

CPP 13: Poster: Crystallization and Self Assembly

Time: Monday 16:30–18:00

Location: Poster C

CPP 13.1 Mon 16:30 Poster C

Block copolymer micelles at the solid-liquid interface

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Micellar solutions of block copolymers have rich phase diagrams, which can be controlled by temperature or polymer concentration. Due to the correlation between structural properties and macroscopic viscosity the phases can be located using rheometry. A salient result of our investigations is that block copolymer micelles may strongly remember their thermal history. In this regard, a different phase behavior depending on whether heating or cooling the sample can be observed.

Further, these amphiphilic systems are highly sensitive to the properties of a solid boundary. We investigated the solid-liquid interface between aqueous solutions of the copolymer EO(20)-PO(70)-EO(20) and solid walls with different chemical treatments. Using neutron reflectometry we depict the influence of surface energy and temperature on the adsorption behavior of single micelles at solid interfaces. To extract the structural arrangements in concentrated solutions we performed Grazing Incidence Small Angle Neutron Scattering (GISANS) and found a distinct dependence of the near-surface micellar ordering on the surface energy.

CPP 13.2 Mon 16:30 Poster C

Phase behavior of nanorods on quasicrystalline substrates

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Quasicrystals are structures with long-range positional and orientational order. However, they cannot be periodic since they possess rotational symmetries such as 5- or 10-fold axis that are forbidden for conventional crystals. These structures lead to new and unique features of matter. Therefore, a lot of effort has recently been initiated to grow atomic quasicrystals on quasicrystalline surfaces. To mimic this situation, 2D light-interference patterns have been used to study the phase behavior of micron-sized colloidal particles in a 2D quasicrystalline potential and new ordered phases have been identified [1,2]. This contribution studies the ordering of nanorods, such as organic molecules, in a quasicrystalline substrate potential. By using Monte-Carlo simulations, we have identified various novel phases. For example, in one phase the centers of mass of the rods order on a hexagonal lattice whereas their orientations display 10-fold symmetry. We demonstrate how these phases are situated in appropriate phase diagrams as a function of the length of the rods, the potential strength, and the particle density.

[1] Mikhael et al., Nature (London) 454, 501 (2008)

[2] M. Schmiedeberg and H. Stark, PRL 101, 218302 (2008)

CPP 13.3 Mon 16:30 Poster C

Structural Characterization of an amorphous-discotic columnar diblock copolymer, Polystyrene-b-Poly(perylene bisimide acrylate)

— ●GAURAV GUPTA¹, PETER KOHN¹, MICHAEL SOMMER², SVEN HÜTTNER², THOMAS THURN-ALBRECHT¹, and MUKUNDAN THELAKKAT¹ — ¹Institute for Physics, Martin Luther University, Halle, Germany — ²Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, Bayreuth, Germany

The property of the block copolymers to self assemble into ordered arrays of micro domains have made them an interesting candidate for the fabrication of nanostructured devices. Amongst the various new materials used in organic electronics, discotic materials self assembling into columnar structures are gaining importance as they exhibit one dimensional charge transport and high charge carrier mobility.

We present here the structural characterization of a semiconductor block copolymer, Polystyrene-b-Poly(perylene bisimide acrylate) PS-b-PPBI using temperature dependent XRD, DSC and TEM with an aim to get an insight of the confinement effects on crystallization. The SAXS measurements reveal that the material is microphase separated forming hexagonally packed PPBI cylinders in PS matrix with a spacing of 21nm between them. From TEM results the diameter of this

cylindrical micro domain is estimated to be 20nm. The WAXS study shows that the monoclinic crystal structure of PPBI does not change upon confinement in these nanodimensional cylinders. The crystalline structure melts at 1750C resulting in an isotropic liquid.

