Welcome to Polyelectrolytes 2006, the 6th of the series of International Symposia on Polyelectrolytes. The meeting program spans from theory to synthesis, characterization and application in the exciting field of polyelectrolytes, hoping the interesting conference will facilitate discussion between scientists from all over the world.

Welcome to the city of Dresden, which is celebrating its 800th anniversary, while at the same time holding the title of Germany’s “City of Science”. Dresden is thus bridging from tradition to innovation. We hope that the meeting will arrange the same bridge, bringing together young and established scientists, reporting exciting results and preparing the ground for new ideas.

## ORAL PROGRAM

| Monday, Sept. 4 | |
|---|---|
| 9:30 to 15:30 | Tutorial<br>(A. Laschewsky, M. Müller, K. Huber, S. Schwarz, R. G. Winkler, U. Scheler) |
| *from 16:30* | *Registration* |
| *to 21:00* | *Welcome Mixer* |

| Tuesday, Sept. 5 | | | Page |
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| 8:30 | | Opening | |
| 9:00 | I-1 | Qi Liao[1], A. V. Dobrynin[2], M. Rubinstein[3]<br>[1] Beijing, China, [2] Storrs, CT, USA, [3] Chapel Hill, NC, USA<br>COUNTERION-CORRELATION INDUCED ATTRACTION IN POLYELECTROLYTE SOLUTIONS | 17 |
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| 9:40 | C-2 | P. Vallat, J.-M. Catala, F. Schosseler, M. Rawiso<br>Strasbourg, France<br>ANNEALED CONJUGATED POLYELECTROLYTES IN POOR SOLVENT: INTERPLAY BETWEEN THE ELECTRONIC STRUCTURE AND THE AVERAGE CONFORMATION | 19 |
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| 11:10 | C-5 | D. V. Pergushov[1], I. A. Babin[1], F. Plamper[2], A. B. Zezin[1], V. A. Kabanov[1], A. H. E. Müller[2]<br>[1] Moscow, Russia, [2] Bayreuth, Germany<br>NOVEL WATER-SOLUBLE INTERPOLYELECTROLYTE COMPLEXES BASED ON POLY(ACRYLIC ACID) STARS | 22 |
| 11:30 | C-6 | S. Strandman, S. Hietala, V. Aseyev, B. Koli, S. J. Butcher, H. Tenhu<br>Helsinki, Finland<br>AMPHIPHILIC PMMA-BLOCK-PAA STARS IN AQUEOUS SOLUTIONS | 23 |
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| 13:30 | C-8 | J. Gummel, F. Cousin, François Boué<br>Saclay, France<br>PROTEIN POLYELECTROLYTE COMPLEXES: STRUCTURES, INTERNAL COMPOSITIONS AND CHAIN CONFORMATIONS DETERMINED BY SANS. | 25 |
| 13:50 | C-9 | A. B. Zezin, V. B. Rogacheva, S. P. Valueva, N. I. Nikonorova<br>Moscow, Russia<br>FROM INTERPOLYELECTROLYTE-METAL COMPLEXES TO POLYMER-METAL NANOSYSTEMS | 26 |
| 14:10 | C-10 | R. G. Winkler[1], A. G. Cherstvy[1, 2]<br>[1] Juelich, Germany, [2] Dresden, Germany<br>CRITICAL ADSORPTION OF POLYELECTROLYTES ONTO CHARGED SPHERICAL COLLOIDS | 27 |
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| 15:30 | I-2 | Ch. Schatz[1], Th. Delair[2], Ch. Pichot[2], A. Domard[2], A. Bionaz[2], J.-M. Lucas[2]<br>[1] Bordeaux, France, [2] Lyon, France<br>VERSATILE AND EFFICIENT FORMATION OF NANO-PARTICLES OF POLYSACCHARIDE-BASED POLYELECTROLYTE COMPLEXES | 30 |
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| 13:20 | | **Poster Session (even numbers)** | |
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| 15:40 | C-44 | R. Müller[1], L. Dähne[2], A. Fery[1]<br>[1] Potsdam, Germany, [2] Berlin, Germany<br>MICROMECHANICS OF HOLLOW POLYELECTROLYTE MICROTUBES AND THEIR TEMPERATURE-INDUCED SHAPE CHANGES | 66 |
| *16:00* | | *End* | |
| *17:30* | | *Sightseeing (starting point: Theaterplatz – end point: Festungsmauern* | |
| *19:00* | | *Dinner Festungsmauern am Brühlschen Garten* | |

| **Friday, Sept. 8** | | | |
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| 9:00 | C-45 | M. Nichifor[1], S. Lopes[2], M. Bastos[3], A. Lopes[2]<br>[1] Iasi, Romania, [2] Oeiras, Portugal, [3] Porto, Portugal<br>FLUORESCENCE AND CONDUCTOMETRIC STUDIES OF THE POLYSACCHARIDE BASED AMPHIPHILIC POLYELECTROLYTES - ALKYL SULFATES INTERACTION | 68 |
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| *10:00* | | *Break* | |
| 10:30 | I-8 | Dan Q[1], D. Rapoport[1], R. von Klitzing[2]<br>[1] Potsdam, Germany, [2] Kiel, Germany<br>INTER- AND INTRAMOLECULAR INTERACTIONS OF POLYELECTROLYTES CONFINED IN THIN LIQUID FILMS | 71 |
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| 12:00 | C-51 | M. Müller[1], W. Ouyang[1], K. Bohata[2], B. Keßler[1]<br>[1] Dresden, Germany, [2] Prague, Czech Republic<br>INFLUENCING POLYELECTROLYTE COMPLEX NANOSTRUCTURE BY CHARGED POLYPEPTIDE CONFORMATION | 75 |
| *12:20* | | *End* | |

## POSTER PRESENTATIONS

# COUNTERION-CORRELATION INDUCED ATTRACTION IN POLYELECTROLYTE SOLUTIONS

*Qi Liao*[1], *Andrey V. Dobrynin*[2], *Michael Rubinstein*[3,] *

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We have developed a necklace model of hydrophobic polyelectrolytes in which the necklace structure consisting of polymeric globules (beads) connected by extended sections of the chain (strings of monomers) appears as a result of the counterion condensation and is caused by the balance of the correlation-induced attraction of condensed counterions to charged monomers and electrostatic repulsion between uncompensated charges. The size of the beads increases with polymer concentration while their number per chain decreases. We predict coexistence of necklaces with different number of beads on a polymer backbone at any polymer concentration. To test this necklace model we performed molecular dynamics simulations of polyelectrolyte chains with degree of polymerization N varying from 25 to 373 and with fraction of charged monomers f=1/3, 1/2 and 1 in poor solvent conditions for polymer backbone. The observed concentration dependence of the bead size supports the assumption of the counterion condensation origin of the necklace structure. The osmotic coefficient of the solutions of polyelectrolytes in poor solvent conditions for polymer backbone exhibits non-monotonic concentration dependence in agreement with 2-zone model predictions. It decreases with increasing polymer concentration in dilute solutions, while it is an increasing function of polymer concentration in the semidilute regime. The Kratky plot of the chain form factor is in excellent agreement with the neutron scattering experiments. We analyze the dynamics of polyelectrolyte in a fully draining regime and find that it is analogous to expected dynamics in polyelectrolyte solutions with full hydrodynamic coupling. In particular, we find the non-monotonic concentration dependence of the relaxation time, predicted by the scaling theory and observed experimentally.

Qi Liao, Andrey V. Dobrynin, and Michael Rubinstein, Macromolecules 39, 1920-1938, (2006).

# CONFORMATIONAL CHANGE OF GIANT DNA WITH ADDED SALT AS REVEALED BY SINGLE MOLECULAR OBSERVATION

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The conformational behaviour of individual giant double-stranded T4 DNA (165.6 kilobase pairs) molecules has been investigated by fluorescence microscopy in a wide range of NaCl concentrations and the results have been compared to theory and other experiments. The measured long-axis length of T4 DNA was transformed into a persistence length and subjected to a power-law analysis, which showed that electrostatic contribution to the persistence length was inversely proportional to the square root of the salt concentration; i.e., it had a linear dependence on the screening length. DNA is generally considered to be a stiff molecule and other experiments have shown a quadratic dependence on the screening length, which is the behaviour predicted by Odijk-Skolnick-Fixman theory for rodlike molecules. T4 DNA, however, is much longer than the persistence length and the linear dependence is interpreted as the behaviour of a flexible chain with electrostatic excluded volume interactions, as has been observed in simulations. The importance of excluded volume effects is also supported by the fluorescence images. An alternative interpretation, namely that the linear dependence is consistent with Le Bret-Fixman theory, may be ruled out, primarily on the account of the observed agreement with Odijk-Skolnick-Fixman theory for somewhat shorter DNA.

# ANNEALED CONJUGATED POLYELECTROLYTES IN POOR SOLVENT: INTERPLAY BETWEEN THE ELECTRONIC STRUCTURE AND THE AVERAGE CONFORMATION

*Perrine Vallat*, Jean-Marie Catala, François Schosseler, Michel Rawiso*

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Conjugated polyelectrolytes are particular polyelectrolytes that have a backbone composed by a conjugation of double and/or triple bonds. The presence of this conjugated backbone has two main consequences. Due to the delocalization of the pi-electrons along the backbone, conjugated polyelectrolytes are strongly hydrophobic. This character is enhanced as soon as the degree of charging is decreased. Second, thanks to the interplay between the electronic structure of pi-electrons and the conformation of the macro-ions [1,2], it becomes possible to study the conformation of polyelectrolytes by UV-visible absorption spectroscopy in the low concentration regime. We are more particularly interested in studying the behavior in poor solvent of hydrophobic annealed polyelectrolytes, i.e. with a dynamic distribution of charges along the backbone. For this study, we have chosen a flexible and annealed polyelectrolyte. Both requirements are fulfilled by synthesizing a polythiophene backbone bearing carboxylic groups on lateral side chains, namely poly(3-thiophene acetic acid) ([(SC4H)-(CH2COOH)]n) [3]. By coupling UV-visible absorption spectroscopy to titration experiments, a drastic color change has been observed as the quality of the solvent is reduced (when the pH of the solution is decreased). An isosbestic point, characteristic of a two-state model, also appears when considering the evolution of the spectra during titration. This observation provides direct evidence for the first-order nature of the transition. This is in agreement with the discontinuous first order transition between a strongly charged extended state to a weakly charged collapsed state predicted by theory [4] and Monte-Carlo simulations on infinitely diluted chains [5]. The observation of this transition is rather complex in the case of saturated polyelectrolytes. Specifically, titration curves are often ambiguous. The conjugated character of such polyelectrolytes is therefore a key to get a better understanding of annealed hydrophobic polyelectrolytes. We will also discuss the influence of several parameters such as temperature, ionic strength and chain length on this hydrophilic/hydrophobic transition for annealed polyelectrolytes in a poor solvent.

[1] K. C. Lim, A. J. Heeger, J. Chem. Phys., 82, 522-530 (1985)
[2] M. Rawiso, J.-P. Aime, J.-L. Favre, M. Schott, M. A. Müller, M. Schmidt, H. Baumgartl, G. Wegner, J. Phys. France, 49, 861-880 (1988)
[3] B. Kim, L. Chen, J. Gong, Y. Osada, Macromolecules, 32, 3964-3969 (1999)
[4] E. Raphael, J.-F. Joanny, Europhys. Lett., 13, 623-628 (1990)
[5] S. Uyaver, C. Seidel, Europhys. Lett., 64, 536-542 (2003)

# INTERACTION BETWEEN HYDROPHOBICALLY MODIFIED POLYMERS WITH DIFFERENT POLYMER CHAIN SIZES AND CYCLODEXTRINS FOLLOED BY FLUORESCENCE

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Poly (acrylic acid) polymers of low (2000 g/mol) and high (450 000 g/mol) molecular weight (MW), hydrophobically modified with pyrene showed have been previously studied and that their behaviour in solution was found to be dependent on the size of the PAA chain, degree of labelling and other factors, such as the pH and the nature of the solvent.[1] In the present study, the interactions between the pyrene-labeled poly(acrylic acid) with two different chain sizes and degrees of labeling, and beta- and gamma-cyclodextrins (beta- and gamma-CD) were studied using absorption and fluorescence (steady-state and time-resolved) techniques. This interaction results in the formation of inclusion complexes between the pyrene groups of the polymer and the cyclodextrins. The absorption and the fluorescence spectra (IE/IM ratio) changes with the addition of gamma-CD but not with beta-CD. In the case of gamma-CD at acidic pH values the inclusion phenomena seems to prevail involving more than one pyrene and thus enhancing ground-state dimmer formation. In the case of interaction of PAAMePy polymers with beta-CD, due to the availability of this CD cavity for a single pyrene unit, the photophysical behaviour of the polymers seems to be kept unchanged with the increase in CD concentration. These data seem to be in accordance with the behaviour found for the interaction of analogous PAAMePy polymers with CDs.[2] In water, the fluorescence decays of the PAAMePy polymers were found to be tri-exponential in the monomer and excimer emission regions, i.e., the presence of two monomers and two excimers was observed. The shorter and the longer decay times were attributed to the decay of monomer species that are able to form excimer and to the decay of free monomers (not able to form excimer).[3] The two other decay times were attributed to two different excimers with different structures with symmetric asymmetric sandwich-like-structures.[4] These data will be presented and discussed by comparison with the behaviour found in water and in organic solvents. Preliminary studies indicate that the decay component attributed to the asymmetric structure increases with of gamma-CD. Acknowledgments Financial support from the Portuguese Science Foundation (FCT) through FEDER and POCI is acknowledged. Telma Costa acknowledges FCT for a Ph. D. grant (SFRH/BD/17852/2004). We thank A. Francisco, Dr. S. Gago and Dr. I. Gonçalves for the help in the synthesis of the labelled polymers.

[1] J. Seixas de Melo, A. Francisco, T. Costa, S. Gago, I. S. Gonçalves, p. 291, in Coloides e Interfases, M.M.V. Salicio, M.D.M. Moreno, Editors. 2005, Ed. Univ. Salamanca: Salamanca.
[2] J. Seixas de Melo, T. Costa, N. Oliveira, K. Schillén, to be submitted.
[3] J. Seixas de Melo, T. Costa, M. G. Miguel, B. Lindman, K. Schillén, J. Phys. Chem. B, 2003, 107, 12605.
[4] J. Seixas de Melo, A. Francisco, T. Costa, A. Maçanita, S. Gago, I. S. Gonçalves, to be submitted.

# SYNTHESIS AND SOLUTION BEHAVIOUR OF STAR-SHAPED POLYELECTROLYTES

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We present the synthesis of star-shaped poly(acrylic acid) (PAA) with 5, 8, 21 and up to approximately 40 arms by Atom Transfer Radical Polymerization (ATRP) applying the core-first approach.[1] We also report the preparation of strong cationic polyelectrolyte stars using the same attempt. Besides saccharide-based initiators a silsesquioxane-based initiator with ca. 58 initiation sites (PDI ~ 1.2) was used as a scaffold for star polymers. That initiator was prepared by esterification of hydroxy-functionalized silsesquioxane nanoparticles with α-bromoisobutyryl bromide and analyzed by MALDI-ToF MS.[2] Both tert-butyl acrylate (tBA) and dimethylaminoethyl methacrylate (DMAEMA) were polymerized with help of this initiator yielding stars with high arm numbers. Consecutive elimination of isobutylene from PtBA with trifluoroacetic acid gave the corresponding poly(acrylic acid) stars. Aqueous GPC revealed that fragments of “four arm” stars partly detach from the silsesquioxane core during the transformation to star-shaped PAA. However, star-shaped PDMAEMA could easily be quaternized without any destruction of the core as shown by dynamic light scattering (DLS). Potentiometric titration of different PAA stars with NaOH was performed in dilute salt-free solution. With increasing arm number the titration curves shift to higher pH values. This is understood in terms of differences in osmotic pressure inside the star, leading to a reversal of the acid base equilibrium and expelling hydroxide into bulk solution.[1] Determining the osmotic coefficient by osmometry of PAA stars with ionization degree $\alpha \sim 0.6$ and different arm numbers shows good agreement with theoretically derived and simulated values.[3] We compare the findings from osmometry with other methods like potentiometry also examining the amount of released counterions. DLS studies of quaternized PDMAEMA stars reveal the expected contraction of the stars with increasing ionic strength. But even at constant ionic strength the stars begin to shrink when adding di- and trivalent counterions. Close to the point where the total charge of the star is saturated with the charge of the multivalent counterions the polymer starts to precipitate. This was also shown by turbidimetric titrations.

[1] Plamper, F.; Becker, H.; Lanzendörfer, M.; Patel, M.; Wittemann, A.; Ballauff, M.; Müller, A. H. E. Macromolecular Chemistry and Physics 2005, 206, 1813-1825
[2] Muthukrishnan, S.; Plamper, F.; Mori, H.; Müller, A. H. E. Macromolecules 2005, 38, (26), 10631-10642
[3] Jusufi, A.; Likos, C. N.; Löwen, H. Journal of Chemical Physics 2002, 116, (24), 11011-11027

# NOVEL WATER-SOLUBLE INTERPOLYELECTROLYTE COMPLEXES BASED ON POLY(ACRYLIC ACID) STARS

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The interaction of star-shaped poly(acrylic acid) ((PAA)x, x = 5, 8, and 21, DPn(arm) = 100) with a strong linear cationic polyelectrolyte, poly-N-ethyl-4-vinylpyridinium bromide (P4VP*EtBr, DPw = 600, 3000), in neutral and alkaline media was examined (pH 7, 9; [NaCl] < 0.3 M). This interaction was shown to result in the formation of water-soluble interpolyelectrolyte complexes (IPECs) if the basemole ratio Z of the aqueous mixtures the oppositely charged polymeric components, Z = [N+] / [COO- + COOH], does not exceed a certain maximum value Z* (Z* < 1), that is, when (PAA)x is present in the system in a certain excess compared to P4VP*EtBr. The values of Z* were observed to decrease with decreasing x as well as with increasing ionic strength of the surrounding solution, the former effect being more pronounced at higher salt concentrations. Sedimentation coefficients and hydrodynamic radii of the formed complex species were found to be either independent of Z (x = 5 and 8) or only weakly dependent on Z (x = 21), thus strongly suggesting that such particles are of characteristic (constant) stoichiometry which appears to be close to Z*. The sizes of the complex species based on (PAA)x with the small numbers of arms (x = 5 and 8) were shown to be considerably larger than those determined for the corresponding original polyelectrolyte stars, clearly indicating that polycation-induced assembly of (PAA)x leading to the formation of aggregates containing several polyelectrolyte stars takes place. At the same time, the size of the complex species resulting EtBr was found to be decisively from the interaction of (PAA)21 with P4VP determined by the degree of polymerization of the cationic polyelectrolyte: hydrodynamic radius of complex particles containing the shorter polycation is close to that determined for (PAA)21 whereas the formation of aggregates containing several polyelectrolyte stars is observed when (PAA)21 interacts with the longer polycation. At [NaCl] > 0.3 M, the interaction between (PAA)x and EtBr was found to be suppressed because of the screening effect of small P4VP* ions. This research was supported by Marie Curie Research and Training Network POLYAMPHI “Self-Organized Nanostructures of Amphiphilic Copolymers” and Russian Foundation for Basic Research (project # 06-03-32696).

# AMPHIPHILIC PMMA-BLOCK-PAA STARS IN AQUEOUS SOLUTIONS

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Amphiphilic block copolymers are capable of forming various nanostructures resembling those observed in nature. The most common of these supramolecular assemblies are spherical micelles, worm micelles, and vesicles.[1,2] As solvent plays an important role in the formation of noncovalent assemblies, changing the solvent composition, ionic strength or pH can induce the self-assembly of block copolymers or trigger the transition between the assembled geometries.[1,3] In this work we have studied the self-assembling of an amphiphilic star block copolymer, 4-arm (PMMA-b-PAA)4 with poly(methyl methacrylate) inner blocks and poly(acrylic acid) outer blocks in aqueous solutions. The association of the amphiphilic PMMA-b-PAA stars in aqueous solutions has been investigated by light scattering using Kratky analysis and by direct visualisation of the solutions by cryoTEM. These methods revealed the presence of nonspherical micellar morphologies in saline solutions. The association of the starlike macromolecules resembles that of charged biopolymers, such as actin, since a balance between attractive and repulsive forces is required for the formation of cylindrical assemblies and can be manipulated by the ionic strength of the solvent.[4]

[1] Zhang, L.; Eisenberg, A. J. Am. Chem. Soc. 1996, 118, 3168-3181, Macromolecules 1999, 32, 2239-2249.
[2] Discher, D.E.; Eisenberg, A. Science 2002, 297, 967-973.
[3] Choucair, A.; Lavigueur, C.; Eisenberg, A. Langmuir 2004, 20, 3894-3900.´
[4] Tang, J.X.; Janmey, P.A. J. Biol. Chem. 1996, 271, 8556-8563.

# COLLAPSE TRANSITION IN SPHERICAL POLYELECTROLYTE BRUSHES IN PRESENCE OF MULTIVALENT COUNTERIONS

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We consider the interaction of multivalent counterions with spherical polyelectrolyte brushes (SPB). The SPB result if linear polyelectrolyte chains (contourlength: 140nm) are densely grafted to colloidal spheres of ca. 100nm in diameter. Dispersed in water the surface layer consisting of chains of the strong polyelectrolyte poly(styrene sulfonic acid) (PSS) will swell. In salt-free solution the osmotic limit is reached in which practically all counterions are confined within the brush as predicted by theory [1, 2]. We have shown that an increase of the ionic strength by adding monovalent salt leads to a gradual decrease of the height L of the surface layer that can be measured by dynamic light scattering [3,4]. Here we demonstrate that trivalent ions (La3+) lead to a collapse in which the surface layer is shrinking drastically. Moreover, the collapse transition within the brush layer is accompanied by the onset of an attractive interaction between the particles. All findings will be discussed on the base of MD-simulations that show that the trivalent ions are strongly enriched within the surface layer. Moreover, we present results of an analytical calculation showing the strong ion exchange within the layer.

[1] Pincus, P. Macromolecules 1991, 24, 2912
[2] O. V. Borisov, T. M. Birshtein, E. B. Zhulina, J. Phys. II (France) 1991, 1, 521.
[3] Guo, X.; Ballauff, M. Phys. Rev. E 2001, 64, 051406.
[4] Mei, Y.; Ballauff, M. Eur. Phys. J. E 2005, 16, 341.

