BP 30: Biomaterials and Biopolymers I (joint CPP/BP)

Time: Wednesday 15:00–18:15 Location: ZEU 222

Invited Talk BP 30.1 Wed 15:00 ZEU 222

Fabrication of 3D Cell Structures Using Self-Folding Polymer Films — •Leonid Ionov — Leibniz Institute of Polymer Research Dresden

Nature offers an enormous arsenal of ideas for the design of novel materials with superior properties and interesting behaviors. In particular, self-assembly and self-organization, which are fundamental to structure formation in nature, attract significant interest as promising concepts for the design of intelligent materials. Self-folding stimuli-responsive polymer films are exemplary biomimetic materials and can be viewed as model systems for bioinspired actuation. Such films, on one hand, mimic movement mechanisms in certain plant organs and, on the other hand, are able to self-organize and form complex 3D structures. These self-folding films consist of two polymers layers with different properties. For such a bilayer to changes its curvature at least one of these polymers, the active one, must change its volume more than the other one in response to changes in the external environmental such as temperature, pH or light. Because of this non-equal expansion of polymers, these films are able to form tubes, capsules or more 3D complex structures. Self-folding polymeric films provide unique possibilities for the straightforward fabrication of fibers with complex responsive architectures and that cannot be achieved using other currently available technologies. In this presentation, new applications of self-folding films for encapsulation and release of cells, 3D cell patterning as well as design of scaffolds will be demonstrated.

BP 30.2 Wed 15:30 ZEU 222

Surface-Nanostructure Induced Structural and Dynamical Properties of Adsorbing Protein Layers — •Thomas F. Keller[1], Robert Schulze[2], Jörg Bossert[2], Mark Kastantin[3], Daniel K. Schwartz[3], and Klaus D. Jandt[3] — [1]Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany — [2]Friedrich Schiller University Jena, Germany — [3]University of Colorado Boulder, USA

Designing implant surface properties on the nanoscale may be one method for tuning the structure and dynamics of adsorbing protein layers. For a set of materials with relevance in the biomedical field, such as ultra high molecular weight polyethylene (UHMWPE), titanium dioxide (TiO_2) and polystyrene-b-poly(ethylene oxide) (PS-b-PEO) block copolymers, we show how advanced materials processing permits the creation of surface nanostructures suitable for guiding adsorbing proteins into lateral arrangements that may also affect their dynamic behavior, as determined from mapping using accumulated probe trajectories (MAPT). By atomic force microscopy (AFM), we observed that 1) the surface nanostructure of native UHMWPE may establish a densely packed, ordered arrangement of fibrinogen, which is one key protein in the implant-induced blood coagulation cascade, 2) adjacent crystalline facets on a nanostructured TiO_2 surface create local adsorption sites that guide fibrinogen into different conformational arrangements, and 3) nanoscale phase domains on block copolymer surfaces may serve as nucleation sites for fibrinogen networks. *Ref.:* **ACS Nano 2011**, 5, 3120; **Adv. Funct. Mater. 2012**, 22, 2617; **Acta Biomater. 2013**, 9, 5810; **Macromolecules 2012**, 45, 4740.

BP 30.3 Wed 15:45 ZEU 222

On the Relationship between Peptide Adsorption Resistance and Surface Contact Angle: A Combined Experimental and Simulation Single-Molecule Study — •Nadine Schwierz[1], Dominik Horinek[1], Susanne Liese[2], Tobias Pirzer[1], Bizan N. Balzer[1], Thorsten Hugel[1], and Roland R. Netz[2] — [1]Technische Universität München, Germany — [2]Freie Universität Berlin, Germany

Controlling the adsorption of proteins and peptides at synthetic surfaces is the ultimate goal for designing biocompatible implants and fouling resistant surfaces. To gain a microscopic understanding of the transition between peptide adsorption and adsorption resistance, the force-induced desorption of single peptide chains is investigated in closely matched molecular dynamics simulations and atomic force microscopy experiments. In both simulations and experiments, the surfaces become adsorption resistant when their contact angle decreases below $\theta = 50°$-$60°$, thus confirming the so-called Berg limit, established in the context of protein and cell adsorption.

Entropy/enthalpy decomposition of the simulation results reveals that the key discriminator between the adsorption of different residues on a hydrophobic monolayer is of entropic nature and thus is suggested to be linked to the hydrophobic effect. Peptide adsorption resistance is caused by the strongly bound water hydration layer and characterized by the simultaneous gain of both total entropy in the system and total number of hydrogen bonds between water, peptide, and surface. This mechanistic insight into peptide adsorption resistance might help to refine design principles for anti-fouling surfaces.

