CPP 34: Crystallization, Nucleation, Self Assembly I (joint session CPP/DY, organized by CPP)

Time: Wednesday 9:30–12:15   Location: H42

Invited Talk   CPP 34.1   Wed 9:30   H42
Polymer crystallization and nucleation: New insights from fast scanning calorimetry — ●Christoph Schick[1], Evgeny Zhuravlev[1], and René Androsch[2] — [1]University of Rostock, Institute of Physics, 18051 Rostock — [2]Martin-Luther-University Halle-Wittenberg, Center of Engineering Sciences, 06099 Halle/Saale

Crystallization commonly starts from a (sub)nanoscale nuclei which eventually growth to a crystal. Classical nucleation theory (CNT) provides a qualitative description of these processes. Nevertheless, CNT often fails to predict nucleation and crystallization on a quantitative level. Differential scanning calorimetry (DSC) is often employed to probe such complex phase transitions. The traditional DSC is limited in its cooling capability to cooling rates below 10 K/s. However, many materials are crystallizing, e.g. during processing, at much faster cooling rates (100 to a few 1000 K/s). Knowledge about the phase transitions on fast cooling is therefore required. Chip based calorimeters cover this range but so far they do not allow to obtain the full information for fast crystallizing materials like PE or PTFE. Faster controlled cooling and heating rates above 106 K/s are therefore required. These novel fast scanning calorimeters were used in combination with conventional DSC to study crystallization of polymers on fast cooling, isothermal crystallization after fast quenches, the efficiency of nucleating agents, the kinetics of crystal nucleation and the kinetics of the glass transition. The basic principle of the new technique and applications to polymeric and non-polymeric materials will be presented.

CPP 34.2   Wed 10:00   H42
Elementary steps of chain folding in a melt of linear polyethylene * a proposal for discussion. — ●Heinz H. W. Preuss — Sedanstr. 6, 31785 Hameln

As far as lamellae of crystalline polyethylene from solution or melt consist of close folded molecular chains (Preuss DPG Spring Meeting 2015, CPP 6.7), one has to find out how the folding can occur. The answer is in the understanding of the limited mobility and flexibility of polymer molecules in a melt. If the molecules are with a large portion nearly close and parallel packed, they can move freely in the direction of their backbone by *worming*(Faraday Discussion 1979, F. C. Frank, p 7 ff., A. Keller, p.146 ff.).In the direction perpendicular to the backbone, molecules have 8,5 % (1/12)of their diameter as average room of move for isomeric exchange of the place of C and H atomes. By simultaneous exchange of some C-H-pairs one can get pairs of folds in an extended chain keeping its general orientation. This would be possible with small molecules neighbouring only and should occur already during polymerization in solution or gas. The expression *adjacent reentry* is in this context a source of missunderstandig, for it provokes the meaning, molecules would move out of the place of junktion in a lamella and would reenter nearby after returning, a probably impossible motion.

CPP 34.3   Wed 10:15   H42
How realistic are *random coils* in HD-PE? Analysis of the closeness of the packing. — ●Heinz H. W. Preuss — Hameln

In a previous talk (CPP 6.7 Spring Meeting 2015) was demonstrated evidence of chain folding in HD-PE after slow cooling from the melt. With an analysis of the density and closeness of Packing including a model experiment with balls close wound with a clothes line one can learn that the density of the melt can be reached only with a high portion (at 80 %) of chain segments beeing nearly close and parallel neigbouring but not with *random coils* understood as balls packed with an entangeled molecular chain. The conformation in the melt should be near to the conformation in the crystal what is easy to be understood with the existence of folded chains in the melt. Compared with the crystal structure in the melt the molecules have 27,6 % more volume and 8,5 % more average distance available for mobility and flexibility. The random coil remains an important abstract mathematical tool, but should not be missinterpreted as if an arbitrarily coiled line could be a correct model of polymer molecules in a melt.

