

## CPP 19: Poster: Crystallization, Nucleation and Self Assembly

Time: Tuesday 18:15–20:15

Location: Poster C

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**The formation of polymeric honeycomb structure in the presence of different organic liquids** — FARID FARAJOLLAHI, MA-SOUD AMIRKHANI, and OTHMAR MARTI — Institute of Experimental Physics, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Micro porous polymer structures have several applications in photonic devices, cell culturing scaffolds and super hydrophobic surfaces. Recently, self assembly of polymers into micro structures have gained more attention and different methods have been suggested for fabrication desirable patterns. Condensation of water on a volatile polymeric solution which called Breath Figure is one of the new method to produce order micro structure. The ability to make order bubble pattern with one step process have provided unique properties for breath figure method.

In this research, we made the micro bubble structure by adding a small amount of different organic liquid to linear polystyrene solution. By adjusting the concentration of organic liquid, the shape and structure of honeycomb pores can be tuned. For different organic liquid, the effect of length of carbon chain on the self assembled pattern have been investigated

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**Transcrystallinity in isotactic polypropylene: synchrotron IR microspectroscopy and microfocus X-ray scattering** — GONZALO SANTORO<sup>1</sup>, SHUN YU<sup>1</sup>, STEPHAN V. ROTH<sup>1</sup>, ULRICH SCHADE<sup>2</sup>, and GARY ELLIS<sup>3</sup> — <sup>1</sup>HASYLAB at DESY, Notkestr. 85, 22607, Hamburg, Germany. — <sup>2</sup>BESSY-II, Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489, Berlin, Germany. — <sup>3</sup>Institute of Polymer Science and Technology, ICTP-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Isotactic polypropylene (iPP) is one of the most widely-used consumer polymers. It is a semicrystalline thermoplastic exhibiting four different polymorphs: the monoclinic  $\alpha$  phase (thermodynamically the most stable and predominant under regular processing conditions), the trigonal  $\beta$  phase (promoted under special processing conditions, like crystallization under shear), the orthorhombic  $\gamma$  phase (present in materials with low molecular weight or regular chain defects) and a mesomorphic phase (a semi-ordered phase) [1]. Moreover, when crystallization takes place in the presence of fibers, transcrystalline morphologies can develop.

This work presents polarization modulated synchrotron IR microspectroscopy and microfocus X-ray scattering studies on the transcrystalline  $\beta$ -cylindritic phase of iPP, showing evidence for lamellar twisting along the growth direction [2,3].

[1] B. Lotz et al. *Polymer* **37**, 22, 4979 (1996).

[2] J. Torre et al. *Macromolecules* **39**, 16, 5564 (2006).

[3] G. Santoro et al. *J. Phys.: Conf. Ser.* **359**, 012005 (2012).

CPP 19.3 Tue 18:15 Poster C

**Unusual crystallization kinetics in poly(1,1-dimethyl silacyclobutane)** — JUNYU LI<sup>1</sup>, SCHÖNBERGER ASTRID<sup>2</sup>, KUTTICH BJÖRN<sup>1</sup>, JOHANNES ELBERT<sup>2</sup>, GALLEI MARKUS<sup>2</sup>, STÜHN BERND<sup>1</sup>, and REHAHN MATTHIAS<sup>2</sup> — <sup>1</sup>Experimental Condensed Matter Physics, TU Darmstadt — <sup>2</sup>Ernst-Berl-Institute for Technical and Macromolecular Chemistry, TU Darmstadt

The crystallization behavior of poly(1,1-dimethyl silacyclobutane) (PDMSB) with molecular weight ranging between 3.000 and 50.000 kilodalton has been studied through Small Angle X-ray Scattering (SAXS), X-ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC). Well-defined PDMSB homopolymers with polydispersity index less than 1.2 have been prepared by living ring-opening anionic polymerization. It has been found that in the cooling process only one crystallization peak was observed by DSC, however, in subsequent heating process two obvious melting peaks appeared. SAXS results show that there is only one long range order. DSC measurements also show that when isothermal crystallization temperature  $T_c$  is low enough, there will be two melting peaks, but only one melting peak when  $T_c$  is high. The value of lower melting peak  $T_{m1}$  increases with  $T_c$ , showing the increase of lamella thickness due to increase of  $T_c$ . However, the value of higher melting peak  $T_{m2}$  stays constant with  $T_c$ . In addition, surface-attached PDMSB on polystyrene particle was

studied. DSC results show that only one melting peak was observed independent of  $T_c$ . Based on these observations, re-crystallization is suggested to explain this interesting phenomenon.