CPP 13.4 Mon 16:30 Poster C

Substrate induced orientation in thin crystalline polythiophene films

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We studied if and to what extent the crystal orientation of poly (3-hexyl thiophene) thin films can be controlled by substrate effects. Regioregular head-to-tail (HT)-coupled P3HT thin films were crystallized on silicon and HOPG (highly oriented pyrolytic graphite) substrates. Surface morphology and crystal orientation were probed by atomic force microscopy (AFM) and X-ray diffraction (XRD). For both substrates, AFM measurements showed edge-on crystalline lamellae separated by amorphous inter-lamellar zones. The surface topography showed characteristic differences for the two substrates. In some cases for graphite, the crystal orientation reflected the three fold rotational symmetry of the underlying substrate indicating epitaxial effects. XRD measurements revealed different crystal orientation for the two cases. On silicon the crystal a-axis stands perpendicular on the substrate, i.e. the layered structure consisting of separated main and side chains is lying parallel to the substrate, while on graphite the crystal b-axis i.e. the π - π stacking direction is oriented perpendicular to the substrate and consequently the main/side chain layered structure aligned perpendicular to the graphite substrate. The orientation on silicon can be attributed to the wetting effects active in high temperature layered phase, on contrary graphite acts as a nucleating surface inducing oriented epitaxial crystallization.

CPP 13.5 Mon 16:30 Poster C

Molecular weight dependence of the crystalline-amorphous superstructure of semi-crystalline polymers

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During crystallization polymers form a crystalline-amorphous superstructure consisting of lamellar crystals with a typical thickness of about 10 nm. 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 equilibrium 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 fact that d_a increases with molecular weight indicates that the semi-crystalline morphology is related to structure of the chains in the amorphous melt before crystallization.

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Crystallization kinetics in colloidal model system obtained by small angle light and bragg scattering - a comparison.

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We study the crystallization kinetics of spherical colloidal particles with a hard-sphere interaction. The particles are composed of cross-linked polystyrene with a linker/monomer-ratio of 1/10 and are suspended in 2-Ethyl-naphthalen with a volume fraction near the melting concentration.

The Bragg light scattering setup allows us to measure a q-range from 4 up to 20 1/um. Further on we have constructed a second machine to measure the scattered light in the small-angle-regime up to 0.7 1/um. Both systems are capable of measuring the full azimuth-angle with a high resolution on the q- and the time-scale giving excellent statistics

which allows us to study the crystallization kinetics of our samples.

We present a comparison of the different scattering techniques and of the determined parameters describing the crystallization scenario. The combination of both techniques gives us the possibility to get a comprehensive picture of the crystallization process in colloidal model systems.

CPP 13.7 Mon 16:30 Poster C

Crystallisation in attractive colloidal Hard Spheres — ●RICHARD BEYER, SARA IACOPINI, THOMAS PALBERG, and HANS JOACHIM SCHÖPE — Johannes Gutenberg-Universität Mainz, Institut für Physik, Staudinger Weg 7, 55099 Mainz, Germany

We study the crystallization kinetics of a mixture of colloidal "hard-sphere" particles and non-adsorbing polymer, in which the polymer induces a "depletion" attraction between the particles. With increasing amount of added polymer the early stages of the crystallization process are modified significantly and the crystallization process is delayed. We observe obvious deviations from a pure rhcp structure factor and a modification in the time trace and of the absolute values of the nucleation rate density.

CPP 13.8 Mon 16:30 Poster C

Influence of Electric Fields on the Phase Behavior of Concentrated Block Copolymer Solutions — ●HEIKO G. SCHÖBERTH^{1,2}, CHRISTIAN W. PESTER¹, KRISTIN SCHMIDT³, KERSTIN A. SCHINDLER^{1,2}, and ALEXANDER BÖKER¹ — ¹Lehrstuhl für Makromolekulare Materialien und Oberflächen and DWI an der RWTH Aachen e.V., RWTH Aachen University, 52056 Aachen, Germany — ²Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany — ³Materials Research Laboratory, University of California, Santa Barbara, USA

We investigate the influence of the electric field on the phase behavior of diblock copolymers in concentrated solutions using synchrotron small-angle X-ray scattering (synchrotron SAXS). When heating the solutions through the order-disorder transition temperature T_{ODT} , we find a significant decrease in T_{ODT} with increasing electric-field strength. In addition we found a temperature regime in which it is possible to switch between the disordered and phase separated state at constant temperature upon application of a moderate electric field.