CPP 34.4   Wed 10:30   H42
Wang-Landau simulation of short single polyethylene chain's "crystallization" — ●Timur Shakirov and Wolfgang Paul —

University of Halle, Halle, Germany

The phase behaviour of polyethylene has been under wide investigation during the last 6 decades. But investigation of single chain crystallization is a technically difficult problem. In the case of molecular dynamics simulations, it is not so easy to distinguish kinetic and thermodynamic effects on chain folding. We present results of a Wang-Landau type Monte Carlo study at thermodynamical equilibrium of folding of a single polymer chain. Our simulations are based on a chemically realistic united atom model [1].

[1] W. Paul, D.Y. Yoon, G.D. Smith. An optimized united atom model for simulations of polymethylene melts. The Journal of chemical physics, 103(4), 1702-1709. (1995)

15 min. break

CPP 34.5   Wed 11:00   H42
Control of homogeneous crystal nucleation in polymers — ●Evgeny Zhuravlev[1], Jürn Schmelzer[1], René Androsch[2], and Christoph Schick[1] — [1]University of Rostock, Institute of Pysics, Wismarsche Str, 43-45, 18057 Rostock — [2]Martin-Luther-University Halle-Wittenberg, Center for Engineering Sciences, 06099 Halle/S., Germany

A summary of recent application of Tammann's nuclei development method [1] to fast crystallizing polymers has been laid out to further address the role of pre-formed homogeneous nuclei on crystallization kinetics as well as semi-crystalline morphology. Making use of the separation in time of homogeneous nucleation and growth in the vicinity of glass transition temperature, the nuclei can be pre-formed using the precision and fast temperature control of a fast scanning calorimeter [2]. Further non-isothermal and isothermal heat treatments of these nuclei largely affects on crystallization kinetics and morphology. Combination of these studies contributes to a better understanding of homogeneous nuclei volume density, thermal stability and reordering kinetics. [1] Tammann, G., Number of nuclei in supercooled liquids. Zeitschrift für Physikalische Chemie 1898, 25, 441-479; [2] Zhuravlev, E., et al., Experimental test of Tammann's nuclei development approach in crystallization of macromolecules. Crystal Growth & Design, 2015. 15(2): p. 786-798.

CPP 34.6   Wed 11:15   H42
Crystallization behavior of nanocomposites based on Polylactide - Rigid Amorphous Phase due to the Nanofiller — ●Jing Leng[1], De-Yi Wang[2], Andreas Wurm[3], Christoph Schick[3], and Andreas Schönhals[1] — [1]Bundesanstalt für Materialforschung und prüfung — [2]IMDEA Materials Institute — [3]University of Rostock, Institute of Physics

Two kinds of synthesized NiAl (NiAl-LDH) and MgAl (MgAl-LDH) layered double hydroxides were melt blended with commercial polylactide to prepare different polymer based nanocomposites. The MgAl-LDH based nanocomposites and NiAl-LDH based nanocomposites have a different but mixed intercalated / exfoliated structure. Based on the different structures, the crystallization behaviors of polymer based nanocomposites were investigated by differential scanning calorimetry (DSC) and temperature modulated differential scanning calorimetry (TMDSC) specificly where the heating and cooling rates were varied in a considerably wide range. In a first step, the cooling rate where crystallization can be completely surpressed is estimated. In a second step, based on a specified temperature program the crystalline fraction (CF), the rigid amorphous fraction (RAF) and the mobile amorphous fraction (MAF) were calculated from the the enthalpy and specific heat capacity in dependence on the concentration of the nanofiller. The rigid amorphous fraction was considered as resulting from the the crystallites and the nanofiller. For the first time both fractions were calculated quantitatively without any additional assumption.