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**Effect of Shear Stress on Crystallization of Isotactic Polypropylene from a Structured Melt** — BIN ZHANG<sup>1,2,3</sup>, JINGBO CHEN<sup>3</sup>, BARBARA HECK<sup>1</sup>, and GÜNTER REITER<sup>1</sup> — <sup>1</sup>Institute of Physics, University of Freiburg, Germany — <sup>2</sup>Hermann Staudinger Graduate School, University of Freiburg, Germany — <sup>3</sup>School of Materials Science & Engineering, Zhengzhou University, Peoples Republic of China

Based on a control of the melt structure at temperatures near but below the equilibrium melting point we investigated the role of shear stress imposed by the wall of the capillary die on crystal morphology of isotactic polypropylene (iPP). The nanoscale bundles of partially ordered chain segments within the quiescent melt at temperatures between the nominal melting temperature ( $T_m$ ) and the equilibrium melting point ( $T_m^0$ ) allowed for the possibility of shear-induced or shear-assisted formation of crystalline cylindrites which were investigated by means of polarized optical microscopy and small/wide-angle X-ray scattering. The SAXS patterns of near melting point structured melt monitored at 180 °C can be fitted by using a form factor for polydisperse cylinders. It was found that the average radius and height of the bundles of partially ordered chain segments was about 17 nm and 40 nm, respectively. For a given structured melt, the number of cylindrites increased with shear stress, concomitantly, the nucleation density of  $\alpha$ -iPP within a single cylindrite structure increased with shear stress at the expense of  $\beta$ -iPP nucleation density.

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**MUSIC-mode AFM of self-assembled oligothiophene fibrils** — MARTIN FEIFER<sup>1</sup>, EIKE-CHRISTIAN SPITZNER<sup>1</sup>, ROBERT MAGERLE<sup>1</sup>, ROMAN MARTY<sup>2</sup>, and HOLGER FRAUENRATH<sup>2</sup> — <sup>1</sup>Chemische Physik, TU Chemnitz, D-09107 Chemnitz — <sup>2</sup>Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

We investigate the structure of self-assembled oligothiophene fibrils, that may be of interest as organic semiconducting nanowires. Spin-coated on a substrate, the fibrils are about 26 nm wide and have an average height of 2.9 nm. For analysis we use multi-setpoint intermittent contact (MUSIC) mode atomic force microscopy (AFM), which provides with unprecedented spatial resolution data on the fibrils nanomechanical properties and gives a detailed insight into the inner structure. The fibrils consist of a rigid core from tetrathiophene terminally attached with oligopeptides that form a soft shell. We also present results on different substrates and discuss their influence on the fibril's configuration. Furthermore we compare results using standard AFM tips to high-resolution data, obtained by super sharp AFM tips.

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**Free energies of fcc, hcp, and bcc phases of hard sphere crystals** — MOHAMMAD HOSSEIN YAMANI and MARTIN OETTEL — Institut für Angewandte Physik, Universität Tübingen, Germany

We use density functional theory of fundamental measure type (FMT) to evaluate the fully unconstrained minimized periodic fcc, hcp and bcc crystal profiles. Previous FMT results in the case of fcc compare very well to simulation results [1]. hcp and fcc differ only in the stacking sequence of hexagonally packed planes of particles, and thus one expects only a small free-energy difference between these two structures. FMT predicts hcp to be more stable than fcc by a free energy difference per particle of the order of  $0.001 k_B T$ . Instead, simulation results show that fcc is more stable than hcp by about the same free energy difference. We rationalize these findings using Stillinger's expansion [2] for the crystal partition function in the number  $n$  of correlated, free particles in a matrix of frozen particles at ideal lattice positions. It turns out that the stability of hcp over fcc holds for a truncation at  $n = 2$ , giving approximately the same hcp-fcc free energy difference as FMT. For a reversal of stability truncation at higher  $n$  is required.

[1] M. Oettel et al., *Phys. Rev. E* **82**, 051404 (2010).

[2] W. G. Rudd et al., *J. Chem. Phys.* **49**, 4857 (1968).

CPP 19.7 Tue 18:15 Poster C

**Crystalline microstructure of thin elastomeric polypropylene films** — ●JULIA SEEMANN, MARTIN NEUMANN, and ROBERT MAGERLE — Chemische Physik, TU Chemnitz, D-09107 Chemnitz

Elastomeric polypropylene (ePP) is a semi-crystalline polymer with a low degree of crystallinity of < 20%. We study with atomic force microscopy (AFM) the crystalline microstructures forming in thin films of ePP crystallised from solution or melt. One objective is to find ideal conditions for the formation of the crosshatch structure. The films were prepared on silicon substrates via spin coating or dip coating and were annealed under inert conditions for a few hours up to 4 weeks at temperatures between 90°C and 150°C. With dip coating, gradient films have been prepared, showing a continuous increase in film thickness over the lateral extent. This allows for correlation of the film thickness with the crystalline microstructure. With increasing film thickness the size of hedrites decreases and their number increases. The degree of crystallinity depends on the annealing temperature and time, which is in line with general trends reported in the literature.

