

SYPE 2: Polyelectrolytes I

Time: Thursday 14:00–17:00

Location: H37

Invited Talk

SYPE 2.1 Thu 14:00 H37
Coulomb and Flory: Fathers of SONS. Polyelectrolytes in Self Organized Nano Systems — ●MARTIEN COHEN STUART — Laboratory of Physical Chemistry and Colloid Science, Wageningen University, P.O. Box 8038, 6700 EK Wageningen, The Netherlands

Supramolecular chemistry exploits the many non-covalent interactions between molecules to create novel and functional structures. A most versatile interaction is the electrostatic force that emerges between ions and polyions. We have seen an enormous activity in recent years to fabricate novel materials using pairs of oppositely charged macromolecules; in particular, fabrication of thin films consisting of polyelectrolyte complexes by controlled deposition in alternating fashion has captured the imagination of many chemists and physicists. The debate concerning the description of these systems in terms of fundamental physical laws and chemical properties is going on.

In the present contribution we exploit the same tendency of oppositely charged chains to form a condensed phase, but we add new features, with the aim to make new complex and functional nanoparticles. The new feature is a 'stop mechanism' that suppresses growth of a macroscopic phase so that only small particles result. Connecting a neutral, water soluble to at least one of the polyelectrolytes participating in complexation, one will get micellar particles, which we call 'Complex Coacervate Core Micelles (C3M's), and which have been denoted as 'Poly Ion Complexes' (PIC's) or 'Block Ionomer Complexes' (BIC's) by others.

SYPE 2.2 Thu 14:30 H37

Pore size distribution in polyelectrolyte multilayers determined by cryoporometry — ●FABIÁN VACA CHÁVEZ and MONIKA SCHÖNHOF — Institut für Physikalische Chemie, WWU Münster, Germany

Permeability and porosity of polyelectrolyte multilayers (PEM) are properties of major interest, as they are crucial for applications in encapsulation, controlled release and membrane separation. In the current work the first pore size distribution of PEM in samples consisting of silica particles coated with poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) is presented. To this end, the Nuclear Magnetic Resonance (NMR) cryoporometry technique was applied. NMR cryoporometry has been successfully applied to various porous systems and, in our approach, we consider polyelectrolyte multilayers as a porous material, where the hydration water can freeze in dependence on the size of water pores. The proton NMR signal of liquid water is analyzed assuming a log normal distribution of motional correlation times. From our results, it is possible to determine the size of water sites in the layers to around 1 nm. In addition, a slight variation with the number of layers is found. The average pore size agrees with cut-off sizes found in permeation experiments.

SYPE 2.3 Thu 14:45 H37

Adsorption of Light and Heavy Water Vapours in Polyelectrolyte Multilayer Films — CHRISTOPHE DELAJON¹, ●THOMAS GUTBERLET², HELMUTH MÖHWALD¹, and RUMEN KRASTEVA¹ — ¹Max-Planck-Institute of Colloids and Interfaces, Wissenschaftspark Golm, 14424 Potsdam, Germany — ²Paul Scherrer Institute, 5232 Villigen, Switzerland

We studied the swelling and the uptake of water (H₂O or D₂O) vapours in polyelectrolyte (PE) multilayer (PEM) samples deposited on solid support (Si wafers) as a function of the isotope nature of the vapour and the charge of the last polymer layer. The samples were prepared with deuterated poly(sodium 4-styrenesulfonate) (dPSS) and poly(allylamine hydrochloride) (PAH). Two types of samples were studied. The sample with a structure Si/PEI/(dPSS/PAH)/dPSS was negatively charged. A positively charged sample was PAH terminated and had the structure Si/PEI/(dPSS/PAH)₆. The film thickness and density were estimated from neutron reflectometry experiments and the results were complemented with in-situ QCM measurements. The swelling of PEM in H₂O and D₂O vapours is the same, but the amount of sorbed water depends on the used water isotope. It is about twice as large in the case of D₂O compared to H₂O. We attribute the effect to the strength of the hydrogen and deuterium bonds formed between the water molecules and the PEM matrix. We also show that the amount of sorbed water depends on the nature of the last layer

which builds the PEM.