CPP 34.7   Wed 11:30   H42
Improved Transferability of Coarse Grained Models for Polymer Crystallization Using Machine Learning — ●Chan Liu[1], Christine Peter[2], Kurt Kremer[1], and Tristan Bereau[1] — [1]Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — [2]Theoretical Chemistry, University of Konstanz,

Konstanz, Germany

Coarse-grained (CG) models, which combine a number of atoms into superatoms or beads, can significantly speed up the simulations and provide reasonable resolution for studying polymer crystallization. One of the major challenges in CG modeling is that the reduction of the number of degrees of freedom makes the resulting coarse models state point dependent; that is, most CG force fields developed from the structures of an atomistic melt are not guaranteed to be transferred to crystalline structures. Thus deriving a transferable CG potential across different thermodynamic states is rather crucial if one want to study the phase behavior of polymeric systems. In this work, we introduce a Machine Learning approach to improve an existing CG model parametrized for a different phase by predicting the deviation between CG and atomistic forces, which can be seen as an external force added on the original CG force field. This model predicts a force on each bead based on the surrounding geometry without projecting it onto pairwise potentials such that it can potentially reproduce many-body contributions. This approach opens the perspective to modeling many-body interactions in CG simulations and thus improve the transferability and accuracy of its force field.

CPP 34.8　Wed 11:45　H42

Double-Crystalline Diblock Copolymer Nanostructures by Crystal Thickening — ●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

Nanostructures of semi-crystalline diblock copolymers (DBCP) can be tailored by controlled crystal thickening. In double-crystalline DBCP, both blocks have the ability to crystallize and, thus, can be used for crystal thickening which was not investigated so far. The aim of the study was to test the hypothesis that the lamellar long period of a linear double crystalline polyethylene-block-poly(ethylene oxide) (PE-b-PEO) can be increased by stepwise annealing of both crystalline phases. Using differential scanning calorimetry, one-step annealing experiments revealed crystal thickening of both crystalline phases, PE and PEO, separately. X-ray scattering experiments showed that PEO crystal thickening did not affect the PE-b-PEOs morphology while PE crystal thickening increased the lamellar long period. Crystal thickening of both phases together was realized by two-step annealing which further increased the lamellar long period as compared to the sole PE crystal thickening. This observation was attributed to a stretching of PEO-blocks triggered by the initial PE crystal thickening that enabled the formation of thicker PEO crystals compared to the one-step annealing of PEO. The defined crystal thickening of double-crystalline DBCP can be used to fabricate tailorable nanopatterns for materials science applications in photonics or the biomedical field.

CPP 34.9　Wed 12:00　H42

Interface & confinement induced order and orientation in thin films of Poly-Caprolactone — ●Wilhelm Kossack[1], Anne Seidlitz[2], Thomas Thurn-Albrecht[2], and Friedrich Kremer[1] — [1]Universität Leipzig, Institute for exp. physics 1,04103 Leipzig — [2]Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, 06120 Halle/Saale

Infrared-transition moment orientational analysis (IR-TMOA), X-ray Diffraction (XRD) measurements and model calculations are combined to study interface and confinement induced order and orientation in thin ($h \approx 11 \times 10^{-6}$ m) films of Poly-caprolactone (PCL) prepared by drop-casting on silicon wafers. Depending on the crystallization temperature, 303 K $\leq T_x \leq$ 333 K, spherulites with a diameter of 1×10^{-6} m $\leq d_S \leq 500 \times 10^{-6}$ m form. Macroscopic order of the crystalline lamellae is imposed by spatial ($d_S > h$) and interfacial interactions and quantified IR-TMOA and XRD pole figures. Both techniques rely on the relative orientation of sample and incident radiation, and measure, in case of PCL, the orientation distribution of *complementary* crystal directions. This allows to (1) correlate the directions of the transition moments with the crystal axes; and (2) estimate the volume fractions of flat- or edge on lamellae as induced by the different interfaces, as well as the fractions of surface-induced- or bulk-nucleated spherulites in dependence on T_x. The contribution of substrate induced spherulitic structures rises with $T_x = 323$ K up to ~ 12 vol%, whereas no indications of edge on lamellae at the free surface are found. The bulk phase, on the other hand, dominates at $T_x \leq 313$ K.