

## CPP 3: Polymer Physics

Time: Monday 13:30–16:15

Location: H3

**Invited Talk**

CPP 3.1 Mon 13:30 H3

**Emulsion Templating: Unexpected Morphology of Monodisperse Macroporous Polystyrene** — ●COSIMA STUBENRAUCH<sup>1</sup>, LUKAS KOCH<sup>1</sup>, SOPHIA BOTSCH<sup>1</sup>, and WIEBKE DRENCKHAN<sup>2</sup> — <sup>1</sup>Institut für Physikalische Chemie, Universität Stuttgart, Deutschland — <sup>2</sup>Institute Charles Sadron, CNRS Strasbourg, Frankreich

We start with a monodisperse, hexagonally close-packed water-in-monomer high internal phase emulsion (HIPE). The polymerization of the continuous monomer phase with a water-soluble initiator leads to a monodisperse, macroporous polymer with an unexpected morphology: the pore cross-sections of this material are closed hexagons and the pore walls consist of three distinctive layers. Though this morphology has already been observed for two different systems, the mechanism leading to it has not been identified yet. Based on new experimental results we propose a surfactant-driven mechanism: excess surfactant is dissolved in the continuous phase, where it emulsifies water from the emulsion droplets. When the polymerization is initiated from the interface, the continuous phase becomes a poor solvent for both the surfactant and the emulsified water. As a consequence, they "flee" from the site of the polymerization (1) towards the water/monomer interface or (2) into the yet unpolymerized inside of the continuous phase. The first process may cause the emulsion droplets to change their shape from spherical to polyhedral and the second process may be responsible for the formation of the three observed layers in the pore wall. We will (a) discuss both processes in detail and (b) present the experimental results that clearly support them.

CPP 3.2 Mon 14:00 H3

**Dissociation degree and pKa value of polyacid systems in solution and coatings determined by FTIR titration** — LUISE WIRTH<sup>1,2</sup>, BIRGIT URBAN<sup>1</sup>, CAROLIN NAAS<sup>1,2</sup>, and ●MARTIN MÜLLER<sup>1,2</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Department Functional Colloidal Materials, Hohe Str. 6, D-01069 Dresden, Germany — <sup>2</sup>Technische Universität Dresden, Department Chemistry and Food Chemistry, D-01062 Dresden, Germany

Dissociation degree  $\alpha$  and pKa of poly(acrylic acid) (PAA) and propionic acid (PA) 0.1 M solutions were determined by FTIR titration and potentiometric (POT) titration concept. Increasing subsequently the pH value from 2 to 12 by adding 1 M NaOH portions, FTIR spectra of PA and PAA show decrease of  $n(\text{C}=\text{O})$  and increase of  $n(\text{COO}^-)$  band due to carboxyl ( $\text{COOH}$ ) and carboxylate ( $\text{COO}^-$ ) groups, respectively. From the respective normalized band integrals  $A$ , the dissociation degree  $\alpha_{\text{R}} = \text{ACOO}^- / (\text{ACOOH} + \text{ACOO}^-)$  can be calculated. pH was plotted versus  $\alpha_{\text{R}}$  and fitted by  $\text{pH} = \text{pK}_a + B \log(\alpha_{\text{R}} / (1 - \alpha_{\text{R}}))$  related to Henderson-Hasselbalch equation with fit parameters pKa and empirical cooperativity factor  $B$ . The slight pKa deviation found for FTIR and POT titration, the respective deviation between monomeric PA and polymeric PAA and the PAA molecular weight trend (PAA-2K, PAA-50K, PAA-450K) are discussed based on the known two-phase model of polyelectrolyte solutions including Gibbs-Donnan potential concept. Furthermore,  $\alpha_{\text{R}}$  of PAA within consecutively adsorbed polycation/PAA multilayer coatings was determined by FTIR titration showing significant effect of the outermost polyelectrolyte layer.

