

CPP 14: Poster: Interfaces and Thin Films

Time: Monday 16:30–18:00

Location: Poster C

CPP 14.1 Mon 16:30 Poster C

Random Block Copolymers in the Bulk and at Selective Surfaces — ●BIRGER STEINMÜLLER and MARCUS MÜLLER — Institut für Theoretische Physik, Georg-August-Universität Göttingen

The disordered phase of a random block copolymer melt shows structural properties which are of interest for the fabrication of fuel cell membranes. In order to observe their behaviour over larger time and length scales than the ones accessible to atomistic simulations, we employ two different coarse-grained models. The Single-Chain in Mean Field (SCMF) model has soft interactions which allow us to equilibrate our systems very fast, whereas the bead-spring Molecular Dynamics model grants us better access to the real dynamics and the structural properties of the melt.

We quantitatively connect these two different models at large length scales so that we can take advantage of the two models' positive properties. For this, we have found parameter values which result in similar mesoscopic behaviour and then used the SCMF configurations as starting points for MD simulations. Additionally, we look at the behaviour of the melt when in contact with a selectively attractive surface. In our simulations, due to compositional fluctuations, we see a new length scale near the surface, the interphase.

CPP 14.2 Mon 16:30 Poster C

Elastic properties of thin transparent polymer films — ●JOHANNES WIEDERSICH, ALEXANDER DIETHERT, PETER MÜLLER-BUSCHBAUM, and WINFRIED PETRY — Physikdepartment E13, TU München, Garching

The method of Brillouin scattering has recently been extended from bulk samples to the application of thin and ultra thin transparent polymer films. The method provides a means to investigate mechanical properties of films with thickness in the nm range in a contactless in-situ manner. Theoretical computations predict a complicated pattern of propagating film and surface guided modes, depending on the thickness and on the mechanical properties of the films, which are spin coated on glass substrates.

We have been able to improve the sensitivity of our Brillouin scattering set-up and extend measurements down to ultra-thin films. The first results on our thinnest films show deviations from the theoretical predictions and indicate that the mechanical modulus deviates from the bulk value for films with thickness on the order of 20 nm.

CPP 14.3 Mon 16:30 Poster C

Polymer chains in confined geometries with long-range correlated disorder. — ●ZORYANA USATENKO — Universität Duisburg-Essen, Fachbereich Physik, Duisburg, Germany — Institute for Condensed Matter Physics, Lviv, Ukraine

The influence of long-range correlated disorder of the form $\frac{1}{r^a}$, where $a < d - 1$ (and r denotes the distance parallel to the surface) in dilute solution of long-flexible polymer chains in a good solvent on the depletion interaction potential and depletion force between two parallel repulsive walls is studied. The calculations are performed in the framework of renormalization group field theoretical approach up to first order of perturbation theory in a double (ϵ, δ) -expansion ($\epsilon = 4 - d$, $\delta = 4 - a$) for ϕ^4 $O(n, m)$ -vector model in the limit $n, m \rightarrow 0$. Besides, the calculations of the monomer density profiles and the density profiles of end points for different regions $L \gg R_g$ and $L \ll R_g$, where L is distance between the walls and R_g - the gyration radius of polymer chain in unrestricted region are performed.

CPP 14.4 Mon 16:30 Poster C

On the Thermodynamics of the 2-dimensional Lamellar Phase of Poly(styrene sulfonate) Adsorbed onto an Oppositely Charged Lipid Monolayer — ●THOMAS ORTMANN, HEIKO AHRENS, JENS-UWE GÜNTHER, and CHRISTIANE A. HELM — Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany

Electrostatic and entropic interactions in monolayers of cationic lipids with adsorbed polystyrene sulfonate (PSS) are studied by isotherms, and grazing incidence X-ray diffraction. Dioctadecyldimethylammonium bromide (DODA) is used as lipid, the PSS concentration is 0.01 mM (with respect to the monomer concentration); the PSS chain length is varied. Bragg peaks attributed to flatly adsorbed, aligned

PSS chains are observed for PSS both beneath the lipids in the solid (chain separation 2-2.7 nm) and in the fluid phase (chain separation 3-6 nm), the latter only if the PSS contour length exceeds 10 nm. The peak position is independent of the chain length. However the isotherms depend strongly on PSS chain length: the surface pressure of the liquid/condensed phase transition is largest for the shortest PSS used (contour length 5.5 nm) and decreases the longer the polymer gets, a limiting value is reached at 25 nm. The latent heat of the phase transition shows nonmonotonic behaviour with an extremum at 8 nm contour length, and levels off at 25 nm. Presumably, for very short PSS chains and large chain separations, the rotational entropy of the electrostatically stretched chains hinders alignment. Even for aligned short chains, the transition enthalpy is affected strongly.

