CPP 23: Poster: Semicrystalline Polymers, Polymer Crystallization and Self-Assembly

Time: Tuesday 18:00–20:00 Location: P2

CPP 23.1 Tue 18:00 P2

Deformationsverhalten einzelner kristalliner Lamellen in elastomerem Polypropylen: Verbiegung, Dehnung und Fragmentation — Mechthild Franke und •Robert Magerle — Chemische Physik, TU Chemnitz, D-09107 Chemnitz

Elastomeres Polypropylen (ePP) zeichnet sich durch einen sehr niedrigen Anteil kristalliner Bereiche aus (10 bis 25%), die als einzelne kristalline Lamellen sowie in Verbünden von Lamellen in einer Matrix von amorphem Polypropylen vorliegen. Wir untersuchen das Deformationsverhalten dieser komplexen Gefügestruktur mit einem in ein Rasterkraftmikroskop integrierten Mikrozugversuch. Freitragende, nur wenige Mikrometer dicke ePP-Filme können damit kontrolliert gedehnt und wieder relaxiert werden; gleichzeitig können Veränderungen der Gefügestruktur an der Oberfläche der Filme mittels Rasterkraftmikroskopie abgebildet werden. Unsere Bildreihen zeigen eine Vielzahl unterschiedlicher Deformationsprozesse kristalliner Lamellen: Verbiegung und Dehnung einzelner Lamellen, Bildung von Knicken bei Dehnung, sowie das Auseinanderbrechen einzelner kristalliner Lamellen in etwa 15 nm große Blöcke. Verzweigungen zwischen Lamellen und epitakitsch darauf gewachsene Tochterlamellen weisen beim Dehnen feste Winkel auf, was zu lokal auxetischem Verhalten einzelner Lamellenverbünde führen kann. Das beobachtete Deformationsverhalten kann sehr gut mit einem Block- und Dehnfugenmodell der kristallinen Lamellen erklärt werden.

CPP 23.2 Tue 18:00 P2

Interplay between semicrystalline microstructure and viscoelastic properties of elastomeric polypropylenes — •Martin Neumann and Robert Magerle — Chemische Physik, TU Chemnitz, D-09107 Chemnitz

We aim at understanding how mechanical stress relaxation is affected by the heterogeneous microstructure of semicrystalline polymers. As a model system we study elastomeric polypropylenes (ePP) with different degrees of crystallinity and different molecular weights. Further control about the microstructure and the entanglement density is provided by the annealing temperature and time. With a microtensile testing setup integrated in a scanning force microscope (SFM) we study the nanoscale deformation processes within the microstructure of $\sim$1 μm thin films of ePP. Series of SFM images taken during straining and relaxation show a large variety of deformation processes: elongation, bending, kink formation, and fragmentation of individual crystalline lamellae into 10 nm large blocks (M. Franke, R. Magerle, to be published). The setup allows for different mechanical testing schemes, such as step-wise straining with simultaneous measurement of the temporal evolution of stress overshoot and relaxation. The stress relaxation process ranges over several hundreds of seconds and it resembles the stress relaxation behavior observed in polymer melts. Other experiments are straining with a constant straining rate, creep experiments at constant stress, and shearing. From this data viscoelastic material parameters, such as the elastic modulus and the elongational viscosity can be determined.

CPP 23.3 Tue 18:00 P2

Multi-Setpoint Amplitude Modulation Atomic Force Microscopy on Soft Materials — •Eike-Christian Spitzner, Christian Riesch, Mario Zerson, and Robert Magerle — Chemische Physik, TU Chemnitz, D-09107 Chemnitz, Germany

We present an approach where pointwise measurement of amplitude and phase as function of tip sample distance is used to reconstruct amplitude modulation atomic force microscopy (AM-AFM) images. From one single-pass measurement, images for almost any amplitude setpoint are reconstructed. Furthermore, the position of the unperturbed surface, and the tip indentation into soft (compliant) specimens is determined. Tip indentation can be used as a depth coordinate to reconstruct depth-resolved cross-sections and volume images of the mechanical properties of the top 20 nm of soft polymeric specimens. The method overcomes most limitations of AM-AFM and allows for a better and more quantitative interpretation of height and phase images. The materials studied include block copolymer microdomains, crystalline lamella in elastomeric polypropylene, surfaces of poly(3-hexylthiophene), and supramolecular aggregates deposited on a substrate.