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**Polymer blend lithography: A versatile method for fabricating nanopatterned self-assembled monolayers** — CHENG HUANG<sup>1,2</sup>, MARKUS MOOSMANN<sup>1,2</sup>, JIEHONG JIN<sup>1,2</sup>, TOBIAS HEILER<sup>1,2</sup>, ●PAUL VINCZE<sup>1,2</sup>, STEFAN WALHEIM<sup>1,2</sup>, and THOMAS SCHIMMEL<sup>1,2</sup> — <sup>1</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology — <sup>2</sup>Institute of Applied Physics and Center for Functional Nanostructures, Karlsruhe Institute of Technology

Polymer blend lithography is introduced as a rapid method to produce patterned self-assembled monolayers on solid substrates featuring different chemical functionalities. For the pattern generation the phase separation of two immiscible polymers, polystyrene (PS) and poly(methylmethacrylate) (PMMA), as a blend solution is used for coating by a spin-coating process. By controlling the spin-coating parameters and conditions, including the humidity, the molar mass of the PS and PMMA, and the mass ratio between the two polymers in the blend solution, the formation of a purely lateral morphology can be reproducibly induced. By selectively dissolving one component, a monolayer copy of the corresponding polymer phase morphology can be created. The patterning process is applied with various functional molecules forming self-assembled monolayers (SAM). This process is suitable for the rapid preparation of quasi two-dimensional nanopatterned functional substrates [1].

[1] Huang, C.; Moosmann, M.; Jin, J.; Heiler, T.; Walheim, S.; Schimmel, T. *Beilstein J. Nanotechnol.* 2012, 3, 620-628. doi:10.3762/bjnano.3.71

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**Deformation mechanisms in semi-crystalline polymers investigated by x-ray scattering** — ●KONRAD SCHNEIDER — Leibniz-Institut für Polymerforschung Dresden, Germany

Depending on the molecular structure the crystallization behaviour of different polymers is different. This is the reason for differences also in the deformation mechanisms of these materials. The lecture compares the deformation mechanisms of different polymers investigated

by simultaneous synchrotron small and wide angle scattering during deformation.

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**Control over crystallization and crystallite orientation in conducting polymer blend films** — ●EVA M. HERZIG<sup>1</sup>, AMMARA AKTHAR<sup>1</sup>, ANNA NAUMANN<sup>1</sup>, CLAUDIA M. PALUMBINY<sup>1</sup>, WEIJIA WANG<sup>1</sup>, SHUAI GUO<sup>1</sup>, GREGORY TAINTER<sup>1</sup>, JAN PERLICH<sup>2</sup>, SHUN YU<sup>2</sup>, STEPHAN V. ROTH<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany — <sup>2</sup>HASYLAB at DESY, 22603 Hamburg, Germany

Various parameters can be exploited to influence the morphology and therefore the performance of conducting polymer blends used in photovoltaic applications [1]. In particular charge transport is anisotropic in many conducting polymers and hence is sensitive to molecular orientation and presence of crystalline domains. Therefore it is highly desirable to have control over crystallization and crystallite orientation. We demonstrate for the well-studied system P3HT:PCBM the response of molecular ordering to the addition of two different passive components. The thorough investigation of these systems, using advanced scattering techniques, spectroscopy and microscopy measurements, allow us to select well-defined preparation protocols to deliberately choose the predominant orientation of crystalline domains in the thin conducting polymer blend films.

[1] M. A. Ruderer, and P. Müller-Buschbaum, *Soft Matter* 7, 5482 (2011)

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**Structure and Dynamics of self-healing model polymers in the melt** — ●ANA RITA BRÁS, MARGARITA KRUTYEVA, WIEBKE ANTONIUS, CLAAS HÖVELMANN, JÜRGEN ALLGAIER, WIM PYCKHOUT-HINTZEN, ANDREAS WISCHNEWSKI, and DIETER RICHTER — Forschungszentrum Jülich, JCNS-1/ICS-1, D52425 Jülich, Germany

One fascinating aspect of a self-assembly of supramolecular polymers carrying functional endgroups is the possibility of controlling the structure, adding functionalities, adjusting the macroscopic properties and taking profit of the non-trivial dynamics associated to the reversibility of hydrogen bonds. The most recent application of these polymers is the self-healing ability. Models of such materials have been synthesized, in which appropriate end-functionalization was performed by using DNA-inspired end-groups like Thymine(Thy)(A) and Diaminotriazine (Triaz)(B). These homoditopic mixtures AA/BB build exclusively key-lock systems A-B. The pre-polymer was polyethylene(glycol)(PEG). Both, Small Angle Neutron Scattering and Neutron Spin-Echo Spectroscopy were performed in the melt allowing to quantitatively access the assembly process. The structure was described for the first time by a Random Phase Approximation generalized to multiblock copolymers consisting of H and D based hydrogen-bonded supramolecular copolymers including interactions. Moreover, it was shown that by NSE the dynamics of hydrogen bonded macromolecules can indeed be accessed. The results could be described in terms of a significantly changed mode structure of the supra-chain based on the suppression of long wavelength Rouse modes. Supported by DFG-SPP1568 and EU-Dynacop