CPP 14.5 Mon 16:30 Poster C

Block Architecture for Neutron Reflectivity Investigation of Internal Interfaces of Polyelectrolyte Multilayers — ●OLAF SOLTWEDEL¹, OXANA IVANOVA¹, MADLEN MÜLLER¹, RALF KÖHLER², and CHRISTIANE A. HELM¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany — ²Helmholtz-Zentrum Berlin für Materialien und Energien, Glienicker Straße 100, D-14109 Berlin, Germany

Polyelectrolyte multilayer (PEM) are built by sequential adsorption of oppositely charged polyelectrolytes, either poly(styrenesulfonate) - pSS and poly(diallyldimethylammonium) - pDADMAC or poly(allylamine hydrochloride) - pAH solutions. Using neutron reflectivity and a two block PEM architecture, one block consisting of protonated polyelectrolyte bilayers only and one of deuterated bilayers, it is possible to quantify unambiguously the scattering length density and the thickness of the respective blocks. Also, the internal roughness of the interface between the blocks is determined. While the total number of deposited layers is kept constant, the ratio between the protonated and the deuterated block is varied systematically. Different growth zones, i.e. the precursor zone adjacent to the substrate, the core zone and the outer zone next to the air can be distinguished. Depending on the polycation used, not only the internal roughness but also the extension of the zones change within the PEM. Also annealing effects, which appear during preparation of PEM and or after treatment with salt solutions, are investigated with this approach.

CPP 14.6 Mon 16:30 Poster C

In situ measurements of polyelectrolyte multilayers using multiple angle ellipsometry: even-odd effects in layer thickness and refractive index — ●PETER NESTLER, STEPHAN BLOCK, and CHRISTIANE A. HELM — Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17489 Greifswald, Germany

We investigate in situ the growth of polyelectrolyte multilayers (PEMs) by sequential adsorption of poly(allyl amine)hydrochloride (PAH) and poly(styrene sulfonate) (PSS) using multiple angle ellipsometry within a liquid cell. The multilayers are built onto RCA cleaned and poly(ethylen imine) (PEI) coated silicon wafers using polyelectrolyte adsorption solutions, whose temperature is controlled between 22 °C and 55 °C and which additionally contain 1 M NaCl or 1 M KCl. After each adsorption step we determine the PEM thickness and index of refraction with high accuracy by measuring the ellipsometric parameters at several angles of incidence. We observe a PEM thickness which is increased by at least 40% with respect to X-Ray reflectometry measurements performed after drying in air. Furthermore we find, that the increase in PEM thickness after an adsorption step shows an even-odd effect which is attributed to an unequal contribution of both polyelectrolytes to the thickness of one bilayer: at 22 °C PSS amounts to more than 60% to the average bilayer thickness, whereas at 55 °C this value reduces to 35%. A similar even-odd effect is observed in the refractive index of the PEM and allows an estimation of the refractive index of a single PSS or PAH layer within one bilayer.

CPP 14.7 Mon 16:30 Poster C

Layer-by-layer fabrication of hierarchical structures in sol-gel templated thin titania films — ●JAN PERLICH^{1,2}, MINE MEMESA³, ALEXANDER DIETHERT¹, EZZELDIN METWALLI¹, WEINAN WANG¹, STEPHAN V. ROTH², ANDREAS TIMMANN², JOCHEN S. GÜTMANN³, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department LS E13, Garching — ²HASYLAB at DESY, Ham-

burg — ³Max-Planck-Institute for Polymer Research, Mainz

Nanostructured titania thin films have gained great popularity in a variety of applications such as coatings, photocatalysis, gas sensing, and photovoltaics. For most of these applications a defined morphology of the titania nanostructures is crucial for the functionality and significantly influences the performance. The morphology determines the volume-to-surface ratio and hence the surface available for interfacial reactions. In order to increase the surface area the fabrication of titania nanostructures with hierarchical order of different structural levels is investigated. The nanostructures are prepared with a diblock-copolymer assisted sol-gel process. By iterative spin-coating of the solution onto silicon substrates a thin polymer-nanocomposite film is deposited and transformed to purely anatase titania nanostructures via calcination. This procedure is repeated three times on top of the substrate. The approach is monitored with grazing incidence small angle X-ray scattering (GISAXS) performed at the synchrotron beamline BW4 of DESY HASYLAB after each fabrication step. With scanning electron microscopy the final hierarchical structure is imaged. From the characterization different structural levels are clearly identified.