CPP 23.4 Tue 18:00 P2

Nucleation and crystallization in polycaprolactone (PCL) — •Andreas Wurm[1], Doris Pospiech[2], and Christoph Schick[1] — [1]University of Rostock, Institute of Physics — [2]Leibniz IPF Dresden e.V.

Crystallization is commonly considered as nucleation followed by a growth process. Nevertheless, a complete description of polymer crystallization is far from being achieved. Here we apply the recently developed technique, differential fast scanning calorimetry (DFSC), for the investigation of polycaprolactone (PCL) of different molecular weights. DFSC allows temperature control of the sample and determination of its heat capacity during temperature treatments at high cooling and heating rates (up to 500,000 K/s). We can derive information about kinetics of crystal nucleation and overall crystallization in the whole temperature region between glass transition and melting temperature.

CPP 23.5 Tue 18:00 P2

Conformational changes of oligo(ethlene glycol) under aqueous conditions during growth and at elevated temperature monitored with PMIRRAS — •Stefan Zorn, Alexander Gerlach, and Frank Schreiber — Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany

Oligo(ethylene glycol) SAMs are a model system for protein resistant SAMs and are subject of comprehensive research for a better understanding of protein resistance. Recent SFG and IR studies show a strong effect of water on the SAM structure and imply a connection of this interaction to the biofouling properties [1]. The exact mechanism, however, is still under discussion. In this study we were able to monitor the growth of hexa(ethylene glycol) SAMs in real-time under aqueous conditions (in-situ) with polarisation modulation infrared spectroscopy (PMIRRAS) using a home built thin liquid layer cell. Fitting of the absorption modes with Gaussians enabled us to determine their area, width and position. We observed a conformational reordering of the OEG moiety from all-trans / helical to predominantly helical and an enhancing crystallinity. In addition, we were able to study the SAM-water interaction in the different growth states. It is the higher the lower the surface coverage [2]. Further, we investigated hexa(ethylene glycol) SAMs at elevated temperatures under in-situ conditions. Our observations contribute to the understanding of biofouling properties and stability of OEG-SAMs and show the possibilities and importance of PMIRRAS in-situ investigations. [1] M.W.A. Skoda et al., Langmuir 23 (2007) 970; [2] S. Zorn et al., PCCP 12 (2010) 8985

CPP 23.6 Tue 18:00 P2

Increasing the disorder-order transition temperature in PS-P2VP diblock copolymers by applying strong electric fields — •Ilja Gunkel and Thomas Thurn-Albrecht — Institute of Physics, Martin Luther University Halle Wittenberg, Halle, Germany

We present temperature-dependent in-situ small-angle X-Ray scattering measurements on symmetric polystyrene-block-poly-2-vinylpyridine (PS-P2VP) diblock copolymer melts in the presence of an electric field. We found that an electric field favors the ordered state in diblock copolymer melts as the temperature of the disorder-order transition (T_{DOT}) was increased by 1 °C in the presence of electric fields with 30 V/μm. This result qualitatively agrees with recent theoretical predictions on the shift of T_{DOT} in electric fields where it was shown that applying an electric field suppresses composition fluctuations thus leading to an increase of the disorder-order transition temperature [1]. However, in concentrated solutions of symmetric PS-PI in toluene T_{DOT} was found to decrease in the presence of electric fields [2]. These different results will be compared and discussed.

[1] Gunkel, I.; Stepanow, S.; Trimper, S.; Thurn-Albrecht, T. Macromolecules 2007, 40 (6), 2186-2191

[2] Schoberth, H. G.; Schmidt, K.; Schindler, K. A.; Boker, A. Macromolecules 2009, 42 (10), 3433-3436.

