SYPE 1: Polyelectrolytes Poster

Time: Wednesday 16:00–18:30 Location: Poster B

SYPE 1.1 Wed 16:00 Poster B

Hollow Polyelectrolyte Multilayer Tubes: Preparation and mechanical charaterisation — •Renate Müller^1, Lars Dähne^2, and Fery Andreas^1 — ^{1}Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Wissenschaftspark Golm, 14424 Potsdam — ^{2}Capsulution NanoScience AG, Volmerstr. 7b, 12489 Berlin

Tubelike hollow structures are of considerable interest for material science, as they can serve as channels for microfluidics, can be easily assembled to meshes for filtration/ sensing or serve as scaffolds for growing tissue, since they provide a high stability in combination with a low weight. Also possible is an encapsulation of chemicals inside the tubes.

Here we present a new route for the preparation of tubes with micrometer sized dimensions by using the well-known Layer-by-Layer technique [1], which enables us to control the wall thickness within few nm and depending on the composition of the multilayer either ending up in stable tubes or a bubble necklace like structure [2]. We characterised the tubes with Fluorescence Microscopy and CLSM, the wall thickness was determined by AFM imaging. The walls' permeability was also studied. The tubes mechanical properties were determined with the AFM colloidal probe technique [3], which were found to be dependent on the AFM probing position and yielded a Young's Modulus of 200 MPa.

1. Decher G. Science 1997; 277 (5330): 1232-1237./ 2. Mueller R, et al. Polymer 2006: submitted./ 3. Fery A, et al. New Journal of Physics 2004; 6: 18-31.

SYPE 1.2 Wed 16:00 Poster B

Preparation and characterization of nanocomposite films with switch effect — •W. Wang^1, A. Laschewsky^2, and P. Müller-Buschbaum^1 — ^{1}TU München, Physik - Department E13, James-Franck-Str. 1, D-85747 Garching, Germany — ^{2}Potsdam Universität, Mathematisch-Naturwissenschaftliche Fakultät, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

Nanostructures based on polymeric materials are of growing interest for numerous applications in electric and optic areas. The goal of this study is the production and characterization of nano-structured thin films with switch effect from encasing inorganic-organic hybrid materials. The central emphasis is to prepare the films with good thermal-mechanical and chemical characteristics. The basis of the production is a sol-gel template based synthesis of ceramic metallic oxide nanoparticles, with which amphiphile diblockpolymer is used as matrix. In the first step, the polymer matrix - poly(styrene-block-N-isopropylacrylamide), which is synthesized by RAFT polymerization, is deposited on the pre-cleaned, oxide covered silicon (100) substrates as well as glass slides by the spin coating technique. As the performance is strongly influenced by the morphology of the films, atomic force microscopy (AFM) is routinely used to monitor the surfaces of polymer films giving rise to a real-space visualization of the surface topography. A meaningful statistical analysis of film thickness and roughness is advantageously performed with conventional X-ray reflectivity measurement.

SYPE 1.3 Wed 16:00 Poster B

Experiments with single colloids — •Kegler Kati^1, Gutsche Christof^1, Salomo Mathias^2, and Kremer Friedrich^1 — ^{1}PAF, Exp. Physik 1, Universität Leipzig, Linnestr.5, 04103 Leipzig — ^{2}Biophysik, Universität Leipzig, 04103 Leipzig

In rheological experiments the flow resistance of single blank or DNA-grafted colloids is determined by Optical tweezers and compared. The degree of swelling of the grafted DNA is adjusted by exchanging the ion concentration of the surrounding medium. For all examined flow velocities one observes an interesting deviation from Stokes law which can betraced back to a shear-dependent conformational change of the brush layer.The ratio of the effective hydrodynamic radii of DNA-grafted and blank colloids shows a pronounced dependence on the flow velocity, but as well on the length of the grafted DNA and the ionic strength of the solvent. The experimental findings are in qualitative agreement with hydrodynamic simulations based on an elastically-jointed chain model. Optical tweezers are employed to measure the forces of interaction between single DNA-grafted colloids. Parameters to be varied are the length of the DNA,the grafting density and the ionic concentration of the surrounding medium. From the measured force-separation dependence an interaction-length at a given force is deduced. It shows in the mushroom regime a scaling with the grafting density which levels off for brushes. For the latter the transition from an osmotic to a salted brush can be traced in detail by varying the ionic concentration in accordance with meanfield theories.