CPP 14.8 Mon 16:30 Poster C

Ordering of amphiphilic particles at a hard wall — ●GERALD ROSENTHAL and SABINE H. L. KLAPP — Institut für Theoretische Physik, Fak. II, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin

We present a numerical calculation of amphiphilic molecules at a hard wall using density functional theory. We focus on the competition between surface field and interaction-induced ordering phenomena. Amphiphilic molecules (e.g. surfactants, Janus-particles) are composed of hydrophilic and hydrophobic segments. We use an effective coarse-grained model, which describes the "surfactants" or Janus-particles as hard spheres with a hydrophilic and a hydrophobic side. This anisotropy is realized by a vector as an internal degree of freedom. The coarse-grained model goes back to Tarazona *et al.* [1]. In our density functional approach we use the White-Bear fundamental measure theory [2] for the hard sphere part and a mean-field approximation for the anisotropic part of the interaction.

[1] A. M. Somoza, E. Chácon, L. Mederos and P. Tarazona, *J. Phys.: Condens. Matter* **Vol. 7**, 5753 (1995).

[2] H. Hansen-Goos and R. Roth, *J. Phys.: Condens. Matter* **Vol. 18**, 8413 (2006).

CPP 14.9 Mon 16:30 Poster C

Modification of the electrical conductivity in conjugated polymer films — ●ANDREAS NATHAN¹, MATTHIAS A. RUDERER¹, ROBERT MEIER¹, HYEOKMIN CHOE¹, ROBERT CUBITT², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department LS E13, James-Frank-Str. 1, 85747 Garching, Germany — ²Institut Laue-Langevin, 6 rue Jules Horowitz, 38000 Grenoble, France

Conjugated polymers in thin films are of great interest for various applications such as organic photovoltaics, organic light emitting diodes and organic field effect transistors. Therefore, the selective modification and control of their electrical conductivity has special importance. Doping of conjugated polymers in particular allows for the adjusting of the conductivity. In polyacetylene the conductivity is increased over a remarkably large range from an insulating to a metallic behaviour.

In this work we prepare thin films of polyacetylene derivatives through solution based processes and test different doping methods. The film thickness is determined with x-ray reflectivity measurements. The electrical conductivity is measured with respect to film thickness and doping. UV/Vis measurements complete our investigations.

CPP 14.10 Mon 16:30 Poster C

Electrical properties of a charge-transfer interlayer modified organic heterojunction — ●SHUWEN YU¹, INGO SALZMANN¹, ANTIJE VOLLMER², and NORBERT KOCH¹ — ¹Humboldt-Universität zu Berlin, Institut f. Physik, Brook-Taylor-Str. 6, 12489 Berlin — ²HZB-BESSY, Albert-Einstein-Str. 15, 12489 Berlin

We investigated the effect of a thin interlayer (ca. monolayer) of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) between prototypical hole and electron transport layers (HTL and ETL) on interface energetics and current transport. As HTL we used 4,4',4''-tris(N,N-diphenyl-amino)triphenylamine (TDATA) and tris(8-hydroxyquinoline)aluminium (Alq3) as ETL, which are commonly employed in organic light emitting diodes. The hole injection barrier into TDATA is 0.5 eV, as measured by photoemission spectroscopy. De-

position of an F4-TCNQ interlayer on top of TDATA does not further change the energy level position. However, after applying the F4-TCNQ interlayer the energy levels of Alq3 deposited on top of TDATA are 0.15 eV closer to the Fermi-level than without the interlayer. Diodes fabricated without interlayer had a 0.6 V higher onset-voltage one order of magnitude lower current density than those with F4-TCNQ. These observations can be rationalized by an increased (non-radiative) electron-hole recombination rate at the modified organic heterojunction and a changed internal electric field distribution.

CPP 14.11 Mon 16:30 Poster C

Active microrheology of (Gibbs) monolayers — ●ULI LANGER and THOMAS FISCHER — Universität Bayreuth, Bayreuth, Germany

We describe the setup of a nano-needle rheometer, in order to measure the surface viscosity of monolayers. The reorientation of nickel nanorods in an external magnetic field is analysed in order to obtain the surface shear viscosity.