CPP 23.7 Tue 18:00 P2

Polymer Blend Lithography: A Method to Generate Monolayer Templates for the Self-Assembled Growth of ZnO Nanostructures — •Jiehong Jin[1], Armin Müller[1], Svetlana Khasminskaya[1], Cheng Huang[1], Jorg Pfeifer[1], Luciana Pitta Bauermann[3,4], Peter Gerstel[3,4], Joachim Bill[3,4], Stefan

Walheim[1,2], and Thomas Schimmel[1,2] — [1]Karlsruhe Institute of Technology (KIT), Institute for Nanotechnology (INT), Karlsruhe, Germany — [2]Karlsruhe Institute of Technology (KIT), Institute of Applied Physics and Center for Functional Nanostructures (CFN), Karlsruhe — [3]Institute for Materials Science, Universität Stuttgart, Germany — [4]Max-Planck-Institute for Metals Research, Stuttgart

A wet-chemical process near room temperature allowing the large-area deposition of nanostructured ZnO films would be attractive for device fabrication. Our approach is 1) to generate a monolayer template on which 2) a nanostructured ZnO layer is assembled. Polymer phase separation during spin coating of a polymer blend is used to generate a purely lateral phase morphology. The selective dissolution of one polymer (Polystyrene) leaves back a polymer mask (PMMA) with holes showing sharp edges. The diameter of the holes depends on the humidity, the molecular weight and film thickness and can therefore be adjusted in the range between 100 nm and several microns. We use these perforated polymer films as lift-off masks for the deposition of self-assembled silane monolayers. The remaining 2-nm-thick pattern can be used as template for the wet-chemical assembly of large-area ZnO nanostructures with thickness of about 50 nm.

CPP 23.8 Tue 18:00 P2

Ellipsometry as a non-destructive tool for in-depth analysis of polymer/fullerene blend films — •Sebastian Engmann, Vida Turkovic, Harald Hoppe, and Gerhard Gobsch — Technische Universitaet Ilmenau, Fakultaet fuer Mathematik und Naturwissenschaften, Institut fuer Physik, Experimentalphysik I, Weimarer Strasse 32, 98693 Ilmenau, Germany

The validity of various optical descriptions/models in relation to the blending ratio of polymer/fullerene blends used in organic photovoltaics has been tested. Fullerene inclusions shape and the degree of polymer crystallinity inside the film have been investigated using Spectral Ellipsometry.

CPP 23.9 Tue 18:00 P2

Self-aggregation of mononucleotides in solution studied by frequency resolved depolarized dynamic light scattering techniques — •Christoph Angermann[1] and Thomas Hellweg[2] — [1]Universität Bayreuth, Physikalische Chemie 1 — [2]Universität Bielefeld, Physikalische und Biophysikalische Chemie

In some cases the rotational diffusion of particles in the nanometer scale is too fast to be easily resolved with conventional photon correlation spectroscopy (PCS) methods. Therefore a custom built depolarized light scattering apparatus equipped with a confocal Fabry-Perot interferometer (FPI) with a free spectral range of 150 MHz was developed. The FPI is used to analyze the scattered light in the frequency domain. This is an important characteristic because the rotational motion of the particles modifies the depolarized component of the scattered light. The original setup was enhanced with an AOM (acousto-optic modulator) instead of mechanical shutters. Due to this enhanced measurement technique, it is easily possible to accumulate the noisy component efficiently leading to an enhancement of the signal to noise ratio. As a proof of principle for the experimental technique we studied interesting self-assembly of mononucleotides in aqueous solution. Self-aggregation phenomena as well as the interaction of the mononucleotides uridine-5'-monophosphate and cytidine-5'-monophosphate can be analyzed precisely.

CPP 23.10 Tue 18:00 P2

Direct estimation of spin diffusion constants by a cross-polarization based method — •Matthias Roos and Günter Hempel — Martin-Luther-Universität, Institut für Physik, Betty-Heimann-Straße 7, D-06120 Halle

Spin diffusion often influences the results of relaxation experiments in dependence of structural and dynamic heterogeneities of the sample. Therefore this phenomenon can be used for the estimation of such heterogeneities. Knowledge of the magnitude of the spin diffusion constant is a precondition for those investigations. Theoretical approaches for the estimation of this constant were used sometimes which however particularly in more mobile phases give rise to some uncertainty. Few experimental attempts for estimating this constant are known. Here we introduce a method which makes use of cross polarization between protons and 13C spins. This method produces holes in the proton magnetization at places where 13C spins are neighboured. During the following waiting time the holes are re-filled. This filling process is caused by spin diffusion; its speed contains information about the spin-diffusion constant. We follow the hole filling process by another cross polarization.

