonal superlattices instead of single-component crystals. Our findings can be rationalized by the occurrence of stable binary crystals LS2, so-called Laves phases, in agreement with computer simulations by Hynninen et al. [2].

[1] Kozina et al., *Soft Matter* 10, 9523 (2014) [2] Hynninen et al., *J. Chem. Phys.* 131, 064902 (2009)

DY 6.7 Mon 11:15 PC 203

Frühe Belege zur Kettenfaltung in Lamellen bei massivem HDPE — •HEINZ PREUSS — 31785 Hameln

Mit dem Oberflächenabriss von aus der Schmelze bei langsamer Ab-

kühlung erstarrten massiven Proben aus Niederdruckpolyethylen (HDPE) gelang die mechanische Trennung der Lamellen längs ihrer Grenzflächen (H.H.W.Preuß, *physica status solidi* Vol. 3, 1963 S. K209 ff.). Dies belegt sowohl, dass die in elektronenmikroskopischen Oberflächenbildern sichtbaren Terrassenstufen tatsächlich die Ränder von Lamellen sind, die sich als relativ selbständige Struktureinheiten in das Probeninnere fortsetzen, als auch die schwächere Bindung der Lamellen aneinander. Zugleich erfährt das Modell der Kettenfaltung (z. B. A. Keller, *Kolloid * Zeitschrift*, 165 (1959), s. 15) eine Bestätigung. Mit dessen Hilfe lässt sich erklären, dass die Molekülketten, welche senkrecht zu den Lamellengrenzflächen orientiert sind, sich in den Lamellen kristallografisch geordnet in den Lamellen unterbringen lassen, obwohl deren Dicke D (8 bis 15 nm) deutlich kleiner ist als die Kettenlänge L .