CPP 14.12 Mon 16:30 Poster C

Interfacial effects on single dye diffusion in ultrathin liquid films — ●DANIELA TÄUBER, FRANK GERLACH, SEBASTIAN SCHUBERT, and CHRISTIAN VON BORCZYKOWSKI — TU-Chemnitz, Institut für Physik, 09107 Chemnitz, and FOR 877

Liquids show layering at solid-liquid interfaces [1], which leads to dynamic heterogeneity in diffusion. Recent observations show additional influence of static heterogeneities of the interface on diffusion.

Here we used Rhodamines to trace the diffusion in ultrathin liquid (TEHOS) films on Si wafers with thermally grown oxide via optical single molecule tracking. Long term observations on thinning films reveal that there is no change in diffusion down to three molecular diameters from the substrate [2]. On the other hand modification of the silanol density on the substrate influenced the fraction of near surface diffusion. Enhancement of diffusion was correlated with the silanol cluster size (ca 0.5 microns) on the heterogeneous substrate.

[1] C.-J. Yu *et al.*, *Phys. Rev. Lett.* **82** (1999) 2326-29

[2] D. Täuber, C. von Borczykowski *et al.*: *Diff. Fund. J.* **12** (2009) accepted

CPP 14.13 Mon 16:30 Poster C

Kinetics studies of lamellar poly(styrene-*b*-butadiene) diblock copolymer thin films during heat treatment — ●ALESSANDRO SEPE¹, ZHENYU DI¹, TILO HOPPE¹, DAVID MAGERL¹, JAN PERLICH⁴, DORTHE POSSELT², DETLEF-M. SMILGIES³, and CHRISTINE M. PAPADAKIS¹ — ¹TU Munchen, Physikdepartment E13, Garching, Germany — ²Institute for Science, Systems and Models, Roskilde University, Denmark — ³Cornell High-Energy Synchrotron Source (CHESS), Ithaca, U.S.A. — ⁴HASYLAB at DESY, Hamburg

Nanostructured block copolymer thin films find a number of applications, especially as templates for anorganic materials, which may be used as optical elements or data storage devices. Thermal treatment has been applied to improve the orientation and the long-range order of the mesostructure.

We have studied thin films of lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) diblock copolymers to elucidate the mechanisms of structural changes induced by thermal treatment and their kinetics. The lamellae initially have the perpendicular lamellar orientation. In-situ, real-time grazing-incidence small-angle X-ray scattering, as well as ex-situ atomic force microscopy and X-ray reflectometry were used. We found that the processes during thermal annealing strongly depend on the treatment temperature: Below the glass-transition temperature of the PS block, the perpendicular orientation is unchanged, whereas above, a more random lamellar orientation is observed and the film surface is flattened.

CPP 14.14 Mon 16:30 Poster C

Very slow breakout crystallization in cylinder-forming diblock copolymer thin films — ●CHRISTINE M. PAPADAKIS¹, CHARLES DARKO¹, ZHENYU DI¹, KORDELIA TROLL¹, EZZ METWALLI¹, ANDREAS TIMMANN², GÜNTER REITER³, and STEPHAN FÖRSTER⁴ — ¹TU München, Physikdepartment E13, Garching — ²HASYLAB at DESY, Hamburg — ³Albert-Ludwigs-Universität Freiburg, Fakultät für Physik und Mathematik — ⁴Universität Hamburg, Department Chemie

In thin polymer films, crystallization often leads to fascinating surface structures. We have investigated the long-term behavior of the crystallization in thin films of cylinder-forming poly(isoprene-*b*-

ethyleneoxide), PI-*b*-PEO. Using optical microscopy, AFM, X-ray reflectometry and grazing-incidence wide- and small-angle X-ray scattering, we have observed very slow breakout crystallization of the PEO. The crystallization of the film was complete only after 150 days. The original hexagonal morphology was destroyed by crystalline lamellae lying in the film plane. The PEO chain stems were perpendicular to the film plane. We attribute this slow breakout to the shortness of the PEO blocks which change from being amorphous in the confinement of the cylinders to twice-folded in the lamellae.

CPP 14.15 Mon 16:30 Poster C

Structural rearrangements in a lamellar diblock copolymer thin film during treatment with saturated solvent vapor — ZHENYU DI¹, DORTHE POSSELT², DETLEF-M. SMILGIES³, and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physikdepartment E13, Garching — ²IMFUA, Roskilde University, Denmark — ³CHESS, Cornell University, USA

The processes during vapor treatment of block copolymer thin films, which is often used for equilibrating film structures, are complex. Solvent not only swells the polymers, but also increases the chain mobility and reduces the interfacial tension between the blocks [1].