SYPE 2.4 Thu 15:00 H37

Elasticity testing of freestanding polyelectrolyte membranes with different charge density — ●INGO DÖNCH, MARC NOLTE, and ANDREAS FERY — Max-Planck-Institut für Kolloid und Grenzflächenforschung, Am Mühlenberg 1, 14424 Potsdam

To build micro scale applications like a sensor or pressure sensitive valve new ways have to enter. It looks realistic to scale sensors down by using known polyelectrolyte membranes. After finding a new way to transfer polyelectrolyte multilayer films stress free to a patterned substrate, it is possible to test different properties of PE-membranes in variable environment, for changing radii. With the existing knowledge of PE-membranes, it is possible to scale down sensors for such applications. The work is primarily specializing in investigating the micromechanical response of the PE-membranes made from PDADMAC/PSS, in these we use PDADMAC with different charge density. The behavior of the resulting membrane patches is dependent only on the thickness of the membrane and the radius of the covered hole. It can be described with simple continuum mechanical models. We generate an osmotic pressure between bulk and the cavities which lead to a bending of the freestanding part of the membrane. This compliance of a fluorescent labeled film can be measured with a confocal microscope. Since the thickness of the multilayer can be precisely controlled in the nanometer range, the compliance of the membrane can also be varied over orders of magnitude. The PE-membranes are also semi-permeable, which makes them sensitive to osmotic pressure differences. Thus they are promising components for future micro-scale membrane sensors.

SYPE 2.5 Thu 15:15 H37

Self-assembly of thermoresponsive polyelectrolyte microgels on polyelectrolyte coated surfaces — STEPHAN SCHMIDT¹, ●THOMAS HELLWEG², and REGINE VON KLITZING² — ¹MPI KGF, Wissenschaftspark Golm, 14424 Potsdam, Germany — ²TU Berlin, Stranski-Lab., Strasse des 17. Juni 124, 10623 Berlin, Germany

PNIPAM-co-poly(acrylic acid) microgels are deposited on poly(ethylene imine) coated silicon wafers using the well known layer-by-layer approach. The obtained surface coverage strongly depends on the degree of charge of the microgels, which is controlled via the pH-value of the used buffer. At intermediate pH (approx. 6) a coverage of about 40 % is obtained and the formation of island structures can be observed. However, placing these surfaces in a similar buffer a second time leads to a complete rearrangement of the structure. Highly ordered surface pattern are obtained. The process is studied in situ using confocal microscopy. In addition ellipsometry and AFM measurements are performed to characterize the prepared surfaces.

SYPE 2.6 Thu 15:30 H37

growth of polyelectrolyte complex nanoparticles: experimental and simulation studies — ●VITALIY STARCHENKO^{1,2}, MARTIN MÜLLER¹, and NIKOLAI LBOVKA² — ¹Leibniz-Institut für Polymer Forschung, Dresden, Deutschland — ²Ovcharenko-Institute of Biocolloidal Chemistry, Kiev, Ukraine

Formation of polyelectrolyte complex (PEC) nanoparticles is of large fundamental interest and has application potential in e.g. biomedicine (drug/protein carrier) and water treatment (flocculation). Monodisperse particles were prepared by mixing cationic poly(diallyldimethylammonium chloride) (PDADMAC) and anionic poly(styrenesulfonate) (PSS) at nonstoichiometric monomer charge ratios followed by consecutive centrifugation, which was characterized by dynamic light scattering (DLS). Using this concept small primary particles of low aggregation number have been suggested to merge to larger secondary particles by attractive dispersive forces, while the colloidal stability and the final particle size is determined by electrostatic repulsion in line with the DLVO theory. To check for the role of the Debye length, we report herein on ionic strength dependence of the particle size. In conformity with theoretical assumptions a model based on Smoluchowski theory, which includes a colloidal potential according to DLVO theory, was developed. This model can be used exclusively for simulation of the coagulation process of particles on the colloid level. Hence, additionally the influence of polyelectrolyte molecular

weight on the particle size was studied to figure out the Debye length dependent contribution on the macromolecular conformation level.

