

CPP 37: Poster Session 2

Polymer Dynamics, Rheology, Polymer Globules, Wetting, Micro- and Nanofluidics, Interfaces and Thin Films, Crystallization, Nucleation and Self Assembly

Time: Wednesday 15:00–19:00

Location: P3

CPP 37.1 Wed 15:00 P3

Interactions between Water and Linear Poly(N-isopropylacrylamide) Chains Around the Phase Transition Investigated by Dielectric Relaxation Spectroscopy — ●MARIEKE FÜLLBRANDT^{1,2}, ELENA ERMILOVA³, ASAD ASADUJJAMAN¹, RALPH HÖLZEL³, FRANK F. BIER³, REGINE VON KLITZING², and ANDREAS SCHÖNHALS¹ — ¹BAM Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin — ²Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin — ³Fraunhofer-Institut für Biomedizinische Technik IBMT, Am Mühlenberg 13, 14476 Potsdam

The molecular dynamics of linear poly(N-isopropylacrylamide) (pNIPAM) in aqueous media are investigated using dielectric relaxation spectroscopy in a frequency range from 0.1 Hz to 100 GHz. Below the lower critical solution temperature (LCST) two relaxation processes are observed located in the MHz and GHz region assigned to the reorientation of dipoles of the solvated polymer segments (p-process) and water molecules (w-process), respectively. Both relaxation processes are analyzed using the Havriliak-Negami (HN) functions taking special attention to the w-process. Above the LCST the dielectric spectra of the pNIPAM solutions resemble that of pure water showing only the high frequency relaxation process of the water molecules with more or less Debye-type behaviour. The non-Debye behaviour of the w-process below the LCST is mainly induced by the interactions between water and pNIPAM chains via hydrogen bonding. The relaxation time and strength of the w-process is studied in dependence on the concentration, temperature and the polymer chain length.

CPP 37.2 Wed 15:00 P3

Different Polymer Architectures under External Oscillatory Forces — ●RON DOCKHORN^{1,2}, TOM GIESSGEN^{1,2}, and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany — ²Technische Universität Dresden, Institut für Theoretische Physik, D-01069 Dresden, Germany

We are studying the force-extension behavior of different polymer architectures (linear chains, ring polymer, 3₁-trefoil knot, two connected or concatenate rings) by using the bond-fluctuation simulation method. First, we apply a constant force f_0 on the chain ends and determine the response of the end-to-end-distance R . The simulation results for the linear and ring structures follow the scaling prediction of the linear $\sim f_0$ and Pincus-regime $\sim f_0^{2/3}$, but the connected/concatenate rings show small deviations. Second, we apply an oscillatory force $f = f_0 + f_a \cdot \sin(\omega t)$ acting on the chain ends and investigate the response of the end-to-end-distance R on the oscillatory frequency ω . An analytical expression for the end-to-end-distance $R(f)$ is derived by using the Rouse model. For the dissipation of energy we are calculating the hysteresis loop $A = \oint df R(f)$ and find a maximum of hysteresis if $\omega \tau_R = 1$ for ideal structures with τ_R as Rouse time which is confirmed by the simulations. The hysteresis for the different polymer architectures follow the predicted trend, but show specific deviations.

CPP 37.3 Wed 15:00 P3

Molecular dynamics of poly(cis-1,4-isoprene) in 1- and 2-D confinement — ●EMMANUEL URANDU MAPESA¹, MARTIN TRESS¹, WYCLIFFE KIPROP KIPNUSU¹, MANFRED REICHE², and FRIEDRICH KREMER¹ — ¹Institute for Experimental Physics I, University of Leipzig, Leipzig, Germany — ²Max-Planck Institute for Microstructure Physics, Weinberg, Halle (Saale), Germany

Broadband Dielectric Spectroscopy - in combination with a nanostructured electrode arrangement - is employed to study thin layers of poly(cis-1,4-isoprene) (PI). PI is further probed in the 2-D confining space of Anodic Aluminium Oxide (AAO) nanopores. We report that while the structural relaxation shows dependence on neither layer thickness nor molecular weight, the normal mode is dramatically influenced by confinement: (i) its relaxation strength is layer-thickness-dependent; (ii) for PI having a molecular weight M_w comparable to M^* (i.e. the critical molecular weight below which Rouse dynamics dominate), the mean spectral position does not shift with layer thickness, (iii) in contrast, when $M_w > M^*$, the relaxation strength and

rate of the normal mode respond to the confinement; (iv) it is demonstrated, for the first time, that the polymer solution from which the thin layers are spincoated has an impact on the chain dynamics; and (v) the extent by which the normal mode is affected depends on the dimensionality of confinement. Put together, these results show that while the chain dynamics are altered in a manifold of ways (due, for instance, to interactions with the confining surface), the dynamic glass transition retains most of its bulk-like nature.

CPP 37.4 Wed 15:00 P3

Photorefractive Effect in Azobenzene-Containing Materials — ●CHRISTOPH MEICHNER¹, LOTHAR KADOR¹, CHRISTIAN PROBST², ROBIN PETTAU², and HANS-WERNER SCHMIDT² — ¹University of Bayreuth, Institute of Physics and Bayreuther Institut für Makromolekülforschung (BIMF), 95440 Bayreuth, Germany — ²University of Bayreuth, Macromolecular Chemistry I and Bayreuther Institut für Makromolekülforschung (BIMF), 95440 Bayreuth, Germany

Azobenzene-based materials are usually used for holographic applications. Recent measurements reveal that they also exhibit a photorefractive effect. It manifests itself in intensity variations of the two transmitted laser beams (488 nm) which are used for hologram inscription (so-called asymmetric two-beam coupling). This effect has its origin in a phase shift between the holographic light intensity grating and the refractive-index grating in the material. The difference to most two-beam coupling experiments in other materials is that the effect arises here without any external electrical field applied. The measurements show that the phase difference is dynamical and varies with time.

CPP 37.5 Wed 15:00 P3

Spatially Resolved Single Molecule Spectroscopy in Thin Semi-Crystalline Polypropylene Films — ●GORDON HERWIG, STEFAN KRAUSE, MARTIN NEUMANN, ROBERT MAGERLE, and CHRISTIAN VON BORCZYKOWSKI — Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Chemnitz, Germany

The fluorescence of a single molecule is a sensitive indicator for its environment. Changes of the fluorescence lifetime, emission wavelength and polarization can report spatial and temporal changes within the vicinity of the dye. Here we report on confocal microscopy studies of single perylene diimides in thin films of semi-crystalline polypropylene with a spatially complex microstructure on the nanometer scale. The velocity of the orientational diffusion is measured and correlated with the information about the dye's local environment. The latter is obtained from high-resolution atomic force microscopy (AFM) images of the specimen's microstructure. Fluorescent particles that are visible in both confocal microscopy and AFM images are used for image registration with high spatial accuracy. This allows us to determine the position of individual dye molecules between crystalline lamellae and provides insight into the dye's local mobility, which is related to the local viscosity within the amorphous regions of polypropylene.

CPP 37.6 Wed 15:00 P3

Single Molecule Reorientation Dynamics in Deformed Polymethylacrylate Melts — ●STEFAN KRAUSE, MARTIN NEUMANN, ROBERT MAGERLE and CHRISTIAN VON BORCZYKOWSKI — Fakultät für Naturwissenschaften, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

The fluorescence of a single molecule (SM) is a very sensitive probe for the molecules environment and changes of the fluorescence lifetime, emission wavelength, and polarization can report spatial and temporal changes in the environment of the fluorescent dye. Here we report on polarization sensitive SM microscopy in thin films of polymethylacrylate (PMA) melts that are stretched in a microtensile testing setup. Functionalized perylene diimide dyes embedded in the PMA film report their molecular reorientation dynamics and changes within their local environment via polarization sensitive SM microscopy. In control experiments we studied the stress-strain behaviour and the stress relaxation of the PMA films. This experiment provides insights into the steric coupling processes between fluorescent probe molecules and

polymer chains which are not accessible with other microscopy techniques. The data show a continuous transition from an unisotropic distribution of orientations to a more isotropic distribution during deformation of the polymer. In addition, the experiment allows for the direct observation of reorientation of the molecules after deformation which is in close relation with the relaxation of the polymer films.

CPP 37.7 Wed 15:00 P3

Structure and Dynamics of High-temperature Polymer Electrolyte Fuel Cells investigated by Neutron Scattering — ●BERNHARD HOPFENMÜLLER¹, OXANA IVANOVA¹, OLAF HOLDERER¹, WIEBKE MAIER², WERNER LEHNERT², REINER ZORN³, and MICHAEL MONKENBUSCH³ — ¹JCNS, Forschungszentrum Jülich GmbH, Outstation at MLZ, Garching, Germany — ²IEK-3, Forschungszentrum Jülich GmbH, Jülich, Germany — ³JCNS-1 & ICS, Forschungszentrum Jülich GmbH, Germany

High-temperature polymer electrolyte fuel cells based on (poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole) membranes (PBI) with phosphoric acid impregnation are a new promising material for high-temperature polymer electrolyte fuel cells (HT-PEFCs). Their operating temperatures are above the boiling point of water. PBI membranes show good chemical resistance and high glass transition temperature (about 700 K). After being loaded with phosphoric acid (PA) such membranes provide very good proton conductivity ($\sim 80\text{mS/cm}$ at 140°C), which increases with an increasing amount of PA in the system [1,2] Different neutron scattering techniques, including back scattering, small-angle-neutron-scattering or time-of-flight-scattering are practical to investigate structure and dynamics in these systems. We will present results obtained from such measurements.

[1] C. Wannek, W. Lehnert, J. Mergel, J. Power Sources 192 (2009) 258. [2] Q. F. Li, J. O. Jensen, R. F. Savinell, N. J. Bjerrum, Progress in Polymer Science 34 (2009) 449.

CPP 37.8 Wed 15:00 P3

ReaxFF reactive force field model for Twin Polymerization — ●THOMAS SCHÖNFELDER¹, JOACHIM FRIEDRICH², STEFFEN SEEGER¹, JANETT PREHL¹, and KARL HEINZ HOFFMANN¹ — ¹Department of Physics, Computational Physics, TU Chemnitz — ²Department of Chemistry, Theoretical Chemistry, TU Chemnitz

Twin polymerization is a new synthesis concept which enables the formation of two different macromolecular structures from organic-inorganic hybrid materials in one single process step [1]. It is characterized by two main process types - electrophilic substitutions contributing to the organic network formation and condensation reactions building the inorganic structure for the reviewed monomer 2,2*-spirobi[4H-1,3,2-benzodioxasiline]. To understand the formation process we develop a first-principles-based ReaxFF reactive force field for C/O/H/Si(S,F,Ti,...).

The corresponding parameterizations known in literature are not able to describe the twin polymerization process to its full extent.

Here, we present out adapted ReaxFF model, so that the first steps of the twin polymerization are captured properly.