# PROTEIN POLYELECTROLYTE COMPLEXES: STRUCTURES, INTERNAL COMPOSITIONS AND CHAIN CONFORMATIONS DETERMINED BY SANS.

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Understanding the mechanisms driving the formation of polyelectrolyte-protein complexes of opposite charges is of a high importance as such complexes are often encountered in biological or industrial issues. A large variety of macroscopic structures can be formed depending on the kinds and strengths of interactions involved in the system. A model system made of lysozyme (positively charged protein) and PSSNa (negatively charged polyelectrolyte) is used and Small Angle Neutron Scattering yields a quite detailed study of this system. Contrast variation and labeling enables to watch separately the protein and the polyelectrolyte inside the complexes and to separate the form of each species from their organization. First, we determine the main structures that can be formed in a system when changing the ratio of negative to positive charges [-]/[+]introduced and the length of the PSS chains at one ionic strength (50mM) and one pH (4.7) [1]. We obtain two main types of structures : (i) For long polyelectrolyte chains, a macroscopic gel is formed and the PSS network still exists but chains are partially shrunk due to cross-linking by lysozyme. (ii) For short polyelectrolyte chains, PSS chains are locally shrunk and do not form a network. Lysozyme and PSS chains are embedded in dense aggregates that arrange in a fractal network. Second, a deeper study of the dense 3-D aggregates formed by small chains is done [2]. Their amount in each species and their water content are precisely determined by matching the contrast of (deuterated) polymer or protein in SANS, yielding the compactness and the inner charge ratio. The complexes show an inner charge ratio always close to 1 and a high compactness. A shell of PSS chains is seen when [-]/[+]introduced > 1. The primary complexes aggregate at a higher scale with a fractal dimension of 2.1 characteristic of Reaction Limited Colloidal Aggregation often found in charged systems. Third, we extend the study of the behavior of the small chains regime to different pH (different charges for the protein) and charge densities on the PSS backbone. For similar [-]/[+]introduced, we obtain a master curve, showing that [-]/[+]inner.~ 1 whatever [-]/[+]introduced. The inner charge stoechiometry of the complexes is thus a general behavior in the system [3]. Finally, the conformation of the chains inside the complexes is determined thanks to a labeling trick and the persistence length is seen to be reduced inside the complexes.

[1] F. Cousin, J. Gummel, D. Ung, F. Boué, Langmuir, 21 (2005) 9675-9688.
[2] J. Gummel, F. Boué, B. Demé, F. Cousin, J. Phys. Chem. B, submitted.
[3] J. Gummel, F. Cousin, F. Boué, in preparation.

# FROM INTERPOLYELECTROLYTE-METAL COMPLEXES TO POLYMER-METAL NANOSYSTEMS

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Complexes of polyamines-transition metal-polycarboxylates were synthesized and their structure, properties and transformations were studied. Such triple complexes were shown to be water soluble or insoluble depending on the ratio of constituent polyelectrolytes and metal. Complexes of polyethyleneimine – $Cu^{2+}$ - polyacrylate were studied in more detail and their structure was determined by ESR. Films of the triple complexes were prepared via sorption of corresponding metal ions ($Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Fe^{2+}$, and so on) by the interpolyelectrolyte complex from aqueous solutions. Ion-exchange capacity was found to be close to the theoretical one for $Cu^{2+}$ ions and slightly lower for other metals. The equilibrium concentration of metal ions is very low so that the sorption proceeds at the ion concentration as low as 10-6 M. Inserting transition metal ions between polyanion and polycation comprising the interpolyelectrolyte complex makes the latter quite stable in alkaline and saline solutions. At the same time metal ions could be set free by the acidification. Metal ions in the wet triple complex films can be reduced to the metal both by electroless and radiochemical reduction. As a result the nanosized metal particles uniformly distributed in the thin films are formed. These materials contain 30-20%wt. of metal. TEM date show that the average size of metal particles is in the interval 3-5 nm, they are amorphous on evidence derived from electron microdiffraction. These metal nanoparticles are easy oxidized in the wet state at the air to form the initial triple interpolyelectrolyte-metal complexes. It opens the possibility to perform multiply reduction-sorption-reduction processes to increase the content of metal particles in interpolyelectrolyte complex matrix. The oxidation of metal nanoparticles does not proceed in the dry nanocomposites. It is possible to prevent the oxidation also in the wet state by the chemical cross-linking of the interpolyelectrolyte matrix via the conversion of some part of interpolymer salt bonds into the covalent amide linkages at the elevated temperature. The structure and properties of the metal nanocomposites such as electron and ion conductivity and magnetizability were studied as well.

# CRITICAL ADSORPTION OF POLYELECTROLYTES ONOT CHARGED SPHERICAL COLLOIDS

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The complexation of charged macroions by oppositely charged polyelectrolytes is a fundamental process in biological systems and many technical applications. Particular examples are the complexation of histone proteins by DNA in nucleosome core particles as well as complexes of polyelectrolytes with charged colloids and micelles. The understanding of the complexation between a polyion and a macroion surface accompanied by screening effects due to counterions and salt posses a major theoretical challenge. Despite significant efforts and progresses, the understanding of charged complexes is still unsatisfactory and lacks behind that of neutral complexes. Certain insight into the complexation process is typically obtained by approximation schemes, e.g., variational calculations, which, however, may lead to controversial results and often apply only in limiting situations such as pointlike particles or large colloidal radii. In this contribution, an exact mean-field solution is presented for the critical adsorption of a flexible polyelectrolyte onto an oppositely charged spherical macroion [1]. Expressions for critical quantities are provided, which are valid for any sphere radius. In particular, in the limit of zero macroion curvature, the results for a planar surface are obtained. In general, we find a significantly different dependence of the critical surface charge density on the Debye screening length than theoretically predicted before, but our predictions are consistent with experimental findings and results of computer simulations. In the strong adsorption limit, when the adsorption energy is large compared to thermal fluctuations of the chain, the adsorbed PE forms well-defined patterns on the sphere surface (rosettes, tennis-ball-pattern, solenoids, etc.). The rearrangement of the PE chains on the sphere is dictated to a large extend by maximization of PE-sphere attraction and minimization of PE-PE repulsion. To determine the interplay between the various energies, usually the superposition of the electrostatic potentials is used, because the calculation of the exact solution for the electrostatic potential and energy created by a nonuniform charge distribution on the sphere can be complicated. Here, results will be presented for certain charge patterns within the Poisson-Boltzmann theory. In particular, the aspect of the overcharging of the complex will be addressed.

[1] R. G. Winkler and A. G. Cherstvy, Phys. Rev. Lett. 96, 066103 (2006)

# THE ROLE OF CHAIN STIFFNESS AND CHARGE DISTRIBUTION IN COMPLEX FORMATION BETWEEN POLYELECTROLYTES AND OPPOSITELY CHARGED COLLOIDS

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We compared the electrostatically-induced binding of small colloids to polyelectrolytes of high persistence length, i.e. chitosan, hyaluronic acid and pectin, with that for more flexible chains of corresponding charge densities, e.g. poly(dimethyldiallylammonium chloride) and copolymers of acrylamide and AMPS. In each case, the onset of complex formation was determined using mixed micelles or proteins with global, or (in the protein case) local, charge opposite to the polymer. The intuitive expectation of higher affinity for the more flexible polymers, also found often in simulations, is tempered by two considerations: (1) the measured persistence length, a reflection of the overall polymer dimenstion per unit contour length, is not necessarily an accurate determinant of local flexibility, and (2) anisotropic colloids such as proteins may present to the polyelectrolyte a complementary charge region of low curvature. For highly flexible chains, the influence of their charge sequence distribution appears to support the ability of loops that facilitate binding while reducing intra-polymer repulsions.

# PH EFFECTS ON WEAK POLYELECTROLYTE AND NANOPARTICLE COMPLEXES INVESTIGATED BY MONTE CARLO SIMULATIONS

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Electrostatically induced interactions between nanoparticles and polyelectrolytes and the resulting complex formation are expected to find important issues (gene therapy, bioengineering, transport of trace pollutants) as well as in industrial applications (purification of water as flocculating water insoluble mixtures). The long range attractive and/or repulsive character of electrostatic interactions between polyelectrolytes and nanoparticles give these complexes specific properties which are partially understood. Owing to the important potential of computer simulations to provide qualitative and quantitative means of understanding the factors that influence polyelectrolytes and nanoparticles interactions, a Monte Carlo approach is used to get an insight into the behaviour of a weak polyelectrolyte with the presence of oppositely charged nanoparticles. By adjusting the solution properties (ionic strength, pH), nanoparticle size and surface charge density, polyelectrolyte persistence length and calculating polyelectrolyte titration curves, it is shown that the presence of oppositely charged nanoparticles significantly modifies the acid/base properties of a weak polyelectrolyte as well as the charge distribution along the polymer backbone and that the solution pH and ionic concentration largely control the polyelectrolyte conformation at the nanoparticle surfaces. Chain stiffness promotes the isolated polyelectrolyte expansion as well as ionization but penalizes the polyelectrolyte adsorption at the nanoparticle surfaces, hence affecting its acid/base behavior. The adsorption/desorption limit as well as the total number of adsorbed nanoparticles which are key parameters for applications in water treatment of polyelectrolyte/nanoparticle mixtures are also investigated.

S. Ulrich, A. Laguecir, S. Stoll: Complexation of a weak polyelectrolyte with a charged nanoparticle. Solution properties and polyelectrolyte stiffness influences. Macromolecules, 2005, 38, 8939-8949

S. Ulrich, A. Laguecir, S. Stoll: Complex Formation between a Nanoparticle and a weak Polyelectrolyte. Monte Carlo Simulations. Journal of Nanoparticle Research 2004, 6, 595-603.

# VERSATILE AND EFFICIENT FORMATION OF NANO-PARTICLES OF POLYSACCHARIDE-BASED POLYELECTROLYTE COMPLEXES

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The research of new gene or drug delivery systems is an exciting challenge not only for biochemists but for physico-chemists as well who find in this application a great opportunity to study the formation of various kinds of structures involving the electrostatic interactions between positive and negative charges of polyelectrolytes. As it was demonstrated in the case of the layer-by-layer approach, these two “bricks” offer unlimited possibilities to built polyelectrolyte complexes (PECs) with well-defined properties. The present contribution focuses on the formation of submicronic particles from the complexation of three charged polysaccharides1-3, chitosan, dextran sulfate and partially N-sulfated chitosan that are a weak polybase, a strong polyacid and a polyampholyte, respectively. The purpose of these biocompatible particles is the in vivo delivery of biomolecules such as DNA, peptides and proteins. A complete study of the complexation conditions was undertaken to point out the relevant parameters affecting the colloidal properties of the particles. The complexation of chitosan and dextran sulfate allows the formation of both cationic and anionic particles through the variation of the molar mixing ratio (n+/n-) of the components. In the case of the amphoteric N-sulfated chitosan, a modification of its charge density with the pH of the media is able to induce the self-complexation of the polymer chains leading to the formation of negatively charged nano-particles. Among the structural parameters of the polymers affecting the hydrodynamic diameter of the PEC particles, the molar mass and the chain flexibility described by the persistence length are the most influent. Others parameters related to medium of the complexation such as the ionic strength or the molar concentration of the polyelectrolytes are less significant. The rate of addition of components is an interesting parameter of the complexation. Traditionally, PECs are formed by adding dropwise the solution of polyelectrolyte to the oppositely charged one 4. Here the one-shot addition of the titrand solution allows to bypass the flocculation of PECs as the molar mixing ratio is close to the unity. Finally, some results tend to prove that PEC particles featured a core/shell structure, the hydrophobic core resulting from the segregation of complexed segments whereas excess component in the outer shell ensured the colloidal stabilization against further coagulation.

[1] Schatz, C. ; Lucas, J.M. ; Viton, C. ; Domard, A. ; Pichot, C. ; Delair, T. Langmuir 2004, 20, 7766
[2] Schatz, C.; Domard, A. ; Viton, C. ; Pichot, C. ; Delair, T. Biomacromolecules 2004, 5, 1882
[3] Schatz, C. ; Bionaz, A. ; Lucas, J-M ; Pichot, C. ; Viton, C. ; Domard, A. ; Delair, T. Biomacromolecules 2005, 6, 1642
[4] Dautzenberg, H. Macromolecules 1997, 30, 7810

# POLYELECTROLYTES IN MICROEMULSIONS: REDUCING, REGULATING AND STABILIZING AGENTS FOR THE NANOPARTICLE FORMATION

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Our research activities were focused on the solubilization of polyelectrolytes (PEL) in water-in-oil microemulsions, and their use as templates for the controlled formation of spherical nanoparticles with diameter smaller than 10 nm. Cationic polyelectrolytes, i.e. poly(diallyldimethylammonium chloride) (PDADMAC) or poly(ethylene imine) (PEI), and anionic polyelectrolytes like polyacrylates (PAA) or carboxymethylcellulose (CMC) can be incorporated into w/o microemulsions without a macroscopic phase separation. Polyelectrolytes of low molar mass can be solubilized in the individual microemulsion droplets, and especially electrostatic interactions between the functional groups of the PEL and the surfactant head groups can increase the stability of the surfactant film, as well as the water solubilization capacity. Therefore, in presence of PEL`s a boostering effect can be observed, and the formation of a bicontinuous phase channel can be induced. The polyelectrolyte-modified microemulsions can be used as a new type of template for the nanoparticle formation. Therefore, the PEL can control the shape and form of the nanoparticles produced, and can stabilize the nanoparticles against coagulation during the solvent evaporation and redispersion process. One can show, that for example PDADMAC-stabilized spherical bariumsulfate nanoparticles of about 6 nm can be redispersed from a sulfobetaine-based microemulsion. In a mixed phosphatidylcholin/sodiumdodecylsulfate (SDS) based microemulsion in presence of PDADMAC the formation of larger aggregates can be suppressed and barite nanoparticles (6 nm in size) can be redispersed. Branched PEI can be used as a reducing and stabilizing agent for the gold nanoparticle formation in a SDS-based microemulsion. After solvent evaporation, PEI-stabilized gold nanoparticles of 8 nm can be redispersed.

J. Koetz, J. Bahnemann, S. Kosmella,
Influence of a Cationic Polyelectrolyte on the Inverse Micellar Region of the Ternary System Sulfobetaine/Water/Alcohol
Journal of Polymer Science:Part A: Polymer Chemistry, Vol. 42 (2004) 742-751

# POLYELECTROLYTE COMPLEXES FORMED IN SEMIDILUTE SOLUTIONS

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Complexes of polyelectrolytes (PE) and different kinds of oppositely charged species (surfactants, macroions, block-copolymers) were studied in semidilute concentration regime. PE studied were poly(acrylic acid) (PAA), poly(diallyldimethylammonium chloride) (PDADMAC), poly(methacrylic acid) (PMAA), poly(ethylene imine) (PEI). PDADMAC, tetradecyltrimethylammonium bromide (TDTMAB), sodium dodecylsulfate (SDS) and polystyrene-block-poly-N-ethyl-4-vinylpyridinium bromide (PS-b-PEVP) were used as complex-forming agents. Dilute-semidilute regime crossover concentrations (C*) in PE solutions were determined by static and dynamic light scattering. Both methods show the change of thermal motion mechanism at C*, while no changes in the mechanism of viscous flow were observed in crossover region. The fluctuative network of entatglements formation occurs at much higher concentration (Ce) as it is shown by viscosity measurements. So two different areas exist in PE solutions: semidilute solution without entanglements (at C*<CCe). The difference between C* and Ce becomes negligible when ionic strength increase or the chain charge decrease. Polyelectrolyte complexes (PEC) in dilute solutions represent individual particles, containing one or several PE chains, i.e. PEC may exist in chain-dispersed or in associated form. Chain-dispersed PEC particles are formed in systems PAA - TDTMAB, PEI - PAA (at pH=5); associated PEC particles appear in PDADMAC - SDS, PMAA – PS-b-PEVP, PEI – PAA (at pH=10) mixtures. In any case the transition from dilute to semidilute solution regime leads to the sharp increase of PEC solutions viscosity and to the appearance of viscosity anomaly. Viscometry data show the network formation in PEC solutions at C*<CCe two-level structure is formed: electrostatic network coexists with entanglement one. The work was supported by the Russian Foundation for Basic Research, grant 06-03-32964.

# ALLYLAMINE BASED POLYAMPHOLYTES

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Noteworthy, cyclopolymerization of allylamine, diallylamine and N-substituted diallylamine with maleic acid yields chemically stable linear and crosslinked polyampholyte systems with regular structure. These polyampholytes are based on low-priced commercial products. In the present communication the synthetic strategy, solution properties and application aspects of alternating polyampholytes based on N,N-dimethyldiallylammonium chloride and maleic acid, N,N'-dimethyldiallylammonium and alkyl (aryl) substituted maleamic acids as well as poly(N,N'-diallyl-N-octadecylamine-alt-maleic acid) are reported. The influence of pH, ionic strength and water-organic solvent mixtures on the viscosity of polyampholytes was shown. The swelling-deswelling behavior of an amphoteric gels composed of maleic acid, N,N'-dimethyldiallylammonium chloride and diallylamine was studied in aqueous and aqueous-salt solutions. Dynamic swelling properties of amphoteric gels in water with and without added salts were measured at various pH including the isoelectric point. The ability of amphoteric gels to swell in saline water allowed to recommend them for application in secondary oil recovery and water desalination. The hydrophobically modified polyampholytes proved to be an efficient pour point depressant, to inhibit the deposition of wax, and to improve the viscosity of waxy crude oils.

[1] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric betaines: Synthesis, characterization and application. Adv.Polym.Sci. 201, 2006.
[2] S. E. Kudaibergenov Polyampholytes: synthesis, characterization and application. New York, Kluwer Academic/Plenum Publishers, 2002, 220 p.

# CHARGE REVERSAL OF COLLOIDAL PARTICLES

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A theory [1,2] and simulations will be presented for the effective charge and zeta ptential of colloidal particles in suspensions containing multivalent counterions. It will be shown that if colloids are sufficiently strongly charged, the number of condensed multivalent counterion can exceed the bare colloidal charge leading to charge reversal. Charge renormalization in suspensions with multivalent counterions depends on a subtle interplay between the solvation energies of the multivalent counterions in the bulk and near the colloidal surface. We find that the effective charge is {\it not} a monotonically decreasing function of the multivalent salt concentration. Furthermore, contrary to the previous theories, it is found that except at very low concentrations, monovalent salt hinders the charge reversal. This conclusion is in agreement with the recent experiments and simulations.

[1] Y. Levin, Rep. Prog. Phys. 65, 1577 (2002)
[2] S. Pianegonda, M. C. Barbosa, and Y. Levin, Europhys. Lett. 71, 831 (2005)

# ADSORBED DENDRITIC POLYELECTROLYTES: INTERACTION FORCES AND ELECTROKINETICS

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The adsorption of higher generation poly(amidoamine) (PAMAM) dendrimers onto flat substrates has been studied by AFM as function of ionic strength and pH. The observed trends in the surface coverage are well described within the effective hard sphere model for random sequential adsorption (RSA). These surfaces, although of random nature, exhibit characteristic length scales in the nanometer range for the distances between adsorbed dendrimer molecules. This approach can be applied not only to flat substrates, but also to colloidal particles. The interaction forces between such heterogeneously charged surfaces were determined by the colloidal probe technique based on the AFM. At large separation distances the interaction forces could be described in terms of diffuse layer overlap with smeared-out charge distributions. By determining the interaction forces between PAMAM-coated colloidal particles in the sphere-sphere geometry, we could demonstrate that the Derjaguin approximation is fulfilled under these conditions. At smaller separation distances the patch charges lead to attractive forces. The results from the direct force measurements can be compared to the ones obtained from the electrophoretic mobility of dendrimer-covered latex particles. By varying the dendrimers dose the surface coverage has been varied, while at the same time the amount of adsorbed dendrimers has been determined by AFM.

# BULK AND INTERFACIAL STUDIES OF POLYELECTROLYTE-SURFACTANT INTERACTIONS: DNA AND OTHER AMPHIPHILIC POLYELECTROLYTES

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The interaction between polyions and oppositely charged amphiphilic ions involves a combination of hydrophobic and electrostatic forces. On the basis of a review of polymer-surfactant association in bulk, the behavior of these mixed systems on solid surfaces is discussed. In particular, we consider the adsorption of mixtures of polyelectrolytes and oppositely charged surfactants on polar and nonpolar surfaces. It is found that, depending on concentration, an ionic surfactant can either induce additional polyion adsorption or induce desorption. Kinetic control of adsorption and, in particular, desorption is typical. Important consequences of this include increased adsorption on rinsing and path dependent adsorbed layers. As an example of an amphiphilic polyelectrolyte we studied DNA. DNA induces surfactant-self-assembly and adsorbs on hydrophobic surfaces, with a low adsorbed amount and with an extended conformation. On addition of a cationic surfactant, the adsorbed amount increases strongly at the same time as DNA compacts. As the surfactant is removed, DNA decompaction may occur. On a hydrophilic anionic surface DNA does not adsorb but adsorption can be induced by a cationic surfactant. Various aspects of the interfacial behaviour of mixed DNA-surfactant systems are presented. These include the study of adsorption on hydrophobic and hydrophilic surfaces by ellipsometry, and the forces between DNA-covered surfaces by surface force apparatus. Different surfactant types are studied including the combination of cationic and anionic surfactant. Both thermodynamic and kinetic aspects are included. Kinetics play a crucial role as shown by an effectively irreversible DNA adsorption.

# SYNTHESIS OF BLOCK COPOLYMER IONOMERS BY CONTROLLED FREE RADICAL POLYMERIZATION, AND THEIR SELF-ASSEMBLY IN AQUEOUS MEDIA

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The diverse methods of controlled free radical poymerization have not only opened an additional and convenient access to block copolymers. They have also enlarged the pool of useful monomers for such polymers considerably. In particular for charged monomers, radical polymerization is much more tolerant than the other established methods, and thus enables the use of up to now unpracticable building blocks. We are currently exploiting these opportunities to prepare novel diblock and triblock tercopolymers containing ionic hydrophilic blocks. Emphasis is given to styrenic as well as acrylic monomers. Our prefered method is the so-called RAFT technique, which is well compatible with most ionic monomers, including sulfonic acids and quaternized ammonium compounds [1]. Moreover, the RAFT method can be performed in water. For the latter case, pH-independent water-soluble RAFT agents were developed [1,2]. Alternatively, uncharged reactive block copolymers are synthesized first, which are transformed into ionic polymers by chemical modification in a second step [3]. Despite some inherent limitations, this strategy simplifies polymer analysis considerably. Furthermore, this strategy is also very practical for the synthesis of charged amphiphilic block copolymers. The direct synthesis of such block copolymer ionomers still poses a particular challenge, but can be realized, too, without the use of protecting groups [2]. The synthesized charged block copolymers were studied with respect to their self-organization in aqueous media [2-5]. Appropriate design of the block copolymer structure enables the fabrication of novel amphiphiles showing complex effects. This comprises for instance internal nanostructuration of micelles and vesicles [3]. Also, stimuli-sensitive associative systems can be prepared [4,5]. Beyond carefully designed diblock copolymers, triblock tercopolymers provide in particular a versatile access to multiple stimuli-sensitive systems. They can undergo stepwise aggregation [5], or can show "schizophrenic" behavior [4,5]. The synthetic strategies and typical problems encountered are discussed, and the rich micellar self-organization of the diblock- and tricopolymers is presented.