BP 30.4 Wed 16:00 ZEU 222

Structural investigation of biomineralization processes in bio(mimetic)-materials by means of solid state NMR — •Anastasia Vyalikh and Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V.

Solid state NMR is applied to study the structure of biominerals. While the 31P solid state NMR spectra of phosphate containing materials represent a single broad line resulting from the diversity of structural motives, 2D heteronuclear correlation (HETCOR) experiments provide signal separation, and therefore can be used to determine the nature of mineral phases and interfacial organic-inorganic structures. The structure formation of biomimetic apatite-gelatine nanocomposites has been revealed, demonstrating the interaction of mineral domains with the organic matrix in the intergrowth region. HETCOR NMR provides resolution for the identification of different phosphate minerals at very early mineralization stages, which do not yet result in crystallite particles visible in imaging and diffraction techniques. The development of different calcium phosphate species in newly formed tissues has been demonstrated, when dental model implants were inserted in the mandible of minipigs and extracted after various healing time. While in mature bone hydroxyapatite, amorphous calcium phosphate and octacalcium phosphate are observed, the earlier stages include in addition ß-tricalcium phosphate and brushite-like structures. We propose a method, which offers identification of biomineral components as well as the information on crystallite dimensionality based on strength of hydrogen bonds in water related structures.

BP 30.5 Wed 16:15 ZEU 222

Elucidating insulin structure at hydrophobic interfaces — •Sergio Mauri[1,2], Tobias Weidner[2], and Heike Arnlods[1] — [1]Surface Science Research Centre, Department of Chemistry, University of Liverpool, UK — [2]Max Planck Institute for Polymer Research, Mainz, Germany

Insulin unfolding and aggregation represents a hot topic for improving the delivery and storage of insulin based drugs.

Human insulin is a small peptide (51 amino acids) that regulates glycemia in the human body. It can be found in the form of hexamers, dimers and monomers: only the latter undergo unfolding and aggregation, forming fibril-like structures (amyloids).

It is generally known that interfaces trigger protein denaturation and eventually aggregation: in particular hydrophobic interfaces (such as the air/water interface) are known to disrupt insulin secondary structure, but the mechanism has not been explained in detail yet, since conventional spectroscopic methods do not have sufficient sensitivity to detect the interfacial protein layer.

Here we address this problem by applying a nonlinear optical technique, infrared-visible sum frequency generation, which is interface sensitive by virtue of optical selection rules and compare it to attenuated total internal reflection IR data at hydrophobic interfaces.

15 min. break

BP 30.6 Wed 16:45 ZEU 222

A theoretical study of intermolecular interactions in crystalline cellulose — •Johannes Hoja and Alexander F. Sax — Department of Chemistry, University of Graz, Graz, Austria

It is often claimed that cellulose I consists of sheets held together by van der Waals interactions and that each sheet consists of chains held together by hydrogen bonds. Since all weak intermolecular interactions consist of electrostatic, exchange, induction, and dispersion contributions we analyze in this study all intermolecular interactions in cellulose in terms of these four interaction contributions. It was shown that dispersion is crucial for the stabilization of alcohol dimers.[1] This justifies the use of a dispersionless density functional and an additional

function that describes the dispersion contribution to the interaction energy for the investigation of the interactions in cellulose Iα, Iβ, and II. For a better understanding of the nature of hydrogen bonds between cellulose chains we investigate model systems of alcohol dimers containing a different number of hydrogen bonds. Especially we study how the dimer stability depends on the intermonomer distance and the topology of the hydrogen bonding networks. For these investigations we use symmetry-adapted perturbation theory based on DFT description of monomers [SAPT(DFT)]. We find that dispersion is not only responsible for the intersheet stabilization but also contributes significantly to the intrasheet interactions. This is in opposition to the general view that only electrostatic interactions are important for hydrogen bonding.

[1] Hoja et al., Chem. Eur. J., DOI: 10.1002/chem.201303528, in press.