[1] Nanocomposites Prepared by Twin Polymerization of a Single-Source Monomer. S. Grund, P. Kempe, G. Baumann, A. Seifert, S. Spange, Angew. Chem. Int. Ed. 2007, 46, 628-632. DOI: 10.1002/anie.200504327

CPP 37.9 Wed 15:00 P3

Relaxation Processes Interpreted as Low-Pass Filters — ●LOTHAR KADOR — University of Bayreuth, Institute of Physics and BIMF, 95440 Bayreuth

Many systems in physics perform relaxation processes upon external stimulation. Examples are glasses investigated with dielectric spectroscopy and fluorescing or phosphorescing chromophore molecules after absorbing appropriate optical frequencies. When the stimulation is modulated, relaxing systems behave like electronic low-pass filters: Low modulation frequencies are transmitted without attenuation, signals of high frequencies are integrated and experience a phase shift. If the relaxation is single-exponentially, there is full equivalence to a simple RC low pass; more complicated relaxation laws correspond to low-pass filters of higher order. Measurements of the relaxation behavior in the frequency domain and the corresponding filtering behavior are interpreted in terms of the Cole-Cole or polar plot. Special situations arise, when the system responds non-linearly to the external stimulation.

CPP 37.10 Wed 15:00 P3

NMR-Investigations of Semicrystalline Polymers — ●RICARDO KURZ — Martin-Luther Universität Halle-Wittenberg, Institut für Physik, Betty Heimann Straße 7, 06120 Halle (Saale)

The dynamics of semicrystalline polymers Poly-Capro-Lactone and Poly-Ethylene-Glycole have been investigated by the approach of solid-state NMR.

CPP 37.11 Wed 15:00 P3

Specific Interactions In A Coarse Grained Hard Sphere Model — ●BENNO WERLICH¹, MARK TAYLOR², and WOLFGANG PAUL¹ — ¹Institut für Physik, Martin-Luther University Halle-Wittenberg, Halle(Saale), Germany — ²Department of Physics, Hiram College, Ohio, USA

We use an off-lattice hard-sphere coarse grained model with a square well (sw) potential for studying structure formation of homopolymer chains. Starting with tangent spheres, shortening of the bond length introduces stiffness. Due to this bond length reduction the spatial structure changed from crystalline to helical-like structures within the lower energy range of the density of states (DOS). We introduce a further interaction where predefined pairs interact via an additional sw potential. This allows the chain to reach lower energy states and leads to a stabilization of additional structures which will be shown in the analysis of thermodynamic functions. For an improved performance for estimating the DOS, the Stochastic Approximation Monte Carlo method is paired with a consecutive Umbrella Sampling.

CPP 37.12 Wed 15:00 P3

In situ x-ray studies of P3HT based bulk heterojunction (BHJ) solidification — ●CHRISTELLE KWAMEN¹, EDUARD MIKAYELYAN¹, PANAGIOTHIS KARAGIANNIDIS², STERGIOS LOGOTHETIDIS², and SOUREN GRIGORIAN¹ — ¹Soft Matter Physics Group, University of Siegen, Siegen Germany — ²LTNF, Physics Department, Aristotle University of Thessaloniki, Thessaloniki Greece

Over the years, the performance of bulk heterojunction (BHJ) polymer solar cells has been shown to be dependent of the local morphology of the active layer. Many processing techniques have been explored to improve the structure of the BHJ layer, passing through solvent, concentration, mixture ratio, thermal annealing etc.(1)

Grazing incidence X-ray diffraction measurements performed on annealed and pristine P3HT:PCBM films showed a strong enhancement of P3HT structure making the (020) peak of π - π stacking visible after annealing. For in situ research, we monitored the solidification of BHJ films where the current-voltage characteristics were recorded simultaneously with GIXD patterns in real time during film formation(2). The structural properties of P3HT-based BHJ and their correlation to electrical performance will be discussed.

This work was partly supported by BMBF (project Nr 05K13PS4).

References: (1)*Al.Ibrahim, M. et al., Appl.Phys.Lett.86 201120(2005) (2)*Grodd L. et al., Macrom. Rapid Comm. 2012, 33(20),1765-1769

CPP 37.13 Wed 15:00 P3

Surface modification, colloidal interaction and the motion of particles — JENNIFER WENZL¹, RYOHEI SETO^{1,2}, and ●GÜNTER K. AUERNHAMMER¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Benjamin Levich Institute for Physico-Chemical Hydrodynamics, New York, NY 10031, United States

A large portion of the goods transported on earth is transported as granulates and powders. With the advances in production techniques of composite materials, the grain size of these powders tends to shrink and reach sizes in the micron and even sub-micron range. For a good processability of the powders their flow behavior is a dominant parameter. The smaller the particles become, the more dominant is the influence of the inter-particle forces on this flow behavior. The macroscopic behavior of such particulate systems is a complex interplay between the internal properties of the particles, their surface properties and the structure the particles form. In this presentation I will focus on the effect of the particle surface and its modification.

I will discuss the influence of surface modification and particle interaction on the mobility of the particles on various length scales. By choosing the appropriate particle chemistry, the interaction between the particles can be tuned from attractive and strongly binding to almost purely repulsive. The structure and mechanical properties of the particle system result from a complex interplay between the particle interaction and the deformation history of the sample. Using mechanical testing and 3D structural analysis of the sample, correlations between

particles interaction and the flowability become visible.

CPP 37.14 Wed 15:00 P3

Spatial distributions of surface energies in porous media: Insights from experiments and simulations on the displacement of immiscible fluids — ●JULIE MURISON¹, THOMAS HILLER¹, BENOIT SEMIN^{3,1}, STEPHAN HERMINGHAUS¹, JEAN-CHRISTOPHE BARET¹, MATTHIAS SCHRÖTER¹, and MARTIN BRINKMANN^{2,1} — ¹Max Planck Institute of Dynamics and Self Organisation, Göttingen — ²Experimental Physics, Saarland University — ³Laboratoire de Physique Statistique, ENS, Paris

Various phenomena observed during immiscible displacement in a porous medium can be related to pore wall wettability. Traditionally the overall wettability of a rock sample is quantified by measuring capillary pressure saturation curves (CPS). To establish a link between these global quantities and the pore-scale distribution of surface energies, we developed a series of model porous media with the same average surface energy, but differing in the typical extension of the wettable surface domains. Complementary to the experiments we use multiple particle collision dynamics (MPCD) to simulate two-phase flow in porous media. The MPCD algorithm is extended to allow for different surface energies to create similar model porous media as used in the experiments. Experimental CPS measurements show that the work dissipated in a complete cycle is monotonically decreasing with the size of the heterogeneities. Imaging of the invading liquid fronts using x-ray tomography revealed front smoothing for small correlation lengths, consistent with a dissipation of energy. The same quantitative behavior is observed in the simulations.

CPP 37.15 Wed 15:00 P3

Study of contact lines moving over heterogeneous surfaces — ●TAK SHING CHAN^{1,2}, DANIEL HERDE², and MARTIN BRINKMANN^{1,2} — ¹Universität des Saarlandes, Saarbrücken, Germany — ²Max Planck Institute for Dynamic and Self-Organization, Göttingen, Germany

We study problems of contact lines moving over heterogeneous surfaces using a lubrication model that incorporates dynamics on many length scales from several nanometers, where hydrodynamic slip plays a significant role, to the size of a system with typical dimensions of a few millimeters. We first consider the problem of a time dependent, oscillating microscopic contact angle and derive the essential relation between the amplitudes of the contact line displacement and the amplitude and oscillation frequency of the microscopic contact angle. We also investigate the problem in which a liquid front is driven by external forces to move over a surface with alternating stripes of different wettability on a plane substrate.

CPP 37.16 Wed 15:00 P3

Depinning mechanism of a droplet contact line on a superhydrophobic surface — ●MARCO RIVETTI^{1,2}, ANAÏS GAUTHIER¹, JÉRÉMIE TEISSEIRE¹, and ETIENNE BARTHEL¹ — ¹Surface du Verre et Interfaces, UMR 125 CNRS & Saint-Gobain — ²Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Göttingen, Germany

It has been demonstrated recently that water droplets on superhydrophobic surfaces may exhibit a strong contact angle hysteresis. Nature offers beautiful examples of both slippery - the lotus leaf - and adhesive - the red rose petal - superhydrophobic surfaces. Several approaches exist in the literature to explain the hysteresis, but most of the models predict the advancing and receding contact angles only under specific hypothesis (i.e. perfect knowledge of the shape of the contact line, given geometry of the surface texture...) In this work we show that the receding motion of the contact line on a textured surface is mediated by the propagation of kinks (step-like defects) all along the perimeter of the drop [1]. We detail the dynamics of this mechanism, and show how the displacement of the contact line and the value of the receding contact angle are affected by the presence of kinks. Our results involve both experiments conducted with water droplets on glass superhydrophobic surfaces and numerical simulations performed with Surface Evolver. We explore the potential of this new concept by assessing the impact of lattice type and texture motive on contact angle hysteresis.

[1] A. Gauthier et al., Phys. Rev. Lett., 110, 046101 (2013)

CPP 37.17 Wed 15:00 P3

Thermal nucleation in ultra thin polymer films on slippery hydrophobic substrates — ●MATTHIAS LESSEL¹, MISCHA KLOS¹, JOSHUA D. MCGRAW¹, OLIVER BÄUMCHEN², and KARIN JACOBS¹ —

¹Saarland University, Experimental Physics, D-66041 Saarbrücken — ²Max Planck Institute for Dynamics & Self-Organization (MPI-DS), D-37077 Göttingen

Spinodal dewetting of thin polystyrene films is subject of many studies (Seemann et al. PRL 2001, Becker et al. Nat. Mat. 2003). Typically, hydrophilic silicon wafers are used as substrates and a no-slip boundary condition is assumed. Here, we modify silicon wafers with self assembled silane monolayers. The silane substrates provide a slip boundary condition and render the surface hydrophobic. Despite the different surface energy, the hydrophobic coating does not change the long-range van der Waals interactions as compared to hydrophilic silicon wafers. Thus, these systems may dewet spinodally. However, in the experiments, a much higher hole density is observed for hydrophobic wafers than is theoretically expected. We find that the hole density on these substrates is influenced by the dewetting temperature and film thickness. The former leads to the hypothesis of thermal nucleation instead of spinodal dewetting as the hole generating mechanism.

CPP 37.18 Wed 15:00 P3

Forced Displacement Experiments in quasi 2D Porous Media. — ●MICHAEL JUNG^{1,2}, MARTA SANCHEZ DE LA LAMA², STEPHAN HERMINGHAUS², MARTIN BRINKMANN^{1,2}, and RALF SEEMANN^{1,2} — ¹Universität des Saarlandes, Saarbrücken, Germany — ²Max Planck-Institute for Dynamics and Self-Organization, Göttingen, Germany

As a model for a forced liquid displacement process into porous media, we study two-dimensional flow experiments in microfluidic devices. The devices and the porous structures are fabricated from oil-resistant UV-curable glue using soft-lithography. The devices were first saturated with oil (silicon oils, fluorinated oils or alkanes) and subsequently the oil was displaced by either a volume or pressure controlled water flush. We observe the global and local dynamic behavior of the advancing liquid fronts and the residual oil distribution using high speed microscopy as function of wettability, viscosity, flow velocity, and geometry of the pore space. Whereas the oil displacement is fairly insensitive to most parameters it shows a pronounced transition depending on wettability. These experimental results are compared to numerical simulations based on multiple particle collisions for analogous pore geometry and wetting conditions.