[1] M. Mertoglu, A. Laschewsky, K. Skrabania, C. Wieland, Macromolecules (2005), 38, 3601
[2] S. Garnier, A. Laschewsky, Macromolecules, (2005) 38, 7580
[3] S. Kubowicz, J.-F. Baussard, J.-F. Lutz, A. F. Thünemann, H. von Berlepsch, A. Laschewsky, Angew. Chem. Int. Ed. (2005) 44, 5262
[4] Arotçaréna, B. Heise, S. Ishaya, A. Laschewsky, J. Am. Chem. Soc. (2002) 124, 3787
[5] M. Mertoglu, S. Garnier, A. Laschewsky, K. Skrabania, J. Storsberg, Polymer (2005) 46, 7726

# EFFECTS OF POLYION CHARGE DENSITY ON POLYION-SURFACTANT ION COMPLEX MORPHOLOGY

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Mixtures of polyelectrolytes and oppositely charged surfactants in aqueous solution phase separate into a dilute phase and a concentrated phase, where the concentrated phase contains most of the polyion and the surfactant. In our lab we have been using the stoichiometric alkyltrimethylammonium surfactant- poly(acrylate) “complex salts” [1, 2] system as simple model systems for investigating the maximum water uptake and the morphology of the resulting complexes. In this work we have investigated the effect of the polyion charge density on the phase behaviour and morphology of cetyltrimethylammonium salts with counterions consisting of copolymers of polyacrylate with uncharged comonomers. To investigate this effect we have used two different approaches; the mixtures of the stoichiometric polyelectrolyte-surfactant complex with additional poly(acrylic acid) in water and the synthesis of random copolymers with charged and uncharged monomers. Two different uncharged monomers were chosen for the random copolymers (NIPAM and DAM); this choice was made so that one was more hydrophobic (NIPAM) than the other less hydrophobic (DAM). The effect of polyion charge density on maximum water uptake and complex morphology is discussed. In both approaches a disordered isotropic phase dominates at low polyion charge density while a cubic liquid crystalline phase dominates at higher polyion charge densities. This qualitatively similar behaviour between the two different approaches is discussed along with the quantitative differences between them.

[1] Svensson et al J. Phys Chem B 2002 106 1013-1018
[2] Svensson et al J. Phys Chem B accepted

# CHARGE CHARACTERISTICS AND STRUCTURAL TRANSITIONS OF POLYELECTROLYTE LAYERS REVEALED BY MICROSLIT ELECTROKINETIC EXPERIMENTS

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Polyelectrolyte (PE) layers are often applied in aqueous environments. In these cases the formation of interfacial electric charge often determines the characteristics of the PE/solution interface. To study surface charge characteristics of flat solid/liquid interfaces we introduced the Microslit Electokinetic Set-up (MES) - a device for the determination of zeta potential and surface conductivity. The potential of microslit electrokinetic measurements for the characterisation of PE layers is demonstrated with selected examples: (i) The electrical properties of poly(acrylic acid) (PAA) brushes were analyzed using the MES. The surface conductivity of these brushes is enormous in case of complete dissociation, accounting for more than 93% of the total measured surface conductivity. However, the mobility of the ions within the brush was estimated from the density of the carboxylic acid groups and surface conductivity data to be only about 14% of that of free ions. (ii) Charge formation and structural transitions of poly(L-glutamic acid) (PGA) layers were studied in KCl solutions of different ionic strength. The data permit to conclude that the helix coil transition as observed for PGA in solution also occurs within the grafted PE layers. The ion mobility within the layer was calculated based on surface conductivity data and optical measurements (ellipsometry) for the case of complete dissociation. The data indicate that the mobility of the ions is reduced to the same extend as in case of the PAA brush.

# POLYELECTROLYTE COMPLEX FORMATION BETWEEN ANIONIC AND CATIONIC NANOGELS IN SALT-FREE AQUEOUS SOLUTION

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Our previous studies [1-5] have demonstrated that polyelectrolyte nanogels based on N-isopropylacrylamide (NIPA) are stably dispersed in both salt-free and salt-containing aqueous solutions even when their charges are fully eliminated. Here, we studied the complex formation in an aqueous salt-free system (pH~3 and at 25 °C) between nanogel particles whose charges are opposite each other. We used anionic gel (AG) and cationic gel (CG) particles consisting of lightly crosslinked NIPA copolymers with 2-acrylamido-2-methylpropane sulfonic acid and with 1-vinylimidazole, respectively. The number of charges per particle was -4,490 for AG and + 20,300 for CG, as estimated from their molar masses (3.33 MDa for AG and 11.7 MDa for CG) by static light scattering and their charge densities (1.35 mmol/g for AG and 1.74 mmol/g for CG) by potentiometric titration. The complexes were formed through addition of AG to CG and vice versa, using turbidimetric titration technique. At the endpoint of the titration, the complex as an aggregate formed based upon "stoichiometric charge neutralization." Further studies of the resulting complexes in the different stages of the titration provided the following aspects: (i) Addition of AG with a hydrodynamic radius (Rh)~119 nm to CG (Rh~156 nm) results in the complex free from aggregation; (ii) In this process, the increase in the added amount of AG leads to a decrease in the Rh of the complex from 156 nm to 80 nm, but an increase in the molar mass from 11.7 MDa to 24 MDa. (iii) When CG was added to AG until 50~60 % of AG is consumed in the complexation, however, the resulting complex has the same size (Rh~80 nm) and the same molar mass (55± 2.5 MDa). To understand these results, we used the following two different models: 'Random model (RM)' in which the added AG particles uniformly bind to all of CG particles in the system via a strong electrostatic attraction; and 'all-or-none model (AONM)' in which a part of the AG particles in the system preferably binds to the added CG particles to neutralize their electric charges, but the other part of AG is uncomplexed and remaining in the system. The complex formations upon addition of AG to CG and of CG to AG were elucidated in terms of RM and AONM, respectively. Also elucidated with these models were the results of electrophoretic light scattering.

[1] Suzuki, H.; Wang, B.; Yoshida, R.; Kokufuta, E. Langmuir 1999, 15, 4283.
[2] Ito, S.; Ogawa, K.; Suzuki, H.; Wang, B.; Yoshida, R.; Kokufuta, E., Langmuir 1999, 15, 4289.
[3] Ogawa, K.; Nakayama. A.; Kokufuta. E. Langmuir 2003, 19, 3178.
[4] Ogawa, K.; Nakayama. A.; Kokufuta. E. J. Phys. Chem. B 2003, 107, 8223.
[5] Ogawa, K.; Sato, S.; Kokufuta. E. Langmuir 2005, 21, 4830.

# PROPERTIES OF PH- AND THERMO SENSITIVE POLYELECTROLYTE MICROGELS

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Thermo- and pH-sensitive microgels combine the charged character of polyelectrolytes and the stimuli-responsive behavior of PNIPAM micro-gels. To build polyelectrolyte microgels N-Isopropyl-acrylamide (NIPAM) is co-polymerized with charged monomers in a batch synthesis. These microgels are then characterized first by pH and conductometric titration. In addition the adsorption behavior of different polyelectrolytes on these microgels is investigated by polyelectrolyte-titration and zeta potential measurements. The results give interesting insights in the interaction between linear polyelectrolytes and charged crosslinked polyelectrolyte-microgels. A second field of investigation is the interaction of polyelectrolyte-microgels and oil/water interfaces. Microgels show pH and temperature adjustable interface behavior due to the different amount of charges. This will lead to a new class of intelligent, functional surfactant-like polyelectrolytes.

# BIOINTERACTIVE FIBRES

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Physical surface engineering with the aid of high molecular weight compounds are of increasing interest for the development of functional materials. Polymers and more specifically polyelectrolytes have also gained attention as a new class of antibacterial agents to prevent the outbreak of bacterial colonization on surfaces, to limit the risk of infection, and also to avoid problems related to for example odour. In the present work the physical adsorption of antibacterial polyelectrolytes on model surfaces has been studied in terms of antimicrobial efficiency. Different functional weak polyelectrolytes have been tested against both gram positive and gram negative bacteria in aqueous solution. The polyelectrolytes exhibiting good antibacterial activity were further evaluated in the immobilised state on solid surfaces. In these experiments the polyelectrolytes were adsorbed onto an oxidized cellulose dialysis membrane that was subsequently tested for antibacterial activity. In order to increase the amount of adsorbed polymer, which would be positive for the antibacterial activity, the polyelectrolyte multilayer technique was used as surface treatment. The antibacterial activity of the treated surfaces was then studied as a function of the amount of functional polyelectrolyte immobilised on the surface. An alternative to the multilayer technique would be to increase the surface charge and to increase the salt concentration during the adsorption. This could easily be achieved with the dialysis membrane approach since the charge of the membrane could be increased by oxidation of cellulose in the membrane to different degrees. By using cellulose membranes as a model surface an optimal value can be found regarding the number of layers and surface charge of the membrane. This can in turn be related to the antibacterial efficiency. The value of the antimicrobial activity shows the difference in viable cell count between a treated material and an untreated material after inoculation and incubation of bacteria.

# POLYELECTROLYTE MOLECULES AT INTERFACES: ATOMIC FORCE MICROSCOPY STUDY

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Due to a long-range character of electrostatic interactions a behavior of single (isolated) polyelectrolyte (PE) chain could be considerably different from the behavior of PE chains within an ensemble of entangled and strongly interacting each other molecules. Because of technical limitations, most of conventional methods (scattering techniques, etc.) usually operate with relatively concentrated PE solutions that precludes understanding of individual molecules. Atomic Force Microscopy (AFM) gives rather unique opportunity in investigations of individual adsorbed PE molecules in both dry state and in solutions; at the same time a description of the collective behaviour of the molecules is also possible through a statistical treatment of the data. However, the adsorption and possibly some other processes occurred during a sample preparation procedure, inevitably cause altering of the chain conformations. Therefore, the understanding of the question, how the! chain conformation observed by AFM correlates with the “solution” conformation, is one of the main issue that will be in the focus. This contribution will overview our recent results in the AFM-study of polyelectrolytes.

# BINDING OF SIMPLE AND SURFACTANT COUNTERIONS BY ISOTACTIC POLY(METHACRYLIC ACID): COMPARISON WITH ATACTIC POLY(METHACRYLIC ACID)

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Isotactic poly(methacrylic acid), i-PMA, exhibits distinctively different solution behavior in comparison with the usual form of PMA, the so-called conventional or atactic PMA, a-PMA. This may be concluded on the basis of a rather limited number of studies on i-PMA [1-5]. Some of the above mentioned differences are the following: (a) i-PMA is a weaker acid than a-PMA; (b) it is insoluble in water below a certain critical degree of ionization [1,2]; (c) potentiometric titration curves of i-PMA show irreversible behavior [3]; (d) there are indications that i-PMA binds counterions to a different extent than a-PMA [4]. In this contribution, we investigate the influence of chain stereoregularity on the binding of simple (sodium, Na ) ions by two forms of PMA, a highly isotactic surfactant (cetylpyridinium, CP PMA and an atactic PMA with a known composition in triad content. Studies were performed at various degrees of neutralization of carboxyl groups on the polyion ranging form 0 to 1. Binding of simple counterions was studied by the help of osmotic coefficient measurements, whereas binding of surfactant ions was evaluated through potentiometric measurements utilizing surfactant-selective membrane electrodes [5]. Surprisingly, the experimental values for osmotic coefficients are very similar and do not suggest any differences in binding of simple monovalent counterions by both stereoregular forms. The experimental osmotic coefficients were compared with predictions of the cell model using cylindrical symmetry. The dimensions of the polyion needed for the calculation were obtained from molecular orbital calculations (see below). On the contrary, pronounced differences were found for the binding of surfactant counterions by i-PMA and a-PMA. At the onset of cooperative binding, the association is stronger with i-PMA as demonstrated by lower critical aggregation concentration, CAC, values and higher values of cooperativity parameters. In contrast, more surfactant is bound by a-PMA in the region where polyion becomes saturated with surfactant ions. The difference is between 20 and 30 %. Results of surfactant ion binding were interpreted by taking into account local chain conformations as obtained from quantum mechanical semiempirical molecular orbital calculations. Greater hydrophobicity and possibly higher charge density of i-PMA on one hand and more flexibility of a-PMA chain on the other are held responsible for these observations.

[1] van den Bosch, E.; Keil, Q.; Filipcsei, G.; Berghmans, H.; Reynaers, H. Macromolecules 2004, 37, 9673-9675.
[2] Loebl, E. M.; O'Neill, J. J. J. Polym. Sci. 1960, 45, 538-540.
[3] Leyte, J. C.; Arbouw-van der Veen, H. M. R.; Zuiderweg, L. H. J. Phys. Chem. 1972, 76, 2559-2561.
[4] L. Costantino, V. Crescenzi, F. Quadrifoglio, V. Vitagliano J. Polym. Sci. Part A-2 1967, 5, 771-780.
[5] Vlachy, N.; Dolenc, J.; Jerman, B.; Kogej, K. J. Phys. Chem. 2006, accepted.

# POLYELECTROLYTE MICROCAPSULES WITH PERMEABILITY, ADHESION AND MECHANICS TUNED VIA IONIC MILIEU AND TEMPERATURE

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Adapting the well-established method of film formation by consecutive adsorption of oppositely charged polyelectrolytes to coat sacrificial colloidal templates one obtains hollow micro- and nanocapsules of defined wall composition (in the nm range), surface and diameter. This enables fine tuning of properties, notably permeability adhesion and mechanics. We will concentrate on controlling of these properties via ionic milieu and temperature, measured by confocal optical and soft X-ray microscopy and colloidal probe force spectroscopy. It is shown that the permeability for macromolecules can be switched via pH and salt, because the internal charge compensation of the polyelectrolyte complex is disturbed. This also affects the mechanical properties, i. e. the Youngs modulus decreases with increasing salt concentration, an! d the effect depends on type of salt qualitatively along the Hoffmeister series. For the system polystyrene sulfonic acid/polydiallyldimethyl ammonium chloride a thermal glass transition near 40 $^{o}$C was observed. It is manifested in an irreversible reduction of capsule diameter, increase of wall thickness, decrease of water content and reversible change of the elastic modulus by two orders of magnitude. The selective adhesion can in turn be established via the outer charge which, in combination with micropatterning, can be used to arrange these capsules on well-defined arrays which may be used for combinatorial arrays.

# DIFFUSION AND BINDING OF PROBE MOLECULES IN SUB-MICRON POLYELECTROLYTE CAPSULE DISPERSIONS MEASURED USING PFG-NMR

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Pulsed field gradient NMR (PFG-NMR) is employed to probe the distribution and dynamics of probe molecules in colloidal dispersions of sub micron hollow polymeric capsules. The capsules are prepared using the layer-by-layer (LBL) self-assembly method of polyelectrolytes onto silica particles, followed by a dissolution of the silica core in hydrofluoric acid. The capsules are permeable for water and small ions, but large molecules, such as polydextran, are found to be in slow exchange between two sites, the capsule interior and the exterior [1]. 1H spin-spin (T2) and spin-lattice (T1) relaxation times of the encapsulated dextran are estimated from combined diffusion-relaxation measurements. The diffusion and relaxation behaviour is explained by a two- site model of free and bound molecules in slow exchange. With both relaxation times the population in either site is calculated and the state of the encapsulated dextran is discussed. Though a high concentration of encapsulated dextran is found, the dextran appears to be in a liquid-like state rather than being immobilized on the capsule wall. On the other hand, small probe molecules such as phenol rapidly exchange through the capsule wall. Here, diffusion echo decays are single exponentials, proving the fast exchange. 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 influenced by an ultrafast relaxation of the bound component. 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. The diffusion and relaxation behaviour is finally analysed by a two- site model of free and bound molecules, where the model is specifically adjusted to the case of ultrafast relaxation of the bound component.

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[1] Adalsteinsson, T.; Dong, W. F.; Schönhoff, M. J. Phys. Chem. B, 108(52), 2004, 20056.

# SOFT AND POROUS THERMORESPONSIVE BUILDING BLOCK FOR LAYER-BY-LAYER ASSEMBLY OF POLYELECTROLYTE MULTILAYERS

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The layer-by-layer (LbL) technique has been devised by Decher [1] in the early 1990s and involves the sequential adsorption of polyanions and polycations onto a charged surface. One of the many advantages of this technique is that it is not restricted by the shape or nature of the substrate. Early works have involved adsorption of polyions on planar substrates, then Sukhorukov [2] and Caruso [3] demonstrated that three dimensional adsorption is possible using spherical particles. Only recently, Caruso [4] successfully uses the LbL technique to coat mesoporous silica particles. So far, polyelectrolyte multilayers have been adsorbed on hard and solid surfaces. In this work we propose to adsorb polyelectrolyte multilayers on soft and porous surfaces of a thermoresponsive poly(N-isopropylacrylamide) (PNiPAM) microgel [5]. We report the optimum conditions for sequential adsorption of polycations and polyanions on different building blocks depending on the location of the charge: (i) neutral core of cross-linked PNIPAM, (ii) a charged core of P(NiPAM-co-AA), AA being acrylic acid, (iii) a core-shell system composed of a neutral PNIPAM core and a charged P(NIPAM-co-AA) shell [5], and (iv) its inverse system composed of a charged P(NIPAM-co-AA) core and a neutral PNIPAM shell. The swelling and deswelling of the microgel after successive layer deposition is followed by measuring the hydrodynamic radius RH using dynamic light scattering, DLS. DLS study reveals that adsorption is template-dependent. Electrophoretic measurements reveal successful charge reversal after deposition of successive polyelectrolyte layer, and confirmed the build-up of the polyelectrolyte multilayers on the microgels. A fluorescent-labelled polyelectrolyte, P(DADMAC-rand-DAPA-labelled rhodamine B) has been used within the multilayer to successfully prove that LbL is possible on soft and porous building blocks.

[1] Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992 , 210, 831.
[2] Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, M.; Buddle, A.; Möhwald, H. Colloids Surf. A 1998, 137, 253.
[3] Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Möhwald, H. Angew. Chem., Int. Ed. 1998, 37, 2201.
[4] Wang, Y.; Caruso, F. Angew. Chem. Int. Ed. 2005, 44, 2888.
[5] Greinert, N.; Richtering, W. Colloid Polym. Sci. 2004, 282, 1146.

# VISUALIZING THE INTERACTION BETWEEN MICROGELS AND OPPOSITELY CHARGED POLYPEPTIDES.

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In the last decade the number of protein and peptide drugs on the market and in clinical trial has increased strongly. Such substances can be difficult to administer to their site of action due to a number of complications and the need to develop functional transporter systems is therefore a fact. One interesting system, playing an important role in nature, e.g., in cellular secretion of hormones and other transmitter substances, is based on polyelectrolyte networks that are able to store large amounts of oppositely charged substances in a small volume and release them upon swelling. Analogously, microgels show a highly cooperative and fast volume transition in response to external stimuli which makes them interesting for storing and administering protein/peptide drugs in a protected environment. We study the interaction of lightly cross-linked poly(acrylic acid) microgel particles with oppositely charged poly-L-lysine (pLys). Our main focus is to investigate the effects of peptide size, pH and salt concentration on the binding, transport and distribution of pLys in gel particles and thereby also to outline the details of the de-swelling process that occur in the polymer network in response to electrostatic binding of pLys. By studying gel particles in the µm-range we are able to straightforwardly visualize the interactions using experimental setups such as micromanipulator-assisted light microscopy and confocal microscopy. We are also interested in changes in peptide conformation upon binding for which circular dichroism spectroscopy is a useful technique. The de-swelling of microgels on incorporation of oppositely charged pLys is strongly influenced by the peptide distribution within the gel particles. This distribution depends trivially on the peptide size, such that a large peptide is excluded from the gel core and restricted to a shell region. More importantly, such inhomogeneous distributions may be reached also in cases where electrostatic interaction between the gel network and the peptide is strong, notably at large charge contrast and low electrostatic screening. The kinetic aspect, that is the transport and distribution of pLys in the gel particles during the de-swelling process, is highly influenced by the salt concentration. A large peptide size and a neutral to high pH is a prerequisite for a significant change in conformation (random coil to α-helix) for pLys upon interaction with poly(acrylic acid) microgels.

# STRUCTURE AND DYNAMICS OR BLOCK IONOMER COMPLEXES

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Our studies during last decade focused on functional polyelectrolyte-based nanomaterials – block ionomer complexes (BIC). These materials have attracted significant attention due to their potential applications in biomedical fields such as delivery of drugs, proteins, and DNA. BIC display three major characteristics. First, they spontaneously form as a result of electrostatic coupling of block or graft polyelectrolytes with oppositely charged molecules including synthetic polyions, DNA, proteins, surfactants, and metal ions. Second, they are stable in aqueous dispersions and have a defined structure with hydrophobic core and hydrophilic shell. Third, they can participate in cooperative polyion interchange reactions with other polyelectrolyte components present in solution resulting in sharp structural transitions. Although these reactions are of great importance for the self-assembly and practical use of BIC no systematic studies in this area have been conducted so far. We use fluorescence techniques to determine rates and directions of these reactions and understand the contribution of the core-shell architecture of BIC to their dynamic properties. Two types of BIC dispersed in aqueous media are studied. The first type is the complexes with insoluble polyion complex core and hydrophilic corona. These BIC are synthesized by reacting "double hydrophilic" block polyelectrolytes containing polyion block and water-soluble nonionic block, such as poly(ethylene oxide), with polyions of opposite charge. Alternatively block polyelectrolytes are first reacted with a condensing agent to produce micelles with cross-linked ionic cores and then these micelles are reacted with the polyions to form the BIC. The second type is the complexes formed by amphiphilic block copolymers containing polyion block and water-insoluble nonionic block, such as polystyrene. Such block polyelectrolytes form micelles with hydrophobic polystyrene core and polyion corona. Addition of oppositely charged polyelectrolytes to these micelles results in formation of BIC with polystyrene core, surrounded by insoluble polyion complex layer and a charged shell of the polyion present in excess. We acknowledge the support of the National Science Foundation DMR-0513699.

# CONTRASTING THE ROLE OF CHITOSAN VALENCE AND CHITOSAN CHARGE DENSITY IN POLYELECTROLYTE COMPLEXATION

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The formation of polyelectrolyte complexes upon mixing of polycations and polyanions is well-known. However, the influence of molecular parameters on the complexation process is still not fully understood. It has been suggested that one important parameter is the polycation charge. Here the influence of chitosan charge density on the formation of complexes with polyanions as compared to total polycation charge was investigated. Two sets of chitosans, each with chitosans of ~ equal valence (charge per molecule) but differing in their charge density were employed to compact the semiflexible polyanions DNA and xanthan. For each chitosan, the degree of ionization was also varied by changing the pH. The resulting complexes were studied with respect to size, zetapotential and morphology. Additionally for DNA-chitosan complexes, the complexation was followed by the ethidium bromide exclusion assay. While all chitosans were able to complex the polyanions, quantitative analysis showed that the relative amount of structures formed depended on the molecular parameters of the chitosan sample. The overall trends in the results indicate that decreasing the chitosan molecular charge density resulted in an apparent increased association constant between chitosan and the polyanion. This finding was consistent for both polyanions, showing that this is not specific to the DNA-chitosan interaction. Furthermore, changes in pH affected the complexes differently than changing the molecular charge density of chitosan.

