

CPP 8: Crystallization and Self Assembly I

Time: Monday 11:00–12:45

Location: H48

Topical Talk

CPP 8.1 Mon 11:00 H48

Mesoscopic structure formation of polymers in cylindrical nanopores — ●MARTIN STEINHART — Institut für Chemie, Universität Osnabrück

Mesoscopic structure formation processes in the one-dimensional confinement of thin-film configurations, such as crystallization of semi-crystalline polymers and microphase separation of block copolymers (BCPs), have been studied intensively. Only recently, the study of polymers in real two-dimensional confinement, as it is imposed by cylindrical nanopores with rigid pore walls, has emerged as a focus of interest in polymer science. Even though gaining predictive understanding as to how two-dimensional confinement modifies structure formation is still challenging, it has already become clear that inside cylindrical nanopores unprecedented mesoscopic architectures with potentially novel functionalities are accessible. As examples in case crystallization of polymers in aligned ensembles of nanopores and the self-assembly of block copolymers will be discussed. Depending on the nucleation mechanism, crystallization may result in macroscopically uniform textures. It is straightforward that polymers confined to nanoporous hosts could be ideal model systems to study polymorphism, interphases and early stages of crystallization. BCPs confined to nanopores have been found to self-assemble into unprecedented nanoscopic domain structures characterized, for example, by helical structure motifs. Studying polymeric materials in cylindrical nanopores might reveal insight into structure formation processes in general and may pave the way for new functional components made of polymeric materials.

CPP 8.2 Mon 11:30 H48

Freezing kinetics in linear pores with disorder — ●DARIA KONDRASHOVA and RUSTEM VALIULLIN — Department of Interface Physics, University of Leipzig, Leipzig, Germany

Recent progress in the synthesis of nanoporous materials with controlled structural properties made it possible to address various phenomena occurring in mesoscale molecular systems. Among them, different aspects of fluid phase transitions could now be related to the structural properties of mesoporous matrices. In this work, we take advantage of the option to prepare mesoporous silicon with linear, tailor-made pores [1] and thus to study the process of freezing of a fluid under well-defined conditions of confinement. The kinetics of this process measured in the material under study are found to be anomalously slow. We suggest a simple thermodynamical model capturing the main features observed in the experiments. In particular, we show that this behavior results from mesoscale disorder in the pore structure, which leads to a broad distribution of local transition rates [2].

1. Khokhlov A. et al., *New J. Phys.* 9, 272 (2007).

2. Dvoyashkin, M., A. Khokhlov, R. Valiullin and J. Kärger, *J. Chem. Phys.* 129, 154702 (2008).

CPP 8.3 Mon 11:45 H48

Gyroid-structured materials via self-assembled copolymer templates — ●MAIK SCHERER¹, PEDRO CUNHA¹, ALEX FINNEMORE¹, EDWARD CROSSLAND², and ULLRICH STEINER¹ — ¹Cavendish Laboratory, University of Cambridge, Cambridge, UK — ²Albert-Ludwigs-Universität Freiburg, Freiburg, Germany

This talk will discuss the nanostructuring of inorganic materials such as titania or single-crystalline calcium carbonate, using porous diblock copolymer thin films with gyroid morphology.

A particularly interesting phase morphology in microphase separated diblock copolymers is the so called double gyroid, where each of the immiscible blocks forms a triply periodic, self-supporting and continuous network or matrix. Together with its high surface area, the gyroid seems to be the perfect three dimensional structure for novel nanodevices.

I will present two approaches for the fabrication of gyroidal thin films employing either thermal annealing of pure PFS-b-PLA polymer or solvent annealing of a binary blend of hPS/PS-b-PI. The removal of one of the polymeric phases yields nanoporous templates. Finally, two examples for the application of these porous films as templates for in-

organic materials will be presented: Firstly, the bioinspired nanostructuring of single-crystalline calcite with feature sizes as small as 37 nm. Secondly, the electrochemical deposition of titanium dioxide within the porous polymer films on a transparent, conducting substrate for high efficiency dye-sensitized solar cells.