CPP 37.19 Wed 15:00 P3

Liquid-liquid dewetting — ●STEFAN BOMMER¹, SEBASTIAN JACHALSKI², DIRK PESCHKA², RALF SEEMANN¹ und BARBARA WAGNER² — ¹Saarland University — ²Weierstrass Institute Berlin

The transient morphologies towards equilibrium of liquid droplets dewetting on another liquid are considered experimentally and theoretically. As liquids short chained polystyrene and polymethylmethacrylate are used which are glassy at room temperature and which can be considered as Newtonian liquids well above their glass transition temperatures. The liquid/air interfaces are imaged in situ by scanning force microscopy whereas the liquid/liquid interface is imaged after solidifying the sample and removing the dewetting polystyrene. Required experimental input parameters like the ratio of surface tensions of the liquid/air and the liquid/liquid interface and the contact angles which are extracted from the equilibrium shapes of the droplets. The transient droplet shapes are modeled by a lubrication approximation. A remarkable independence of the transient shapes on the start conditions was found theoretically for sufficiently 'mature' droplets which allows for a quantitative comparison with experimental droplet morphologies, whereas both theoretical results describe the experimental results quantitatively.

CPP 37.20 Wed 15:00 P3

Porous hybrid materials structured with breath figure templating — ●ALI HASSAN, VOLKER KÖRSTGENS, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

Solution casting and spin-coating of polymer solution in volatile solvents can lead to honeycomb-like porous structures if performed under conditions of high relative humidity due to changed wetting conditions. The surface structures known as breath figures are induced by an array of water droplets condensing on the surface without coalescing. In the last stage of the film forming process the water droplets evaporate and a porous structure remains. In this study polyacrylate based thin films are combined with inorganic nanoparticles to obtain hierarchical structured surfaces. The achieved coatings have the potential as a photon scattering functional layer in photovoltaic devices. The

films are characterized with UV/vis spectroscopy and the distribution of pores and nanoparticles in the polymer layers is investigated with optical and scanning electron microscopy.

CPP 37.21 Wed 15:00 P3

Interfacial and Wetting Behavior during In-Mold Printing — ●MARTIN DEHNERT¹, EIKE-CHRISTIAN SPITZNER¹, AGNIESZKA KALINOWSKA², MICHAEL GEHDE², ALEXANDER BÖDDICKER³, UTA FÜGMANN³, ARVED CARL HÜBLER³, and ROBERT MAGERLE¹ — ¹Chemische Physik, Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Germany — ²Professur Kunststoffe, Fakultät für Maschinenbau, Technische Universität Chemnitz, Germany — ³Print- und Medientechnik, Fakultät für Maschinenbau, Technische Universität Chemnitz, Germany

In-mold printing enables decoration of plastic parts during injection molding [1]. The image is pad printed onto the surface of the injection mold, the plastic melt is injected, and during solidification and part removal the ink is transferred to the plastic part. The understanding of wetting and adhesion of the ink on the mold and on the plastic part is essential for a successful implementation of this new printing process. We study the involved interfacial phenomena during in-mold printing of polypropylene with optical microscopy, laser scanning microscopy, and atomic force microscopy. The flow patterns of the ink give insight into the physical processes during the ink transfer. We observe different phenomena on the micro- and nanometer scale, such as wetting of the ink on the mold and on the solidified plastic part, as well as adhesion between the ink, the polymer and the mold surface. A Taylor-Saffman instability of the ink indicates the fluid state of the ink and the shrinkage of the polymer during solidification of the plastic part. [1]Härtig T. et al. *Kunststoffe international* 3/2013

CPP 37.22 Wed 15:00 P3

Microemulsion on model surfaces, study of wetting behavior and uptake capacity — ●SALOMÉ VARGAS-RUIZ¹, CHRISTOPH SCHULREICH², ALEXANDRA ABRAHAM¹, MARTIN JUNG³, REGINE V. KLITZING¹, THOMAS HELLEWEG², and STEFAN WELLERT¹ — ¹Stranski Laboratory, Technical University Berlin, Str. d. 17.Juni 124, 10623 Berlin, Germany — ²Physical Chemistry III, University Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany — ³Armed Forces Scientific Inst. f. NBC Protection, Humboldtstraße1, 29633 Munster, Germany

We present microemulsion systems as a new and effective cleaning medium for surfaces contaminated with highly toxic organophosphate compounds. The effectiveness of the microemulsions as cleaning agents depends not only on their ability to extract and solubilized the contaminant from the treated area, but also on the initial interactions of these complex fluids and the solid surface. Hence, we study the wetting and uptake processes of microemulsion on model surfaces, constituted by functionalized silicon wafers and porous polymer films of poly(butyl methacrylate-co-ethylene dimethacrylate). It was established that independent of the surface treated, the structure and the concentration of oil in the microemulsion have the major impact on the studied processes. According to the obtained results, we formulate a set of microemulsions able to wet and penetrate surfaces with wide range of chemical nature and morphologies.

CPP 37.23 Wed 15:00 P3

Capillary leveling of stepped perturbations in thin viscous films — ●MARCO RIVETTI¹, THOMAS SALEZ², STEPHAN HERMINGHAUS¹, and OLIVER BÄUMCHEN¹ — ¹Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Göttingen, Germany — ²Laboratoire de Physico-Chimie Théorique, UMR Gulliver 7083 CNRS & ESPCI, Paris, France

Leveling occurs in thin liquid films if the free surface has a non-constant curvature. The consequent flow is driven by local curvature gradients and resisted by viscosity, and it is well described in the lubrication theory through the thin film equation. We here revisit recent developments and present new experiments on the capillary leveling of thin polymer films where the initial non-equilibrium profile is given by a Heaviside function (i.e. a step geometry) [1]. Experimental profiles for several film geometries and molecular weights are measured during relaxation. The leveling is shown to be self-similar, in agreement with theoretical predictions. An analytical solution of the profile has been obtained for small steps, when linearization of the problem is possible [2]. For steps comparable to the thickness of the film we present numerical solutions of the thin film equation which show good agreement with the experiments. We will also discuss the possible transition from

leveling to the spreading regime occurring for ultra-thin films.

[1] J.D. McGraw *et al.*, *Phys. Rev. Lett.* **109**, 128303 (2012)

[2] T. Salez *et al.*, *Phys. of Fluids* **24**, 102111 (2012)

CPP 37.24 Wed 15:00 P3

Micro-optical lens array for ultrahigh-throughput fluorescence detection in droplet-based microfluidics — ●JISEOK LIM^{1,2}, PHILIPP GRUNER¹, JEREMY VRIGNON¹, CHRISTOS S. KARAMISTOS², MANFRED KONRAD², and JEAN-CHRISTOPHE BARET¹ — ¹Max Planck Institute for Dynamics and Self-organization, Am Fassberg 17, D-37077 Goettingen, Germany — ²Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, D-37077 Goettingen, Germany

Droplet-based microfluidic systems are promising platforms for high-throughput screening applications. Elementary methods for droplet production, incubation, fusion, and sorting, have been developed over the past years to provide parallelized droplet manipulation required for these applications. Detection systems have so far been poorly parallelized, setting up a bottle neck for the increase of throughput. We demonstrate the design and integration of droplet-based microfluidic devices with microoptical element arrays for enhanced detection of fluorescent signals. We show that the integration of microlenses and mirror surfaces in these devices results in an 8-fold increase of the fluorescence signal and in improved spatial resolution [1]. Finally, we demonstrate that the developed system can be used to detect beta-galactosidase activity of single E.coli cells in 100pL droplets. We reached a throughput more than 100 000 droplets per second, an analytical throughput larger than those obtained using flow cytometry [2]. References: [1] J. Lim *et al.*, *Lab Chip*, **13**, 1472-1475 (2013) [2] J. Lim *et al.*, *Appl. Phys. Lett.*, **103**, 203704 (2013)

CPP 37.25 Wed 15:00 P3

Dense Colloidal Suspensions in Microfluidic Flow — ●PHILIPP KANEHL and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin

Dense colloidal suspensions in a pressure driven flow accumulate in the center of the microchannel. Binary mixtures partially demix depending on their densities [1]. In very dense colloidal systems, one observes oscillations in the colloidal flow velocity which is attributed to transient jamming. The oscillations ultimately become irregular when increasing density further [2].

To develop a theoretical understanding of all these effects, we simulate hard disks under pressure-driven flow in two dimensions using the mesoscale simulation technique of Multi-Particle Collision Dynamics which is an efficient particle-based solver of the Navier-Stokes equation.

In our simulations, we reproduce the experimental observations that a binary suspension segregates into its two species. Whereas at equal densities the larger colloids accumulate in the center, this behavior is reversed when smaller colloids are in the majority and reach a critical density. In sufficiently dense, monodisperse suspensions we obtain the observed oscillations in narrow channels. We monitor both fluid and colloidal flow and thereby explore the role of fluid permeation. In addition, in the transient jamming regime we determine the size distribution for the jammed regions and also look for force chains.

[1] D. Semwogererea and E. R. Weeks, *Phys. Fluids*, **20**, (2008).

[2] A. I. Campbell and M. D. Haw, *Soft Matter* **6**, (2010).

CPP 37.26 Wed 15:00 P3

Effect of Wettability on Water-Oil Front Progression in Porous Media — ●ALEN KABDENOV^{1,2}, HAGEN SCHOLL¹, KAMALJIT SINGH^{2,3}, MARCO DI MICHIEL³, MARIO SCHEEL³, STEPHAN HERMINGHAUS², and RALF SEEMANN^{1,2} — ¹Saarland University, Experimental Physics, D-66041 Saarbrücken, Germany — ²Max Planck Institute for Dynamics and Self-Organization, D-37073 Göttingen, Germany — ³European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France

The effect of wettability on the progression of a water front forced into an initially oil filled porous medium is explored using ultrafast X-ray tomography. The wettability of the porous media was controlled using different cleaning and coating procedures, different bead material or using different combinations of experimental fluids. It is shown that for smaller contact angles, the front progresses in a compact shape without any oil trapping and a single pore-volume of water flood is sufficient to reach the final state. By contrast, the front roughens in the case of larger contact angles, and forms several enlarged fingers due

to front stopping at smaller throats. When forcing the water front into a porous media with locally varying wettability the less wettable volumes are bypassed or bridged in the first water flush and are eventually penetrated by water at a late stage of the water flush.