# COMPLEXES OF POLYELECTROLYTE-NEUTRAL DOUBLE HYDROPHILIC BLOCK COPOLYMERS WITH SURFACTANTS, POLYELECTROLYTES AND PROTEINS

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Double hydrophilic block copolymers with sodium poly[sulfamate-carboxylate)-isoprene] polyelectrolyte blocks and poly(ethylene oxide) neutral blocks were synthesized by a combination of anionic polymerization and post polymerization functionalization methodologies. The presence of the anionic polyelectrolyte block facilitates formation of complexes with dodecyltrimethylammonium bromide, a low molecular weight cationic surfactant, with quaternized poly(2-vinylpyridine), a cationic polyelectrolyte, as well as with lysozyme, a globular cationic protein at physiological pH. Soluble complexes are formed in aqueous solutions with appropriate choice of the structural characteristics of the double hydrophilic block copolymer and of the stoichiometric ratios. The self-assembly properties of these complexes formed in the different cases are studied using a gamut of physicochemical techniques, including static, dynamic and electrophoretic light scattering, fluorescence spectroscopy and atomic force microscopy. Their structural aspects are investigated as a function of the physicochemical parameters of the systems like stoichiometry, pH and ionic strength. The investigated systems can serve as models for the design of functional polyelectrolyte based colloids.

[1] S. Pispas J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 606.

# SURFACTANT-POLYELECTROLYTE INTERACTION IN CROSSLINKED POLY(ACRYLIC ACID) GELS

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Earlier studies have shown that gels based on crosslinked poly(acrylic acid) spontaneously absorb cationic surfactants [1]. The strong interaction between the cationic surfactant micelles and the anionic polyacrylate network [2] limits the osmotic swelling of the gels, resulting in volume changes of up to 100 times compared to a surfactant free system. Since the amount of surfactant available is kinetically limited, the entire gel cannot collapse at once. Instead, the outer part of the gel will collapse first, forming a dense, rubber-like skin around a swollen core [3]. For microgels and dodecyltrimethylammoniumbromide (DoTAB), the deswelling can be successfully modeled using ion exchange kinetics [4]. Since the two phases formed (skin and core) are part of the same network, they cannot separate like the non-crosslinked polymer would and they therefore influence each other's equilibrium states, resulting in a less swollen core and less dense skin [4]. Describing the partial collapse of the network as well as the deswelling kinetics is crucial to understanding the interaction of the surfactant and the crosslinked polymer. We have now studied the interaction of dodecyl- and cetyl-trimethylammonium bromide with both millimeter and micrometer sized crosslinked poly(acrylic acid) gels. In the kinetic studies we have compared our experimental data (gel volume versus time) with calculations based on a semi-empirical model [5], using the experimental parameters (gel size, surfactant concentration, flow rate etc) for each gel. The millimeter sized gels have also been studied using small angle X-ray scattering (SAXS) to elucidate the microstructure of the polyelectrolyte-surfactant complexes at different surfactant and electrolyte concentrations. The aim of the work is to build a base for future development of controlled release drug vehicles, using the dense collapsed phase as a diffusion barrier.

[1] Hansson, P., Langmuir, 1998, 14, 2269
[2] Hansson, P., Langmuir, 2001, 17, 4167
[3] Hansson, P.; Schneider, S.; Lindman, B., J. Phys. Chem. B, 2002, 106, 9777
[4] Nilsson, P., Hansson, P., J. Phys. Chem. B, 2005, 109, 23843
[5] Göransson, A.; Hansson, P., J. Phys. Chem. B, 2003, 107, 9203

# AGGREGATION OF COLLOIDAL PARTICLES BY OPPOSITELY CHARGED POLYELECTROLYTES

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Polyelectrolytes adsorb strongly on oppositely charged particle surfaces, and thereby control their aggregation behaviour. With increasing polyelectrolyte dose, the surface is progressively neutralized, passes through a point of zero charge (PZC), and finally accumulates the opposite charge (i.e., overcharging). Particle aggregation is governed by this adsorption process, and leads to fast aggregation at the PZC, and slow aggregation at low and high polymer dose. The aggregation depends strongly on the salt level. Presence of salt accelerates the aggregation near the PZC, and slows it down away from it. The aggregation further strongly depends on the molecular mass of the polyelectrolyte. In the slow regime, the suspension becomes less stable with increasing molecular mass. These trends are very generic, as found by careful electrophoresis and light scattering studies with many different polyelectrolyte and particle systems. Two systems will be particularly highlighted, namely poly(styrene sulfonate) and amidine latex, and poly(amidomine) dendrimers and sulfate latex. These two systems demonstrate the mentioned trends very clearly. The results can be interpreted qualitatively in terms of lateral heterogeneities of the adsorbed polyelectrolyte layers. Finally, it will be shown that coadsorption of ions plays is very important in the adsorption of polyelectrolytes on oppositely charged surfaces and the corresponding charge neutralization process.

# A THEORY OF THE POLYELECTROLYTE PERSISTENCE LENGTH BASED ON EULER BUCKLING

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To understand better the role of electrostatics on the rigidity of a polyelectrolyte $A$, we define $A^*$, the null isomer of the polyelectrolyte, as the hypothetical structure that would result from A if all its charge sites bore zero charge. For the purposes of theoretical analysis, we model $A^*$ as identical to $A$ but supplemented by a longitudinal compression force equal in magnitude but oppositely directed to the stretching (tension) force on $A$ caused by charge-charge repulsions. The null isomer $A^*$ then becomes an elastically buckled form of the charged polyelectrolyte. On this basis, we derive a nonadditive relationship between the persistence length $P$ of the polyelectrolyte and the persistence length $P^*$ of its null isomer. From the formula obtained, which contains no adjustable parameters, we can predict the value of $P^*$ if $P$ is known, and we can predict the ionic strength dependence of $P$ under the assumption that $P^*$ does not depend on ionic strength. For DNA, the predicted value of $P^*$ and the log $c$ salt dependence are consistent with the copious data available. Alternate models of the Odijk-Skolnik-Fixman type, including one by the author, are considered and provisionally rejected on grounds supported both by theory and experiment that the nonelectrostatic persistence length inherent in OSF theories may in fact be largely electrostatic in origin.

# TEMPERATURE INDUCED COLLAPSE OF ALKALINE EARTH CATION – POLYACRYLATE ANION COMPEXES

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Polyacrylate anions (PA) and derivatives thereof are used to inhibit CaCO3 precipitation and are promising additives to control formation of carbonate nano-particles. The origin of this applicability lies in specific interactions between the carboxylate functions along the PA chain and those metal cations, which participate in inorganic particle formation. In the presence of soluble alkaline earth salts, the PA chains itself precipitate with the respective metal cations. The resulting precipitation threshold denoted as the critical metal cation concentration increases with increasing PA content. Extended investigation of dilute NaPA solutions approaching this precipitation threshold revealed drastic changes of the PA coil dimensions.[1] Along such approaches, the PA coils decrease in size and, if the threshold is crossed, adopt a fully collapsed sphere. Recent thermodynamic experiments[2] and computer simulations[3] indicated that the driving force of ! these processes is entropic in nature. Inspired by these findings, we launched supplementary experiments to investigate the impact of temperature on the structure of the dissolved PA chains in the presence of alkaline earth cations. To this end, dilute solutions of high molecular weight NaPA chains were analysed at variable amounts of alkaline earth cations. The overall amount of cationic charges was kept constant at a level of 0.01M by addition of NaCl. The alkaline earth cations were introduced by replacing the corresponding amount of Na cations. Thus, a cascade of intermediates with varying extent of shrinking became accessible. Successively, selected intermediates were subdued to temperature changes in a regime of $15°C < T < 40°C$ and, along this temperature variations structural changes of the PA coils were recorded by means of various scattering techniques, among them combined static and dynamic light scattering. As a major result we could unambiguously demonstrate that the polyelectrolyte chains can be reversibly collapsed and extended by increasing and decreasing the temperature respectively.

[1] Schweins, R. ; Lindner, P. ; Huber, K. Macromolecules 2003, 36, 9564
[2] Sinn, C. G. ; Dimova, R. ; Antonietti, M. Macromolecules 2004, 37, 3444
[3] Molnar, F. ; Rieger, J. Langmuir 2005, 21, 786

# EFFECTIVE CHARGE OF POLYELECTROLYTES, COUNTERIONS AND COMPLEXES

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The charge of polyelectrolytes in solution usually is smaller than the nominal charge because the thermal energy of the counterions is too small for all of them to leave the macromolecule. A combination of PFG NMR, that yields the diffusion coefficient and thus the hydrodynamic friction, and electrophoresis NMR, that yields the electrophoretic mobility of molecules and complexes in solution, provides a way to determine the effective charge of the molecule or complex [1,2]. Since the NMR experiment is performed with spectral resolution, the moving species are identified, which permits to investigate polyelectrolyte and counterion simultaneously. For the example of poly(diallyldimethylammonium chloride) (PDADMAC) and perfluorinated succinic acid [3] and a sulfonated poly(aramide) and pyridine the effect of counterion condensation has been proven directly. A fraction of the counterions moves in the electric field with the oppositely charged polyelectrolyte. On the time scale of the experiment there is fast exchange between free and condensed counterions which results in a weighted average for both the diffusion coefficient and the electrophoretic mobility. The extension to a three-dimensional experiment permits the investigation of samples with a wide distribution of sizes and charges.

[1] U. Scheler, in H.S. Nalva (ed.) ‘Handbook of Polyelectrolytes and their applications’, American Scientific Publishers (2002)
[2] Ute Böhme, Ulrich Scheler, Colloids and Surfaces A, 222, (2003), 35
[3] Ute Böhme, Ulrich Scheler, Macromolecular Symposia, 211, (2004), 87

# WATER SOLUBLE POLYMERS AS CRYSTALLIZATION REGULATORS. THE INFLUENCE OF MALEIC ACID COPOLYMERS ON THE SEPARATION OF I NORGANIC SALTS

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Water-soluble polymers and polyelectrolytes (WSPEL) are known to affect the crystal habit of scale-forming minerals and their rates of deposition. The ability of WSPEL to act as crystallization inhibitors or activators is a relatively recent but promising subject that was already exploited in several applications. Metal carbonates, especially calcium carbonate ($CaCO_3$), were chosen as one of the standard model systems due to their abundance in nature and also their important industrial application [1, 2]. Remediation of $CaCO_3$ scale formation in geothermal wells and other industrial processes, reducing of the precipitation of $CaCO_3$ during washing treatments by adding polycarboxylic acids as builders, preventing downhole and topside mineral scale formation in oil fields are some examples of WSPEL abilities. The preparation of thin films of $CaCO_3$ crystals on solid matrixes (cellulose, chitosan, chitin) in the presence of WSPEL was reported as a biomimetic method to imitate the structure of pearl. Polyelectrolytes with carboxylic groups were demonstrated as effective inhibitors of Ca phosphate crystal growth. Their effects on the nucleation (induction period), crystal growth, and morphology of hydroxyapatite precipitated from solutions of the lattice ions were examined [3, 4]. Another interesting application could be the control of crystal growth in drug suspensions [5]. In our contribution we analyse the influence of WSPEL on the crystallization/separation of inorganic or organic salts. Then a series of results are presented regarding the influence of maleic acid copolymers with different comonomers in the crystallization of $CaCO_3$ and the formation of hydroxyapatite in the presence of a maleic acid copolymer.

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[1] Amjad Z., Ed., Water Soluble Polymers: Solution Properties and Applications, Kluwer, Boston, (1998).
[2] Agarwal, P., Berglund, K. A., Crystal Growth & Design (2004), 4, 479.
[3] Amjad Z., Ed., Calcium Phosphates in Biological and Industrial Systems, Kluwer, Boston (1998).
[4] Tsortos A., Nancollas G. H., J. Colloid Interf. Sci. (2002), 250, 159.
[5] Raghavan S. L., Trividic A., Davis A. F., Hadgraft, J., Int. J. Pharmaceutics (2001), 212, 213.

# FLEXIBLE POLYELECTROLYTES WITH MONOVALENT SALT

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We present a model for describing flexible polyelectrolytes in a good solvent and in the presence of monovalent salt. The molecule composed by N monomers is characterized by the end to end distance $R_e = b\ (Z\text{-}1)^{\gamma}$ and the number of associated counterions n. At high temperatures the polyelectrolyte behaves as a neutral polymer ($\gamma = 0.588$). Decreasing the temperature, the macromolecule changes from this extended configuration ($\gamma = 0.588$) to a stretched form ($\gamma \sim 1$). At even lower temperatures, above the Manning condensation threshold, the polyelectrolyte collapses ($\gamma \sim 0.3$). Our results show good agreement with simulations.

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# WATER-SOLUBLE FUNCTIONAL POLYMERS WITH ABILITY TO REMOVE IONS FROM AQUEOUS SOLUTION IN CONJUNCTION WITH ULTRAFILTRATION MEMBRANES

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The removal and separation of toxic and environmentally relevant ions are a technological challenge respect to industrial and environmental applications. A particular emphasis is given to the study the water-soluble polymers (WSP)-ion interactions, under different experimental procedures, through the liquid-phase polymer based-retention (LPR) technique, which combines the WSPs and membrane filtrations [1-3]. These WSPs containing ligand groups are called polychelatogens. This method is based on the separation of inorganic species bound to the polymers from non-complexed ions . According to that, we have prepared water-soluble homo- and copolymers by radical polymerization from vinyl monomers. Some polymers were also commercial reagents. The polymers studied are: poly(acrylamido glycolic acid), poly(acrylic acid), poly(2-acrylamido-2-methyl-1-propane sulfonic acid), poly(aspartic acid), poly(3-methacryloylamine)propyl trimethyl ammonium chloride, poly(3-methacryloylamine)propyl trimethyl ammonium chloride-co-acrylic acid), poly[(acryloxy) -ethyl]trimethyl ammonium chloride, poly[(2-acryloxy)ethyl] trimethyl ammonium methyl sulfate. These polymers were purified and fractionated by ultrafiltration membranes with different molecular weight cut off and characterized by FT IR and NMR spectroscopy. The ion retention ability of these polychelatogens was investigated for the metal cations: Cu(II), Co(II), Ni(II), Pb(II), Cd(II), Zn(II), Al(III), and Cr(III) in the pH range between 1 and 7 depending on the solublity properties of the metal ions. The polychelatogens as polycations were investigated to remove anionic arsenic species, particularly from As(V). The effect of the filtration factor, Z, defined as the ratio between the volume in the filtrate Vf and the volume in the cell Vo on the affinity for the metal ions and the arsenic(V) was investigated. The As(V) is more strongly retained between pH 6 and 8). From the ion retention data the maximum retention capacity (MRC) was subsequently determined. The metal ion retention capabilty depended on the pH and filtration factor, Z. Usually as increases the pH increases the metal ion retention capacity. it is related with the higher affinity of the anions to form complexes with the metal cations. Possible polymer-ion interaction mechanisms are suggested.

The authors thank to FONDECYT (Grants No 1030669 and No 3050057) and CNRS-CONICYT (No 18641) the financial support.

[1] Spivakov B.Ya., Shkinev V.M., Geckeler K.E, Puer Appl. Chem. 1994, 66, 632.
[2] Rivas B.L., Geckeler K.E, Adv. Polym. Sci. 1992, 102, 171.
[3] Rivas B.L., Pereira E.D., Moreno-Villoslada I., Progr. Polym. Sci., 2003, 28, 173

# PREDICTING THE OSMOTIC PRESSSURE OF SOLUTIONS OF SEMI-FLEXIBLE FINITE POLYELECTROLYTES

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In this contribution we perform a systematic analysis of different effects which influence the counterion distribution in a polyelectrolyte solution via computer simulations. We first review a recently proposed self-consistent geometry optimized cell model approach to study osmotic properties of stiff-chain polyelectrolyte solutions. In contrast to the usual monotonic Poisson-Boltzmann prediction, the cell model predicts correct non-monotonic dependence of the osmotic coefficient on concentration. A lower degree of polymerization is found to reduce significantly the counterion condensation in a typical dilute strong polyelectrolyte. The results agree quantatively with simulations of a corresponding many-body bulk system up to a dense semi-dilute regime. We then analyze a number of factors which can affect the osmotic properties for model parameters resembling that of a typical synthetic rod-like (PPP) polyelectrolyte which has been the subject of a number of investigations recently [2,3]. We compare our simulation results with experimental data and predictions of the Poisson-Boltzmann (PB) theory for an infinitely long rod. Incorporation of the electrostatic correlations to the model is found to decrease the osmotic coefficient by some 5-7 per cent. A decrease twice smaller than that is observed upon including chain flexibility into the model. The residual salt also decreases the osmotic pressure and this effect is more noticeable at low polymer and high salt concentration. The osmotic coefficient calculated in the simulations at different densities for a realistic bulk system of finite macroions was found to be much higher than that predicted by the PB theory. It also exceeded the experimental values by a factor of about two [4]. This overshoot suggests existence of a binding energy of the order of 5kT which retains the counterions in the condensed state. Under the assumption that the experimental results are correct, one is lead to the conclusion that the model assumption of pure Coulomb interactions in a uniform dielectric background need to be improved.

[1] D. Antypov, C. Holm, Phys. Rev. Lett. 96, 088302 (2006).
[2] C. Holm, M. Rehahn, W. Oppermann, M. Ballauff, in Advances in Polymer Science 166, ed. M. Schmidt, Springer, New York, 2004.
[3] M. Deserno, C. Holm, J. Blaul, M. Ballauff, and M. Rehahn, Euro. Phys. Journal E 5, 97-103 (2001).
[4] D. Antypov, C. Holm, Osmotic coefficient calculations for dilute solutions of stiff-chain polyelectrolytes, submitted.

# EFFECTIVE MACROION CHARGE, STRUCTURE, AND DYNAMICS OF HIGHLY ASYMMETRIC ELECTROLYTES

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We study static and electrokinetic properties of highly asymmetric electrolyte solutions using advanced computer simulations. The solutions are modeled on the level of the primitive electrolyte model, where all charged species are considered explicitly. The dynamic properties of polyelectrolyte solutions are modeled using a combined lattice Boltzmann / Langevin dynamics method [1], which enables hydrodynamic interactions. The central goal of the work is to find a systematic way to predict the dependence of macroscopic properties of polyelectrolyte solutions on the macroion concentration. We analyze the structure of the ionic double layer around the macroion and discuss the relation between the static effective charges and electrokinetic (zeta) potential of the latter. We define a set of dimensionless parameters (renormalized macroion charge and effective scaled screening length), which allow an universal description of structure and electrokinetic properties of highly asymmetric electrolytes in a wide range of conditions in terms of single macroion characteristics [2]. This approach is applied to conditions of (i) counterion dominated screening that appear, for example, at low salt and finite macroion concentrations, and (ii) screening with a multivalent salt, where the mean field theories are unsuccessful. In particular, we describe effective charge and electrophoretic mobility reversal for macroions immersed in a multivalent salt solution and its correlation with the solution stability. We demonstrate the validity of the approach for description of polyelectrolyte solutions and colloidal dispersions [2,3].

[1] V. Lobaskin, B. Duenweg, C. Holm, J. Phys.: Condens. Matter, 16, S4063 (2004)
[2] V. Lobaskin, B. Duenweg, M. Medebach, T. Palberg, C. Holm, cond-mat/0601588
[3] M. R. Stukan, V. Lobaskin, C. Holm, O. I. Vinogradova, Phys. Rev. E 73, 021801 (2006)

# NANOSTRUCTURED POLYELECTROLYTE BRUSHES GRAFTED ONTO POLYMER SUPPORTS

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Extreme ultraviolett (EUV) lithographic exposure of polymer substrates followed by graft polymerisation of a second polymer is a powerful technique to create micro- and nanopatterns of polymer brushes [1,2]. In this work we report on the formation of patterned brushes of poly(glycidyl-methacrylate) (poly-GMA), their chemical modification to turn them into poly-electrolytes, and the deposition of polyelectrolyte multilayers on such structured substrates. Exposures of 100 μm thick ETFE films were performed using 92 eV EUV radiation at the Swiss Light Source (SLS), either through shadow masks to create microstructures, or in a EUV interference set-up to form periodic structures with nanometer scale resolution. The patterns of radicals created near the surface of the films serve as initiators for the subsequent radical polymerisation of glycidylmethacrylate. As described earlier [1-3], the height of the grafted structured is depending on the exposure dose and on grafting parameters such as reaction temperature and monomer concentration. The obtained structure height ranges from a few tens to of nanometers for nanostructures up to several hundred nanometers for microstructures. Sulfonation of the grafted brushes was achieved by reaction with sodium hydrogen sulfite as confirmed by contact angle and XPS measurements. AFM measurements were used to characterize the nanostructured brushes before and after sulfonation. Periodic structures down to 200 nm period appeared well resolved after sulfonation, indicating the stable anchoring of the brush on the fluoropolymer support. A slight swelling of the structures was observed which is consistent with the increased molecular weight and water uptake of sulfonated poly-GMA. In first measurements of structured polyelectrolyte brushes after deposition of multilayers, which were composed of polystyrene-sulfonic acid and polyallyl-amine, the nanostructures appeared still well resolved, indicating that thin layers were deposited which mainly follow the surface topography of the structured brush. The influence of different conditions of the polyelectrolyte multilayer deposition is currently under investigation.

[1] H.P. Brack, C. Padeste, M. Slaski, S. Alkan, H. H. Solak, J. Am. Chem. Soc. 2004, 126 (4), 1004.
[2] C. Padeste, H. H. Solak, H.P. Brack, M. Slaski, S.A. Gürsel, G.G. Scherer, J. Vac. Sci. Technol. B, 2004, 22 (6), 3191.
[3] C. Padeste, P. Farquet and H.H. Solak, Microelectron. Eng., in press.

# POLYELECTROLYTES INSIDE VIRAL CAPSIDS

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The structural organization of viruses is characterized by simplicity and economy. At a minimal level, the viral genome, which is composed of a number of RNA or DNA molecules that are either single stranded or double stranded, is surrounded by a spherical or cylindrical protein shell composed of many copies of almost identical proteins. The linear size of the virus genome can be tens of microns and is large compared to the diameter of capsid, usually in the range of tens of nanometers, so the genome must undergo a high degree of condensation during viral assembly. Structural features of genomes confined inside viral capsids and the thermodynamics of the encapsidation of the genome into the viral capsid have been examined by using coarse-grained model solved by Monte Carlo simulations. The capsid was modeled as a spherical shell with embedded charges and the genome as a linear jointed chain of oppositely charged beads, and their sizes corresponded to those of a scaled-down T=3 virus. Counterions were explicitly included, but no salt was added. The encapisdated chain was found to be predominantly located at the inner capsid surface, in a disordered manner for flexible chains and in a spool-like structure for stiff chains. The distribution of the small ions was strongly dependent on the polyelectrolyte-capsid charge ratio. The encapsidation enthalpy was negative and its magnitude decreased with polyelectrolyte length, whereas the encapsidation entropy displayed a maximum when the capsid and polyelectrolyte had equal absolute charge.