CPP 3.3 Mon 14:15 H3

**New nanoscale gradient copolymer films fabricated via initiated chemical vapor deposition (iCVD)** — ●STEFAN SCHRÖDER, ALEXANDER M. HINZ, OLEKSANDR POLONSKYI, THOMAS STRUNSKUS, and FRANZ FAUPEL — Kiel University, Institute for Materials Science, 24143 Kiel, Germany

Many structures found in the natural world are based on organic gradients. To reproduce these structures, polymers are an excellent choice, as they also enable the formation of gradient copolymers. This study reports on the fabrication of such gradient copolymers in the form of thin films via initiated chemical vapor deposition (iCVD). Solvent-free deposition and the mild deposition conditions are only two of the advantages of iCVD in order to produce high-quality polymer thin films on large-area substrates, complex geometries as well as temperature-sensitive samples. In addition, the process enables the combination of comonomers which typically lack a common solvent. For the transfer of the gradient film approach to the lower nanoscale, a detailed understanding and control of the vapor phase kinetics are required.

This is solved in this study by a novel in-situ quadrupole mass spectrometry (QMS) extension combined with supporting ab-initio/density functional theory (DFT) calculations. It offers a better insight into the underlying reaction kinetics and enables enhances process control during the deposition. This facilitates the fabrication of gradient copolymer films with film thicknesses below 30 nm. They show completely new physical and chemical properties, which cannot be obtained with materials currently in use.

**Invited Talk**

CPP 3.4 Mon 14:30 H3

**Structural Transitions of Molecules on Surfaces** — ●ANGELIKA KÜHNLE — Physical Chemistry I, Department of Chemistry, University Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

Molecular self-assembly constitutes a versatile strategy to create functional molecular structures at surfaces. Conventionally, self-assembly is associated with structures in thermodynamic equilibrium. In this talk, several examples will be given for molecular structures that are explained by thermodynamic equilibrium. However, observed structures might be kinetically trapped, and structural transitions can be induced by annealing. On the (111) surface of copper, dimolybdenum tetraacetate (MoMo) molecules are shown to undergo a reversible phase transition of molecular islands (2D solid phase) into mobile molecules (2D gas phase). Interestingly, while this phase transition is usually associated with heating, the mobilization of the MoMo molecules presented here is observed upon cooling. In this talk, the molecular-scale origin of this inverse phase transition is discussed.

**15 min. break**

CPP 3.5 Mon 15:15 H3

**Tack Properties of Pressure-Sensitive Adhesive-Coated Fiber Assemblies** — ●VOLKER KÖRSTGENS, JORGE CORELLA PUERTAS, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

For the mechanical characterization of the adhesive bond of pressure-sensitive adhesives one has to take into account the geometry of the adherents and the kind of stress applied. We present a technique, which allows for the measurement of tack for assemblies of fibers coated with pressure-sensitive adhesives using customized cylindrical composite stamps [1]. Key element of the method is the proposed technique to achieve monolayers of parallel-aligned fibers as a fiber assembly. With the adapted probe tack test we investigated the tack properties of a polymer blend of poly(vinylpyrrolidone-co-vinylacetate) and polyethylene glycol (PEG) coated on human hair. This composition serves as a simple model system for hair styling products. The influence of different PEG contents and of the humidity on the tack is demonstrated. Nylon fibers with different diameters are studied as references. [1] V. Körstgens et al., ACS Appl. Polym. Mater. 2, 3189-3195 (2020).

CPP 3.6 Mon 15:30 H3

**Thermoporometry Characterization of Mesoporous Materials: A Kernel-Based Approach** — ●HENRY R. N. B. ENNINFUL, DIRK ENKE, and RUSTEM VALIULLIN — Leipzig University, Leipzig, Germany

Detailed characterization of the structure of mesoporous solids presents key insights into the tailored design for various industrial applications such as catalysis, molecular separations and adsorption, among others.