CPP 8.4 Mon 12:00 H48

Small Angle X-Ray Scattering Study of Thermodynamic and Conformational Changes in Ion-Containing Symmetric Diblock Copolymers — ●ILJA GUNKEL^{1,2} and THOMAS THURN-ALBRECHT² — ¹Max Planck Institute of Microstructure Physics, Halle, Germany — ²Institute of Physics, Martin Luther University Halle Wittenberg, Halle, Germany

We present temperature-dependent SAXS measurements on two different symmetric block copolymers with added salt (Lithiumtriflate, LiCF₃SO₃). For both studied systems, Polystyrene-b-Poly-2-vinylpyridine (PS-b-P2VP) and Polystyrene-b-Polyethyleneoxide (PS-b-PEO), the salt selectively dissolved in one block leading to large increases of the order-disorder transition temperatures (T_{ODT}). In addition, the lamellar thickness of these ion-containing block copolymers nontrivially changed above a certain salt concentration - in PS-b-P2VP the lamellae became thicker whereas their thickness decreased in PS-b-PEO. Using basic arguments of the thermodynamics of block copolymers we were able to separate the ion-induced increase of T_{ODT} due to a higher incompatibility between the different blocks from changes in the thickness of the lamellae at T_{ODT} resulting from changes in the conformation of the ion-containing blocks.

CPP 8.5 Mon 12:15 H48

Arrays of Core-Shell Nanorods from ABC Triblock Copolymers — ●MARCUS BÖHME¹, BHANU NANDAN¹, MANFRED STAMM¹, MARKUS GALLEI², and MATTHIAS REHAHN² — ¹Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden — ²Technische Universität Darmstadt, Ernst-Behrl-Institut, Petersenstr. 22, 64287 Darmstadt

Recently Poly-(styrene-b-ferrocenylsilane-b-2-vinylpyridine) (PS-b-PFS-b-P2VP) triblock copolymers have been reported to form core-shell like cylinders under certain solvent annealing conditions in thin films via microphase separation[1]. Here, we present our studies on structure formation in a similar polymer when applying thermal annealing using SAXS, GISAXS and SEM. Furthermore, we present our efforts to transfer the obtained structure into isolated core-shell nanorods by dissolving the matrix polymer in a selective solvent. [1] V. P. Chuang, C. A. Ross, J. Gwyther, I. Manners, *Adv. Mater.* 21 (37), 3789-3793, (2009)

CPP 8.6 Mon 12:30 H48

Structure formation of triphilic block copolymers micelles in water — KARSTEN BUSSE, SAMUEL KYEREMATENG, and ●JÖRG KRESSLER — Nat.Fak. II, Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle (Saale)

The micelle formation in water of a new type of triphilic block copolymers [1] (hydrophilic poly(glycero monomethacrylate) PGMA + hydrophobic poly(propylene oxide) PPO + fluorophilic fluorodecyl F) in different compositions like ABC or CABAC structure was investigated by light and Neutron scattering.[2] The hydrophobicity of the PPO part is temperature and molecular weight dependent. The micellar structure depends on the composition of the block copolymer and temperature, and different behaviors can be observed. Due to the temperature dependence of the solubility of the PPO block in water, a collapse of the PPO should appear during heating within the observed temperature range between 5 and 60 °C. This should lead to a shrinking of the core. Depending on the length of the hydrophilic part, the shell can increase in size, due to better solubility. The aggregation behavior of two pentablock copolymers with different hydrophilic amount have been investigated in more detail by NMR, AFM, and TEM.[3]

References 1. Kyeremateng, S. O.; Amado, E.; Blume, A.; Kressler, J. *Macromol. Rapid Commun.* 2008, 29, 1140. 2. Kyeremateng, S. O.; Busse, K.; Kressler, J. in preparation 3. Kyeremateng, S. O.; Kressler, J. in preparation