# SOLID-LIQUID SEPARATION WITH AGGREGATING CATIONIC POLYMER SYSTEMS

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Solid-liquid separation by coagulation and flocculation is an important part of many well-established technical processes, using highly-hydrophilic linear polyelectrolytes with excellent water-solubility as processing aids. Nevertheless, there are still two essential deficiencies in this field. First, the polyelectrolyte concentration window, providing an efficient flocculation, is often very narrow. Thus, restabilisation of the particles by polymer overdosing due to steric or electrosteric effects takes place easily. Second, several separation problems are not sufficiently solved up to now. So, the flocculation of suspensions, containing small particles with low charge density, together with higher amounts of additives, often fails. These disadvantages may be overcome, using associating or aggregating cationic polyelectrolytes as flocculants. A significant enhancement of the flocculation properties can be achieved by introduction of hydrophobic functionalities into the polyelectrolyte backbone, thus increasing the surface activity and allowing the formation of aggregates. Poly-(vinylbenzyl-trialkyl-ammonium chloride)s as well as poly(methacryloyloxyethyl-dimethyl-alkyl-ammonium chloride)s, containing alkyl substituents of different hydrophobicity, show a decrease of the apparent charge density up to 50% with increasing hydrophobicity and molecular weight. Increasing ionic strength enhances this effect, and aggregates with an average size of about 1 µm were observed. Flocculation investigations with stable kaolin dispersions as well as polystyrene latices with different particle size and surface charge density reveal higher amounts of adsorbed polymers and a substantial broadening of the flocculation window with increasing polymer hydrophobicity. With decreasing charge density of the substrate, hydrophobic interactions play a more profound role within the flocculation process. Obviously, due to a more compact conformation of these polymers in solution and at the interface. Again, a further efficiency increase was observed at higher ionic strength. Using these polymers, some technical waste waters could be clarified for the first time.

# POLYDADMAC WITH HIGH MOLECULAR WEIGHTS – SYNTHESIS AND USE AS FLOCCULANT

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The purification of municipal and industrial waste water requires the separation of suspended solids, which in general means flocculation with subsequent filtration or centrifugation. Flocculation aids are necessary to accelerate flocculation. Currently, copolymers from acrylamide and cationic acrylic esters are applied since they can be polymerized to the high molecular weights required (higher than 1 million g/mol) without difficulties. However, a large part of incidental waste water possesses pH-values ranging between 7 and 10. Acrylic polymers are sensitive to hydrolysis, accompanied by a loss in efficacy, in this range. Hence, there exists a considerable demand for hydrolytically stable alternative polyelectrolytes. The objective of our work was to provide poly(diallyldimethylammonium chloride) (polyDADMAC) with the required molecular weights to act as flocculation agent. Normally, the molecular weight of polyDADMAC is kinetically limited to about 400.000 g/mol. Two approaches to overcome these limitations are introduced: the use of small amounts of special bifunctional monomers and a special redox-initiation system consisting of peroxodisulfate and an amine, which enables the reinitiation of polymer chains already formed. The combination of these approaches in an inverse emulsion polymerization led to polymers with molecular weights in the range between 1 and 2 million g/mol (Mw). Techniques to ensure the long-term stability of the inverse polyDADMAC dispersions will be presented. It will be shown, that the process developed is transferable to a technical scale without problems. Experimental data regarding the flocculation performance of the polymers (kaolin sedimentation [KSD] and capillary suction time [CST]) demonstrate the advantages of the new polyDADMACs. They can be used without loss of performance in systems with extreme pH-values and/or high salt contents as well as at elevated temperatures (>40°C). Moreover, the flocculation interval is considerably expanded, i.e. the risk of overdosage, which may cause restabilization of dispersed solids, can be minimized.

# MICROMECHANICS OF HOLLOW POLYELECTROLYTE MICROTUBES AND THEIR TEMPERATURE-INDUCED SHAPE CHANGES

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Tubelike hollow structures of micron diameter are of considerable interest for material sciences, where they can serve for example as building blocks for microfluidic systems and combine large surface area with simpler handling on macroscale (in the form of meshes). We show the fabrication of hollow tubes made from Polyelectrolyte multilayers by the layer by layer technique. We coat fiber templates which can be subsequently dissolved without destroying the multilayer coating, which results in the formation of hollow tubes, whose diameter is determined by the fiber diameter, while the length can be chosen by fiber cutting prior to coating. We have investigated the tube's response to external forces using afm force spectroscopy. Individual tubes can be tested and we can quantitatively model the force data using analytic continuum models. In previous work, we have found pronounced temperature effects for multilayer systems that indicate that the meting temperature of certain multilayers can be reached in aqueous solution [1]. We have investigated the effect of multilayer melting on the tubes' shape and find that it triggers non-trivial shape changes, such as the formation of pearl-necklace type structures.

[1] R. Müller, K. Köhler, R. Weinkamer, G. B. Sukhorukov and A. Fery, Macromolecules, 2005, 38: 9766

# SOLUTION PROPERTIES OF CHARGED DESIGNED COPOLYMERS

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We discuss advances that have recently been achieved in the computer simulation and theoretical understanding of solutions of designed hydrophobic polyelectrolytes. We consider a recently developed approach, called conformation-dependent sequence design, which is based on the assumption that a copolymer obtained under certain preparation conditions is able to "remember" features of the original conformation in which it was built and to store the corresponding information in the resulting sequence. The focus is on the so-called "proteinlike" copolymers with specific chemical sequences resembling those known for soluble proteins. Such copolymers exhibit large-scale compositional heterogeneities and long-range statistical correlations between monomer units. Using computer simulation techniques, the processes of coil-to- hydrophobic attraction and Coulomb interactions as well as to their specific chemical sequence, globule transition, aggregation of the charged protein like copolymers, and counterion condensation are studied in detail. The main attention is paid to the influence of the counterions of different charge on the aggregation of the copolymers. Due to a complex interplay between proteinlike polyelectrolytes having hydrophobic groups can readily adopt stable spherical-shaped globular conformations and can be protected against large-scale intermolecular aggregation in selective (polar) solvents. For solutions containing monovalent counterions, we find three different temperature regimes, which are characterized by a different behavior of Coulomb energy, chain sizes, and pair correlation functions. In this regime corresponding to counterion condensation, we observe a solution of non-aggregating polymer globules which form a stable array resembling a charge-stabilized (micro)suspension or microgel phase. Multivalent counterions considerably increase the aggregation of the chains, which form in their presence the finite size aggregates built up from several polyions. However, the striking feature of the aggregation is that this process does not appear to lead to macroscopic phase separation. The mechanism that prevents the phase separation is discussed.

# FLUORESCENCE AND CONDUCTOMETRIC STUDIES OF THE POLYSACCHARIDE BASED AMPHIPHILIC POLYELECTROLYTES - ALKYL SULFATES INTERACTION

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Aqueous systems containing polyelectrolytes and oppositely charged surfactants have been extensively studied due to their applications in food, cosmetic or pharmaceutical industries. Surfactant self-aggregation in the presence of polyelectrolytes occurs at a lower concentration (cac) than the cmc of the free surfactant. In the systems containing amphiphilic polyelectrolytes, the electrostatic interaction between charged species is accompanied by hydrophobic interaction between polymer and surfactant hydrophobic groups. This results in the simultaneous occurrence of species self-aggregate and mixed aggregates [1] We have previously synthesized and characterized the self-assembly of a new class of amphiphilic cationic polyelectrolytes obtained by chemical modification of neutral polysaccharides. These amphiphilic polymers (PCn) have pendant N-Cn-N,N-dimethyl-N-(2-hydroxypropyl) - ammonium chloride groups with n = 8-16 and form self-aggregates in aqueous solutions by intra- or intermolecular hydrophobic interactions between their pendant alkyl chains. Their interaction with alkyl sulfates has been studied by titration calorimetry, turbidimetry and viscosity [2-4]. In the present study, we use several fluorescence techniques and conductometric measurements to further investigate the characteristics of the aggregates formed in the systems containing dextran based polyelectrolytes (DCn) and alkyl sulfates (SCn, n =8-16), as a function of the chemical structure of the components and their relative concentrations. Fluorescence measurements allowed the estimation of surfactant cac, its aggregation number, and cooperativity or the surfactant self-aggregation. Conductometric measurements supplied qualitative evaluations of the surfactant binding ability, the strength of the binding and the extent of counterion release by binding. The results showed that the binding in all systems starts at very low surfactant concentration and the strength of the binding depends mostly on the hydrophobicity of the polymer. The prevalence of the mixed micelles to surfactant self-aggregates increases with the increase in the length of alkyl chain belonging to both surfactant and polymer. The cooperativity of surfactant self-aggregation is specific to the pair polymer-surfactant, and is more significant for the pairs DC8-SC16 and DC16-SC8. The size of the surfactant self-aggregates decreases with the increase in the polyelectrolyte hydrophobicity.

[1] Polymer-Surfactant Systems. Kwak, J. C. T. Ed; Marcel Dekker, NY, 1998.
[2] M. Nichifor, M. Bastos, A. Lopes. J. Phys.Chem. B,108, 16463, 2004.
[3] G. Bai, M. Nichifor, A. Lopes, M. Bastos. J. Phys. Chem. B, 109, 518, 2005.
[4] G. Bai, M. Nichifor, A. Lopes, M.Bastos. J. Phys.Chem. B,109, 21681, 2005

# PH-EFFECTS IN COMPLEXATION AND BLENDING OF POLY(CARBOXYLIC ACIDS) WITH NON-IONIC POLYMERS

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Weak polymeric acids, acting as proton-donating polymers, form interpolymer complexes (IPC) stabilized by hydrogen bonds with nonionic proton-accepting polymers in aqueous and organic solutions. In the present communication the role of solution pH in the complex formation between poly(carboxylic acids) and non-ionic polymers will be discussed and existence of critical pH phenomena in these binary mixtures will be demonstrated. It has been found [1-3] that the formation of colloidal dispersions of hydrophobic interpolymer complexes and their further precipitation is observed below the first critical pH of complexation ($pH_{crit1}$). Above this value, but below the second critical pH of complexation ($pH_{crit2}$), the products of interaction are more hydrophilic and form transparent solutions. Above the $pH_{crit2}$ the polymers do not interact with one another and the binary system is homogeneous in diluted solutions. The critical $pH_1$ is suggested to be a criterion for evaluation of the complex formation ability of non-ionic polymers with respect to poly(carboxylic acids) [1-4]. The complexation ability of different classes of water-soluble non-ionic polymers such as polyethers, polyalcohols, polyacrylamide and its derivatives, cellulose ethers has been analyzed and some of the general features have been revealed. A new classification of interpolymer complexes based on critical pH values and ionic strength effects will be presented. The effects of solution pH on the possibility to prepare polymeric films based on blends of poly(carboxylic acids) and non-ionic polymers will be also discussed [1-3]. The miscibility-immiscibility transitions caused by pH changes were found to affect the final properties of the polymeric films. Different ways of these blends cross-linking and their application as mucoadhesive drug delivery systems will be demonstrated.

[1] Khutoryanskiy V.V., Dubolazov A.V., Nurkeeva Z.S., Mun G.A., Langmuir 20, 9, 3785-3790 (2004).
[2] Nurkeeva Z.S., Mun G.A., Dubolazov A.V., Khutoryanskiy V.V., Macromol. Biosci., 5, 424-432 (2005).
[3] Dubolazov A.V., Nurkeeva Z.S., Mun G.A., Khutoryanskiy V.V., Biomacromolecules, in press (2006).
[4] Nurkeeva Z.S., Mun G.A., Khutoryanskiy V.V., Macromol. Bioscience, 3, 283-295 (2003).

# TEMPERATURE INDUCED SOFTENING OF POLYELECTROLYTE MULTILAYER CAPSULES: A TOOL FOR ENCAPSULATION

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Multilayers formed by the alternating adsorption of oppositely charged polyelectrolytes [1] have attracted much interest because of the variety of possible applications. By assembling the film on spherical charged substrates and subsequent dissolution of the template, microcapsules are obtained. They consist of a free multilayer not attached to a substrate, thus having enough space to rearrange. The temperature dependent behavior of polyelectrolyte microcapsules consisting of different polyions was investigated. Above a certain softening temperature [2] at which the polyelectrolytes start to rearrange, they show a pronounced odd-even effect of size with layer number [3]. The thermodynamically most stable state of the multilayer film is mainly determined by a balance between surface tension and electrostatic forces within the polymer shell. Capsules with dominating surface tension shrink uniformly with increasing temperature until they form solid spherical particles. In parallel to this shrinkage and the concomitant wall thickness increase the water content within the multilayer is drastically reduced as measured by means of transmission x-ray microscopy. The thickening and densification of the multilayer observed upon heating offer a unique tool to fine-tune the permeability of capsules over a remarkable range. Thus, temperature treatment can be used to encapsulate low-molecular weight substances.

[1] G. Decher, Science 1997, 277, 1232.
[2] R. Müller, K. Köhler, R. Weinkamer, G.B. Sukhorukov, A. Fery, Macromolecules 2005, 38, 9766.
[3] K. Köhler, D.G. Shchukin, G.B. Sukhorukov, H. Möhwald, J. Phys. Chem. B 2005, 109, 18250.

# INTER- AND INTRAMOLECULAR INTERACTIONS OF POLYELECTROLYTES CONFINED IN THIN LIQUID FILMS

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Thin liquid films are the building blocks of many macroscopic systems (e.g. foams, emulsions), and they affect the stability and functions of them. The forces between the opposing interfaces depend on the composition of the film interfaces and of the film fluid. Two interesting aspects of liquid films will be presented: 1) Correlation between interfacial forces and stability of thin liquid films and 2) the spatial confinement of colloidal dispersions within thin films [1].

In the measurements presented in the paper, a polyelectrolyte solution is confined in a thin liquid film. The question is how the chain structuring changes with respect to the bulk.

The sum of interactions between the film surfaces is determined quantitatively by the disjoining pressure isotherm (disjoining pressure *vs.* film thickness) and it is measured by varying the outer pressure or force in a so-called thin film pressure balance (TFPB) or in a Colloidal Probe AFM (CP-AFM). With TFPB foam films and wetting films can be studied and in a CP-AFM a liquid film between two solid interfaces is investigated.

At low polyelectrolyte concentration the films show a continuous drainage with increasing outer pressure, while thin liquid films of semi-dilute polyelectrolyte solution result in an oscillating pressure curve due to a structure formation of the polyelectrolyte chains in the interfacial regions. A comparison of the force oscillation with the structure peak of SANS or SAXS spectra show that the chain distance and the correlation length are the same in both geometries [2,3]. It means that the polyelectrolyte concentration remains constant during the confinement. But confinement effects are visible in fluorescence measurements which probe the local polyelectrolyte concentration within the film [4].

In order to modify the interactions between the fluid and the interface the solid surface is pre—coated with polyelectrolytes of different charges and viscoelasticity [5]. The air/water interface is varied by the adsorption of different amphiphiles [6]. The results show a strong influence of the surface composition on the film thickness, but the structure formation within the film core seems to be unaffected.

[1] R. v. Klitzing, A. Espert, A. Colin, D. Langevin, Colloids and Sufaces A 176 (2001) 109.
[2] R. v.Klitzing, B. Kolaric, W. Jaeger, A. Brandt, Phys. Chem. Chem. Phys. 4 (2002) 1907.
[3] D. Qu, S. Garnier, J.S. Pedersen, A. Laschewsky, H. Möhwald, R. v. Klitzing, Macromolecules, submitted.
[4] D. Rapoport, D. Anghel, G. Hedicke, H. Möhwald, R. v. Klitzing, J. Phys. Chem B, submitted.
[5] K. Ciunel, M. Armelin, G.-H. Findenegg, R. v. Klitzing, Langmuir 21 (2005) 4790.
[6] B. Kolaric, W. Jaeger, G. Hedicke, R. v. Klitzing, J. Phys. Chem. B 107 (2003) 8152.

# ADSORPTION OF WELL-CHARACTERISED POLYDIALLYL-DIMETHYLAMMONIUMCHLORIDE (DADMAC) ONTO SIO2 SURFACES FROM WATER

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Abstract A set of five different specially prepared polyDADMAC samples (28, 63, 112, 303 and 623 kD) have been characterised with the aid of NMR-diffusion, dynamic light scattering and size-exclusion chromatography measurements. The results show that the polymers have narrow molecular mass distributions and the NMR diffusion and dynamic light scattering data show a generally good agreement when comparing the diffusion coefficients for different salt concentrations and molecular mass. An estimation of the molecular mass from the different methods, at high salt concentrations, shows a good agreement. The adsorption of the different polyelectrolytes at the siliconoxide/water interface was further determined at different salt concentrations with two different methods. Stagnation Point Adsorption Reflectometry (SPAR) was used to determine the adsorbed amount of polyelectrolyte in (mg/m2) and a Quartz Crystal Microbalance (QCM) was used to determine the adsorbed amount of polyelectrolyte and the amount of water immobilised by the polyelectrolyte. In this way the amount of water as well as the amount of polyelectrolyte in the adsorbed layer could be determined. The results show that the polyDADMAC with a molecular mass lower than 300 kD adsorb in a very compact structure at low salt concentrations. At salt concentrations around 0.01 M NaCl the adsorbed structure changes for these polyelectrolytes and the concentration of polyelectrolyte was as low as 20% by weight for the 63 kD and 28 kD polymers. At higher salt concentrations, where non-ionic interactions between the polyelectrolyte and the surface starts to dominate, the structure changes again and the amount of water in the adsorbed layer decreases for polyelectrolytes with a molecular mass in the range of 63 kD to 300 kD. For polyelectrolytes with a molecular mass larger than 300 kD, i.e. 303 kD and 623 kD, the amount of water in the adsorbed layer stays rather constant around 50% and increases only slightly at the highest salt concentration for the 303 kD polymer. Finally the binding of nano-silica particles to the pre-adsorbed polylelectrolytes was determined with the QCM method in order to test the importance of the structure of a polymer layer on the interaction with a nano-particle layer. It was found that the adsorbed amount of silica particles was higher the higher the adsorbed amount of polyDADMAC in the first layer, irrespective of molecular mass and salt concentration.

# LINEAR VS. EXPONENTIAL GROWTH OF POLYELECTROLYTE MULTILAYERS; AN OPTICAL REFLECTOMETRY STUDY

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It is known that the formation of multilayers of polyelectrolytes of alternating charge can be followed in situ by means of stagnation point optical reflectometry [1,2]. In this study, the abovementioned method was applied for investigations of the distinction between linear and exponential (or superlinear) build-up mechanisms of polyelectrolyte multilayers with special emphasis on the influence of ionic strength of solution on such process. In our experiments we used two typical pairs of polyelectrolytes known in the literature for predominantly linear (poly(allylamine hydrochloride) / poly(sodium 4-styrenesulfonate)) and exponential (poly-L-lysine hydrochloride / poly-L-glutamic acid) growth. As the solid substrate, we used silica in the form of silicon wafers carrying an oxide layer. We investigated the formation of polyelectrolyte multilayers in both systems at different ionic strengths and in the presence of different salts. As the supporting electrolyte we used potassium chloride and potassium nitrate. We observed that in both investigated systems the ionic strength significantly influences the growth pattern. In the PAH/PSS system, at lower ionic strength (e.g. 10 mM) the growth is approximately linear and at higher Ic (e.g. 300 mM) the growth is exponential. On the other hand, when we analysed the PLL/PGA system, at all investigated ionic strength the formation of multilayers was characterized by exponential growth. Additionally, the obtained results were compared with the results obtained earlier for the formation of multilayers in other systems.

[1] D. Kovačević, S. van der Burgh, A. de Keizer and M. A. Cohen Stuart, Langmuir, 18 (2002) 5607-5612.
[2] D. Kovačević, S. van der Burgh, A. de Keizer and M. A. Cohen Stuart, J. Phys. Chem. B, 107 (2003) 7998-8002.
[3] J. M. Garza, P. Schaaf, S. Muller, V. Ball, J.-F. Stolz and J.-C. Vogel, Langmuir, 20 (2004) 7298-7302.

# EFFECTS OF DEPOSITION TEMPERATURE ON INTERNAL ORDER OF POLYELECTROLYTE MULTILAYERS

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Polyelectrolyte multilayers are prepared by consecutively adsorbing poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) from aqueous KCl and NaCl solution (1 mol/L) at different temperatures, between 5 and 60 °C. The films are characterized by X-ray and neutron reflectometry, using selectively deuterated PSS layers. When the preparation solution is heated, the film thickness increases up to a factor of three. At low temperature, the internal roughness is about 40 % of the thickness of a polycation/polyanion layer pair, the same result as obtained when the bilayer thickness is controlled by varying the salt content in the deposition solution. Starting at 35 °C (films from KCl solution) or 45 °C (films from NaCl solution), the internal roughness grows indicating increasing layer interpenetration, a feature which may be attributed to the theoretically predicted changes of the polymer conformation in solution from extended configuration to pearl-necklace or even globular structures on deterioration of solvent quality.

# INFLUENCING POLYELECTROLYTE COMPLEX NANOSTRUCTURE BY CHARGED POLYPEPTIDE CONFORMATION

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Polyelectrolyte (PEL) complexes (PEC) are self-assembled systems and can be prepared by two methods: (i) mixing oppositely charged PEL in solution leads to dispersed nanoparticles known from the work of Bungenberg de Jong, Kabanov and Dautzenberg and (ii) consecutively adsorbing those PELs at solid interfaces results in PEL multilayer (PEM) films known from the work of Decher and Möhwald. PEC particles (i) and PEM films (ii) show significant correlations in the adopted nanostructure, although both products can be apparently different on the macroscopic level. Herein we report on the influence of PEL molecular stiffness on the nanostructures of PEC particles and PEM films. For that charged homopolypeptides like cationic poly(L-lysine) (PLL) and anionic poly(L-glutamic acid) (PLG) were used, whose conformations can be changed from random coil to a-helix [1-3] by salt type or pH value. PLL and PLG were combined with flexible polyanions (PA) like poly(vinylsulfate) (PVS) or copolymers of maleic acid (PMA-X) and flexible polycations (PC) like PDADMAC and PEI, respectively. in-situ ATR-FTIR, AFM, circular dichroism (CD) and dynamic light scattering (DLS) were used for the characterization of surface and bulk phase and interaction to analytes. As a result AFM images on both PLL containing solution casted PEC particles (a) and consecutively adsorbed PEM films (b) [2-3] show elongated structures for the a-helical conformation, while coiled PLL caused spherical PEC particles and isotropically structured PEM films. Conformation and orientation of PLL was determined by IR spectroscopy and circular dichroism. Those particles and films can be used as nanocarriers, cell mimics or nanostructured biomimetic coatings. Results on their interaction with proteins are included.