CPP 37.27 Wed 15:00 P3

Influence of monomeric structure on the slip boundary condition of polymeric liquids — ●MISCHA KLOS, SEBASTIAN BACKES, MATTHIAS LESSEL, and KARIN JACOBS — Saarland University, Experimental Physics, D-66041 Saarbrücken

With further miniaturization of microfluidic devices the role of the solid/liquid interface gets more important for the flow dynamics. Our experiments probe slippage using the dewetting process of thin polymer films on hydrophobic substrates [1]. As hydrophobic coatings we use amorphous polymers (AF1600, AF2400) and different types of highly ordered self-assembled silane monolayers on top of silicon substrates. On silane surfaces, polystyrene (PS) of low molecular weight shows slip lengths up to micrometers [2]. On AF1600, no significant slip is observable. Recent studies using scattering techniques reveal an ordering of the PS side chains at the solid/liquid interface depending on the structure of the substrate [3]. The situation changes if PMMA or PVP are used: The side groups of PS feature a homogeneous electron environment, yet those of PVP are disturbed by a nitrogen atom, PMMA has no side rings at all. The dewetting experiments show that the slip effect is less pronounced in systems with PVP or PMMA. X-ray scattering methods supplement those findings and give further insight to the slippage mechanism at the solid/liquid interface.[1]O. Bäümchen, et.al., J Phys Condens Matter 24 (2012) 325102 [2]R. Fetzer, et. al, Europhys Lett 75 (2006) 638 [3]P. Gutfreund, et. al.,Phys Rev E 87 (2013) 012306

CPP 37.28 Wed 15:00 P3

Shape and wrinkle analysis of deflated elastic capsules — ●JONAS HEGEMANN, SEBASTIAN KNOCH, and JAN KIERFELD — Department of Physics, Technische Universität Dortmund, 44227 Dortmund, Germany

Elastic capsules, prepared from droplets or bubbles attached to a capillary (as in a pendant drop tensiometer), can be deflated by suction through the capillary. We study this deflation and show that a combined analysis of the shape and wrinkling characteristics enables us to determine the elastic properties in situ. Shape contours are analyzed and fitted using shape equations derived from nonlinear membrane-shell theory to give the elastic modulus, Poisson ratio and stress distribution of the membrane. We include wrinkles, which generically form upon deflation, within the shape analysis. Measuring the wavelength of wrinkles and using the calculated stress distribution gives the bending stiffness of the membrane. We compare this method with previous approaches using the Laplace-Young equation and illustrate the method on polymerized octadecyltrichlorosilane (OTS) capsules. Our results are in agreement with the available rheological data.

CPP 37.29 Wed 15:00 P3

Characterisation of a novel splitting geometry for microdroplets — ●MICHAEL MOSKOPP, MICHAEL HEIN, JEAN-BAPTISTE FLEURY, and RALF SEEMANN — Experimental Physics, Saarland University

For applications in droplet based microfluidics it is essential to manipulate individual droplets. Along with coalescence, sorting and mixing of their contents the splitting of droplets is a crucial basic operation. Besides its employment in practical applications the physical process of droplet pinch off is still not completely understood. The most straight forward way to split droplets is to use channel geometries where they normally break into two parts. We report a novel splitting geometry with a broad main channel which subdivides into three narrow split channels. Thus a droplet is forced to split into three smaller compartments of different volumes along its flow direction. For an experimental study of this geometry the droplet-length and -velocity and the width ratio of the split channels were varied. Several regimes of different splitting characteristics were observed for each channel geometry. At low drop velocities the breakup mechanism is dominated by surface tension and capillary driven relaxation. However at higher flow velocities this relaxation process is negligible. Thus, in this case the splitting can be explained by geometrically cutting the droplet. Understanding droplet splitting in different geometries is crucial for design of future applications.

CPP 37.30 Wed 15:00 P3

Monitoring the Kinetics of Interfacial Polymerizations using Microfluidics — ●INGMAR POLENZ, QUENTIN BROSSEAU, and JEAN-CHRISTOPHE BARET — Am Fassberg 17, 37077 Goettingen

Interfacial polymerization (IFP) techniques known since the 1960s offer a facile route for the rapid production of solid shells along emulsion droplets for the encapsulation of both hydrophilic and hydrophobic ingredients under mild conditions. However, due to the high particle size range gained at common IFP processes still there is a lack of reliable quantitative information on the polymerization kinetics and understanding the governing mechanisms that affect the shell formation and thus the capsule properties.

We use microfluidic PDMS devices for monitoring interfacial polymerization process at emulsion droplets by measuring the interfacial deformation which is induced by a hydrodynamic shear stress caused by consecutively arranged construction chambers. This method allows us to measure the microencapsulation fast-kinetics and precisely compare the reactivity of certain components at the IFP. We study the formation of polyurea microcapsules (PUMCs); shell formation occurs at the oil-water interface by an immediate reaction of amines, dissolved in the aqueous phase, and isocyanates that are dissolved in the oily phase. We find that at the initial shell formation both monomers of this IFP contribute equally to the overall encapsulation rate. We also quantify the retarding effect of surfactants on the encapsulation kinetics. The observations clearly indicate our monitoring device to be a powerful tool for the study of interfacial polymerization kinetics.

CPP 37.31 Wed 15:00 P3

Flow rectification in glass nanopores — NADANAI LAOHAKUNAKORN¹, SANDIP GHOSAL², and ●ULRICH F KEYSER¹ — ¹Cavendish Laboratory, University of Cambridge, JJ Thomson Ave, CB3 0HE Cambridge, UK — ²Northwestern University, Evanston, IL60208-3109, USA

Fluid jets are found in nature at all length scales from microscopic to cosmological. Here we report on an electroosmotically driven jet from a single glass nanopore about 75 nm in radius with a maximum flow rate around 15 pL/s. A novel anemometry technique allows us to map out the vorticity and velocity fields that show excellent agreement with the classical Landau-Squire solution of the Navier-Stokes equations for a point jet [1]. We observe a phenomenon that we call flow rectification: an asymmetry in the flow rate with respect to voltage reversal. Such a nanojet could potentially find applications in micromanipulation, nanopatterning, and as a diode in microfluidic circuits.

[1] N. Laohakunakorn, B. Gollnick, F. Moreno-Herrero, D.G.A.L. Aarts, R.P.A. Dullens, S. Ghosal, and U. F. Keyser. A Landau-Squire Nanojet. Nano Letters 13(11): 5141-6 (2013)

CPP 37.32 Wed 15:00 P3

On the Dynamics of Polymer Brushes — ●MICHAEL LANG¹, RON DOCKHORN^{1,2}, MARCO WERNER^{1,2}, TORSTEN KREER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany. — ²Institute of Theoretical Physics, Technische Universität Dresden, Zellescher Weg 17, 01062 Dresden, Germany

We analyze the relaxation dynamics of densely grafted layers of polymer chains under good solvent conditions by Monte Carlo simulations. We find anisotropic monomer mean square displacements when comparing the directions parallel and perpendicular to the grafting plane at intermediate time scales. Our analysis further reveals that the chains relax from the free end towards the innermost monomers. A plateau is observed for the bond-autocorrelation function that grows exponentially in time for the innermost monomers of the brush. Our observations indicate that chain retraction might be the dominating mechanism for the long time relaxation of densely grafted chains.

CPP 37.33 Wed 15:00 P3

Crystallinity Determination of Poly(3-hexyl thiophene) Thin Films by Means of Fast Scanning Calorimetry — ●JENS BALKO¹, SOPHIE SEIDEL¹, ANDREAS WURM², CHRISTOPH SCHICK², and THOMAS THURN-ALBRECHT¹ — ¹Institute of Physics, Martin-Luther-University Halle-Wittenberg, 06120 Halle, Germany — ²Institute of Physics, University of Rostock, 18057 Rostock, Germany

Poly(3-hexyl thiophene) (P3HT) is a common polymer semiconductor, often used as material or component in organic field effect transistors or solar cells. The crystallinity of this semicrystalline material is among other parameters governing the electronic mobility. Fast scanning calorimetry allows studying samples with masses ranging from

several ng to μg and scanning rates not accessible by conventional DSC. Using the extrapolated reference melting enthalpy of a 100% crystalline material obtained in bulk¹, we determined the crystallinity in thin films of a commercial P3HT. The mass of the thin film samples was determined by calibrating the heat capacity in molten state. The crystallinity decreases by a factor of 5 starting from the bulk value for thick films down to films having 25 nm thickness. Cooling rate dependent measurements indicate that the reduced crystallinity is not due to a change in crystallization kinetics.

¹ J. Balko et al., resubmitted to *Macromolecules*

CPP 37.34 Wed 15:00 P3

Evidence of random copolymer adsorption at fluctuating selective interfaces from Monte-Carlo simulation studies — ●IGOR GAZUZ and JENS-UWE SOMMER — Leibniz-Institut für Polymerforschung Dresden e. V., 01069 Dresden

We performed Monte Carlo simulations of a binary, strongly separated mixture of A- and B-type homopolymers with some amount of random AB copolymers added. We show that the copolymers tend to localize at the interface between A and B species. We also simulated random copolymers in a one-component surrounding and compared the free energy to the case of copolymers at the interface. The result shows that interface adsorption is energetically clearly favored compared to bulk micellization, contrary to the conclusion made in literature. We calculate the reduction of the interface tension due to copolymers and check the theoretical predictions for the adsorption mechanism and scaling laws made in the previous works, where ideal interfaces were considered.

CPP 37.35 Wed 15:00 P3

Influence of Substrate-Solvent Interactions on Strongly Adsorbed Polymer Layers — ●DANIEL GEIGER, KIRSTEN DAMMERTZ, MASOUD AMIRKHANI, and OTHMAR MARTI — Institute for Experimental Physics, University of Ulm

Adsorption of poly(methyl methacrylate) (PMMA) on solid substrates forms pseudobrush-like layers. It was found, that even though the adsorption energy of a single chain segment is relatively low, such a layer can be practically irreversibly adsorbed [1] and cannot be removed by rinsing with solvent. Often, e. g. in lithography, such a residual layer is a crucial issue.

We investigated the adsorption of porous monolayers of PMMA on mica and silicon. This enables interaction of the solvent with the substrate leading to a translation and agglomeration as well as partial removal of the polymer on mica. That is not only possible by using the solvent chloroform, but also when using water, in which PMMA is insoluble. Additionally, we observed that annealing has a minor effect on the adsorption strength of such a layer. If applied to a dense layer, washing doesn't cause dewetting or removal of the film.

On silicon substrates movement for both applied liquids is suppressed, but a collapse of single chains was observed when rinsed with water.

[1] P. Frantz and S. Granick, *Kinetics of Polymer Adsorption and Desorption*, Phys. Rev. Lett., 66, 899-902, 1991

CPP 37.36 Wed 15:00 P3

Complex macrophase separated nanostructure induced by microphase separation in lamellar diblock copolymer thin films — JIANQI ZHANG¹, DORTHE POSSELT², KONSTANTINOS KYRIAKOS¹, SEBASTIAN JAKSCH¹, JAN PERLICH³, DETLEF-M. SMILGIES⁴, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching — ²IMFUFA, Roskilde University, Denmark — ³DESY, Hamburg — ⁴Cornell University, Ithaca, NY, USA

Complex, macrophase-separated structures in thin films may be prepared from binary blends of diblock copolymers. We have investigated the nanostructures of thin films spin-coated from binary blends of compositionally symmetric poly(styrene-*b*-butadiene) (P(S-*b*-B)) diblock copolymers having different molar masses using atomic force microscopy (AFM) and grazing-incidence small-angle X-ray scattering (GISAXS) after spin-coating and after subsequent solvent vapor annealing. The as-prepared thin films from these binary blends feature mainly perpendicular lamellae in the one-phase state, indicating that the higher molar mass diblock copolymers dominate the lamellar orientation. The lamellar thickness decreases linearly with increasing volume fraction of the low molar mass diblock copolymer. After solvent vapor annealing, well-defined macrophase separated nanostructures appear which feature parallel lamellae near the film surface and

perpendicular ones in the bulk.

CPP 37.37 Wed 15:00 P3

PPMA-PMMA block copolymer thin films with modified gold nanoparticles — ●DIETER JEHNICHEN¹, DORIS POSPIECH¹, GUPING HE¹, PETER FRIEDEL¹, JIANQI ZHANG², CHRISTINE M. PAPADAKIS², and JAN PERLICH³ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²Technische Universität München, Physik-Department, Garching — ³DESY Photon Science, Hamburg

Diblock copolymers show phase separation on mesoscopic length scales and form a wealth of ordered morphologies in both bulk and thin films resulting in nanostructured polymer surfaces. These may serve as templates for the controlled assembly of nanoparticles.