SYPE 1.4 Wed 16:00 Poster B

Conductivity spectra of polyphosphazene based polyelectrolyte multilayers — •Yahya Akgöl^1, Christian Hofmann^1, Yunus Karatas^2, Cornelia Cramer^1, Hans-Dieter Wiemhöfer^2, and Monika Schönhoff^1 — ^{1}Institut für Physikalische Chemie und SFB 458, WWU Münster, Germany — ^{2}Institut für Anorgansiche und Analytische Chemie und SFB 458, WWU Münster, Germany

Polyphosphazenes are promising materials for application as polymer electrolytes with a high ion conductivity die to their flexible backbone. Here, polyelectrolyte multilayers are built up from ionically modified polyphosphazenes by layer-by-layer assembly of a cationic and an anionic polyphosphazene (PAZ+ and PAZ-). In comparison, multilayers of poly (sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) are investigated. Frequency-dependent conductivity spectra are taken in sandwich geometry at controlled relative humidity. Conductivity spectra of ion conducting materials generally display a dc plateau at low frequencies and a dispersive regime at higher frequencies. Dc conductivity values, which can be attributed to long range ionic transport, are on the order of $10_{-}10$ Scm$_{-}1$ to $10_{-}7$ Scm$_{-}1$ and strongly depend on relative humidity. For PAZ+/PAZ- multilayers the dc conductivity is consistently larger by one decade as compared to PSS/PAH layers. The dispersive regime shows a frequency-dependence, which is deviating from the typical behaviour found in most ion conducting materials.

SYPE 1.5 Wed 16:00 Poster B

Effective charge of polyelectrolytes as a function of the solvent permittivity — •Ute Böhme and Ulrich Scheler — Leibniz Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

One important issue in polyelectrolyte research is the determination of the effective charge, the charge which is capable of interacting with other molecules or solid surfaces. Due to counterion condensation the nominal charge is significantly reduced, depending on the nominal charge density of the polyelectrolyte, potential additional salt ions, the pH and the dielectric properties of the solvent. The effective charge of polyelectrolytes in organic solvents with varying dielectric constants has been derived from a combination of electrophoretic mobility and diffusion coefficient [1], both obtained from PFG NMR experiments. Decreasing permittivity of the solvent results in a drastically reduced effective charge and in changing conformation of the polyelectrolytes simultaneously.

[1] U. Scheler, in H.S. Nalva (ed.) *Handbook of Polyelectrolytes and their applications*, American Scientific Publishers (2002)

SYPE 1.6 Wed 16:00 Poster B

Diffusion and binding of phenol in sub-micron polyelectrolyte capsule dispersions measured using PFG-NMR — •Rudra Prosad Choudhury and Monika Schönhoff — Institute of Physical Chemistry and Graduate School of Chemistry, WWU Münster, Germany

The distribution and dynamics of phenol molecules in colloidal dispersions of sub micron hollow polymeric capsules is investigated by pulsed field gradient NMR (PFG-NMR). The capsules are prepared by self-assembly of polyelectrolytes onto silica particles, followed by dissolution of the silica core in HF. Here, diffusion echo decays are single exponentials, proving the fast exchange of phenol between a free site and a capsule-bound site. However, apparent diffusion coefficients extracted from the echo decays depend on the diffusion time, which is typically not the case for the fast exchange limit. We attribute this to the presence of a particular regime, where apparent diffusion coefficients are observed, which are influenced by an ultrafast spin relaxation in the bound site. Indeed, relaxation rates of phenol are strongly enhanced in the presence of capsules, indicating binding to the capsule wall rather than encapsulation in the interior. We present an analysis in terms of a combined diffusion-relaxation model, where exchange times can be determined from diffusion and spin relaxation experiments even in this particular regime, where the exchange is fast. Based on the ultrafast relaxation in the bound site, the apparent diffusion coefficients become sensitive to the diffusion time. The results show an increase of exchange rates with phenol concentration.