[1] M. Müller, B. Keßler, K. Lunkwitz, J. Phys. Chem., 107 (32), 8189-8197 (2003)
[2] M. Müller, T. Reihs, B. Keßler, H.J. Adler, K. Lunkwitz, Macromol. Rapid. Commun., 25(3), F56-F57 (2004)
[3] M. Müller, T. Reihs, W. Ouyang, Langmuir, 21(1), 465 (2005)

# PHASE TRANSITIONS IN THE POLYELECTROLYTE GEL WITH COUNTERIONS DIFFERING IN SIZE

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There are many of experimental publications on the investigation of the polymer systems with counterions differing in size. As the counterions both single halogen ions $Cl^-$, $Br^-$, $I^-$ or metal ions $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Ag^+$, and more complicated compounds like tetraalkylammonium and aminomethylanthracene and different surfactants are used. On the other hand, the effect of the size of counterions was not studied theoretically yet. In this paper the influence of the size of counterions on the collapse of polyelectrolyte gel is studied. The possibility of ion pair formation between charged groups of the gel and counterions is also taken into account. The model of monomer units, counterions and ion pairs as hard spheres of different radius is considered. Volume interactions between monomer units and counterions, counterions and ion pairs, monomer units and ion pairs, counterions themselves and ion pairs themselves are taken into account. The free energy of volume interactions is calculated using the virial expansion. The second and third virial coefficients are calculated. The collapse has been investigated for different potentials of interaction between the particles. The influence of the dielectric constant of the system on the collapse has also been investigated. It was found, that the volume interactions between counterions are not important for the behavior of the weakly charged polyelectrolyte gel. If the dielectric constant is big, the transition from swollen into collapsed state is discontinuous for the network with small counterions. When the counterions become larger, the transition becomes continuous. If the monomer units-counterions and counterions- counterions interactions are repulsive, the increase of the size of counterions leads to the shift of the transition towards poorer quality of the solvent and to increasing of the swelling coefficient. If the monomer units-counterions and counterions-counterions interactions are attractive, the swelling coefficient decreases with increasing of the counterion's size. If the dielectric constant is small, all point counterions form ion pairs, and large quantity of large counterions remains free. Therefore the gel with point counterions behave like neutral gel in this case, and the behavior of the gel with large counterions does not depend on the dielectric constant.

# SELF-ASSEMBLING OF AMPHOLYTE DENDRIMERS IN COMPLEX GELS

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Triple systems consisting of polyelectrolyte hydrogel (lightly cross-linked highly swollen sodium poly (2-acrylamido-2-methylpropanesulphonate) or poly(N-diallyl-N-dimethylammonium chloride)), ionic surfactant (Sf) (dodecyl- or cetylpyridinium chloride and respectively sodium dodecylbenzosulfonate) and ampholyte dendrimers of 1-4th generations (containing inner tertiary amino groups and peripheral carboxylic groups) have been studied. It was found that complex gels formed via the active sorption of the ampholyte dendrimers by the oppositely charged polyelectrolyte hydrogels can interact with Sf to produce Sf-dendrimer complexes inside the cross-linked matrix. Depending on pH values of the surroundings the molecules of the ampholyte dendrimers can bear as negative (pH>pI, only the outer carboxylic groups are charged) as positive charge (pH).

# HYDROGEL MATERAILS AND TECHNOLOGY FOR WASTEWATER PURIFICATION

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Amphoteric hydrogels are finding increased use in separation and enrichment technologies through combined adsorption, chelating and ion-exchange processes [1,2]. We have developed novel high swellable betaine type gels, the main advantages of which are: i) high swelling degree in water; ii); high metal adsorption capacity); iii) easy desorption of metal ions in the media of mineral acids; iv) reusability; v) longevity and durability of hydrogel materials. It was found that the adsorbed metal ions can be released from the gel matrix at the isoelectric point of amphoteric gel due to the realization of "forcing out effect" [1,2]. The salient property of amphoteric gels to swell in salt-containing water and deswell under the imposed externally DC electric field was used for developing of wastewater purification technology.

[1] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric betaines: Synthesis, characterization and application. Adv.Polym.Sci. 201, 2006.

[2] S.E. Kudaibergenov, Polyampholytes: synthesis, characterization and application. New York, Kluwer Academic/Plenum Publishers, 2002, 220 p.

# MICROGELS CONTAINING ZNO NANOPARTICLES

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Preparation of the temperature and pH-sensitive hybrid microgels containing ZnO nanoparticles is reported. The synthesis of ZnO nanoparticles in the presence of two different microgels poly(N-vinylcaprolactum-co-acetoacetoxyethyl methacrylate) (VCL/AAEM) and poly(N-vinylcaprolactum-co-acetoacetoxyethylmethacrylate-co-N-[3-dimethylamino)propyl]-methacrylamide)(VCL/AAEM/PDMAPMAm) has been studied. It has been found that these microgels act as the container for deposition of ZnO nanoparticles, under the specific reaction conditions, leading to the formation of hybrid microgels. Change in the colloidal stability, temperature sensitivity and swelling-deswelling behaviour of these microgels after the inclusion of ZnO particles has been studied. A close relationship between changes in properties of hybrid microgels with the loaded ZnO content is reported. Higher ZnO content leads to the lower colloidal stability of composite particles in water. Microscopic studies pr! ove the inclusion of nanoparticles into microgels. It has been found that prepared microgels have tendency to form composite films on solid substrates after water evaporation, with homogenous distribution of ZnO nanoparticles in polymer matrix.

# POLYMER–DYE INTERACTIONS AS A TOOL FOR STUDYING PHASE TRANSITION

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During the last forty years, macromolecules have been investigated intensively, due to their enormous applications that cover almost all segments of human life, e.g. from food to material and pharmaceutical technology. For both theoretical and practical reasons, a thermo sensitive polymer attracts special attention . In aqueous solution, the poly N-alkylacrylamide undergoes a phase transition, above a lower critical solution temperature (LCST) of 32 °C. For such polymers, the microenvironment polarities near the main chains change considerably with the phase transition. Since its discovery, this phase transition has been well-studied by various methods especially with calorimetry. Studies involving the addition of fluorophores in the matrix indicated that the micro environmental polarity near the main chain of poly(NIPAM) decreased above 32 °C as compared to that below 32 °C. They also support the view point that the phase transition is due to the collapse of an open coil to a more globular structure. At the same time the changing of polymer conformation induces of changing of hydration shell around the molecule causing differences in water structure around the polymer and within the polymer globule. Fluorescence techniques are especially popular due to their selectivity in signal detection, all the way down to the single molecule level, as well as their high sensitivity to the environmental changes. Recently, numerous publications have dealt with the physical properties of polymers investigated by using single molecule detection methods.. Since Single Molecule Spectroscopy completely eliminates the averaging inherent to ensemble measurements, it is possible to observe the heterogeneities and local fluctuations of the polymer network. We aim, in this paper, to report on the wealth of information obtained by investigating the phase transition of a NIPAM network within bulk and at the single molecule level. Experiments were performed by measuring the emission of a carbocyanine water soluble dye (S0522).We were able to observe the influence of the polymer motion below and above the transition point on the emission properties of the single dyes and their changes in anisotropy during the transition. These investigations also reveal structure of NIPAM as well as structure of water inside NIPAM pocket above phase transition.

# SWELLING BEHAVIOR OF POLYELECTROLYTE HYDROGELS

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The equilibrium swelling behavior of cross-linked polyelectrolyte gels has been investigated by means of a scaling analysis combined with molecular-dynamics simulations of a coarse-grained bead spring model. To do this, idealized defect-free networks with a diamond-like topology of the crosslinking have been considered at the Theta-point and under good solvent conditions. In all cases the counterions were treated explicitly. A multitude of systems covering the range between strongly and very weakly charged gels were examined for both solvent qualities, in order to provide a basis for a detailed scaling analysis. For this we varied the amount of charges in the system, the length of the network chains and the strength of the electrostatic interactions for both solvent qualities over a wide range of parameters. We find that current theories only apply in the limit of weak electrostatics and suggest corrections based on the microscopic interplay of the systems' components, which are accessible in a simulation and allow to model successfully our "measured" data. The resulting swollen structures can be described by mechanical theories, after taking charge renormalization properly into account. Consequences for hydrophobic polyelectrolyte backbones will be discussed as well and compared to polyelectrolyte conformations in poor solvent for the backbone.

B. A. Mann, R. Everaers, C. Holm, K. Kremer, Europhys. Lett. 67, 786 (2004)
B.A. Mann, C. Holm, K. Kremer, J. Chem. Phys. 122, 154903 (2005).

# THERMODYNAMICS OF POLYELECTROLYTE GEL/OPPOSITELY CHARGED COLLOID INTERACTIONS

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A new thermodynamic model of the interaction of linear polyelectrolytes and polyelectrolyte hydrogels with oppositely charged surfactant and proteins will be presented. The model, which is fairly detailed, makes it possible to compare the relative importance of electrostatic, excluded volume, and elastic interactions. Results from model calculations will be presented and compared with experimental data. The talk will focus on the following aspects: 1) The nature of the cohesive force in ‘complex salts’, and the influence of the polyion degree of polymerization and linear charge density on the stability and structure of complex salts, 2) The importance of phase coexistence in cross-linked gels and its relation to network elasticity, and the question of thermodynamic stability of collapsed surface phases (core/shell).

# MONTE CARLO SIMULATIONS OF POLYELECTROLYTE GELS: THE EFFECT OF OPPOSITELY CHARGED SPECIES AND NETWORK TOPOLOGY ON SWELLING

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Hydrogels swell in pure water due to the osmotic pressure created by the presence of network counterions. Such gels response to changes in the surrounding solution, e. g., and shrink on being immersed in salt solution and collapse on being immersed in surfactant solutions due to micellar aggregation inside the hydrogel. It is also known that the internal topology of the gel (such as the fraction of network chains and the distribution of crosslinker in the network) can greatly influence hydrogel swelling. We have used Monte Carlo simulations to study how gel swelling depends on the presence of oppositely charged particles and the network topology. In all simulations we have employed a coarse-grained model, with explicit counterions in a periodicly bounded simulation cube. The deswelling of diamond lattice gels in the presence of either a 1:1 or a 1:2 simple salt was studied and results qualitatively compared against the Flory-Rehner-Donnan theory. The theory is shown to hold for gels in a 1:1 salt but shows worse agreement for divalent counterions. We have also shown how the collapse of diamond lattice hydrogels is affected by the presence of macroions of varying charge and radius. The collapse is described in terms of osmotic pressure, excluded volume and polyelectrolyte-macroion attraction terms. The swelling of trimodal networks (hydrogels made from three known lengths of polymers) have been simulated. Trimodal networks are found to swell less than the corresponding monomodal networks. The relative stretching of chains in the trimodal and monomodal gels has been discussed. By successively unclipping monomodal network chains we have studied the effect of the reduction of elastic network chains on gel swelling. All hydrogel networks swell compared to the ideal case when the elastic network fraction of chains is reduced. This effect is described by an increase in chain entropy and a decreased elastic restoring force contribution of the infinite network. Preliminary results for randomly cross-linked hydrogels in solution are presented. The resulting hydrogel has a low fraction of elastic network chains and a homogeneous distribution of crosslinker particles and thus swells less than an ideal diamond lattice gel. We use graph theory to explain the reduced swelling capacity of these 'real' hydrogels. The swelling/deswelling as a function of salt and network type will also be presented.

Monte Carlo Simulations of Defect-Free Cross-Linked Gels in the Presence of Salt
Edgecombe, S.; Schneider, S.; Linse, P. Macrimilecules; 2004; 37(26); 10089-101000.

Monte Carlo Simulations of Crosslinked Polyelectrolyte Gels with Oppositely Charged Macroions
Edgecombe, S.; Linse, P. Langmuir; (Accepted); 2006;

# ADSORPTION OF MACROMOLECULES TO RESPONSIVE SURFACES

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The phenomenon of polymer, or protein, adsorption to substrates, like lipid bilayers, is very relevant in biophysics, since many biological processes occur at interfaces involving these components. It is also of major technological importance. The adsorption of macromolecules at planar or spherical substrates is an intermediate step in fabrication of drugs or gene delivery vehicles. Also, and due to its unique structure, DNA is a good candidate for future nanodevices such as templates, biosensors, or semi-conducting molecules. This has prompted to a great interest in the study of DNA at interfaces. It has been observed, by fluorescence microscopy, that DNA adsorbs onto catanionic vesicles and cationic liposomes, in a compacted conformation, whereas it presents an extended conformation when adsorbed at cationic lipid bilayers deposited on a glass substrate. These experimental results have prompted a Monte Carlo study where we analyse the interaction of a negatively charged polyion with a surface consisting of sets of negative and positive charges, which are allowed to move in the xy plane, simulating the lateral diffusion of lipids in membranes, and also to protrude individually into the "solution". It is shown that the adsorption behaviour is determined by the length and stiffness of the polyelectrolyte, overall charge of the membrane, and mobility of charges in a non-trivial manner. When the membrane retains some positive charge, the discrimination based on the stiffness is low, but less flexible polyelectrolytes show a higher degree of adsorption if the charges are frozen, compatible with a smaller loss in internal entropy, while in the case of mobile charges adsorption is still almost complete, irrespective of the intrinsic stiffness. When the membrane becomes neutral or slightly negative the general view is that flexible polyions adsorb better for both mobile and frozen charges than stiffer ones. These findings go beyond the conventional adsorption behaviour of a polyion at homogeneously charged surfaces. When individual protrusions are considered the adsorption of the polyelectrolyte is further enhanced. The surface response to the adsorbing macromolecule is two-fold: (i) the displacement of the surface particles out of the surface plane and towards the macromolecule and (ii) the polarization of the surface with the concentration of positive charges near the oppositely charged molecule. This is further illustrated by the use of a macroion.

# WETTING OF AQUEOUS MIXTURES OF ANIONIC SURFACTANTS AND A CATIONIC POLYELECTROLYTE ON POLYMER SURFACES

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The wetting behaviour of aqueous surfactant/polyelectrolyte mixtures on polymer surfaces of different hydrophobicity (in terms of surface energy) was systematically investigated. Anionic surfactants sodium laureth sulfate (LES) and sodium lauryl sulfate (SDS) and cationic polyelectrolyte hydroxyethylcellulose (HEC) were used in this study. Static and dynamic contact angles of aqueous surfactant/polyelectrolyte mixtures as well as those of their individual components were measured in the pre- and micellar concentration range of surfactants at constant polyelectrolyte content on Parafilm and polyethylenterephthalate (PET) surfaces. The static contact angle on Parafilm is slightly slowed down with increasing surfactant concentration, reaches a maximum value in the concentration range depending on surfactant type, and then decreases towards to the higher concentration values. On moderately hydrophobic PET, the static contact angle decreases with increasing concentration within the whole concentration region investigated. The wetting behaviour will be discussed with reference to the charge ratio of individual components in the mixture (i.e. n-/n+). The surface modification of both polymer surfaces caused by adsorption of surfactant/polyelectrolyte complexes was investigated, as well. The advancing contact angle of water on modified Parafilm surface decreased compared to the initial one whereas the PET surface becomes more hydrophobic as a result of adsorption of surfactant/polyelectrolyte complexes.

# INTERACTION OF GLOBULAR MODEL PROTEINS WITH BINARY POLYELECTROLYTE BRUSHES

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Mixed brushes of oppositely charged polyelectrolytes are representing a special case of responding surfaces which are sensitive to changes of the pH value in aqueous environment. The polyelectrolyte brushes used were composed of the two oppositely charged polyelelctrolytes poly (2-vinylpyridine) (P2VP) and polyacrylic acid (PAA) and the in-situ properties and surface characteristics, as surface charge, surface tension, extent of swelling of these brush layers are described . To test the behaviour of the polyelectrolyte brushes when coming into contact with biosystems, protein adsorption experiments with globular model proteins (α-chymotrypsin and α-lactalbumin) were performed at different pH values and salt concentrations of the buffer solutions. The influence of the pH value and the buffer salt concentration on the adsorbed amount, the structure of the protein layers and the interfacial tension during protein adsorption as well as the protein adsorption mechanism in reference to recently developed theories about protein adsorption on polyelectrolyte brushes will be discussed.

# STRENGTH OF FLOCS FORMED FROM CLAY MINERAL PARTICLES IN THE PRESENCE OF POLYELECTROLYTES

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The settling characteristics of a suspension and strength of flocs have important role in phase separation used in water treatment and clarification. These characteristics depend on the solid concentration, the tendency of particles to cohere, floc size, shape and density as well as shear conditions. The kinetics of flocculation of bentonite and kaolin suspensions by cationic polyelectrolytes, the growth, destruction and re-growth of flocs in a flow system as well as the influence of floc strength on settling characteristics as a function of the polymer dose, solid content and stirring conditions have been studied. To characterise the degree of aggregation measurements of fluctuations of light transmittance in suspensions by PDA-2000 Dispersion Analyser were used. It has been shown that an increase in the applied shear causes an increase in the degree of particles aggregation up to stirring at 300-500 rpm, while at further increase of the stirring intensity the size of aggregates decreases. The biggest and most stable aggregates are formed at condition of alteration of slow (50 rpm) and fast (500 rpm) stirring the suspension. Processes of aggregates formation, growth, destruction and subsequent restoration depend on the change of conformation and packing density of macromolecules in adsorbed layers located in aggregates of particles with changes the polymer dose and applied shear values. The settling characteristics of the suspensions were measured before and after the stirring test using the intensity of transmitted light determined by spectrophotometric method. Flocs resistance to shear was tested using a Standard Shear Test Stirrer. A simple mathematical model was developed to characterise the flocs destruction during the stirring and a parameter was selected as indicator of settling characteristics. Its dependence on flocculation conditions and floc strength was studied. Kaolin floc characteristics and the influence of flocculation conditions were also analysed using photosedimentation method. The floc density function was established for different polyelectrolyte doses and stirring conditions.

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# CHARACTERISING SELF-ASSEMBLED MONOLAYER FILMS OF PH-RESPONSIVE DIBLOCK COPOLYMER MICELLES

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A diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-block-poly(2-(diethyl amino)ethyl methacrylate) (PDMA-PDEA) can form pH-responsive micelles reversibly in aqueous solution: PDMA-PDEA exists as unimers under an acid condition, while in alkaline solution it forms core-shell micelles with the hydrophobic PDEA chains located in the cores and the hydrophilic PDMA chains forming the micelle coronas [1]. When adsorption is investigated from the micellar solutions, the adsorbed layer structure at either a mica/aqueous solution or silica/aqueous solution interface shows an adsorbed layer of micelles [2-4]. Interestingly, however, titration to a lower pH is not seen to completely degrade this layer even when the bulk structures would be completely disaggregated. Rather, we see that: (i) the adsorbed micelles seen at high pH are observed to "open" at low pH (due to protonation of the hydrophobic PDEA core chains); and, (ii) the original core-shell adsorbed micelles appear to be reformed on returning to high pH [2, 3]. In this presentation, we report evidence for the self-assembly of PDMA-PDEA micelles at a silica/aqueous solution interface. The effects of repeated exposure to acidic/alkaline water on the adsorbed micelle structures are also presented.

[1] Bütün, V.; Armes, S. P.; Billingham, N. C. Polymer (2001) 42, 5993.
[2] Webber, G. B.; Wanless, E. J.; Armes, S. P.; Tang, Y.; Li, Y.; Biggs, S. Adv. Mater. (2004) 16, 1794.
[3] Webber, G. B.; Wanless, E. J.; Armes, S. P.; Biggs, S. Faraday Discuss. (2005) 128, 193.
[4] Sakai, K.; Smith, E. G.; Webber, G. B.; Schatz, C.; Wanless, E. J.; Bütün, V.; Armes, S. P.; Biggs, S. Submitted.

# BUNDLE FORMATION IN POLYELECTROLYTE BRUSHES

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Bundle formation in the vertically oriented polyelectrolytes 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. At 0.5 Molar monomer concentration and without added salt, 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.

# ADSORPTION OF POLYELECTROLYTES AT OPPOSITELY CHARGED SURFACES

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The adsorption of highly charged polyelectrolytes onto oppositely charged planar surfaces is investigated by means of Monte Carlo simulations [1]. Flexible as well as rod-like (i. e., rigid) polyelectrolytes are considered. The effects of image forces stemming from the dielectric discontinuity at the substrate interface are also taken into account. It is demonstrated that for sufficiently long chains, the adsorption of polyelectrolytes is considerably larger with rod-like polyelectrolytes than with flexible ones. On the other hand, when image forces are present flexible and rod-like polyelectrolytes get adsorbed with a similar strength.

[1] R. Messina, J. Chem. Phys., VOL. 124, 014705 (2006)

# ISOTOPE EFFECT IN THE ADSORPTION OF LIGHT AND HEAVY WATER VAPOURS IN POLYELECTROLYTE MULTILAYER FILMS

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Isotopic replacement in chemical compounds is a common method used in physics, chemistry and biology which enables local investigations up to the scale of a single atom. The method is important for techniques as NMR spectroscopy or neutron scattering. Although the physical properties of the compounds vary with their isotopic composition, it is commonly assumed that the isotopic modification does not alter the chemical properties of the materials. We studied the sorption of light (H2O) and heavy (D2O) water vapours in polyelectrolyte (PE) multilayer (PEM) films prepared on solid support from polystyrenesulfonate (PSS) and polyallylamine hydrochloride (PAH) using the Layer-by-Layer technique. We showed by means of scattering (neutron and X-ray reflectometry) and gravimetric (Quartz Crystal Microbalance) experiments that the isotope effect is far from negligible. The swelling of PEM in H2O and D2O vapours is the same, but the amount of sorbed water strongly depends on the used isotope, being twice as high in the case of D2O. The volume fraction of sorbed H2O is comparable with the volumetric change of the film thickness. No effect of the isotope exchange in the PE molecules used to build the PEM was observed. Well pronounced dependence on the nature of the last PE layer was detected. The different uptake of D2O and H2O in PEM cannot be explained only by the different physical properties of the two isotopes. A preliminary model which may explain the observed effect was proposed. The results should be taken into account when new materials based on PEM are characterized or their loading properties are studied. The effect itself may be used to develop new sensing materials responsive to vapours with different isotope content. We have shown the isotope effect being larger than a factor of two which can also have a strong influence on the chemistry and physics of other nanoporous systems.

# THERMOSENSITIVE SURFACE COATINGS BASED ON PNIPAM MICROGELS ADSORBED ON PEI LAYERS

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In the present contribution the formation of PNIPAM microgel based surface coatings and their properties will be discussed. The microgels contain acrylic acid as co-monomer and their charge can be easily controled by changing pH. In this way it is possible to control the interaction of the particles with a poly(etylene imine) coated substrate. We present a procedure to obtain closed microgel coatings which change their thickness and hence their reflectance as a function of temperature. In contrast to coatings obtained with linear PNIPAM block-copolymers the swelling and de-swelling of the microgel layers is fully reversible. This type of new composite material seems to be promising with respect to applications as sensor.