Furthermore we can also induce an order-order-transition. We synthesized different block copolymers with compositions close to the predicted phase boundaries. Due to the lower free energy of aligned anisotropic microdomain structures parallel to the electric field, we can induce a transition from the metastable hexagonally perforated lamellae to the lamellae phase under strong electric fields. In addition for an isotropic cubic gyroid phase, which cannot be aligned, a transition to aligned cylinders is found.

CPP 13.9 Mon 16:30 Poster C

Fabrication and Characterization of Two Dimensional Ordered Arrays of Mesoscopic Latex Particles on Solid Sur-

faces — ●ZÜLEYHA YENICE and REGINE V. KLITZING — Stranski-Laboratorium für Physikalische und Theoretische Chemie - Institut für Chemie TU Berlin, Sekr. TC 9 Strasse des 17. Juni 124 D-10623 Berlin

Textured surfaces of controlled morphology and periodicity are of great significance for many areas of science and technology.

The aim of the present work is to control the distance between particles in a 2D lattice. The deposition of the particles on to the wafer is accruing by spin coating technique [1]. Here the effect of the particle size, different rotational speed, type of solvent and different concentrations of the latex particles in the suspension were examined. For morphological observation an atomic force microscope (AFM) operating in the tapping mode was used.

It was observed that different ionic strengths of the solvent leads to different structures on the surface, the distances between deposited particles decrease with increasing ionic strength. This phenomenon can be explained by the classical DLVO model theory. It was also observed that the viscosity and the evaporation rate of the solvent effects the structure on the surface. However, there is a lack of information about the preparation of high ordered colloidal arrays with the interparticle distance ranging from 10 nm to 100 nm.

[1] P. Jiang, M. J. McFarland. J. Am Chem. Soc. 2004,126, 13778-13786

CPP 13.10 Mon 16:30 Poster C

Photo-initiated Growth of sub-7 nm Silver Nanowires within a Chemically Active Organic Nanotubular Template — ●D.M. EISELE¹, H. V. BERLEPSCH², C. BÖTTCHER², K.J. STEVENSON³, D.A. VANDEN BOUT³, S. KIRSTEIN¹, and J.P. RABE¹ — ¹Humboldt-Universität zu Berlin — ²Freie Universität Berlin — ³University of Texas at Austin

Silver nanowires are highly promising quasi 1-dimensional nanostructures for a variety of applications in electronics, photonics and catalysis, as well as for sensors. However, it remains a challenge to control their diameters in the interesting range below 10 nm, where their electronic properties begin to deviate substantially from the bulk. Here, it is reported that self-assembled uniform nanotubular J-aggregates of amphiphilic cyanine dye C8S3 [1] can be used as chemically active templates for the photo-initiated fabrication of silver nanowires by reduction of silver salt. The silver ions are reduced by oxidizing the template.[2] Due to the uniformity of the templates, crystalline silver wires have been obtained exhibiting a highly homogeneous diameter of (6.4±0.5) nm and lengths exceeding a micron. The nanotubular templates act as structure-directing agents and also as localized chemical reductants for silver ions. They may be functionalized further, e.g. with optoelectronically active polycations, providing access to quasi 1-dimensional organic/inorganic hybrid structures with well defined metallic nanowires as a core. [1] D. M. Eisele et al., Nature Nanotech. 4 (2009) 658; [2] J. L. Lyon et al., J. Phys. Chem. C 112 (2008) 1260.