15 min. break

Invited Talk SYPE 2.7 Thu 16:00 H37

Bundling Phenomena in Semiflexible Polyelectrolytes — ●CHRISTIAN HOLM^{1,3}, MEHMET SAYAR², and BERK HESS³ — ¹Frankfurt Institute for Advanced Studies, Johann Wolfgang Goethe - Universität, Frankfurt, Germany — ²Koc University, College of Engineering, Istanbul, Turkey — ³Max-Planck-Institut für Polymerforschung, Mainz, Germany

We present the results of extensive computer simulations performed on solutions of monodisperse charged rod-like polyelectrolytes. In the first part of the talk we investigate the bundle formation of DNA-like semiflexible generic polyelectrolytes. DNA is known to aggregate in the presence of multivalent cationic condensing agents into toroidal and bundle like structures. We study a coarse-grained semiflexible bead-spring model in the presence of trivalent counterions, using a combination of parallel tempering and hybrid Monte Carlo techniques. Our results show that for small values of the electrostatic interaction the solution mostly consists of dispersed single rods. In the second part of the talk we investigate the bundle formation in solution of hydrophobically modified sulfonated poly(p-phenylene) oligomers (PPP) via atomistic simulations in the presence of Na and divalent Ca counterions. We show that the basic packing of the PPP oligomers does not change upon increase of the counterion valency, but the interaction among bundles goes from repulsive to attractive.

SYPE 2.8 Thu 16:30 H37

Bundle Formation in Polyelectrolyte Brushes — ●JENS-UWE GÜNTHER¹, HEIKO AHRENS¹, STEPHAN FÖRSTER², and CHRISTIANE HELM¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany — ²Institut für Physikalische Chemie, Universität Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Bundle formation in the vertically oriented chains of poly(styrene sulfonate) (PSS) within polyelectrolyte brushes is studied with grazing

incidence diffraction as function of grafting density and ion concentration. The brush thickness determined with X-ray reflectivity amounts to 30-50% of the contour length. As predicted theoretically, bundle formation can be induced by adding divalent ions, ie CaCl₂. However, at 0.5 Molar monomer concentration and without added salt, already bundles are observed. Then, a bundle consists of two chains and is 5 nm long. On the addition of up to 1 M CsCl in the subphase the aggregation number increases up to 20 whereas the bundle length approaches a limiting value, 2 nm. We suggest that the bundle formation is determined by a balance between long-ranged electrostatic repulsion, whose range and amplitude is decreased on salt addition, and a short-ranged attraction.

SYPE 2.9 Thu 16:45 H37

Collapse of highly charged polyelectrolytes by dipole-dipole interactions — ●ANDREY CHERSTVY and ROLAND WINKLER — IFF, Forschungszentrum Jülich, D-52425 Jülich, Germany

Although collapse of highly charged polyelectrolytes (pe) was considered in a number of theoretical [1,2] and simulation [3-5] studies, some questions about effect of added salt and scaling relations for compact state remain open. We consider the influence of electrostatic (el) and dipole-dipole (dd) interactions on properties of flexible highly charged pes [6]. The dd interactions of pe segments are due to condensed counterions. We sum screened el and dd interactions along pe assuming that Gaussian statistics is weakly perturbed [7]. Attractive averaged dd interactions used are akin to Keesom energy. For weakly charged pe (below Manning limit), pes are swelled due to el repulsion of monomers. As condensation of counterions sets in, attractive dd interactions start to counteract el repulsion and trigger chain compaction into globules. We study onset on collapse as a function of chain length and salt conc. Scaling relations for size of the globule depending on pe charge density are obtained, with and without excluded volume interactions. We treat also the persistence length of dipolar chain and scaling relations for dense aggregates.

[1] H. Schiessel et al., MM 31 7953 (1998). [2] A.G. Cherstvy et al., JPCB 106 13362 (2002). [3] R.G. Winkler et al., PRL 80 3731 (1998). [4] R.G. Winkler et al., PRE 66 021802 (2002). [5] R.G. Winkler New J. Phys. 6 11 (2004). [6] A.G. Cherstvy and R.G. Winkler, in preparation. [7] S. Lifson et al. JPolSci XI 409 (1953).