# FORMATION, CHARACTERIZATION AND APPLICATION OF POLY(4-VINYLPYRIDINE) N-ALKYL QUATERNIZED MONOLAYERS SUPPORTED ONTO SI WAFERS

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The adsorption behavior of bromide salts of poly(4-vinylpyridine) N-alkyl quaternized with linear aliphatic chains of 2, 4 and 5 carbon atoms, P4VPyC2, P4VPyC4 and P4VPyC5 respectively, onto Si wafers has been studied by means of ellipsometry, contact angle measurements and atomic force microscopy (AFM). Solutions of P4VPyC2, P4VPyC4 and P4VPyC5 were prepared in the concentration range of 0.01 g/L to 2.0 g/L in the ionic strength of 0.001 mol/L NaCl or 0.1 mol/L NaCl. P4VPyC2, P4VPyC4 and P4VPyC5 with average molecular weight MW of 60 000 g/mol were prepared as described elsewhere [1]. Independent on the aliphatic side chain length, the adsorbed amount was low (1.0 +/- 0.1 mg/m$^2$) under low ionic strength. Upon increasing the ionic strength the adsorption was favored, reaching a mean plateau value of 1.9 +/- 0.2 mg/m$^2$. These findings indicate that the adsorption follows the screening enhanced adsorption regime [2], where the adsorption is not driven by electrostatic interaction. Interestingly, the advancing contact angles increased as the aliphatic side chain length decreased. P4VPyC2 and P4VPyC5 covered Si wafers presented mean advancing contact angles of (67 +/- 5)o and (44 +/- 4)o, respectively . These findings suggest that P4VPyC2 chains are more mobile, exposing their hydrophobic portions to the air, than P4VPyC5 chains. Polymer covered Si wafers are rougher than bare Si wafers, as evidenced by AFM images and contact angle measurements. Regions of ordered domains could be observed by AFM. In a second step, the immobilization of bovine serum albumin (BSA) and lysozyme (LSZ) onto P4VPyC2, P4VPyC4 and P4VPyC5 covered Si wafers has been investigated by means of ellipsometry and AFM. These proteins have been chosen as model proteins because BSA has isoelectric point (pI) at pH 5.3 and LSZ at pH 11 [3]. The experiments have been performed at pH 7, under neutral conditions BSA is negatively charged, while lysozyme is positively charged.! For a constant protein concentration of 1.0 g/L, BSA adsorbed similarly (7.5 +/- 0.5 mg/m$^2$) onto P4VPyC2, P4VPyC4 and P4VPyC5 covered Si wafers. On the contrary, the adsorbed amount of LSZ onto P4VPyC2, P4VPyC4 and P4VPyC5 covered Si wafers amounted to (0.13 +/- 0.05) mg/m$^2$, (0.90 +/- 0.05) mg/m$^2$ and (1.4 +/- 0.1) mg/m$^2$, respectively. Therefore, LSZ adsorbed preferentially onto a more hydrophilic surface. These findings were confirmed by AFM images.

[1] M. D. Úrzua, H. E. Rios, Polymer International 2003, 52, 783.
[2] Van de Steeg, H.G.M., Cohen Sturat, M.A., de Kaizer, A., Bijterbosch, B.H. Langmuir 1992, 8, 2538.
[3] Hollmann, O., Czeslik, C. Langmuir 2006, 22, 3300.

# GUANOSINE MOLECULES DEPOSITED ON THE SURFACE OF MICA AND STUDIED USING ATOMIC FORCE MICROSCOPY

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The guanine specific molecular structure enables the formation of self-assembled structures with guanosine-quartets (G-quartet) as the basic building units. G-quartets are also building blocks of quadruplex DNA configurations that appear in various guanosine rich segments of the DNA and play a vital role in several biological processes. In aqueous solutions and in the presence of different counterions the disc shaped G-quartets can stack on top of each other to form 1D columnar aggregates known as "G-wires". Recent studies have shown that various surface architectures made from "G-wires" can be used for fabrication of photo- and electro-active molecular electronic devices [1-3]. An important step for exploration of guanosine based surface architectures is to control their surface deposition methods. In relation to this problem we investigated the deposition of the guanosine 5'- monophosphate (GMP) on the freshly cleaved muscovite mica. The starting GMP material was in the form of sodium or potassium salt. The solutions were prepared by dissolving the GMP salts in pure water at different mass concentrations. In order to prepare surface structures we used the dip coating method followed by a subsequent drying of the substrate. The resulting surface structures were analysed with the atomic force microscopy (AFM). We studied the effect of concentration and influence of counterions on the surface architecture. Our results indicate that the formation of single "G-wires" and multi-layered surface structure strongly depend on the mass concentration of the depositing solution.

[1] Gottarelli, G., Spada, G. P., The Chem. Rec. 4: 39-49 (2004).
[2] Vesenka, J., Henderson, E., AIP Conference Proceedings 640:109-122 (2002).
[3] Marsch, T. C., Vesenka, J., Henderson, E., Nucl. Acids, Res.23, (4), (1995).

# INTERACTIONS OF OPPOSITE CHARGE POLYELECTROLYTES AT THE SOLID / LIQUID INTERFACE

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Our interest in this work was focused on the study of layer-by-layer adsorption regularities of cationic polyelectrolyte polydiallyldimethylammonium chloride (PDDA) of two different molecular weights (Mw = 400000-500000 (HMW) and Mw = 100000-200000 (LMW)) and anionic polyelectrolyte polyacrylic acid sodium salt (Mw = 2100). The investigation was carried out on fused quartz surface by capillary electrokinetic method. The adsorption kinetics for cationic and anionic polymers was studied in concentration range from 10-5 g/l up to 10-1 g/l. The dependence of the first adsorbed layer structure was investigated on the formation conditions such as concentration of PE (CPE), flow velocity of solution through the capillary during the adsorption, layer formation time. The structure of adsorbed layers depended on the molecular weight of PE: HMW PE adsorbed in conformation with loops and tails in all concentration range investigated and LMW PE adsorbed in flat confirmation up to C = 10-3 g/l. For cationic PE the adsorption was irreversible in all range of concentrations studied. The adsorption of anionic PE leads to the surface overcharge. The value of negative charge depends on PAA and PDDA concentration and the time of the first adsorbed layer formation. Due to the anionic polyelectrolyte adsorption the structure of CPE adsorbed layers changed: deformation of bilayer structure increased, significant swelling took place. This swelling decreased as a function of time. The investigation of PAA desorption showed that in all cases the adsorption of molecules are very strong and also irreversible.

# ADSORPTION OF POLYELECTROLYTES ON OPPOSITELY CHARGED POROUS MICROSPHERES

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The impact of macromolecule constitution and electrostatic dimensions on the adsorption of cationic model polyelectrolytes (PEL) on oppositely charged porous microspheres suspended in aqueous media is demonstrated. The contour length (L) of the PEL, the chemical structure of the substituents at the ionic group, the ionic strength of the solution (I), and the average pore radius of the adsorbent (R) are considered as variable. Information from adsorption isotherms quantitatively reveal how PEL, adsorbent, and medium characteristics affect the adsorbed amount and surface coverage. Electrostatic exclusion was proven as long as the Debye length (lD) exceeds R, even if L was considerably smaller than the pore diameter. A polyelectrolyte charge to surface charge ratio (CR) was derived and served to evaluate the surface occupancy. It is applicable to the two limiting cases: adsorption only on the porous microsphere outer surface and additional adsorption inside the pores. For CR>1 the PEL molecules do not occupy the surface completely whereas for CR<1 the surface is over occupied. Moreover, three models are proposed to illustrate the adsorption behavior. The findings are seen as valuable contribution to basic research in the field of PEL. Precise data, which were not available before, are provided for comparison with theoretical models and simulations. Overall conclusions may be useful for technical applications such as surface modification, chromatographic processes, or materials development.

V. Malinova, Doctoral thesis N°3244, EPFL 2005

# OPTICAL TWEEZERS TO MEASURE FORCES OF INTERACTION BETWEEN SINGLE (DNA-GRAFTED) COLLOIDS

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Optical tweezers are experimental tools with extraordinary sensitivity in its determination of the position of a micrometer-sized colloid and its measurement ( 50 fN) of forces acting on it. Experiments are reported in which, the forces of interaction between two identical DNA-grafted colloids are measured on approach to each other. Parameters to be varied are the grafting density of the DNA-brushes (1250 - 300 molecules per colloid ), the length (1000 basepairs (bp) - 6000 bp) of the double-stranded DNA-chains and the concentration and valency of the ions in the surrounding medium. Further experiments are carried out to measure under similar conditions as above the interaction between one DNA-grafted and one blank colloid. The results are discussed with respect to the different brush regimes.

# STRUCTURAL ANALYSIS OF POLYELECTROLYTE FILM ABSORBING METAL ION BY SAXS UTILIZING WITH X-RAY ANOMALOUS DISPERSION EFFECT.

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It is well known that polyelectrolyte film changes its property by absorbing metal ions: for example, electric conductivity of Nafion film decreases by absorption of the metal ions. Therefore, it is important to elucidate the structural change of polyelectrolyte film by absorbing metal ions. Small-Angle X-ray scattering (SAXS) is one of powerful tools to observe the structure in nano-scale. Even though the SAXS gives us information of the electron density distribution in the nano-scale, it is very difficult to derive distribution of a certain atom, such as a metal ion, from the SAXS data. In turn, because the spatial resolution of the SAXS (>10 A) is less than that of ordinary X-ray diffraction methods (<1A), it is impossible to distinguish high electron density domain by high density aggregation of material from that by aggregation of heavier atoms in the electric density fluctuation. In order to solve this problem, we utilize X-ray anomalous dispersion effect to the SAXS method: the SAXS is observed by sweeping the incident X-ray energy around the absorption edge of the target atom. In this case, the part of scattering profile concerning about the distribution of the target atom could be changed because the only atomic form factor of the target atom is drastically changed around the absorption edge. In the presentation, we report a distribution of Cu ion in Nafion, which is observed with this new method.

Structure Investigation of Metal Ions Clustering in Dehydrated Gel using X-ray Anomalous Dispersion Effect: J. Phys. Soc. Jpn, vol.72 (2003) 2110-2113, Y.Soejima, S.Kuwajima, M.Sugiyama, M.Annaka, A.Nakamura, N.Hiramatsu and K.Hara.

# AMINO STARCHES AS PH-SENSITIVE SURFACE COATING: SYNTHESIS AND APPLICATION

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Polymeric material with response to external stimuli such as pH and/or temperature have attracted much attention as supramolecular switchers. The former case is represented by a couple of different structures, displaying a pH-sensitive solution behaviour in aqueous systems. Typical examples are acrylate terpolymers containing tertiary amine functionality. Polyelectrolytes from renewable resources such as cationic starch or carboxymethyl starch are widely-used as ecologically friendly alternative for some synthetic polymers. Combining different starch structures with pH-sensitive functionality should trigger a dramatic change in solubility, too. So we aimed at the development of starch based tertiary amines as pH-responsive coating material. Homogeneous etherification of degraded or carboxymethylated starch yielded a couple of compounds with the desired pH-dependent solubility. The diisopropylamino group turned out to be the most favourable function in this respect. This was shown by pH-dependent turbidimetry. Additionally this principle was proved for two-component polyelectrolyte complexes. As an application example solid spherical surfactant mixtures were coated with different amounts of amphiphilic polymer or the corresponding polyelectrolyte complex in a fluidised bed. The resulting coated "particles" were analysed by measuring the surface tension in a dishwasher-like temperature and ionic strength regime. The efficiency of this coating was proved by comparing with commercial material in a real dishwasher. The starch coated surfactant displayed a better performance than the double amount of a commercially coated surfactant.

# HIGHLY CATIONIC STARCHES: MODIFICATION OF CELLULOSE FIBERS TOWARD HIGH FILLER TECHNOLOGY IN PAPERMAKING

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Modification of cellulose fibers via adsorption of highly functionalized 2-hydroxy-3-trimethylammoniumpropyl starch chloride (cationic starch) with degree of substitution (DS) in the range from 0.25 to 1.54 was investigated by electrokinetic measurements and fillers retention tests. It was found that the adsorbed amount of cationic starch at the plateau of the isotherm only slightly depends on the DS of the derivative and more remarkably on the amylose/amylopectin ratio. All studied cationic starches significantly improve kaolin particles retention in comparison with untreated fibers and fibers modified by low-substituted commercial starch. Balancing efficiency of performance and costs of starch cationization, we have concluded that the optimum DS of the cationic starch for cellulose modification in papermaking lies in the range 0.6-0.7, where filler loading up to 500 mg/g can be reached at a level of starch additions of 0.5-0.6 %.

# POLYELECTROLYTES WITH PHOSPHORIC ACID GROUPS BASED ON NATURAL POLYMERS

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Polysaccharides are natural polymers (biopolymers) that rise from a wide variety of vegetable or animal resources or are produced by microorganisms. The derivatization is a usual way to modify and improve the properties of polysaccharides. In our contribution we report new results regarding the polyelectrolyte behaviour of some phosphorylated polysaccharides which could be successful partners in applications such as crystallization modulators or interpolyelectrolyte complexes formation. The polyelectrolyte behaviour was studied using the following methods: - potentiometric titration with mono and divalent bases, in present or absent of low molecular salt. The interpretation of potentiometric curves was performed with Henderson-Hasselbach relation: $pKa = pH + \log[(1-\alpha)/\alpha]$ were Ka - apparent dissociation constants; $\alpha$ – degree of ionisation. The dissociation constants pK0 was estimated from extrapolation of $pKa = f(\alpha)$ curves; - conductometric titration with mono and divalent bases. The transport coefficients of the monovalent and divalent counterions and the equivalent conductance of polyanion were calculated; - viscosimetric measurements. Acknowledgement: The financial support of RELANSIN Program of the Romanian Ministry of Education and Research, project CEEX 46/2005.

[1] D.M. Suflet, G.C. Chitanu, V.I. Popa, "Phosphorylation of polysaccharides. New results on synthesis and characterisation of phosphorylated cellulose", Reactive and Functional Polymers, in press.
[2] D.M. Suflet, G.C. Chitanu, V.I. Popa, "Polyelectrolytes with phosphoric acid groups based on natural polymers", Polyelectrolytes 2004, Amherst, USA 14-18 iunie 2004.
[3] G.C. Chitanu, M. Rinaudo, M. Milas, J. Desbrières, A. Carpov, Langmuir, 1999, 15, 4150.

# CYCLODEXTRIN-ANIONIC POLYSACCHARIDE HYDROGELS; SYNTHESIS, CHARACTERIZATION AND INTERACTION WITH BIOLOGICAL ACTIVE SUBSTANCES

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Hydrogel microparticles have been prepared through co-crosslinking of cyclodextrin and carboxymethyl or sulfopropyl pullulan with a new bifunctional reagent: 3-(glycidoxypropyl)trimethoxysilane. Have been prepared samples with various ratios of cyclodextrin/ anionic polysaccharide and various amounts of crosslinking agent. The hydrogel microparticles were characterized through water swelling behavior, conductimetric titrations, scanning electron microscopy. The retention of biological active substances can occur both by their inclusion in cyclodextrin inner cavities and in the pores of hydrogels, as well as through electrostatic forces of anionic charged polyelectrolyte. The performances in inclusion/ elution of molecules can recommend the cyclodextrin/ anionic polysaccharide microparticles as chromatographic or controlled release drug systems supports.

# DYNAMIC LIGHT SCATTERING STUDY ON THE CALF VITREOUS BODY

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The vitreous body is a tenuous gel that contains collagen and Na-hyaluronate. The fraction of the polymer network is only about 1-2 %, and the remaining is water. Therefore, large amount of water is sustained within the dilute polymer network. The vitreous body has a complex structure, in which the highly flexible Na-hyaluronate is considered to be interwoven by semi-rigid network of collagen threads. Many studies performed to date have suggested that Na-hyaluronate, which has a coil shape, is uniformly distributed throughout the three-dimensional network of collagen fibers that form the triple helix in the vitreous body. However the structural properties of the vitreous body has not been determined. And essentially no investigations on the dynamics and phase equlibrium properties of the vitreous body, however, have been performed to verify indisputably that the vitreous body is indeed a gel network. In this study, the microscope laser light scattering spectroscopy is applied to investigate the structural and dynamical properties of the gel network in the calf vitreous body. It is natural to consider the collagen motion is the coupled with the dynamics of Na-hyaluronate, therefore we develop the equation for the mode coupling of flexible Na-hyaluronate and semi-rigid network of collagen. From the observations of the dynamics of light scattered by the calf vitreous body, intensity autocorrelation functions that revealed two diffusion coefficients, D(fast) and D(slow), were obtained. We developed the theory for describing the density fluctuation of the entities in the vitreous gel system with Na-hyaluronate polymers filled in the meshes of collagen fiber network. The dynamics of collagen and Na-hyaluronate explains two relaxation modes of the fluctuation. The diffusion coefficient of collagen obtained from D(fast) and D(slow), is very close to that in aqueous solution, which suggests the vitreous body is in the swollen state. The diffusion coefficients were found to be dependent on the position (surface or central part) of the vitreous body from which the scattered light sampled. The inhomogeneous distribution of Na-hyaluronate and collagen and the shell structure of the vitreous body were suggested. Together with experimental and theoretical results of dynamic light scattering, we discuss the elastic properties of the calf vitreous body.

[1] T. Matsuura, Y. Hara, S. Maruoka, S. Kawasaki, S. Sasaki and M. Annaka, Macromolecules, vol. 37, 7784 (2004)
[2] T. Matsuura, Y. Hara, F. Taketani, E. Yukawa, S. Maruoka, S. Kawasaki, and M. Annaka, Biomacromolecules, vol. 5, 1296 (2004)

# MULTILAYERED AND BULK FILMS BASED ON HYDROGEN-BONDED COMPLEXES AND BLENDS OF POLY(ACRYLIC ACID) AND METHYLCELLULOSE

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Interaction between poly(acrylic acid) and methylcellulose in aqueous solutions leads to the formation of hydrophobic interpolymer complexes (IPC), stabilised by hydrogen bonds. In this communication we will report three different approaches for preparing polymeric materials based on poly(acrylic acid) and methylcellulose. The first approach is based on casting solution mixtures of the two polymers without pH adjustment and subsequent drying in air, which results in bulk polymeric film formation. The second approach utilises mixing polymer solutions under acidic conditions leading to the formation of interpolymer complexes in the form of a dispersion, which gradually precipitates. In the third approach, thin multilayered IPC films can be prepared via layer-by-layer sequential adsorption of poly(acrylic acid) and methylcellulose on the surface of glass under acidic conditions. The materials prepared have been characterised by infrared spectroscopy, differential scanning calorimetry, scanning electron microscopy and solubility/swelling property testing. The potential applications of these materials in dosage forms design will be discussed.

# OLIGONUCLEOTIDE PH SENSITIVE NANOCONSTRUCT- ENSEMBLE AND SINGLE MOLECULE INVESTIGATIONS

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DNA, regardless its biological importance, is one of the most favorite building block for designing complex nano structures because oligonucleotides offer a unique way of controlling the molecular intra and intermolecular interactions throughout highly specific Watson -Crick complementarity's . The final goal of structural DNA nanotechnology is to build nanoscale objects, motors and devices, from DNA itself as from its self assembly in periodic arrays that perform motion induced by external stimuli. Up to date, different synthetic DNA nano structures are well described as promising candidates to serve as construction materials in nanosciences.. The subject of our research is the investigation, by fluorescence optical techniques, of a specifically designed construct made of two specific oligonucleotide chains with specific sequences that offers a controllable duplex – triplex transition by changing pH Up to our knowledge presented construct is one of the most humble and simple oligonucleotide structure, which allows the pH-dependent transition between a double and a triple DNA helix. At the basic pH = 9, the oligonucleotides have an elongated shape due to the repulsive interactions between the sequentially ordered bases in the backbone. This state is defined as the opened state. Decreasing the pH changes the electrostatic and hydrogen interactions between the bases and induces a bending of the single strand and formation of the triplex structure (also called the closed state). In order to study this global transition between the opened and the closed states at the ensemble and single molecule levels, using fluorescence techniques, a dye-quencher pair was introduced into the system: the dye (rhodamine green) and the quencher (Dabcyl - 4-[[4-(Dimethylamino)phenylazobenzoic acid) were inserted at positions 3 prime of the single strand (B) and 3 prime of the strand A, respectively.

# NEW ASPECTS ON THE INTERACTION BETWEEN DNA AND SURFACTANTS: COVALENT GELS AND AMINO-ACID BASED SURFACTANTS AS TRANSFECTION AGENTS

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DNA interacts differently to cationic surfactants than other anionic polyelectrolytes, for reasons which are not well understood. A number of anomalies on DNA-cationic surfactant systems have been identified including a "double cooperativity" in binding and an unexpected difference between single- and double-stranded DNA. On the basis of a review of previous studies, we analyze the results of our two quite different, but interrelated, ongoing investigations. In one of these, we prepare covalent DNA gels by chemical cross-linking and examine their swelling behavior in the presence of cationic surfactants and several other cosolutes, ranging from simple electrolytes to polymers and proteins. In the other, we investigate the interactions between DNA and novel divalent cationic amino-acid-based surfactants, including certain biological effects. In covalent DNA gels, in the presence of surfactants, there is no effect below the CAC, the critical association concentration, where surfactants start to self-assemble at the DNA chain. The CAC values are the same as for simple DNA solutions. On subsequent addition of an anionic surfactant the gels reswells to the initial value. These and other observations show interesting correlations with the compaction-decompaction of individual DNA chains. Between gels based on single- and double-stranded DNA there are striking differences. In contrast to classical cationic surfactants, an arginine-based divalent surfactant appears to be without any significant toxicity. Since it also can considerably enhance transfection efficiency, a closer study of the interactions with DNA was undertaken. This included studies of compaction and phase separation phenomena and characterization of the particles formed with respect to gross morphology and internal structure.

DNA-Cationic Surfactant Interactions are Different for Double and Single Stranded DNA, Rosa, Dias, Miguel, Lindman, Biomacromolecules, 2005, 6, 2164-2171.

Interaction between DNA Covalent Gels and a Cationic Surfactant, Costa, Hansson, Schneider, Lindman, Miguel, Biomacromolecules.

Amino acid-based catanionic surfactant systems: spontaneous formation of vesicles and dispersed cubosomes and hexasomes particles, Rosa, Infante, Miguel, Lindman, Langmuir.

# ADSORPTION OF THE FLEXIBLE SALIVARY PROTEINS STATHERIN AND PRP1 TO CHARGED SURFACES. A MONTE CARLO SIMULATION STUDY.

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Due to the inherent surface activity of proteins, adsorption usually takes place at almost any type of surface in contact with a biological fluid. The process proceeds quickly and a monolayer is usually formed within seconds or minutes. It is well known that this initial layering monitors subsequent biocolloid adhesion and biofilm growth; hence the formation of the initial protein layer is an important clue in order to understand and control biofilm growth. Oral biofilms, usually referred to as dental plaque, constitute a major research field due to the importance in dentistry in particular for the understanding of the development of plaque and related diseases, such as caries or periodontal disease. We have systematically over the last years studied key proteins in saliva and their role in the formation of the initial protein layer on surfaces in contact with saliva. Proteins of importance are statherin and the acidic proline rich protein PRP1. These are known to be responsible for maintaining the calcium balance in saliva and hence to affect e.g. remineralisation of the enamel. In addition, they have also been reported to be involved in mediating specific interactions with oral micoorganisms thereby modulating plaque growth. Structural properties of statherin and the acidic proline rich protein PRP-1 of salivary origin in bulk solution and adsorbed onto charged surfaces have been studied by Monte Carlo simulations. A simple coarse-grained model system with focus on electrostatic interactions and short-ranged attractions among the uncharged amino acids has been used. The effect of a short-ranged attractive interaction between the proteins and the surfaces and how it affects the adsorbed amounts on the surfaces will be discussed. The simulations results will be compared with data from ellipsometric studies.