We investigate diblock copolymers from poly(*n*-pentyl methacrylate) and poly(methyl methacrylate), P(PMA-*b*-MMA) having different block lengths and compositions. In bulk, they form lamellae or hexagonally packed cylinders [1]. For film thicknesses lower than the repeat distance of the bulk morphology, standing cylinders are observed using atomic force microscopy and grazing-incidence small-angle X-ray scattering. In contrast, for higher film thicknesses, lying cylinders are found. Gold nanoparticles assemble at the interfaces and result in some cases in severe changes of the thin film structure.

1. D. Jehnichen et al., *Z. Kristallogr. Suppl.* **30**, 485 (2009).

CPP 37.38 Wed 15:00 P3

Sensing Adhesion on the Nanoscale - Revealing the Contact Formation of Biomimetic Microstructures — ●JENS W. NEUBAUER¹, JOHANN ERATH¹, DIRK-MICHAEL DROTLEF², ARÁNZAZU DEL CAMPO², and ANDREAS FERY¹ — ¹Universität Bayreuth, Bayreuth, Germany — ²Max-Planck-Institut für Polymerforschung, Mainz, Germany

Evolution has led to various bio-surfaces with specific functionalities. Mimicking the models of nature, the properties of man-made materials can be improved as well. For instance, adhesion can be enhanced by microstructuring of surfaces, as shown for gecko mimicked structures. To understand this effect the stress distribution in the contact area is of special interest.

Therefore, we developed a method for the detection of local contact stresses on biomimetic microstructured surfaces. This mechano-responsive system consists of a fluorescently labeled polymer brush. Its response to pressure loads was calibrated using an atomic force microscope. The brush response is sensitive to low pressures (10 kPa) with a spatial resolution better than human skin (1 μm). Under stress steric interactions arise in the polyelectrolyte brush. We investigated these interactions and compared them with existing polymer brush theories.

Using this polymer-based sensor, we studied the adhesive enhancement of microstructured surfaces combining a commercial setup (PVM-A, GeSim, Germany) with a confocal microscope. Hence, we were able to control the contact formation of the microstructured surface.

CPP 37.39 Wed 15:00 P3

Structure of adhesive-adherent interfaces probed by neutron scattering — ●MARKUS SCHINDLER¹, STEPHAN PRÖLLER¹, THOMAS GEUE², JEAN-FRANCOIS MOULIN³, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str.1, 85748 Garching — ²Laboratory for Neutron Scattering, ETHZ & PSI, 5232 Villigen, Switzerland — ³Helmholtz Zentrum Geesthacht, MLZ, Lichtenbergstr. 1, 85747 Garching

Pressure sensitive adhesives (PSAs) are widely used in everyday applications, industries and medicine. Individually tailored compounds exist for many fields of application. The interactions between an adherent and the polymer adhesive can lead to the establishment of an enrichment layer of one of the PSA's components close the interface. To investigate these buried interfaces neutron scattering is the technique of choice due to its high penetration, e.g. compared with X-rays. We present results from neutron scattering experiments, both TOF-GISAXS and neutron reflectivity, revealing the inner structure of the surface-near regions and buried interfaces of a model PSA in contact with an adherent. This model PSA is the statistical copolymer P(EHA-*stat*-MMA), the adherent of choice is silicon, pre-treated with different cleaning routines. We find very different near-interface enrichment layers for the different buried interfaces.

CPP 37.40 Wed 15:00 P3

Magnetic susceptibility of thin films of ferrocene containing polymers — ●HAIKO DIDZOLEIT¹, MARKUS GALLET², JOHANNES

ELBERT², MATTHIAS REHAHN², and BERND STÜHN¹ — ¹TU Darmstadt, Experimental Condensed Matter Physics — ²TU Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie

We focus on amphiphilic ferrocene block copolymers (here poly(vinyl ferrocene)-*b*-poly(vinyl pyridin), PVFc-P2VP) and their magnetic susceptibility depending on the oxidation state in thin films. These films are prepared as Langmuir monolayers on a water substrate and as Langmuir-Blodgett multilayer films on a solid silicon substrate. The structure of the films are monitored by X-Ray reflectivity in situ (water subphase) and ex situ (silicon substrate) and analysed in terms of standard models. In the reduced state the structure of the Langmuir monolayers is dominated by the P2VP block partner and strongly ruled by the surface pressure in the monolayer. The oxidised state induces conformational changes of the ferrocene moiety leading to a swelling of the polymer film on solid substrates and to increased solubility in water leading to a collapse of the Langmuir monolayers. Besides the altered structure on solid substrates we find a switching from diamagnetic to paramagnetic susceptibilities (measured by SQUID magnetometry) in dependency on the oxidation ratio of the ferrocene complex. The impact of the degree of order in the multilayer polymer film on the strength of the magnetic response of the thin films will be discussed.

CPP 37.41 Wed 15:00 P3

Salt Induced Reduction of Lysozyme Adsorption at Behenic Acid Membranes — •HOLGER GÖHRING, MICHAEL PAULUS, and METIN TOLAN — Fakultät Physik/DELTA, Technische Universität Dortmund, D-44221 Dortmund

Lipid membranes serve in biological cells as boundaries between intracellular and extracellular regions. Many biological processes taking place at membranes are associated with the adsorption of proteins. We present a study on the adsorption behaviour of the protein lysozyme at behenic acid films. In the case of electrostatic interaction between proteins and membranes, the screening effect of salt ions can be used to control the adsorption. Therefore we focus the investigation on the effect of NaCl on the adsorption of lysozyme. By varying the salt concentrations the electrostatic interaction between the positively charged proteins and the negatively charged head groups of the behenic acid is altered resulting in a decreased lysozyme adsorption with rising NaCl concentration. The adsorption process is investigated by x-ray reflectivity measurements, which allow the determination of the electron density profiles of thin layers at the liquid – gas interface.

CPP 37.42 Wed 15:00 P3

Surface Dynamics of Liquid, Thin Polymer Films — •FAN-YEN LIN, HANS-JÜRGEN BUTT, and WERNER STEFFEN — Max Planck Institute for Polymer Research, P.O. Box 3148, 55128 Mainz, Germany

The emerging technique of resonance enhanced dynamic light scattering (REDLS)[1] was used to study the motions of polymer chains in thin polymer films at different length scales. The polybutadiene (PB) we measured is close to a Newtonian or ideal viscous polymer liquid at room temperature ($T_g+125^\circ\text{C}$). The surface dynamics found can be described by a hydrodynamic capillary wave model[2].

Our studies show the surface dynamics to be strongly suppressed when the length scale is below 25nm. We observe a stiffening behavior decreasing the length scale and by this increasing the confinement. The overall behavior of the dynamics can be explained by a three layer model, bulk behavior in the middle, a more mobile layer at the polymer-air interface and a less mobile layer at the solid substrate-polymer interface.

1, Plum MA, Menges B, Fytas G, Butt HJ, Steffen W, Rev. Sci Instr. 2011, 82, 015102

2, Kim H, Rühm A, Lurio LB, Basu JK, Lal J, Lumma D, Mochrie SGJ, and Sinha SK, Phys. Rev. Lett. 2003, 90, 068302

CPP 37.43 Wed 15:00 P3

Flexibility investigations on low-temperature processed nanostructured polymer/titania hybrid films — •TOBIAS WIDMANN, WEIJIA WANG, and PETER MÜLLER BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

On the way to green energy, hybrid solar cells show great potential. They combine a conducting polymer with an inorganic semiconductor and therefore have advantages of both materials. The flexibility is one of the most promising properties of hybrid solar cells, which ensures the production by a roll-to-roll process and in large scale. Hence, in this work the flexibility of low temperature processed hybrid thin films

is investigated. A porous film structure is synthesized by incorporating a titania precursor into a diblock copolymer which functions as the template. Thereafter it is deposited on a flexible substrate and a bending test is implemented by a custom made machine. The alteration of the bare titania structure and the hybrid film structure due to bending is investigated with optical microscopy and SEM and correlated with photophysical properties probed with UVvis and PL.

CPP 37.44 Wed 15:00 P3

Einfluss der Oberflächensegregation auf die nanomechanischen Eigenschaften von Polystyrol-Polybutadien-Mischungen — •MARTIN SCHINDLER, MARTIN DEHNERT and ROBERT MAGERLE — Chemische Physik, Fakultät für Naturwissenschaften, Technische Universität Chemnitz, D-09107 Chemnitz, Deutschland

In dünnen Filmen von Mischungen aus Polystyrol (PS) und Polybutadien (PB) Homopolymeren führt die Anreicherung von PB an der Oberfläche von PS-reichen Domänen zu einer Veränderung der nanomechanischen Eigenschaften ihrer Oberfläche. Wir haben dies mittels Multi-Set Point Intermittent Contact mode Rasterkraftmikroskopie untersucht, wobei wir das Volumenverhältnis von PS und PB sowie die Schwingungsamplitude der AFM-Spitze systematisch variiert haben. Die Eindringtiefe der Spitze nimmt auf PS-reichen Bereichen mit zunehmendem PB-Anteil zu, was wir als eine Zunahme der Dicke der PB-Benetzungsschicht an der Oberfläche interpretieren. Bei kleinen Schwingungsamplituden kommt es nur zu einer attraktiven Wechselwirkung zwischen Spitze und Probe und die Kurven der dissipierten Energie weisen sowohl auf PS- wie auch PB-reichen Bereichen der Probe einen parabelförmigen Verlauf auf, der typisch für viskoelastische Materialien ist. Tiefenprofile der effektiven Federkonstante zwischen Spitze und Probe zeigen anschaulich die unterschiedliche Größe der attraktiven und repulsiven Bereiche der Spitze-Probe-Wechselwirkung auf PS und PB reichen Bereichen.

CPP 37.45 Wed 15:00 P3

Stability limits of n-nonane calculated from MD-interface-simulations — •STEPHAN BRAUN¹, ATTILA IMRE², and THOMAS KRASKA¹ — ¹University of Cologne, Institute of Physical Chemistry, Luxemburger Str. 116, D-50939 Köln — ²HAS Centre for Energy Research, H-1525 POB 49, Budapest

Based on molecular dynamics simulation of the vapor-liquid interface, the classical thermodynamic spinodal for n-nonane is estimated. The determination of the spinodal is based on properties of the liquid vapor interface. This method relates the tangential pressure component through the vapor*liquid interface to the van der Waals loop in the two-phase region of the phase diagram. By application of the thermodynamic stability criteria, the location of the spinodal can be determined. Up to now the applicability of this method was demonstrated for substances such as Lennard-Jones Argon, carbon dioxide or methanol but not for molecules with a highly anisotropic shape. The choice of n-nonane as investigated molecule originates from the question whether a deviation from the spherical symmetry of a molecule affects the prediction of the stability limit data. One might expect that anisotropic properties of the molecules influence the tangential pressure profile and hence the spinodal. As a result, we find that the estimated stability limit data for n-nonane are consistent within the experimental data available for the homologous series of the n-alkanes. It turns out that the slight alignment of the molecules parallel to the interface reported in the literature does not affect the method of transferring interface properties to the bulk phase stability limit.