SYPE 1.7 Wed 16:00 Poster B

The Influence of Secondary Interactions during the Formation of Polyelectrolyte Multilayers: Layer Thickness, Bound Water and Layer Interpenetration — •Manesh Gopinadhan[1], Oxana Ivanova[1], Heiko Ahrens[1], Jens-Uwe Günther[1], Roland Steitz[2], and Christiane A. Helm[1] — [1]Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany — [2]Hahn-Meitner Institut, Glienicker Strasse 100, D-14109 Berlin, Germany

With X-ray and neutron reflectivity the structure and composition of polyelectrolyte multilayers from poly (allyl amine) (PAH) and poly (styrene sulfonate) (PSS) is studied as function of preparation conditions (salt concentration and solution temperature). The onset of a temperature effect occurs at 0.05 M NaCl (Debye length less than 1 nm). At 1 M salt, the film thickness increases by a factor of three on heating the deposition solution from 5 to 60°C. The PAH/PSS bilayer thickness is independent of the kind of salt (NaCl or KCl) yet its composition is different (more bound water for NaCl). At low T, the internal roughness is 33% of the bilayer thickness, it increases to 60% at high T. The roughening is accompanied by a total loss of bound water. At which temperature the roughening starts is a function of the kind of salt (50°C for NaCl and 35 °C for KCl). The strong temperature dependence and the eventual loss of bound water molecules can be attributed to the hydrophobic force. However, there is an isotope effect since the loss of bound water is less pronounced in the deuterated layers.

SYPE 1.8 Wed 16:00 Poster B

Deposition and nanostructure of poly(ethyleneimine)/poly(acrylic acid) multilayers in dependence of polyelectrolyte concentration — •Martin Müller, Bernd Kessler, and Wuye Ouyang — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden

Polyelectrolyte (PEL) multilayers (PEM) of poly(ethyleneimine)/poly(acrylic acid) (PEI/PAC) were reproducibly deposited in an automated flow cell and studied in dependence of the adsorption step z and PEL concentration cPEL by in-situ ATR-FTIR spectroscopy and AFM. Quantitative information on the deposited amount and PEL composition was provided based on the integrated areas of characteristic IR bands of either PEI or PAC. Varying cPEL between 0.001 M and 0.1 M resulted in a maximum PEM deposited amount for moderate cPEL. Evidence for the release of outermost located PEI upon PAC immersion (even step) and of outermost PAC upon PEI immersion (odd step) was obtained. AFM images on the surface deposits for PEM-10 revealed smaller structural features for low and high cPEL and larger ones for moderate cPEL. The found cPEL dependent deposition and morphological features are suggested to be determined by a competition of two types of electrostatic attraction: between the outermost PEL and the underlying PEM zone (PEM formation and stability) (i) and between the outermost PEL and the immersed one (PEM rupture and solution complexation) (ii) mediated by Debye length and PEL supply. Applications are related to both charged and nanostructured surfaces for selective drug or protein interaction.

SYPE 1.9 Wed 16:00 Poster B

Layer-by-layer Polyelectrolyte films containing magnetite nanoparticles: Construction and magnetic properties — •Marjolein Neeleman and Andreas Fery — Max-Planck-Institut für Kolloid und Grenzflächenforschung, Am Mühlenberg 1 14424 Potsdam

Magnetic ultrathin membranes are of interest for various applications ranging from data storage to the biomedical field. We have investigated the construction of such membranes using the well-established electrostatic layer-by-layer deposition. This method allows to build up nanoscale surface coatings by alternating adsorption of poly(allylamine hydrochloride) (PAH) and magnetite nanoparticles from aqueous solutions. We have characterized the dependence of the structure of these coatings on deposition parameters like salt concentration of the adsorption solution using atomic force microscopy and X-ray reflectivity. We find that depending on the deposition conditions both linear film growth and exponential film growth can be observed for this system. Finally, hollow magnetic capsules were produced by coating dissolvable core particles with multilayers and subsequently dissolving the particles under conditions that do not destroy the multilayer. With a magnetic balance the magnetic moment of the resulting microcapsules was studied. We find an almost linear increase of the magnetic moment with the number of bilayers applied to the cores, which demonstrates that our method allows producing membranes of well defined magnetization.