We have investigated the structural changes in thin films of lamellar poly(styrene-*b*-butadiene) diblock copolymers during treatment with saturated cyclohexane vapor, a solvent slightly selective for polybutadiene. Using real-time, in-situ grazing-incidence small-angle X-ray scattering (GISAXS) [2], the swelling and the rearrangement of the lamellae were investigated with a time resolution of a few seconds. After a few minutes in vapor, a transient state with a more well-defined and more long-range ordered lamellar orientation was encountered. Additional parallel lamellae formed because of the increased degree of coiling of the polymers in the swollen state. Eventually, the film became disordered.

[1] C. M. Papadakis et al., *Langmuir* 24, 13815 (2008). [2] D.-M. Smilgies et al, *Mater. Res. Soc. Symp. Proc.* 1147, OO01-01 (2009) [3] Z. Di, et al., *Macromolecules*, accepted.

CPP 14.16 Mon 16:30 Poster C

Density and Viscosity at the polymer-solid interface — EICKE TILO HOPPE, DAVID MAGERL, and CHRISTINE M. PAPADAKIS — TU München, Physikdepartment E13, Garching

Close to the interface between a polymer film and a solid, the polymer properties may deviate from the bulk. This change in physical behavior is of importance for the adhesion of polymer coatings to solids, e.g. in medical implants or in paints.

The aim of the project is the investigation of the influence of the polymer-solid interaction on the physical properties of the polymers near the interface. The focus lies in the correlation between the change of density and viscosity of the polymer near the interface.

Polybutadiene melts on dry thermally oxidized silicon are studied as a model system. The changes in density and viscosity are investigated by neutron reflectometry and fluorescence correlation spectroscopy. To tune the interface interactions between substrate and polymer melt, the substrate surface is modified by different silanizations.

CPP 14.17 Mon 16:30 Poster C

How do co- and counter ions affect thin aqueous films? — NATASCHA SCHELERO and REGINE V. KLITZING — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Germany

The specific effects of electrolytes are omnipresent in all systems and processes based on liquid water. For instance the question arises, why salty water is foaming in a more pronounced way than salt free water. Therefore, the effect of addition of different types of salt on the (de)stability and functionality of single thin aqueous films (foam films) is of interest.^{1,2} Within this work the stability and the interactions between film surfaces is determined in a so-called thin film pressure balance (TFPB). This apparatus is normally used to investigate free-standing symmetrical foam films. In recent studies our group showed that a TFPB also can be used for the investigation of wetting films (air/water/solid)³. This method has been successfully used to proof negative charges at the air water interface.^{1,4} Further on, we will present a new insight into ion specific effects in foam films and wetting films.

[1] K. Ciunel, M. Armélin, G.H. Findenegg, R. v. Klitzing, *Langmuir* 2005, 21, 4790 [2] C.L. Henry, C.N. Dalton, L.Scruton, V.S.J. Craig, *J. Phys. Chem. C* 2007, 111, 1015 [3] R. v. Klitzing, *Adv. Coll. Interf. Sci.* 2005, 114/115, 253 [4] K. Hänni-Ciunel, N. Schelero, R. v. Klitzing, *Faraday Discussion*, 2009, 141, 41

CPP 14.18 Mon 16:30 Poster C

Molecularly imprinted PPy for the voltage-dependent uptake and release of L-glutamate in neutral pH — KATHRIN FUCHS, ELIZABETH VON HAUFF, and JÜRGEN PARISI — University of Oldenburg, Department of Physics, Energy and Semiconductor Research Laboratory, Carl-von-Ossietzky Str. 9-11, 26129 Oldenburg, Germany

For medical or biological applications, a device, which can control the concentration of a specific biomolecule in solution, is of great interest. Therefore, polypyrrole (PPy) is analysed with respect to the voltage-dependent uptake and release of L-glutamate, an important neural transmitter in the human nervous system. Additionally the effect of glutamate diffusion out of the film is investigated.

The PPy is electrochemically deposited on Au-coated electrodes utilizing an aqueous solution containing the monomer pyrrole and sodium L-glutamate. For some examinations, the PPy was electrochemically overoxidized using a phosphate buffer solution and thereby creating glutamate selective cavities. Such overoxidized PPy films have been described as having selective properties regarding the L-conformation of glutamate at low pH [1]. In this study, the uptake and release of glutamate resulting from a voltage sweep and having a mass change of the polymer film in neutral pH solution as a consequence is measured using an electrochemical quartz crystal microbalance (EQCM), while the diffusion of glutamate out of the polymer film is determined using UV/Vis-spectroscopy.