CPP 37.46 Wed 15:00 P3

Controlling adsorption of semiflexible polymers to planar and curved substrates — •TOBIAS ALEXANDER KAMPMANN and JAN KIERFELD — TU Dortmund, Germany, NRW

We study the adsorption of semiflexible polymers such as polyelectrolytes or DNA on planar and curved substrates, e.g., spheres or washboard substrates via short-range potentials using extensive Monte-Carlo simulations, scaling arguments, and analytical transfer matrix techniques. We show that the adsorption threshold of stiff or semiflexible polymers on a planar substrate can be controlled by polymer stiffness: adsorption requires the highest potential strength if the persistence length of the polymer matches the range of the adsorption potential. On curved substrates, i.e., an adsorbing sphere or an adsorbing washboard surface, the adsorption can be additionally controlled by the curvature of the surface structure. The additional bending energy in the adsorbed state leads to an increase of the critical adsorption strength, which depends on the curvature radii of the substrate struc-

ture. For an adsorbing sphere, this gives rise to an optimal polymer stiffness for adsorption, i.e., a local minimum in the critical potential strength for adsorption, which can be controlled by curvature. For two- and three-dimensional washboard substrates, we identify the range of persistence lengths and the mechanisms for an effective control of the adsorption threshold by the substrate curvature.

CPP 37.47 Wed 15:00 P3

Influencing optical properties and the morphology in thin polymer films consisting of P3HT, PFO und MEH-PPV by adding small amounts of high-boiling solvent additives — ●MARKUS REICHENBERGER — Universität Bayreuth, Lehrstuhl EP2

If admixing a few volume percent of higher boiling point additives to a solution with constant polymer concentration and solvent, impact on optical transitions, electronic properties and film morphology is resulting. It is shown how this modification of the polymer solution affects thin films of P3HT. The investigation is carried out by different spectroscopical methods and various techniques of surface analysis. Diiodooctane, dichlorobenzene and octanedithiole are used as exemplary high-boiling additives. The effect of incorporating diiodooctane on films made of PFO and MEH-PPV gives approximately equivalent results as in P3HT films: By admixing a small amount of an arbitrary high boiling point additive to the polymer solution, one can control the fraction of amorphous and aggregated phase, hence potentially the charge transport, in the spin-coated polymer film. Many a time in the literature one observes an high energetic peak at 2.12 eV, respectively 585 nm, in the photoluminescence spectrum of thin P3HT films. Recent results are able to clarify the origin of this peak.

CPP 37.48 Wed 15:00 P3

Heteroepitaxial growth of C60 on a substrate: a kinetic Monte Carlo study — ●CHRISTOPHER WÄCHTLER, NICOLA KLEPPMANN, and SABINE H. L. KLAPP — Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Thin crystalline fullerite films are currently of high interest as candidates for applications in semiconductor devices. Therefore a good understanding of the growth mechanisms and of the influence of parameters like temperature and the underlying substrate is mandatory.

Experimental data [1] leads us to examine the heteroepitaxial growth of fullerenes on mica. Based on transition state theory and previous studies of C60 epitaxy [2] we use kinetic Monte Carlo simulations to reproduce the experimental results under the same experimental conditions, i.e. temperature, deposition rate and substrate size. In this study we analyze the influence of the substrate on the system dynamics during deposition and subsequent relaxation on a real-space surface on experimental time scales. The systems of lateral extension of 500 to 2000 nm show a Volmer-Weber mechanism and grow near the thermodynamical equilibrium. Morphological quantities such as island density and layer coverage are used to characterize the simulated films. We also investigate the influence of strain on the growth mode of fullerenes grown on a substrate with a lattice constant that is incommensurable to the C60 fcc crystal.

[1] H.-G. Busmann et al., Surf.Sci. 289, 3, (1993).

[2] S. Bommel, N. Kleppmann et al., submitted to PRL

CPP 37.49 Wed 15:00 P3

Nanoparticle distribution and domain orientation in nanoparticle / block copolymer composite thin films — ●ANDRIY HORECHYY¹, BHANU NANDAN², DIETER JEHNICHEN¹, MICHAEL GÖBEL¹, MANFRED STAMM^{1,3}, and DORIS POSPIECH¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — ²Department of Textile Technology, Indian Institute of Technology Delhi, New Delhi, India — ³Technische Universität Dresden, Physical Chemistry of Polymer Materials, Dresden, Germany

Block copolymers (BCP) which microphase separate into various morphologies, are widely used as templates for organizing nanoparticles (NP) into 1D, 2D and 3D-periodic structures. In NP/BCP thin films the thermodynamics that governs the BCP morphology becomes more complex as compared to the bulk, mainly due to the interfacial effects that occur at polymer/substrate and/or polymer/air interface.

In this work we studied and compared the effects of chemical composition of BCP on distribution and lateral arrangement of nanoparticles dispersed in BCP thin films, and influence of such nanoparticle-associated effects on the orientation of BCP domains. By changing the chemical composition of BCP constituents, different lateral and orthogonal distributions of nanoparticles are realized. Presence of

nanoparticles at polymer/substrate or polymer/air interface changes the effective surface energy and promotes domain re-orientation regardless of whether selective or non-selective NP/polymer interactions are involved. We acknowledge funding by Deutsche Forschungsgemeinschaft (DFG).

CPP 37.50 Wed 15:00 P3

Crystalline and J-aggregated state of semiconducting polymer: thin polycrystalline polyaniline films — NATALIA GOSPODINOVA¹, OLGA OMELCHENKO^{1,2}, ELENA TOMŠÍK¹, and ●OLGA GUSKOVA³ — ¹Institute of Macromolecular Chemistry AS CR, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic — ²A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31 Leninsky prospect, 199071 Moscow, Russian Federation — ³Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

Thin polycrystalline polyaniline films according to two dimensional WAXS data are constituted from fibril-like crystals. Full-atomistic molecular dynamics simulation confirms that water-mediated hydrogen bonds are responsible for the self-assembling of aniline oligomers in the fibril direction. Polycrystalline films show a reversible red shift of long-wavelength optical maximum from 570 to 800 nm upon water adsorption. Similarly to dyes long-wave absorption can be attributed to J-like liquid crystalline phase, superficial formation of which is governed by water-mediated intermolecular hydrogen bonding. Thus, a dominating role of hydrogen bonds in crystalline and J-aggregate design of semiconducting polymer has been shown [1].

[1] O. Omelchenko, E. Tomšík, A. Zhigunov, O. Guskova, O. Gribkova, N. Gospodinova // Macromol. Chem. Phys. 2013. DOI: 10.1002/macp.201300429.

CPP 37.51 Wed 15:00 P3

AFM Observation of Heterogeneous Nucleation in Epitaxially Crystallized Polymers — ANN-KRISTIN LÖHMANN, ●MARTHA SCHULZ, JANA RÜDEL, THOMAS HENZE, and THOMAS THURN-ALBRECHT — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg

We present a microscopic study of heterogeneous nucleation in epitaxially crystallized polymers. Instead of randomly occurring nuclei leading to a spherulitic growth, we find a different mechanism in the case of epitaxy. Crystallization starts from an ordered interfacial layer that is stabilized above the bulk melting point. This layer wets the interface and acts as a nucleus which induces the unusual highly oriented lamellar structure of the crystalline film. Ultrathin films of LLDPE, HDPE and PCL crystallized epitaxially on graphite were studied at temperatures close to the polymer melting point. The AFM measurements at high temperatures were performed in the net-attractive oscillation state [1] of Intermittent Contact Mode. The stabilized interface layer can be found in all of the studied systems with differences in morphology, thickness and stabilized temperature range.

[1] T. Henze, K. Schröter, and T. Thurn-Albrecht, Nanotechnology 23, 245702 (2012).

CPP 37.52 Wed 15:00 P3

Automatic, optimized interface placement in Forward Flux Sampling simulations — ●KAI KRATZER¹, AXEL ARNOLD¹, and ROSALIND J. ALLEN² — ¹Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart, DE — ²SUPA, School of Physics, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

With Forward flux sampling (FFS) rare events like crystallization phenomena in equilibrium or non-equilibrium systems can be simulated by driving the system from its initial state to the final state via a set of interfaces in phase space. The efficiency as a combination of computational cost and statistical error of FFS depends on the locations of these interfaces. We present two methods for placing the interfaces automatically at optimal locations and on-the-fly during the simulation, without knowledge of the underlying energy landscape of the physical system. Using these methods only the borders of the initial state and the final state in terms of an order parameter must be defined. Then, the simulation finds its own way through phase space by means of inexpensive exploring simulations. This facilitates the setup of an FFS simulations and increases the efficiency of FFS tremendously by placing more interfaces at bottlenecks of the system where the probability of advancement is lower. The method aims at establishing a constant flux through all interfaces, which not only maximizes the efficiency, but also avoids biasing due to bad sampling at interfaces with very low fluxes.

CPP 37.53 Wed 15:00 P3

Micellar solutions of novel thermoresponsive diblock copolymers — ●LUKAS AUGSBACH¹, KONSTANTINOS KYRIAKOS¹, ANNA MIASNIKOVA², ANDRÉ LASCHEWSKY², ZHENYU DI³, PETER MÜLLER-BUSCHBAUM¹, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching — ²Universität Potsdam, Institut für Chemie, Potsdam-Golm — ³Jülich Centre for Neutron Science, Outstation JCNS, MLZ, Garching

Amphiphilic diblock copolymers with a thermoresponsive block self-assemble into thermoresponsive micelles in aqueous solution. Poly(methoxydiethyleneglycol acrylate) (PMDEGA) is a novel thermoresponsive system, which exhibits cloud points, T_{cp} , in the range 35-45 °C [1]. This system shows peculiar behavior, such as a broad transition region. Moreover, the collapse of the micellar shell has not yet been detected.

Here, we report on small-angle neutron scattering (SANS) experiments on a micellar solution of P(S-*b*-MDEGA) (PS stands for polystyrene) around T_{cp} . The focus is on the structural changes at the cloud point, such as the micellar radius and the correlation of the micelles. At the cloud point, significant structural changes are observed, and the transition occurs over a broad temperature range with intermediate stages, in agreement with previous results on similar PMDEGA systems [2].

[1] A. Miasnikova, A. Laschewsky *J. Polym. Sci. Part A: Polym. Chem.* 2012, **50**, 3313

[2] A. Miasnikova, et al., *Langmuir* 2012, **28**, 4479

CPP 37.54 Wed 15:00 P3

Core-Shell Brush Copolymers with Poly(propylene oxide)-*b*-poly(ethylene oxide) Side Chains — ●CHRISTINA PSYLLA¹, KONSTANTINOS KYRIAKOS¹, JUNPENG ZHAO², STERGIOS PISPAS², and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching — ²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Graft copolymers with densely grafted side chains are known as brush copolymers. Brush copolymers with poly(*p*-hydroxystyrene) (PHOS) as the backbone and poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO) in the side chains, have recently been synthesized and show micelle formation as well as thermoresponsive behavior in aqueous solution [1]. Their multibranched molecular structure may affect their micellization behavior in aqueous solution compared to simple diblock copolymers but also their self-assembly in the bulk.

