

CPP 6: Thin Films

Time: Monday 14:00–17:00

Location: ZEU 160

CPP 6.1 Mon 14:00 ZEU 160

Mimicry of natural structural colours — ●MATHIAS KOLLE¹, MAIK SCHERER¹, HEATHER WHITNEY², and ULLRICH STEINER¹ — ¹Cavendish Laboratories, University of Cambridge, UK — ²School of Biological Sciences, University of Bristol, UK

For many organisms in nature intense and distinctive colours play an important role in inter- and intra-species communication. The most impressive natural colours arise from micrometre- to nanometre-sized structures, which often consist of intrinsically transparent materials. Most of the underlying physical principles that create colour from mere transparent materials are well understood and the challenge lies in applying them to create artificial replicas of natural photonic structures.

Outstanding structural colours result in general from a balanced combination of various optical effects. We aim to create coatings based on nature-similar structures that optimally exploit different optical effects such as multilayer interference, diffraction from lateral structures as well as fluorescence. Efficient, simple procedures such as nanoimprinting and nanosphere-lithography and a variety of polymers and inorganic materials are used and will be subject of this presentation. Structural colour coatings promise a wide range of applications only to mention unique labels in security applications to protect for instance credit cards, passports or banknotes from forgery.

CPP 6.2 Mon 14:15 ZEU 160

Surface enrichment layers in pressure sensitive adhesive films — ●ALEXANDER DIETHERT¹, STEPHAN V. ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik Department LS E13, James-Franck-Str.1, 85748 Garching (Germany) — ²HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg (Germany)

Pressure sensitive adhesives (PSAs) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers. Typically, two or three different monomers are combined to balance the different requests of the PSA. The adhesive properties of the PSA films are mainly determined by surface-near regions. However, detailed structural information about this region is still missing.

In the presented work we focus on PSA model systems of statistical copolymers consisting of two different types of monomers: a tacky monomer (e.g. ethyl hexylacrylate) and a glassy monomer (e.g. methyl methacrylate). The PSA films were prepared with solution casting.

From a naive point of view, one would have expected homogenous films which are characterized by the average monomer composition. To investigate the surface structure, we probed the density profile perpendicular to the PSA surface using x-ray reflectivity (XRR). We detected an oscillating composition profile depending on the chosen monomers, the molecular weight of the polymer and the sample age.

Lateral structures within the surface near region are probed with grazing incidence small angle x-ray scattering (GISAXS).

CPP 6.3 Mon 14:30 ZEU 160

Electron irradiation on thin polymer films and its use for biosurface engineering — ●SINA BURKERT, UHLMANN PETRA, and MANFRED STAMM — Leibniz-Institut für Polymerforschung Dresden e.V. Hohe Str. 6, 01069 Dresden

Surface-active materials have been attracting considerable attention in recent years. Especially the tuning of thin polymer films at surfaces has achieved high interest for applications in micro- and nanotechnology, as well as in biotechnology. In this work we will present the effect of electron irradiation on polymer brushes, which represent thin functional films. Those films have shown to be a versatile tool to create, in dependence on the grafting density and chemical composition, e.g. as mixed brushes, stable responsive functional coatings. It is possible to switch the surface properties of a mixed film between the properties of two incompatible polymers by external stimuli, such as temperature. During electron irradiation specific modifications of the respective polymers occur, which have been investigated by various characterization techniques and will be discussed in detail. The knowledge about the interaction of specific polymer brushes with electrons was then used to control the physico-chemical brush properties and to generate a lateral wettability gradient within the film. Those modified surfaces influence protein adsorption in a special manner, which will be also discussed in this contribution. In terms of application in

biotechnology first results of cell growth experiments will be presented.

CPP 6.4 Mon 14:45 ZEU 160

Brillouin spectroscopy on thin polymer films — ●JOHANNES WIEDERSICH, ALEXANDER DIETHERT, PETER MÜLLER-BUSCHBAUM, and WINFRIED PETRY — Physikdepartment E13, TU München, Garching

Conventional Brillouin light scattering spectroscopy is a versatile tool for the contact free investigation of mechanical properties of polymers. This makes Brillouin scattering an interesting method for the investigation of thin films, where contact methods have difficulties discerning contributions from the thin film and the substrate. Substantial progress of the Brillouin light scattering technique allows acquisition from scattering volumes in the femto litre range, and thus from films merely tens of nm thick.

We present our first results on Brillouin spectroscopy on thin, transparent polymer films on a glass substrate. Depending on the sample thickness (in the range from less than 100 nm up to bulk dimensions) we observe several film-guided phonons, propagating parallel to the surface.