BP 30.7 Wed 17:00 ZEU 222

Biomodified, stimuli responsive surface coatings based on polymer brushes — •Evmorfia Psarra[1,2], Ulla König[1], Klaus-Jochen Eichhorn[1], Manfred Stamm[1,2], and Petra Uhlmann[1] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — [2]Technische Universität Dresden, Physical Chemistry of Polymer Materials, Dresden, Germany

The main focus of this work is the surface biofunctionalization of ultrathin, stimuli responsive polymer brushes grafted to model surfaces. Different polymer brushes either composed out of a pH responsive component, the Poly(acrylic) acid (PAA), and/or a temperature responsive material, the Poly(N-isopropyl acrylamide) (PNIPAAm) are used to investigate the Arg-Gly-Asp (RGD) peptide binding to the brush surface. Using PNIPAAm mixed with PAA polymer material in order to generate binary brushes will help to create smart surface coatings which are hiding or exposing their functionalities by changing the temperature from physiological (37°C) to room temperature. Binary brushes functionalized with cell-signaling molecules, can lead to intelligent stimuli-responsive bio-nanosurfaces, able to regulate cell adhesion and function. Here we are presenting detailed surface analysis results for the PNIPAA-PAA RGD modified system.

BP 30.8 Wed 17:15 ZEU 222

Microtopographic substrates for controlling cell adhesion at the nanoscale — •Laith Kadem, Julia Purtov, Constanze Lamprecht, and Christine Selhuber-Unkel — Biocompatible Nanomaterials, Institute for Materials Science, University of Kiel

Diblock-copolymer micelle nanolithography has in recent years proven to be a valuable tool for controlling the adhesion of cells at the nanoscale by offering a control over spacing variation in binding sites of single-cell adhesion receptors. Here we present a novel method to additionally control binding sites spacing on regular micropatterns. We use a micro-structured topography on Si substrates that can be easily produced with photolithography followed by wet etching. Performing a diblock-copolymer micelle nanolithography procedure on such substrates introduces nanoparticle arrays of different densities and spacings in the pattern provided by the microtopography in a single-step. With this technique, we can achieve spacing variations in the micropattern of up to 25 nm. The microstructured domains patterned with nanoparticle arrays were biofunctionlized with RGD ligands in order to make them attractive for integrin binding in order to further study the effect of ligand spacing on cell adhesion. Thus, our micro-patterned nanostructured surfaces now provide a versatile platform for studying cellular adhesion processes that are influenced by micro-nanostructured ligand spacing and density.

BP 30.9 Wed 17:30 ZEU 222

Thermal Melting of Protein Beta Sheet Crystals — Andreas Wurm[1], Evgeny Zhuravlev[1], Xiao Hu[2], David Kaplan[2], Peggy Cebe[2], and •Christoph Schick[1] — [1]University of Rostock, Institute of Physics, Germany — [2]Tufts University, Medford MA, USA

The remarkable stability that makes silk useful in garments and surgical sutures has impeded efforts by scientists to study its thermophysical properties. Here, we use fast scanning chip calorimetry and report the first reversible thermal melting of protein beta-pleated-sheet crystals, exemplified by silk fibroin. Heating nanogram-sized samples at 2000K/s, allowed us to avoid thermal decomposition, and demonstrate that beta-pleated-sheet crystals melt to become random coils, helices and turns. We establish that following melting silk can be recrystallized into beta-pleated-sheets, and remelted. The similarity between thermal melting behavior of beta-pleated-sheet crystals and crystals of synthetic polymers is confirmed. Significance for controlling beta-pleated-sheet content during thermal processing of biomaterials is envisioned based on these findings. Demonstration of reversible thermal transitions in silk, the most beta-pleated-sheet-enriched and stable protein, suggests important new insights can also be gained with the broader range of proteins where beta-pleated-sheets serve as critical control points in structural transitions.

Invited Talk BP 30.10 Wed 17:45 ZEU 222

Biopolymer Network Mechanics: Nonlinearity and Hierarchy. — •Cornelis Storm — Department of Applied Physics and Institute for Complex Molecular Systems, Eindhoven University of Technology, The Netherlands.

Biological materials possess some remarkable mechanical properties. Cells and tissues can adjust, remodel, stiffen, soften, in some cases even pack up and leave when circumstances require action. Surprisingly, most systems that exhibit this stunningly complex response, such as the cytoskeleton inside cells and the extracellular matrix, share a common design: under a microscope, they are crosslinked, hierarchical networks of biological polymers. Even more surprisingly, many of the in vivo behaviors can be reproduced in vitro in reconstituted proteinaceous polymer gels. Many of these systems, most notably collagen, play a purely structural role in living organisms. In other words, their function *is* their mechanical response. Biopolymer networks are therefore particularly suited to begin to understand the complex relationship between structural design and functionality in living systems.

In this seminar, I will discuss our efforts to bridge the gap from microscopic structure to macroscopic mechanical response of such nonlinear systems using collagen as an example. Towards the end, I will discuss our first steps towards controlling the nonlinear mechanical properties of biomimetic synthetics.