[1] B. Deore, Z. Chen, and T. Nagaoka, *Analytical Sciences*, 15, 827, 1999

CPP 14.19 Mon 16:30 Poster C

Temperature-dependent structure transitions in thin smectic liquid crystalline films — BENJAMIN SCHULZ, CHRISTIAN BAHR, and STEPHAN HERMINGHAUS — MPI for Dynamics and Self-Organization, Bunsenstr. 10, 37073 Göttingen

Thin films of smectic liquid crystals are known to show the formation of self-organized structures if they are subjected to antagonistic boundary conditions [1]. Such structure formations are promising systems as templates for the lithography of photonic crystals [2]. For this reason, a deeper understanding of the conditions that evoke different types of such structures is necessary for further applications of liquid crystal films.

We study films of about 300 nm in thickness of the liquid crystal 8CB near its transition between the smectic-A and the nematic phase using AFM and optical microscopy/polarized light microscopy. Below the actual phase transition temperature, we find structural changes in both the internal structure of the film and the surface topography. Depending on the film thickness, we can identify up to three different structures in the smectic phase. The liquid nature of our system should allow for a straightforward minimization of the free energy. However, near the second-order transition to the nematic state this seems to be a delicate process as we observe different structures. This behaviour could result from major changes of the elastic properties of the film in the vicinity of the transition.

CPP 14.20 Mon 16:30 Poster C

Alignment Mechanism of SVT Polymer Thin Films and its 3-Dimensional Characterization: A Combined QIS-SFM Imaging Study — CLEMENS LIEDEL¹, MARKUS HUND², VIOLETTA OLSZOWKA², and ALEXANDER BÖKER¹ — ¹Lehrstuhl für Makromolekulare Materialien und Oberflächen and DWI an der RWTH Aachen e.V., RWTH Aachen University, D-52056 Aachen, Germany — ²Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany

We observe the direct current electric field induced alignment in thin polymer films with cylindrical morphology basing on a hexagonal superstructure.

So far, little is known about the exact mechanism leading to microdomain orientation of polymer systems in the border region between cylinders and perforated lamellae. Here, we describe quasi *in-situ* scanning force microscopy (QIS-SFM) measurements on thin films of a linear polystyrene-*b*-poly(2-vinylpyridine)-*b*-poly(*tert*-butyl methacrylate) triblock copolymer under an electric field. The alignment process is followed using a new SFM design which enables solvent vapor and electric field treatment after each scanning cycle.

The orientation mechanism is studied and compared to the mechanisms in lamellar block copolymer morphologies. Rotation and nucleation-and-growth mechanisms and defect movement, basing on a hexagonal superstructure, are observed leading to a long-range or-

dered morphology of aligned core-shell cylinders.

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CPP 14.21 Mon 16:30 Poster C

Self Stratification in polymer blend films during spin-coating — ●CHENG HUANG¹, JÖRG PFEIFER¹, STEFAN WALHEIM¹, and THOMAS SCHIMMEL^{1,2} — ¹Institute of Nanotechnology (INT), Northern Campus, Karlsruhe Institute of Technology (KIT) — ²Institute of Applied Physics, Southern Campus, Karlsruhe Institute of Technology (KIT)

The phase separation process of PS/PMMA blend during spincoating from a Methy-Ethyl-Ketone (MEK) solution is studied. The polymer blend dissolved in this solution forms a purely lateral structure on a hydrophilic substrate with PS cylinders in PMMA matrix. Our results of time-resolved in situ reflectometry, post cast ellipsometry and SEM(scanning electron microscope) cross-sectional analysis point in the direction of a transient triplelayer formation during the spin-coating process which then transforms via an instability into the final lateral morphology. A purely horizontally layered situation in the dry state can also be tuned by process parameters. Humidity, spin rate and the concentration of the polymer blend solution are the most important parameters which define the final structure. The PS or PMMA phase was later selectively dissolved and the film was subsequently used as a lithographic Mask for further applications.