Applications to liquid crystals and polymers (amorphous and crystalline regions) are demonstrated. In a liquid crystal (7CB) the diffusion process could be proven as being one-dimensional.

CPP 23.11 Tue 18:00 P2

Self-Assembled Monolayers of Heteroarene Macrocycles — •Stefan-Sven Jester, Eva Sigmund, and Sigurd Höger — Rheinische Friedrich-Wilhelms-Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn

Nanoscale shape-persistent macrocycles based on dithiophene corner units, linked via phenylene-ethynylene-butadiynylene units, are synthesized. Self-assembled monolayers of macrocycles of different ring sizes (n=3-6) are investigated using scanning tunneling microscopy at the solid-liquid-interface.

CPP 23.12 Tue 18:00 P2

Oligomers and Cyclooligomers of Rigid Phenylene-Ethynylene-Butadiynylenes: Synthesis and Self-Assembled Monolayers — •Stefan-Sven Jester, Natalia Shabelina, Stephan M. Le Blanc, and Sigurd Höger — Rheinische Friedrich-Wilhelms-Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn

Starting from the same bisacetylene, different reaction conditions (palladium or copper catalysis) selectively yield cyclic or acyclic oligomers with n=2-6 linked by freely rotating corner units. STM images of self-assembled monolayers reveal the difference in the adsorption behavior of the acyclic and cyclic oligomers.

CPP 23.13 Tue 18:00 P2

Monolayer Patterns for Templated Self-Assembly of ZnO Films with Nanoscale Resolution — •Svetlana Khasminskaya[1], Armin Müller[1], Jiehong Jin[1], Cheng Huang[1], Jorg Pfeifer[1], Luciana Pitta Bauermann[3,4], Peter Gerstel[3,4], Joachim Bill[3,4], Stefan Walheim[1,2], and Thomas Schimmel[1,2] — [1]Karlsruhe Institute of Technology (KIT), Institute for Nanotechnology (INT), Karlsruhe, Germany — [2]Karlsruhe Institute of Technology (KIT), Institute of Applied Physics and Center for Functional Nanostructures (CFN), Karlsruhe — [3]Institute for Materials Science, Universität Stuttgart, Germany — [4]Max-Planck-Institute for Metals Research, Stuttgart

Lithographically defined self-growing ZnO films were prepared by a bioinspired chemical bath deposition technique (CBD). We observed a high selectivity of ZnO deposition: Teflon-like per-fluoro-decyl-trichlorosilane (FDTS) monolayers repelled ZnO primary particles, whereas amino-functionalized areas of the substrate were selectively covered by a highly anisotropic, oriented, and compact ZnO film with a thickness of 50 nm. The size of the primary particles in our methanol-based solution was approximately 2.5 nm. On the amino substrate they formed agglomerates not larger than 30 nm. Monolayer patterns made by polymer blend lithography were templated with an edge resolution of 30 nm.[1].

[1] L. Pitta Bauermann et al.; Langmuir, 2010, 26 (6), pp 3774-3778

CPP 23.14 Tue 18:00 P2

Morphological study of Langmuir films of Polyglutamate — •Renate Reiter[1], Frédéric Wintzenrith[2], and Günter Reiter[1] — [1]Physikalisches Institut, Universität Freiburg, Germany — [2]Ecole Polytechnique, France

Langmuir monolayers are ideal systems for experimental studies of two dimensional physical phenomena. Poly-γ-benzyl-L-glutamate (PBLG) forms rigid rods with flexible side chains when it is in α-helical conformation. Liquid crystalline- and gel-phases have been observed in organic solvents. When these hydrophobic molecules are confined to the air water interface, the rods lay down flat and can form network-like structures. We want to understand the mechanisms governing the formation of these structures. With a Langmuir trough we investigated phase transitions in such PBLG- layers by recording surface pressure (π) versus area (A) isotherms. Furthermore, the temporal evaluation of π gave valuable information on relaxation processes. The obtained film morphologies were visualized directly on the water surface by means of BAM and, after film transfer onto solid substrates, with AFM. Our results strongly suggest that isotherms recorded in the standard way do never represent equilibrated states. At constant area, a complex, non-uniform decay of π in time was observed indicating molecular rearrangement. At high packing densities π slowly decays to zero. Surprisingly, even after such relaxation, a layer with fibrillar morphology was transferred. Moreover, the isotherms showed intricate hysteretic and relaxation behavior. Can we achieve nematic-like structures in quasi 2D films?