We report here on small-angle and wide-angle X-ray scattering experiments on several copolymers of various architectures and compositions, carried out in a wide temperature range. In the bulk, significant effects of the chain architecture, i.e. the sequence of PEO and PPO in the side chains and whether the side chains are diblock or random copolymers, and the volume fraction of PPO on the crystalline structure of the PEO block and on the microphase formation are observed.

[1] J. Zhao et al. *Macromolecules* **43**, 1771 (2010)

CPP 37.55 Wed 15:00 P3

Novel thermoresponsive block copolymers of various architectures - a fluorescence correlation spectroscopy investigation of the micelle formation — ●KONSTANTINOS KYRIAKOS¹, CHRISTINA PSYLLA¹, SARAH OTTINGER¹, ANNA MIASNIKOVA², ANDRÉ LASCHEWSKY², PETER MÜLLER-BUSCHBAUM¹, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching — ²Universität Potsdam, Institut für Chemie, Potsdam-Golm

Amphiphilic copolymers with a thermoresponsive block in aqueous solution self-assemble into micelles with a thermoresponsive shell. Poly(methoxy diethylene glycol acrylate) PMDEGA is a new thermoresponsive polymer, which exhibits a cloud point in the range 35-45 °C, i.e. within the most interesting physiological window [1,2]. However, the characteristics of the transition at the cloud point are very different from the ones of the often studied poly(N-isopropylacrylamide) (PNIPAM).

We report here on fluorescence correlation spectroscopy (FCS) experiments on very dilute solutions of various P(S-*b*-MDEGA) block copolymers differing in chain architecture: a diblock, a triblock and a three-arm star copolymer. It was found that, below the cloud point, all three polymers form micelles above the critical micelle concentration (CMC) and have similar hydrodynamic radii.

[1] Miasnikova, A., Laschewsky A. *J. Polym. Sci. Part A: Polym. Chem.*

50, 3313 (2012)

[2] Miasnikova, A. et al. *Langmuir* **28**, 4479 (2012)

CPP 37.56 Wed 15:00 P3

Influence of the Crystallization Kinetics on the Morphology and Mechanical Properties of Poly- ϵ -Caprolactone — ●ANNE SEIDLITZ¹, YONGFENG MEN², and THOMAS THURN-ALBRECHT¹ — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Germany — ²State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, China

When a sample is crystallized under isothermal conditions, the crystallization process can be slow (slow regime) or fast (fast regime) compared to the dynamics of the chains in the melt. In the slow regime the chains in the melt should be able to disentangle during crystallization, whereas in the fast regime the chains have no time to dissolve the entanglements. We investigated the influence of the crystallization regime on the morphology and mechanical properties of PCL. We performed tensile measurements in combination with SAXS experiments to investigate the structure and nonlinear mechanical properties. Samples with different molecular weights were isothermally crystallized at different temperatures to reach both regimes. While the morphology is nearly unaffected by the crystallization temperature, we observe a systematic change in the tensile properties, probably caused by a difference in entanglement density between the two crystallization regimes.

CPP 37.57 Wed 15:00 P3

Crystallinity investigations on an aqueous-processable conducting polymer for applications in environmentally friendly organic solar cells — ●STEPHAN PRÖLLER^{1,2}, VOLKER KÖRSTGENS², DANIEL MOSEGUÍ GONZÁLEZ², YUAN YAO², SHUN YU³, STEPHAN V. ROTH³, EVA M. HERZIG¹, and PETER MÜLLER-BUSCHBAUM² — ¹TU München, MSE, Lichtenbergstr. 4, 85748 Garching — ²TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching — ³DESY, Notkestr. 85, 22603 Hamburg

When assembling organic solar cells, organic solvents are used which are often even toxic and cause the technology not to be as 'green' as intended to be. Therefore, polymers being processable in non-toxic solvents such as water are of high interest as donor material in the active layer of organic solar cells. One possible polymer is poly[3-(potassium-6-hexanoate)thiophene-2,5-diyl] (P3P6T), a derivate of P3HT. Next to optical properties like absorption and band gap, the crystallinity of polymer films is of special interest in order to obtain efficiently working solar cells. For high charge carrier mobility, local scale ordering appears to be essential. Therefore, detailed studies on the crystallinity of P3P6T and the dependence on annealing temperature are performed. The thin films are prepared via spin coating and solution casting. The optical properties are investigated using UV/Vis spectroscopy. Crystallinity investigations are performed using XRD and GIWAXS measurements.

CPP 37.58 Wed 15:00 P3

Light hinders ordering in polyaniline — ELIZAVETA ALEKSEEVA, ELENA TOMŠÍK, and ●NATALIA GOSPODINOVA — Institute of Macromolecular Chemistry AS CR, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Liotropic liquid crystalline state with features of chromonic mesophase [1] and J-aggregates [2] is shown to precede formation of highly crystalline self-oriented polyaniline films during water evaporation. Importantly, that not only increase of temperature but also exposition to non-polarized light substantially hinders self-assembly into liquid crystalline state which is prerequisite for formation of fibril-like crystals building polycrystalline polyaniline films. X-ray diffraction, optical microscopy and optical absorption spectroscopy have been employed in this study.

[1] J. Lydon, *Liquid Crystals*, 2011, **38**, 11-12, 1663-1681, and references therein

[2] S. E. Sheppard, *Rev. Mod. Phys.* 1942, **14**, 303.

CPP 37.59 Wed 15:00 P3

Polyaniline as an indicator of the non-clustered water in ionic liquids — ●ELENA TOMŠÍK, ELIZAVETA ALEKSEEVA, and NATALIA GOSPODINOVA — Institute of Macromolecular Chemistry AS CR, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Reversible red-shift of long-wavelength absorption accompanying adsorption of water by thin polycrystalline polyaniline films is considered to be a sign of superficial water-promoted formation of liquid crys-

talline phase. Moreover, this effect is favored by the presence of highly hydrated ions which destroy clustered water. Such simple optical test has been used by us to detect the presence of the non-clustered water in the ionic liquids. Correlation between structure of anions/cations composed ionic liquid and content of non-clustered water is revealed.

CPP 37.60 Wed 15:00 P3

Diffusion einzelner Polymerkristalle in Polypropylen niedriger Taktizität — ●MARTIN NEUMANN, STEFAN KRAUSE und ROBERT MAGERLE — Technische Universität Chemnitz, Chemische Physik, Chemnitz, Deutschland

Elastomeres Polypropylen mit geringer Taktizität hat einen Kristallinitätsgrad von nur 15% und bildet isolierte Kristalle, die in einer amorphen Schmelze eingebettet sind. Rasterkraftmikroskopische Untersuchungen an 60 nm dünnen Filmen liefern mit hoher Ortsauflösung und angemessener Zeitauflösung Bildserien der Veränderungen an der Filmoberfläche. Wir beobachten, dass die isolierten Kristalle nicht ortsfest sind sondern auf Zeitskalen von Stunden und Tagen diffundieren. Aus den Bildserien lassen sich Trajektorien der Kristalle bestimmen, welche Aufschluss über die zu Grunde liegenden Diffusionsprozesse geben. Die Trajektorien können als Translationsdiffusion von Partikeln in einem Flüssigkeitsfilm mit einer Viskosität von $\eta = 10^4$ Pa·s beschrieben werden, die im Bereich der von Polymerschmelzen oberhalb des Glasübergangs bekannten Viskositäten liegt. Die kumulative Verteilung der Diffusionsgeschwindigkeit deutet darauf hin, dass gleichzeitig verschiedenartige Diffusionsprozesse mit unterschiedlichen Diffusionskonstanten stattfinden.

CPP 37.61 Wed 15:00 P3

Comparison of the metastable and the stable phase of eicosane via thermal analysis. — ●CARLO DI GIAMBATTISTA, JÖRG BALLER, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg

Upon cooling from the melt eicosane ($C_{20}H_{42}$) exhibits a transition to a metastable orthorhombic phase (rotator I). This metastable phase was investigated by classic Differential Scanning Calorimetry (DSC) and Temperature Modulated DSC (TMDSC). From these measurements thermodynamic quantities as the latent heat of transition and the frequency dependant complex specific heat capacity could be drawn. These were then compared to the stable reference state (trigonal) in the same temperature region. Additional experimental methods (Polarisation Optical Microscopy, X-Ray Diffraction...) were used to get a systematic insight to the processes at hand.

CPP 37.62 Wed 15:00 P3

Monte-Carlo Simulations on the CH_4/CF_4 mixture — JOYJIT CHATTORAJ¹, TOBIAS RISTHAUS², ●OLIVER RUBNER¹, STEFAN GRIMME², and ANDREAS HEUER¹ — ¹Institute of Physical Chemistry, University of Münster, Germany — ²Institute of Physical and Theoretical Chemistry, University of Bonn, Germany

It is known, though not understood at all, that methane and perfluoromethane are immiscible below 95K and behave thus similar to other mixtures of hydrocarbons and perfluorinated molecules. In this work we want to study the mixing/unmixing of CH_4/CF_4 in order to unveil the mechanisms that lead to this behaviour.

For the interaction potentials of CH_4-CH_4 , CF_4-CF_4 and CH_4-CF_4 We performed extensive dispersion corrected DFT-calculations which were carefully benchmarked against very accurate CCSD(T) results. These potentials were then approximated by simple spherical potentials (e.g. of the Lennard-Jones type). The approximations were controlled by comparing the experimental structure factor and dynamical properties with Monte-Carlo simulations. We then used different Monte-Carlo-approaches from literature that are well established for studying the mixing/unmixing behaviour of molecular systems to investigate the phase diagram of CH_4/CF_4 at different temperatures. By comparing the results of the DFT-potentials with those of the approximated spherical potentials we were able to determine the influence of the anisotropy of the molecules on the unusual unmixing behaviour of this system.

CPP 37.63 Wed 15:00 P3

Crystallization dynamics of pentanol in silica nanopores — ●DANIEL RAU, FABIAN SCHÖN, and ROLF PELSTER — Experimentalphysik, Universität des Saarlandes

We present a dielectric study on the crystallization dynamics of n-pentanol in electrochemically etched porous silica with pore diameters

$d_{P1} \approx 7$ nm and $d_{P2} \approx 14$ nm. On slow continuous cooling (< 0.05 K/min), we observed a glass transition instead of crystallization while we find a partial recrystallization upon reheating. This behaviour reflects the different temperature dependences of nucleation and crystal growth. In addition, we studied the crystallization dynamics under isothermal conditions after quenching (≈ 2 K/min) the sample. It is seen that there is a maximum of the crystallization rate far below the bulk melting point.

CPP 37.64 Wed 15:00 P3

Wang-Landau simulation of polymer melts phase behaviour — ●TIMUR SHAKIROV and WOLFGANG PAUL — Martin Luther Universität, Halle, Deutschland

Phase transitions in polymer melts are under intensive investigation during last years using both theoretical and experimental methods. But Wang-Landau simulations of polymer melts wasn't successive and concerned mainly single chains and dilute systems or lattice models. We present results of off-lattice Wang-Landau simulation of melts of linear semi-flexible chains with stiffens bond potential. Simulated phase behavior of such system corresponds to known results of molecular dynamics simulation and can be estimated for model systems which maximal to minimal number of state ratio is over few thousands of magnitude.