CPP 14.22 Mon 16:30 Poster C

High Aspect Ratio Constructive Nanolithography with a Photo-Dimerizable Molecule — MATTHIAS BARCZEWSKI¹, ●ALEXANDER FÖRSTE¹, STEFAN WALHEIM¹, TOBIAS HEILER¹, ALFRED BLASZCZYK^{1,2}, MARCEL MAYOR^{1,3}, and THOMAS SCHIMMEL^{1,4} — ¹Institute of Nanotechnology (INT), Northern Campus, Karlsruhe Institute of Technology (KIT) — ²Department of Commodity Science, Poznan University of Economics, Poland — ³Department of Chemistry, University of Basel, Switzerland — ⁴Institute of Applied Physics, Southern Campus, Karlsruhe Institute of Technology (KIT)

A major challenge in constructive nanolithography is the preservation of the lateral resolution of a monolayer-thick template pattern while amplifying it to a structure with a thickness above 10 nm. Our approach of photoinduced, constructive, reversible nanolithography, is based on nanografting within a coumarin-derivative thiol (CDT) solution using the tip of an atomic force microscope (AFM). By photodimerization and the formation of disulfide bonds, the CDT polymerizes in a single-step process. We demonstrate the highest lateral resolution in constructive nanolithography at thicknesses above 10 nm (40nm lateral resolution at 12 nm thickness, aspect ratio: 0.3).

CPP 14.23 Mon 16:30 Poster C

Self-Alignment of Block Copolymers on Chemically Patterned Substrates — ●TOBIAS HEILER¹, ROLAND GRÖGER¹, STEFAN WALHEIM¹, and THOMAS SCHIMMEL^{1,2} — ¹Institute of Nanotechnology (INT), Northern Campus, Karlsruhe Institute of Technology (KIT) — ²Institute of Applied Physics, Southern Campus, Karlsruhe Institute of Technology (KIT)

Chemical patterns were made by nanoshaving polymer brush layers on silicon oxide. The contrast in polarity between brush surface and exposed silicon oxide was used to control the phase morphology of an amphiphilic block copolymer film. The two components of the block copolymer, as well as the surface of the chemically patterned substrate possess a high contrast in polarity, so that a defect tolerant pattern replication in the polymer film is observed after a short (vapor-)annealing process. Polybutadiene-based block copolymers and polystyrene brushes were used.

CPP 14.24 Mon 16:30 Poster C

Influence of connectivity on the entropic stiffness of tethered membranes — ●MARCO WERNER^{1,2} and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden, Germany — ²Technische Universität Dresden - Institute for Theoretical Physics

We investigate the static and dynamical properties of tethered structures like membranes and fractal polymer objects using the Bond-Fluctuation-Model in three-dimensional space. Tethered structures can be characterized by the spectral dimension depending on their connectivity. For two-dimensional polymers (perfect membranes) we confirm the picture of an entropic stiffness induced locally by excluded volume interaction, which in turn causes a flat state on larger scales [Y.Kantor and K.Kremer, *Phys. Rev. E* 48(4), 2490, (1993)]. On

the other hand we found fractal structures e.g. Sierpinski gaskets to be crumpled and their fractal dimension to agree with mean-field arguments [M.E.Cates, *Phys. Rev. Lett.* 53(9), 926, (1984)], whereas Sierpinski carpets are asymptotically flat like perfect membranes. Indeed we found mean field arguments to be self consistent for Sierpinski gaskets but not for Sierpinski carpets. Thus the lower critical dimension for tethered membranes might be below 2 as indicated by an ϵ -expansion [J.A.Aronovitz and T.C.Lubensky, *Phys. Rev. Lett.* 60(25), 2634, (1988)].

CPP 14.25 Mon 16:30 Poster C

Effect of chain architecture on microdomain orientation in thin films of block copolymer supramolecular assemblies — ●BHANU NANDAN and MANFRED STAMM — Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, 01069 Dresden

The phase behaviour of supramolecular assemblies (SMA) formed by poly(4-vinylpyridine)-b-polystyrene-b-poly(4-vinylpyridine) (P4VP-b-PS-b-P4VP) triblock copolymer with 2-(4'-hydroxybenzeneazo)benzoic acid (HABA) was investigated with respect to the molar ratio (X) between HABA and 4VP monomer unit. The results were compared with SMAs formed by a PS-b-P4VP diblock copolymer of similar composition as the triblock but half the molecular weight to ascertain the effect of chain architecture on microphase separation. In bulk, both the di- and triblock SMAs showed composition dependent morphological transitions which could be tuned by HABA/4VP molar ratio. In thin films also, both the di- and triblock SMAs showed more or less similar morphological transitions depending on X. Interestingly, the domain orientation of the cylindrical or lamellar microdomains in the SMAs was influenced by the chain architecture of the block copolymer. After chloroform annealing whereas the diblock SMAs showed in-plane orientation of the domains, triblock SMAs showed perpendicular domain orientation. The perpendicular orientation of the microdomains in triblock was favored since it allowed the mid PS blocks to acquire normal distribution of loop and bridged conformations. *This research was supported by the priority program of DFG (SPP1165, Project No. STA324/31).