SYPE 1.10 Wed 16:00 Poster B

Molecular weight dependence of PEO permeation through the walls of hollow polyelectrolyte capsules — •Rudra Prosad Choudhury[1], Petrik Galvosas[2], and Monika Schönhoff[1] — [1]Institute of Physical Chemistry and Graduate School of Chemistry, WWU Münster, Germany — [2]Faculty of Physics and Earth Sciences, University of Leipzig, Germany

The exchange dynamics of polyethylene oxide (PEO) in colloidal dispersions of hollow polymeric capsules is stidued by pulsed field gradient (PFG)-NMR and diffusion-relaxation correlation spectroscopy. The capsules are prepared by self-assembly of polyanions and polycations onto silica particles, followed by dissolution of the silica core in HF. In PFG-NMR two echo decay components with diffusion coefficients corresponding to free PEO and capsules, respectively, are found. In addition, relaxation- diffusion correlation spectra reveal two peaks with different diffusion coefficients, but almost identical relaxation times. This implies the presence of mobile PEO chains in the capsule interior. From variations of the diffusion time, the exchange behaviour is analysed by a two- site exchange model of free and encapsulated PEO. Exchange times and permeation rates through the capsule wall are extracted for different molecular weight. Permeation rates are decreasing with increasing molecular weight of PEO. While for short chains (Mw $<$ 10000 Da) the dependence on Mw is strongly pronounced, another, less pronounced dependence is found for larger Mw. This suggests a transition between two different mechanisms of permeation as the molecular weight is increased.

SYPE 1.11 Wed 16:00 Poster B

Measurement of long-ranged steric forces between polyelectrolyte covered surfaces — •Stephan Block and Christiane Helm — Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany

Colloidal Probe Technique (CPT) is used to investigate the distance dependent interaction force between polyelectrolyte coated surfaces in salt solutions between 0.1 mM and 1 M, with the polyelectrolyte layers adsorbed from 1 M NaCl solution. As polyelectrolytes poly(allylamine) hydrochloride (PAH), Poly-L-Lysine (PLL) and poly (styrene sulfonate) (PSS) are used, the latter on Si surfaces which are positively charged by silanization.

The repulsive surface forces are more long-ranged with decreasing salt concentration and their decay length always exceed the Debye length. It can be described by the theory of Alexander and de Gennes for interacting surfaces covered with neutral anchored polymers. Apparently, the polyelectrolyte layer is swollen and loops and tails of the adsorbed polyelectrolyte layer dangle into the solution.

There is no approach-separation hysteresis and no influence of the history of the experiment, ie if the salt concentration is increased or decreased by several orders of magnitude. The situation is very different from the well-known flat polyelectrolyte adsorption layers obtained from salt free solutions, where the interaction force is purely electrostatic.

SYPE 1.12 Wed 16:00 Poster B

Direct evidence of Layer-by-Layer assembly of polyelectrolyte multilayers on soft and porous temperature sensitive PNiPAM-microgel using fluorescence correlation spectroscopy — •John Erik Wong[1], Walter Richtering[1], and André Laschewsky[2] — [1]RWTH Aachen University — [2]Potsdam University

We describe the Layer-by-Layer assembly of polyelectrolyte multilayers on soft and porous temperature-sensitive poly(N-isopropylacrylamide) (PNiPAM) microgel. Microgels are not hard and rigid but rather soft and porous particles and polyelectrolytes can not only interdigitate with each other during multilayer formation but also interpenetrate with the microgel. Because of this difference, there could be concerns about the feasibility of the Layer-by-Layer technique on these systems. The argument being that the layer being deposited is stripping the underlying layer instead of anchoring to the latter, and common methods of characterizing film growth on particles such as zeta-potentials will still show *successful* charge reversal.

To address this issue, we used two differently labeled-polyelectrolytes during the deposition. Due to the small size of the microgel (400 nm) studied, we cannot distinguish between polyelectrolytes adsorbed on or in the microgel. However with fluorescent correlation spectroscopy we can clearly distinguish between free labeled-polyelectrolytes and those that are bound to the microgel. Dual-color correlation confirms the presence of both polyelectrolytes bound to the same particle while fluorescence imaging (on a dry sample) provides the visual proof.