CPP 6.5 Mon 15:00 ZEU 160

"Micro-structure - Macro-response" Relationship in Swollen Block Copolymer Films — JULIA GENSEL and ●LARISA TSARKOVA — Physikalische Chemie II, Universität Bayreuth, Bayreuth 95440, Deutschland

We present experimental evidence on the correlation between micro-structure and macro-response of diblock copolymer films towards swelling in a selective solvent. The starting morphology of poly(styrene)-*b*-poly(2-vinylpyridin) (SV) films has been adjusted by the fast quench from selective or non selective solvents. The structure at films surface was characterized by scanning force microscopy (SFM), while grazing-incidence small-angle X-ray scattering (GISAXS) measurements have been used to access the microstructure in the interior of the films. The swelling under controlled atmosphere of selective solvent was monitored by *in-situ* spectroscopic ellipsometry. The long-term annealing under atmosphere of a selective solvent (toluene) revealed up to 10% stronger swelling of the films with the initial bulk lamella morphology as compared to the films with the non-bulk micellar phase. Moreover, we observed clear dependence of the degree of swelling on the film thickness in a thickness range of 0.5-10 layers irrespective to the initial microstructure. These findings bring novel insights into the solvent processing of block copolymer films and indicate roots for designing nano-structured responsive materials.

CPP 6.6 Mon 15:15 ZEU 160

Highly Ordered Block Copolymer Templates for the Generation of Nanostructured Materials — ●ERATHIMMANNA BHOJE GOWD¹, BHANU NANDAN¹, MANFRED STAMM¹, NADJA C BIGALL², and ALEXANDER EYCHMÜLLER² — ¹Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany — ²Physical Chemistry, TU Dresden Bergstrasse 66b, 01062 Dresden, Germany

Among many different types of self-assembled materials, block copolymers have attracted immense interest for applications in nanotechnology. Block copolymer thin film can be used as a template for patterning of hard inorganic materials such as metal nanoparticles. In the present work, we demonstrate a new approach to fabricate highly ordered arrays of nanoscopic inorganic dots and wires using switchable block copolymer thin films. Various inorganic nanoparticles from a simple aqueous solution were directly deposited on the surface reconstructed block copolymer templates. The preferential interaction of the nanoparticles with one of the blocks is mainly responsible for the lateral distribution of the nanoparticles in addition to the capillary forces. Subsequent stabilization by UV- irradiation followed by pyrolysis in air at 450 °C removes the polymer to produce highly ordered metallic nanostructures. This method is highly versatile as the procedure used here is simple, eco-friendly and provides a facile approach to fabricate a broad range of nanoscaled architectures with tunable lateral spacing.

CPP 6.7 Mon 15:30 ZEU 160

Single molecule tracing to analyze the surface morphology

of block-copolymer thin films — ●MUSTAFA YORULMAZ¹, ALPER KIRAZ¹, and ADEM LEVENT DEMIREL² — ¹Department of Physics, Koç University, Rumelifeneri Yolu, 34450 Sariyer, Istanbul, Turkey — ²Department of Chemistry, Koç University, Rumelifeneri Yolu, 34450 Sariyer, Istanbul, Turkey

Single molecules are sensitive reporters that can provide detailed information on their host matrices. In our studies, Terrylene molecules are embedded in Polybutadiene-Polyethylene Oxide (PB-PEO) block-copolymer thin films which reveal cylindrical channels of PB (diameters of ~40-80 nm) that are oriented parallel to the substrate inside the PEO matrix[1]. Samples are prepared by spin coating a Terrylene/Toluene (~20 nM) and PB-PEO/Toluene (~40 mg/mL) mixture on cover glass. Thin films are then annealed for better channel formation. Terrylene molecules are monitored by using the total internal reflection fluorescence (TIRF) microscopy technique. TIRF microscopy images are then recorded with an Electron Multiplied Charge Coupled Device camera (Hamamatsu-Imagem). Our experiments revealed single molecule traces matching the thin film morphology observed in AFM images. In some of the traces, single molecules are also observed to switch between parallel cylindrical channels. Mean square displacement curves also revealed parabolic dependences to the lag time, suggesting directed diffusion within the channels. This is attributed to the variations in the channel diameters in those cases. [1] M. Y. Yuce, A. L. Demirel, and F. Menzel, *Langmuir* 21, 5073-5078 (2005).

15 min. break

CPP 6.8 Mon 16:00 ZEU 160

Thermoresponsive PNIPAM Microgel Films — ●ANNA BURMISTROVA, MATTHIAS KARG, MARTIN MEDEBACH, and REGINE VON KLITZING — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Strasse des 17. Juni, 10623 Berlin