CPP 23.15 Tue 18:00 P2

Einflüsse von Polymeren auf die Kollagenassemblierung — •Nora Haufe[1], Doreen Naumburger[1], Sébastien Garnier[2], Günter Scherr[2], Volker Bach[2] und Michael Mertig[1] — [1]Professur für Physikalische Chemie, Mess- und Sensortechnik, TU Dresden, 01062 Dresden — [2]BASF SE, 67063 Ludwigshafen

Kollagen ist die wichtigste strukturgebende Komponente der Haut. Daher wird bovines Typ I Kollagen als Modell erforscht, um die Gerbung besser zu verstehen.

Die *in vitro* Assemblierung ist eine Untersuchungsmethode, die Informationen auf molekularer Ebene sowie höheren Struktureinheiten zuläßt. Sie gibt Aufschluss über Wechselwirkungen von Monomeren bishin zu Fibrillen und stellt daher ein geeignetes Betrachtungssystem dar.

Polymere beeinflussen diesen Prozess. Polyethylenglycol und Polyacrysläure als zwei nichtgerbende Polymere und die nachgerbende Polymethacrylsäure wurden vergleichend zum kovalent bindenden Glutaraldehyd untersucht.

Spektroskopische und mikroskopische Untersuchungen werden parallel genutzt, um Rückschlüsse auf Wechselwirkungen in den verschiedenen hierarchischen Niveaus zu ziehen. Veränderungen der Assemblierungskinetik können in Abhängigkeit von Menge und Art des Polymers durch Trübungsmessungen detektiert werden. Mittels Rasterkraftmikroskopie werden morphologische Unterschiede der gebildeten Fibrillen untersucht.

CPP 23.16 Tue 18:00 P2

Behaviour and Assembly of Janus Particles in Confined Systems — •Julie Murison and Matthias Schröter — Max Planck Insitute of Dynamics and Self Organization, Göttingen

Half hydrophobic Janus Particles were created using a pickering-style emulsion. The degree of Hydrophobicity was controlled using different surfactants to create a portfolio of beads. Self Assembly of these particles at the air/water and oil/water interfaces was studied using X-ray Tomography. Beads are found to form micelle like structures within the bulk and create distinct regions of wettability. The packings are useful to model natural porous systems of heterogeneous wettability such as petroleum reservoirs.

CPP 23.17 Tue 18:00 P2

Supramolecular Self-Assembly of Hydrogen Bonded Bis-Urea Based Molecules — •Roozbeh Shokri[1,2], Ashok Narladkar[2], Laurent Simon[2], Fraçois Vonau[2], Laurent Bouteiller[3], and Günter Reiter[1,4] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany — [2]Institut de Science des Matériaux de Mulhouse (IS2M-LRC7228), 4 rue des Frères Lumière, 68093 Mulhouse, France — [3]Laboratoire de Chimie des Polymères, UMRb7610, Université Pierre et Marie Curie, 4 place Jussieu, 75252 paris CEDEX 05, France — [4]Freiburg Institute for Advanced Studies (FRIAS), 79104, Freiburg, Germany

The process of self-assembly has been investigated by AFM analysis for three different bis-urea substituted toluene molecules, EHUT, 3EOUUT and C12EHUT with different side chains. Indirect measurements (neutron-scattering,...) and calculations led to conclude that in solution EHUT molecules can form long supramolecular nanotubes at specific conditions of temperature and concentration. Here, we studied the possibility to stabilize these nanotubes on a surface and see them directly by AFM. Our study, however, presents evidences for layered structures on mica with a quantized step-height of around 2 nm. We prove that within these layers the molecules are organized in a unique upward conformation and form ribbons through hydrogen bonding. Molecules with different side-groups, 3EOUUT and C12EHUT showed characteristic lamellar and triangular morphologies when deposited on graphite, reflecting the 3-fold anisotropy of the atomic lattice of graphite. The second layer in registry with the first layer was observed.