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High Density Magnetic Nanorods via Electrodeposition in Block Copolymer Thin Film Templates — ●MARCUS BÖHME, BHANU NANDAN, and MANFRED STAMM — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden

Recently, we presented a Nanotemplate based on the Supramolecular Assembly of poly-(styrene-b-4-vinylpyridine) with 2-(4'-hydroxybenzeneazo)benzoic acid[1]. One possible application of these templates is the creation of high density magnetic rod arrays to overcome the superparamagnetic limit in magnetic storage devices. Requirements for possible application are long range order and homogeneous filling of the individual pores.

Here, we present our results on increasing the long range order via solvent vapor treatment and filling the template pores with magnetic materials, e.g. cobalt, via electrochemistry. [1]A. Sidorenko, I. Tokarev, S. Minko, M. Stamm; *JACS* 125, 12211-12216, (2003)

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Supramolecular assembly of poly(styrene)-b-poly(4-vinylpyridine) and 1-pyrenebutyric acid in thin film and their use for nanofabrication — ●BIPLAB KUMAR KUILA and MANFRED STAMM — Department of Nanostructured Materials, Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany.

Block copolymer(BCP)based supramolecules are prepared by attaching small additive molecules in to the side chains of one of the BCP blocks1. BCP-based supramolecules also microphase separate similar to block copolymer into arrays of microdomains, tens of nanometers in size. Here, we have studied the supramolecular assembly of 1-pyrenebutyric acid(PBA)with PS-b-P4VP [Poly(styrene-block-(4-vinylpyridine)). The supramolecular assembly of PS-b-P4VP with PBA resulted the switching of block copolymer morphology from cylinder to lamella in thin film due to compositional change.PBA will make supramolecules with the P4VP block due to strong hydrogen bonding between the carboxylic group of 1-pyrenebutyric acid and pyridine ring of P4VP. After fabricating the thin film from the supramolecules, the minor component PBA can be easily removed by dissolving the thin film in ethanol to transform the block copolymer thin film into nanotemplate or membrane for practical application. We have also observed that these nanotemplates can be used for the fabrication of

arrays of nanowire of different functional material like metal or semiconductor. Reference: I.Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. J. Am. Chem. Soc. 2003, 125, 12211.

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Functionalization of Nanostructures via Covalent Binding of Molecules — •THOMAS BAUMGÄRTEL, HARALD GRAAF, and CHRISTIAN VON BORCZYKOWSKI — Center of Nanostructured Materials and Analytics, Institut für Physik, TU Chemnitz, 09107 Chemnitz, Germany

Anchoring functional molecules or nanoparticles to silicon substrates is a field of increasing interest as it can be employed to create tuneable and well-defined surfaces with various properties and functions. The formation of e.g. self-assembled monolayers of molecules on silicon or silicon oxide surfaces is a process which is basically understood and can be carried out using different chemical routes. However, if such a chemical surface functionalization is carried out in a multi-stage procedure on confined geometries, e.g. nanostructures, there are many problems to be dealt with. Amongst others it is desirable to anchor the molecules via covalent bonds which are much more stable compared to physisorption or electrostatic binding. We will report on the creation and functionalization of nanostructures on SAM-terminated

silicon surfaces using different types of molecules and chemical routes. The nanostructures are produced by AFM-induced local anodic oxidation of the silicon. The generated structures are characterized by AFM and Kelvin Probe Force Microscopy. Nanostructures functionalized with optically active molecules or nanocrystals are additionally investigated using spectrally and temporally resolved confocal microscopy.

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Mapping sub-surface features in heterogenous polymers — •EIKE-CHRISTIAN SPITZNER, CHRISTIAN RIESCH, and ROBERT MAGERLE — Chemische Physik, TU Chemnitz, D-09107 Chemnitz

We study tip-sample interaction during scanning force microscopy (SFM) in intermittent contact mode on thin films of polystyrene and polystyrene-*block*-polybutadiene block copolymer swollen in chloroform vapor as well as semicrystalline polypropylene. We measure pointwise amplitude and phase as function of tip-sample distance (apd curves) and determine conservative and dissipative contributions to the interaction process. In addition we obtain the amount of tip indentation into the polymer film. As a result, maps of apd curves provide depth resolved information about structures at and beneath the surface. The accessible depth is limited by the maximal tip indentation that can reach values up to 30 nm for very soft materials.