CPP 37.65 Wed 15:00 P3

An improved model for the simulation of patchy particles — ●REINT HIERONIMUS and ANDREAS HEUER — Westfälische Wilhelms-Universität Münster, Institut für physikalische Chemie, Corrensstrasse 30, 48149 Münster, Germany

For the simulation of Janus particles and patchy particles the Kern-Frenkel model is widely used. However, this potential has severe shortcomings since energetically different configurations may yield the same model energy. To improve the potential, we supplemented the energy by an appropriately chosen factor which takes the patch distance into account. Using this potential, we performed Monte-Carlo simulations to investigate the self-assembly of Janus particles in two- and three-dimensional systems. We studied the phase formation depending on parameters such as temperature, density, patch number and patch size. The results were compared to the standard Kern-Frenkel model.

CPP 37.66 Wed 15:00 P3

Vapor-liquid nucleation of water investigated by molecular dynamics simulation — ●MARTIN WAGNER and THOMAS KRASKA — Institute for Physical Chemistry, University of Cologne, Luxemburger Str. 116, D-50939 Köln, Germany

The homogeneous nucleation of water vapor is investigated by molecular dynamics simulation. The investigation of water is of special interest because of the formation of hydrogen bonds which are expected to influence the nucleation. Starting from a homogeneous stable vapor phase the system is super-cooled by quenching in short time. The quench is initialized by changing the kinetic energy of a carrier gas, which then cools down the water system by molecular collisions leading to the onset of water nucleation. From the analysis of the cluster statistics and their development, the nucleation rate as well as the nucleation barrier and the critical cluster size are calculated. Besides regular water also heavy water is investigated and compared to the regular water data. The differences are compared to experimental data for both systems.

CPP 37.67 Wed 15:00 P3

Kinetics of nucleation and crystallization of poly(ϵ -caprolactone) * multiwalled carbon nanotube composites — ●EVGENY ZHURAVLEV¹, ANDREAS WURM¹, PETRA PÖTSCHKE², and CHRISTOPH SCHICK¹ — ¹University of Rostock, Institute of Physics, Rostock, Germany — ²Leibniz Institute of Polymer Research Dresden, Dresden, Germany

The nucleation efficiency of multi-wall carbon nano-tubes (MWCNT) in poly(ϵ -caprolactone) (PCL), as an example, was tested for a wide range of temperatures and cooling rates and compared to the efficiency of homogeneously formed nuclei. The temperature range below the maximum of crystallization rate is generally not accessible for non-isothermal cooling experiments because the sample becomes amorphous at the needed cooling rates. Isothermal experiments after fast quenches extend the temperature range down to and below the glass transition. The employed differential fast scanning calorimeter (DFSC) allows cooling at rates up to 100,000 K/s and precise control

of isothermal conditions in the time range from 10^{-4} to 10^4 s. Heterogeneous crystal nucleation dominates at low supercooling, revealing a significant dependence of crystallization rate on MWCNT concentration. No saturation of the nucleation activity at a MWCNT loading of 0.2 to 0.5 wt% was observed. At high supercooling, where homogeneous nucleation is prevalent, the addition of MWCNT does not enhance neither reduce the crystallization rate. At the temperature of maximum homogeneous nucleation rate, formation of homogeneous nuclei always dominates crystallization.

CPP 37.68 Wed 15:00 P3

In situ Observation of the Ordering Process in Semicrystalline Diblock Co-polymer Thin Films — ●PENG ZHANG¹, GONZALO SANTORO¹, SHUN YU¹, SARATHALAL KOYILOTH VAYALIL¹, STEPHAN ROTH¹, and TIANBAI HE² — ¹Deutsches Elektronen-Synchrotron, Notkestraße 85, D-22607 Hamburg, Germany — ²State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

The ordering process allows for explaining the structure transitions during polymer crystallization. However, the absence of the clear illustration of the underlying structure evolution on the nanoscale makes this theory not yet commonly accepted. We address this issue and in situ studied the surface structure evolution of PB-b-PCL diblock copolymer thin films with AFM and microbeam grazing incidence small angle X-ray scattering (GISAXS). We successfully prepared PB-b-PCL thin films with regular microphase structure by thermal treatment. Then, we in situ studied the underlying structure evolution during crystallization using AFM and GISAXS (PETRA III, DESY) combined with hot stage. GISAXS is a reliable method to in situ study the underlying structure evolution in thin film because of its fast time-resolution ability and statistical relevance. We present our in situ results on the ordering process and correlated structure evolution during crystallization. (1) Strobl, G. Eur. Phys. J. E 2000, 3, 165. (2) Zhang, P.; Wang, Z.; Huang, H.; He, T. Macromolecules 2012, 45, 9139. (3) Muller-Buschbaum, P. Anal Bioanal Chem 2003, 376, 3.

CPP 37.69 Wed 15:00 P3

Temperature dependent crystallization of iPP: a combined SIST-AFM study — ●LISA UBERLACKER, THOMAS FISCHINGER, and SABINE HILD — Institute of Polymer Science, JKU, Linz, Österreich

The crystallization process of semi-crystalline polymers can be divided in three stages: nucleation, growth and perfection of the crystal structure. At homogeneous and/or heterogeneous nuclei the polymer chains begin to organize and are folding in parallel segments, so called lamellae. The growth occurs radially and results finally in spherulites. This structure formation especially the thickness and perfection of lamellae is influenced strongly by temperature. Stepwise isothermal segregation technique (SIST) is a suitable method to determine the perfection of the lamellae - forming und thickening - during various temperature stages of semi-crystalline polymers like isotactic polypropylene. The method requires several isothermal crystallization steps. Isotactic polypropylene samples with different molecular weight distributions were examined with five isothermal crystallization steps in a range from 145°C to 105°C. The obtained melting endotherms were converted in lamellae thickness distributions using the Gibbs-Thomson equation. For validation the lamellar thicknesses were determined by scanning force microscopy. The comparison between samples with different molecular weight distribution (MWD) and crystallization temperatures show that samples with broader MWD form thinner lamellae than in the samples with smaller MWD. Determine the influences of the single crystallization temperatures on the lamellae forming higher crystallization temperatures obtain thinner lamellae

CPP 37.70 Wed 15:00 P3

First order phase transition at Random Close Packing of spheres — ●FRANK RIETZ¹, CHARLES RADIN², HARRY L. SWINNEY³, and MATTHIAS SCHRÖTER¹ — ¹Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Goettingen, Germany — ²University of Texas at Austin, Department of Mathematics — ³University of Texas at Austin, Center for Nonlinear Dynamics

The name Random Close Packing refers to the experimental observation that some ways of packing of monodisperse beads (like vertical vibration or sedimentation) cannot exceed a volume fraction of about 64%. There are several competing theories for this phenomenon. However, it is possible to surpass the random close packing limit by cyclic shearing [1]. We investigate the three-dimensional distribution of par-

ticles in such a shear cell. Below the Random Close Packing density the packing compacts by reconfiguring particles in denser but disordered arrangements. At Random Close Packing the compaction process saturates involving all particles in tetrahedral-like configurations. These structures are locally dense however compose not the maximum global density that is achievable for spheres. Further increase of the density is only possible by large-scale bead rearrangements that lead to crystalline nuclei and ordered particle ensembles. From the distribution of local volumes around every sphere a first order phase transition is observed. The transition is visible in the polytetrahedra network, angular order parameter, local clusters, and Voronoi shapes.

[1] Nicolas; Eur. Phys. J. E 3, 309 (2000).

CPP 37.71 Wed 15:00 P3

Tagged Chain Rotational Dynamics of Segments in Entangled Polymers — ●MARIE-LUISE TRUTSCHEL, ANTON MORDVINKIN, and KAY SAALWÄCHTER — Institut für Physik - NMR, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

We used simple NMR techniques to probe the dynamics of entangled polymer chains. We measured the orientational autocorrelation function (OACF) for different molecular weights of polybutadiene (tagged chain) in bulk and diluted in deuterated matrix of polymers of variable molecular weight in order to investigate the influence of constraint release processes. Earlier work concentrated on the dynamics in regime II-IV [1, 2, 3], while an extension of our technique allows us to reach regime I. The transition from regime I to II will be studied and compared with the value of τ_e known from theory.

[1] Vaca Chávez, Saalwächter, PRL 104, 198305, 2010.

[2] Vaca Chávez, Saalwächter, Macromolecules 44, 1549-1559, 2011

[3] Furtado et al., Macromolecules, 2014, DOI: 10.1021/ma4021938

CPP 37.72 Wed 15:00 P3

Determining the stereochemistry and key excitations in the CD spectra of organic molecules by theoretical methods — ●ZLATKO BRKLJACA¹, DAVID M. SMITH^{2,3}, and ANA-SUNČANA SMITH^{1,2} — ¹Institut für Theoretische Physik, Universität Erlangen-Nürnberg, Erlangen, Germany — ²Institute Ruder Bošković, Zagreb, Croatia — ³Computer Chemie Centrum, Universität Erlangen-Nürnberg, Erlangen, Germany

Circular dichroism (CD) spectroscopy is one of the most useful methods for the determination of the absolute configuration of optically active molecules, which is one of the key aspects of molecular stereochemistry. However, since the CD spectrum very strongly depends on the molecular flexibility of the chromophores, the interpretation of the experimental data is challenging, and hence theoretical modelling is necessary to properly assign the absolute configurations. In a recent study we have shown that a combination of replica exchange molecular dynamics, clustering procedure, and TD-DFT methods can provide a general framework for the calculation of the CD spectra of flexible molecules. We find that successful modelling of CD spectra requires systematic treatment of the solvent induced polarisation. We validate our methodology by finding excellent agreement with the experimental spectra of 3 novel compounds, namely rhodomirtals 1-3, for which we successfully determine the absolute configurations. We furthermore apply our method to flexible peptides and explore how the predominant amide and aromatic excitations shape the overall result.

CPP 37.73 Wed 15:00 P3

Interaction of semiflexible filamentous virus particles with freestanding lipid membranes — ●ANASTASIA B. ARTEMIEVA, PETRA SCHWILLE, and EUGENE P. PETROV — Max Planck Institute of Biochemistry, 82152 Martinsried, Germany

Recently, an unexpected phenomenon [1] of membrane-driven coil-globule transition of DNA macromolecules electrostatically adsorbed to strongly charged freestanding cationic lipid bilayers [2] has been observed experimentally. To elucidate the effect of the polyelectrolyte persistence length in membrane-driven polyelectrolyte condensation, we study the behavior of much stiffer semiflexible *fd* virus particles ($l_p \sim 2.2 \mu\text{m}$) electrostatically adsorbed on freestanding cationic lipid membranes. At low membrane charge densities, membrane-adsorbed *fd* virus particles behave as semiflexible filaments in 2D. However, at higher membrane charge densities, membrane-driven interactions are strong enough to induce the membrane-driven collapse of the relatively stiff *fd* virus particles, which agrees with the predictions of the recent theory of membrane-driven polyelectrolyte condensation [3]. Further, for *fd* virus particles adsorbed at higher surface densities on weakly charged membranes we observe a new effect of membrane-driven self-

organization of the virus particles into long linear chain aggregates.

[1] C. Herold, P. Schwille, and E. P. Petrov, *Phys. Rev. Lett.* **104** (2010) 148102.

[2] C. Herold, G. Chwastek, P. Schwille, and E. P. Petrov, *Langmuir* **28** (2012) 5518.

[3] A. G. Cherstvy and E. P. Petrov, *PCCP* (2014) in press.