Thermoporometry, as a characterization technique, suffers from some inaccuracies which make it lag behind gas sorption for textural characterization.

Herein, we present a kernel-based approach for the thermoporometry characterization approach which accounts for a varying non-frozen layer thickness due to pore curvature and temperature and thermal fluctuations in especially, very small pores. Additionally, with the help of the serially-connected pore model (SCPM), we reveal disorder in cylindrical pores whose complex morphology results in cooperativity effects in thermodynamic phase behavior.

References [1] Enninful et 2019, *Frontiers in Chemistry*, doi: 10.3389/fchem.2019.00230. [2] Enninful et 2020, *Microporous and Mesoporous Materials* 309, 110534.

CPP 3.7 Mon 15:45 H3

**Columnar Stacks of Azobenzene Stars Under Irradiation - Photoisomerization Kinetics and Light-Induced Defects** — ●MARKUS KOCH, MARINA SAPHIANNIKOVA, and OLGA GUSKOVA — Institute Theory of Polymers, IPF Dresden, Germany

Azobenzenes (azo) are a class of molecules that photoisomerize between their trans and cis state, causing dramatic conformational changes. These chromophores are widely used to add light-responsive properties to various microscopic or macroscopic systems. The object of this study is a star-shaped molecule (TrisAzo) containing three azo groups connected via a BTA group. TrisAzo not only has a rich photoisomerization behavior [1]. In polar media, these molecules self-assemble into supramolecular structures, that undergo a reversible morphological transition upon UV-Vis light irradiation [2]. Our study focuses on modeling these systems via fully atomistic MD simulations. In particular, we investigate the effects of UV-Vis light on columnar TrisAzo stacks [3]. Using a detailed simulation approach, we can closely reproduce the photoisomerization kinetics in these systems. Moreover, the results demonstrate how light induces defects in the columns and how this is related to the intermolecular interactions of stacked TrisAzo molecules. We thank the German Research Foundation (DFG) for financial support, project GU 1510/5-1.

[1] M. Koch et al. *J. Phys. Chem. B* 121 (37), 8854-8867 (2017)

[2] S. Lee et al. *Langmuir* 29 (19), 5869-5877 (2013)

[3] M. Koch et al. *Langmuir* 35 (45), 14659-14669 (2019)

CPP 3.8 Mon 16:00 H3

**Free energy considerations in confined heterocatalysis in a supported ionic liquid phase** — ●TAKESHI KOBAYASHI<sup>1</sup>, HAMZEH KRAUS<sup>2</sup>, FELIX ZIEGLER<sup>3</sup>, MICHAEL BUCHMEISER<sup>3</sup>, NIELS HANSEN<sup>2</sup>, and MARIA FYTA<sup>1</sup> — <sup>1</sup>Institute for Computational Physics, University of Stuttgart — <sup>2</sup>Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart — <sup>3</sup>Institute of Polymer Chemistry, University of Stuttgart

The high potential of performing heterocatalysis in a confined mesoporous media within a supported ionic liquid phase (SILP) is studied using Molecular Dynamics (MD) simulations. Specifically, we investigate the possibility of immobilizing catalytic molecules in confined media in a biphasic solution consisting of an ionic liquid (IL) and heptane as the second phase within a pore with a lateral size of about 5 nm. Divalent cationic Ru-alkylidene N-heterocyclic carbene catalysts are placed in the solution. We were able to monitor the immobilization of the catalysts within the IL for achieving higher turnover rates in the catalytic reactions. We further analyze the accumulation and diffusion of the molecules within the pore, the influence of steric and IL-specific effects, the structuring of a solvent environment, and their synergistic interactions with the catalytic molecules. The free energy calculations reveal that the catalytic reaction must occur at the interface between the heptane and the IL. Our investigations are supported by experimental evidence and provide a deeper understanding of the inherent details that control a rational design of a linker-free catalyst immobilization in nanometer-sized templates for catalytic applications.