During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering [1]. These polymer particles show thermoresponsive behaviour and can therefore be classified as "smart" materials. We synthesize monodisperse PNIPAM microgel with different contents of acrylic acid (AAc) to receive thermosensitive as well as pH-sensitive particles [2,3]. The films were prepared by spin coating and dip coating methods. Characterisation has been done using Atomic Force Microscopy (AFM) and ellipsometry. While AFM allows obtaining information about the particle size and arrangement [4], ellipsometry focuses on the overall film thickness [4]. In order to study the films under various conditions such as temperature and solvent composition we used liquid cells which allowed studying the surfaces against solution. The results show that the way of preparation and external stimuli like pH, ionic strength and temperature influences strongly the film structure. The internal correlation length was measured by SANS. [1] K. Kratz, T. Hellweg, W. Eimer, *Polymer* (2001) 42, 6531. [2] S. Höfl, I. Zitzler, T. Hellweg, S. Herminghaus, F. Mugele, *Polymer* (2007) 48, 245. [3] S. Nayak, L.A. Lyon, *Angew. Chem.* (2005) 117, 7862. [4] S. Schmidt, H. Motschmann, T. Hellweg, R. v. Klitzing, *Polymer* (2008) 49, 749.

CPP 6.9 Mon 16:15 ZEU 160

Stability of smectic films in water — ●YASUTAKA IWASHITA¹, CHRISTIAN BAHR¹, RALF SEEMANN^{1,2}, and STEPHAN HERMINGHAUS¹ — ¹MPI for Dynamics and Self-Organization, D-37073 Goettingen — ²Experimental Physics, Saarland University, D-66041, Saarbruecken

Free-standing smectic films in air, consisting of plane layers parallel to the film surfaces (homeotropic alignment), have been widely studied for decades [1]. In liquids like water, on the other hand, such stable films have not been observed due to the planar alignment of thermotropic liquid crystals (LCs) at the interface. However, it has been shown that LCs can align homeotropically at the interface to water with the aid of surfactants [2]. An advantage of this system is the tunable anchoring potential via the concentration of the surfactant [3].

Here we focus on smectic-A (S_A) films of the cyanobiphenyl series (nCB , $n = 10$ and 12) in water stabilized by a surfactant, monoolein. These systems show surface smectic ordering at the LC-water interface in a range of about 2 K above the isotropic - S_A transition temperature, T_A [3]. First we studied smectic films separating water droplets in microfluidic channels: the foam-like structure made up by the water droplets shows a coarsening time which diverges as $T \rightarrow T_A^+$. The voltage for electrocoalescence of the water droplets also increases towards T_A . In addition, we demonstrate the generation of large-area ($5 \times 5 \text{ mm}^2$) S_A films showing layer-by-layer thinning on heating around T_A .

[1] P. Pieranski *et al.*, *Physica A* **194**, 364 (1993).

[2] J.M. Brake *et al.*, *Langmuir* **19**, 6436 (2003).

[3] C. Bahr, *Phys. Rev. Lett.* **99**, 057801 (2007).

CPP 6.10 Mon 16:30 ZEU 160

Ion specific effects in 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] 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)[2]. A great advantage of measurements of asymmetrical films is that one can modify the charge of both interfaces independently e.g. by charged polyelectrolytes. The stability of aqueous wetting films on a solid substrate depends on the charge of the substrate and on the ionic strength of the liquid. These results indicate that the force within a water film is controlled by electrostatic interactions[3] and give evidence for 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, *et al.* *Langmuir* 2005, 21, 4790 [2] R. v. Klitzing, *Adv. Coll. Int. Sci.* 2005, 114/115, 253 [3] K. Hänni-Ciunel, *et al.* *Soft Materials*, 2007, 5, 61 [4] K. Hänni-Ciunel, N. Schelero, R. v. Klitzing, *Faraday Discussion*, 2008, in press

CPP 6.11 Mon 16:45 ZEU 160

Tuning of interactions in foam films from oppositely charged polyelectrolyte/surfactant mixtures — ●NORA KRISTEN¹, VASILE SIMULESCU¹, REINHARD MILLER², and REGINE V. KLITZING¹ — ¹Stranski-Laboratorium, TU Berlin, Berlin, Germany — ²Max Planck Institute of Colloids and Interfaces, Potsdam-Golm, Germany

Polyelectrolyte/surfactant mixtures in foams play an important role in many technical applications, e.g. in decalcification processes and cosmetics. In order to control the properties of the foam it is important to investigate single free-standing foam films. A quantitative measure of the interactions between the two opposing film interfaces is the disjoining pressure, which is the sum of repulsive electrostatic, attractive van der Waals and steric forces. The disjoining pressure as a function of film thickness is measured with a Thin Film Pressure Balance.

In this work we study the interactions between polyelectrolytes and surfactants in foam films at low surface charge. To tune the surface charge the concentration of negatively charged polyelectrolyte is varied. Starting with a cationic surfactant films with positively charged surfaces are formed. With the addition of more polyelectrolyte the surface charge is reduced and then reversed. Low and high polyelectrolyte concentrations induce the formation of thick Common Black Films but what happens at very low surface charges? Is a thin Newton Black Film formed or does the film break? Results on the stability of films with different polyelectrolytes are presented and compared with surface tension and elasticity measurements. The effect of polyelectrolytes is compared to the influence of their monomers.