# TAILORING SURFACE PROPERTIES OF THERMORESPONSIVE MICROGEL WITH NATURAL POLYELECTROLYTES

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The layer-by-layer (LbL) technique has been devised by Decher [1] in the early 1990s and involves the sequential adsorption of polyanions and polycations onto a charged surface. Synthetic polyelectrolytes such as poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH) or poly(sodium 4-styrene sulfonate) (PSS) have been widely studied for surface modification of various templates, planar as well as spherical. This has opened up doors for potential biomedical applications, and given momentum towards the assembly of natural polyelectrolytes [2] for biocompatibility. In this work we adsorb natural polyelectrolyte multilayers on soft and porous surfaces [3] of a thermoresponsive poly(N-isopropylacrylamide) (PNiPAM) microgel. The polyelectrolytes studied are poly(l-lysine), poly(l-glutamic acid), chitosan, and dextran sulphate. We report the optimum conditions for sequential adsorption of these natural polycations and polyanions on different building blocks depending on the location of the charge: (i) neutral core of cross-linked PNIPAM, (ii) a charged core of P(NiPAM-co-AA), AA being acrylic acid, (iii) a core-shell system composed of a neutral PNIPAM core and a charged P(NIPAM-co-AA) shell, and (iv) its inverse system composed of a charged P(NIPAM-co-AA) core and a neutral PNIPAM shell. The swelling and deswelling of the microgel after successive layer deposition is followed by measuring the hydrodynamic radius RH using dynamic light scattering, DLS. Depending on the core/core-shell structure of the microgel, DLS study reveals new features of the modified microgel surface: adsorption of these natural polyelectrolytes impart a permanent hysteresis to the thermoresponsivity of the microgel. Electrophoretic measurements reveal successful charge reversal after deposition of successive polyelectrolyte layer, and confirmed the build-up of the polyelectrolyte multilayers on the microgels. A fluorescent-labelled polyelectrolyte, FITC-labelled Poly(l-lysine) has been used within the multilayer to successfully prove that LbL is possible on soft and porous building block.

[1] Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992 , 210, 831.

[2] (a) Picart, C. ; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavalle, P. Proc. Natl. Acad. Sci. USA 2002, 99, 12531. (b) Boulmedais, F.; Bozonnet, M.; Schwinté, P.; Voegel, J. C.; Schaaf, P. Langmuir 2003 , 19, 9873.

[3] Wong, J. E.; Richtering, W. Prog. Colloid Polym. Sc. (in press).

# NOVEL MAGNETIC NANOPARTICLES SHELL ON A THERMORESPONSIVE MICROGEL CORE

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Recent advances in the synthesis of magnetic nanoparticles (MNPs) [1] have triggered their promising application to nanobiotechnology. In the search for biofunctional MNPs, several parameters have to be optimized for real applications. As drug-delivery vehicles, encapsulated MNPs would have to achieve high surface-to-volume ratio both for maximum magnetic density as well as high drug storage capacity, high affinity and selectivity to readily recognise and attach to targeted cells, fast delivery capabilities, and a good colloidal stability. Here, we report encapsulated MNPs onto poly(N-isopropylacrylamide) (PNiPAM) [2]. PNiPAM is a microgel with a high surface-to-volume ratio and a lower critical solution temperature (LCST) around 32 °C, i.e. it goes from a hydrophilic water-soluble coil to a hydrophobic water-insoluble globule above the LCST. Using the layer-by-layer (LbL) technique [3] we successfully assemble polyelectrolyte multilayers (PEMs) on the microgel imparting it with either positive or negative charges on the surface [4], and decorate the PEMs shell with MNPs. Positively charged MNPs were synthesized by co-precipitation technique, while the negatively charged MNPs were obtained similarly but in the presence of poly(acrylic acid) (PAA). The PEs used are poly(diallyldimethylammoniumchloride) (PDADMAC) and poly(styrenesulfonate) (PSS). Electrophoretic measurements confirm charge reversal at every stage of layering; giving zeta potentials of +30mV, -30mV and almost neutral on deposition of the PDADMAC, PSS, and the MNPs respectively. Dynamic light scattering (DLS) studies give a consistent hydrodynamic radius of around 300nm for the magnetic-coated microgel at 25 °C, and most importantly, reveal that thermoresponsivity in the latter is preserved. This unique combination of thermosensitivity and magnetism opens up novel perspectives towards remotely controlled drug carriers. Preliminary results obtained by cell incubation tests using tumor cells will also be discussed.

[1] Khalafalla, S. E.; Reimers, G. W. IEEE Trans. Magn. 1980, 16(2), 178.
[2] Schild, H. G. Prog. Polym. Sci. 1992, 17, 163.
[3] Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992, 210, 831.
[4] Wong, J. E.; Richtering, W. Prog. Colloid Polym. Sc. (in press).

# MAGNETIC NANOPARTICLE–POLYELECTROLYTE INTERACTION: A LAYERED APPROACH FOR BIOMEDICAL APPLICATIONS

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Magnetic nanoparticles (MNPs) [1] offer some unique advantages as sensing, image enhancement, and site-specific drug delivery. However, the size, charge, and surface of these MNPs strongly affect their applicability in the majority of the envisioned biomedical applications. It is important that the systems are biocompatible and capable of being functionalized for recognition of specific target sites in the body, hence the surface modification of the MNPs with polyelectrolytes (PEs). In this work we report two different surface modification methods. One approach is to prepare the MNPs from iron salts in aqueous solutions in the presence of PEs to impart an in-situ PE coating. Uncoated MNPs have positively charged surface, so the PEs used are either negatively charged (poly(acrylic acid) (PAA) [2] and poly(styrenesulfonate) (PSS)) or neutral (dextran). Charge overcompensation is observed in the former case as confirmed by charge reversal obtained from electrophoretic measurements. However in the latter case, the zeta potential is neutral, showing that the dextran sheath effectively shields the charges on the MNPs. Transmission electron micrographs (TEM) show that the MNPs remained discrete. The X-ray diffraction (XRD) patterns indicate that binding of PEs do not result in any phase change. Magnetic measurement reveals the MNPs are superparamagnetic, and their saturation magnetisation is only slightly reduced after PE binding. The second approach is to coat the MNPs with PE multilayers using the layer-by-layer technique [3]. The PEs used are polyethylenimine (PEI), poly(diallyldimethylammoniumchloride) (PDADMAC) and PSS. Electrophoretic measurements confirm charge reversal at every stage of layering. After every PE layer we observe not only an increase in size of the particles but also in the size distribution. Measurements from dynamic light scattering (DLS), superconducting quantum interference device (SQUID) and thermogravitometry analysis (TGA) will also be discussed. Preliminary results obtained by cell incubation tests using tumor cells and yeast cells show promising results. Fluorescence micrograph shows immediate attachment of MNPs to the yeast cells, and they successfully aligned themselves in the presence of an external magnetic field.

[1] Khalafalla S. E.; Reimers, G. W. IEEE Trans. Magn. Mag. 1980, 16, 178.
[2] Liao, M. H.; Chen, D. H. J. Mater. Chem., 2002, 12, 3654.
[3] Decher, G. Science 1997, 277, 1232.

# SOLUBILIZATION OF CARBON NANOTUBES IN WATER USING AMPHIPHILIC BLOCK POLYELECTROLYTES

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The solubilization of pristine carbon nanotubes in water by amphiphilic block copolymer, composed of a hydrophobic block and a heparin mimetic anionic polyelectrolyte block is presented. The synthesis of the block copolymer by combination of anionic polymerization high vacuum techniques and post polymerization reactions is described. The solubilization scheme involves the formation of a complex between the pristine carbon nanostructures and the polystyrene block due to hydrophobic interactions. The polyelectrolyte block keeps the PS/carbon nanostructure hydrophobic part in solution. Structure of the aforementioned hybrids at different levels is investigated by TEM, AFM and spectroscopic techniques. The universal nature of the solubilization protocol will be discussed in detail. The polyelectrolyte character of the above hybrid materials and their potential use in the field of nanotechnology will be also discussed.

# REVERSIBLE SUPRAMOLECULAR REORGANIZATIONS OF POLY (N-ETHYL-4-VINYLPYRIDINIUM BROMIDE) – SODIUM DODECYL SULFATE COMPLEXES

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Water-soluble complexes of poly(N-ethyl-4-vinylpyridinium bromide) (PEVP) and sodium dodecylsulfate (SDS) are known to exist either in the form of molecularly dispersed particles including only one macromolecule or highly aggregated species comprising at least 40 PEVP chains and about 20000 SDS ions. Supramolecular organization of PEVP-SDS complex (PSC) species in aqueous solutions was found to be determined by PEVP polymerization degree and the reaction mixture composition. This work is devoted to the study of supramolecular realignments of PEVP-SDS complexes in aqueous solutions upon change of the temperature and (or) complex concentration. The data of static and dynamic laser light scattering indicate that elevation of the temperature or complex concentration promotes aggregation of the complex species while highly aggregated complex particles completely disaggregate up to molecularly dispersed state upon decrease of the temperature. Aggregation/dissaggregation processes are completely reversible: return of the temperature to the initial value results in retrieval of the particle size distributions. The value of critical aggregation concentration (cac) of SDS in the presence of PEVP estimated by solubilization of water-insoluble dye Oil Yellow OB is about 5x10-5 M SDS in the whole temperature range studied (3 °C - 40 °C). Moreover, high-speed sedimentation studies indicate that composition of the complexes is also independent of the temperature. It means that reversible structural realignments of PEVP-SDS complexes that take place in solutions upon change of temperature and (or) PSC concentration represent aggregation or disaggregation of PSC species of the constant composition. Macrophase separation is observed upon additional heating of the samples to the temperature that is approximately 10 °C higher than the temperature at which the beginning of PSC aggregation is observed. The data of elemental analysis of precipitates indicate that the composition of insoluble complexes coincides with the limiting composition of soluble complexes. It means that phase separation induced by increase of the temperature is not accompanied by disproportionation as it is in the case of phase separation upon increase of the reaction mixture composition. This research is supported by Russian Foundation for Basic Research (project code 05-03-32492a).

# COMPLEX FORMATION BETWEEN POLYSTYRENE-B-POLY (METHACRYLIC ACID) MICELLES AND LINEAR POLY(2-VINYLPYRIDINE) IN SOLUTION.

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Block copolymer polystyrene-block-poly(methacrylic acid), PS-PMA, self-assembles into fairly monodisperse micelles when dissolved in 1,4-dioxane-rich mixture with water. Poly(2-vinylpyridine), PVP, chains interact strongly with micelle-shell blocks via hydrogen bond in organic media, and form large polydisperse clusters in the solution. When water content in the solution increases during dialysis against basic aqueous buffers, the clusters split into fairly monodisperse particles. The aqueous solutions of PS-PMA/PVP micelles were studied by a combination of light scattering, atomic force microscopy and fluorescence methods for various solution compositions, pH of aqueous buffers, PVP content and PVP chain length with respect to that of PMA blocks.

# SELF-ASSEMBLY OF POLY(ACRYLIC-ACID)-BLOCK-POLY(ACRYLIC ACID-GRAD-STYRENE) GRADIENT COPOLYMER IN AQUEOUS SOLUTIONS

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Behavior of poly(acrylic acid)-block-poly(acrylic acid-grad-styrene) PA-b-(PA-g-PS) gradient copolymer was studied in aqueous solutions using static and dynamic light scattering, fluorescence spectroscopy and atomic force microscopy. It was found that the gradient polymer self-assembles in aqueous solutions due to poor solubility of PS-rich ends of the PA-g-PS block. Unlike micelles, formed by PS-b-PA block polymers in aqueous solutions, these self-assembled structures are not in kinetically frozen state (the PA-b-(PA-g-PS) copolymer is directly soluble in alkaline buffers, whereas aqueous solutions of PS-b-PA copolymers must be prepared indirectly, e.g., by dialysis from mild selective solvents). Both light scattering and atomic force microscopy show the presence of two types of PA-b-(PA-g-PS) particles in the solution, whose size is strongly concentration-dependent. Acidimetric fluorescence titrations of alkaline aqueous solutions of PA-b-(PA-g-PS) aggregates marked with an amphiphilic fluorescent indicator, 5-(N-dodecanoylamino) fluorescein (DAF), revealed a considerable increase in pKa of DAF. This observation supports the assumption that the aggregates have a micelle-like core-shell structure, in which the fluorescent probe is bound close to the hydrophobic core and the shift of its pKa is caused by an additional energy required for a protone release from the negatively charged PA shell to the bulk solution.

# POLYMERIZATION OF IONIC MONOMERS IN SOLUTIONS OF SURFACTANT AS A NEW METHOD OF POLYELECTROLYTE-SURFACTANT COMPLEXES SYNTHESIS

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Synthesis and investigation of polyelectrolyte – oppositely charged surfactant complexes (PSC) is actively developing direction in polyelectrolyte chemistry. The great interest to the complexes is caused by the opportunities of their practical application, for example in the field of wastewaters treatment. Common method of PSCs preparation is mixing of polyelectrolyte with surfactant in aqueous solution. We have shown that template polymerization of water soluble monomers in aqueous solutions of oppositely charged surfactants is an alternative method of synthesis of PSCs with substantially different properties in comparison with the common ones. Polymerization of 1,2-dimethyl-5-vinylpyridinium methyl sulfate and N,N,N,N-trimethyl(methacryloyloxyethyl)ammonium methyl sulfate was studied in aqueous solutions of sodium dodecyl sulfate (SDS) in the wide range of monomer and SDS concentrations. It was found that template mechanism of polymerization is observed at SDS concentration above cmc. Indeed, if SDS concentration is close to CMC, slight increase of polymerization rate is observed, while further elevation of SDS concentration results in sharp decrease of polymerization rate indicating the template kinetic effect. Molecular mass of the polymerization product is 3–4 times lower in the case of template polymerization in comparison with the product of polymerization in pure water that was carried out at the same concentrations of initiator and monomer. Dilution of the template polymerization product results in formation of PSCs. PSCs prepared either on the base of diluted template polymerization product or on the base of corresponding polyelectrolytes obtained by common free radical polymerization ("common PSCs") were studied by static and dynamic light scattering, turbidimetry and viscosimetry. It was found in particular that the complexes prepared by template polymerization are water-soluble up to Z=[SDS]/[PE]=0.85–0.95 while the common PSCs are water-soluble only up to Z=0.5. We believe that such difference is caused by the template control during polymerization leading to significant change of the polymer microstructure.

# SOLUBILITY AND HYDRODYNAMICS OF POLYELECTROLYTE – SURFACTANT STOICHIOMETRIC COMPLEXES IN ORGANIC SOLVENTS

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Polymer - colloid stoichiometric complexes are formed by polyelectrolyte (P) and surfactant of opposite charge (S) at the equimolar ratio. The polymer - colloid complexes have amphiphilic character and are capable of limited swelling in water and in organic solvents of various polarity. Thus it is established that there is no correlation between the complex solubility and dielectric constant of the solvent. Nevertheless stoichiometric complexes can be dissolved in the organics which are capable to solvate both polar and nonpolar groups, for example, in chloroform. Molecular and hydrodynamic properties of the complexes based on the super high-molecular poly-N, N-dimethyl-N-benzyl(oksyethylmethacryloyl)ammonium chloride were investigated in the individual and mixed solvents by methods of viscosimetry, sedimentation and light scattering. The prepared complexes have ultrahigh molecular mass ((3.0 - 4.4)×107), value of hydrodynamic radius is about 100 nm and also they do not form intermolecular associates in chloroform. It was found that solutions of the complexes in chloroform and methanol show polyelectrolyte behavior with complex concentration decrease. One can suppose that polyelectrolyte behavior appears owing to presence of chain effective charge even in low polar solvents that leads to electrostatic pushing and coil swelling. The increase of hydrocarbons content in the chloroform/hydrocarbon mixture results in compacting of the coil, and it is connected with lower solvation of ionic pairs. Therefore solubility of the complexes and coil swelling is provided with weaken of interionic interactions. Association of polycomplex macromolecules with another amphiphilic molecules - oil-soluble surfactants - accompanies with additional solvation of ionic pairs and polar groups that provides the additional coil swelling and high solution viscosity.

# SOLID-LIQUID SEPARATION OF OIL-BASED DRILLING MUDS

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A novel method employing polyelectrolyte lattices to improve the solid-liquid separation of oil-based drilling muds has been developed and implemented on the field scale. Oil-based drilling muds serve several functions in a littoral drilling process, including lubricating and cooling the drill bit, suspending and transporting cuttings, maintaining well-bore stability, controlling fluid loss to the formation, and buoying the drill string. These oil-continuous functional fluids are typically inverse emulsions (W/O) containing both intentional and adventitious water, suspended solids and surface active species. Mechanical methods are used to remove suspended cuttings during drilling operations; however, fine suspended solids can eventually accumulate to the point where the drilling fluid properties have been sufficiently compromised such that it is no longer useable. Conventional solid-liquid separation technologies, including centrifugation, do not provide at this point a sufficient basis for remediation of the waste mud without very significant dilution of the waste mud. Such a dilution approach can result in additional environmental problems. Previous attempts to improve the solid-liquid separation of waste oil-based drilling muds, using a variety of chemicals including aqueous solutions of polyelectrolytes, proved to be inadequate in large-scale applications. This poster demonstrates the use of a combination of a demulsifying surfactant and polyelectrolyte latex particles to effectively flocculate the solids in waste oil-based drilling muds, allowing greatly improved solid-liquid separations through a conventional centrifuge. The recovered liquid phase is sufficiently clean that it may be directly recycled into making fresh drilling mud. The flocculation process is driven by the attraction and adhesion of polyelectrolyte latex particles to the hydrophilic solids suspended in the oil-continuous mud. This process may be qualitatively understood in terms of wettability differences; however, a more complete description involves attention to a more complex set of interfaces and interactions. Successful application of a commercial-scale technology based on this mechanism will be highlighted.

# WEAK POLYELECTROLYTE/NANOPARTICLE COMPLEXES : SIMULATED ANNEALING IN A GRAND CANONICAL MONTE CARLO APPROACH.

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Monte Carlo simulations are used to study two different models of a weak linear polyelectrolyte in presence of nanoparticles: (i) a rod-like and (ii) a flexible polyelectrolyte. The use of simulated annealing computation technique has made possible to simulate polyelectrolyte chain in presence of several nanoparticles and generate dense and equilibrated complexes without being trapped in local minima weak polyelectrolyte. Titration curves are calculated and the influence of the ionic concentration, surface charge density and number of adsorbed nanoparticles on the polyelectrolyte/nanoparticles complexes are systematically investigated. It is shown that the complex formation modifies the acid/base properties of the polyelectrolyte, promoting monomer deprotonation. The balance of attractive and repulsive interactions on the complex conformation and nanoparticle distribution along the polyelectrolyte backbone as well as the polyelectrolyte stiffness are discussed. Comparison of the two polyelectrolyte models provides an important insight into the polyelectrolyte flexibility influence on the complex formation. Flexible polyelectrolyte promotes the formation of dense structure in which the polyelectrolyte chain acts as a polymeric glue for the nanoparticles. The influence of the charge mobility along the polyelectrolyte, number of adsorbed nanoparticles as well as the overcharging are also discussed.

# DYNAMIC PHENOMENA IN AQUEOUS PIBX-B-PMAAY MICELLAR AND IPEC SOLUTIONS

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Up to now only few investigations of dynamics of block copolymer systems have been reported. Mostly copolymers with a hydrophobic block with Tg above room temperature have been investigated (PS-PAA, PS-PMAA,…). Here the dynamic processes of the aqueous solutions are hindered due to the glassy state of the PS core of the micelle. In our case we employ polyisobutylene (PIB) as the core-forming block, that should exist in a liquid-like state (Tg ≈ -55 °C). Therefore changes in the solution parameters (pH, salt concentration) could have an effect not only on the corona, but also on the core of the micelle, i.e. one expects a dynamic behaviour of such aggregates. This should also have an effect on the aggregation number. Also Interpolyelectrolyte Complexes (IPECs), formed by the polyelectrolyte in the corona of the micelle – poly(methacrylic acid) (PMAA) – with quaternized poly(4-vinylpyridine) (P4VPQ) have been investigated with respect to their kinetics. At pH = 7, water-soluble complexes are formed up to a Z –value (Z = [P4VPQ]/[PMAA], the basemolar concentrations of the cationic polyelectrolyte and ionic block of the copolymer are given in brackets) of 0.4 – 0.5; beyond this value precipitation occurs. Their complexes are stable at low salt concentrations. However, beyond a certain NaCl concentration, the complexes dissolve, thereby reforming the originally present copolymer micelles and molecularly dissolved polyelectrolyte. This can be proven by different types of measurements, including SANS, turbidimetric titration, titration with a sodium-selective electrode and stopped-flow in combination with SAXS. Kinetic investigations of the formation and the dissociation of the complex show an overlay of a fast mixing process, followed by a slower process. The faster one is believed to be the diffusion of individual copolymer molecules coupled to the diffusion of the polycation and the salt into or out of the micelle. The slower one could be a kind of dynamic rearrangement of the block copolymers to form the finally stable aggregates. Thermodynamic investigations on the enthalpy of formation of the IPEC as well as thermodynamic data from titrations are planned to give a deeper insight into the processes occurring during formation and salt-induced dissociation of such complex macromolecular assemblies.

[1] D. Pergushov, E. Remizova, J.Feldthusen, A. Zezin, A.H.E. Müller, V. Kabanov; Novel Water-Soluble Micellar Interpolyelectrolyte Complexes, J. Phys. Chem. B, 2003, 107, 8093-8096

[2] D. Pergushov, E. Remizova, M. Gradzielski, P. Lindner, J. Feldthusen, A. Zezina, A.H.E. Müllere, V. Kabanov; Micelles of polyisobutylene-block-poly(methacrylic acid) diblock copolymers and their water-soluble interpolyelectrolyte complexes formed with quaternized poly(4-vinylpyridine); Polymer, 2004, 45, 367–378

# OPPOSITELY CHARGED SPB

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Polyelectrolyte – surfactant complexes are considered to be a new class of highly ordered polymer materials with novel properties different from them in pure solutions of the components. In the present work we investigated complex formation between spherical polyelectrolyte brushes (SPB) with the styrene sulfonate (SS) functional groups and sodium counter-ions and oppositely charged surfactant molecules of cetylthrimethylammonium bromide (CTAB). The water-soluble complexes of SPB with CTA+ counter-ions were prepared in a wide range of a polyelectrolyte concentration varying surfactant content in the systems. The systems were comprehensive studied by the Cryogenic TEM, dynamic and electrophoretic light scattering, small angel X-ray scattering and conductivity methods. The binding of surfactant monomers by the SPB promotes a partial shrinkage of the polyelectrolyte shell at a small concentration of CTAB in the system. The further concentration increase of the amphiphilic component leads to the formation of minimicelles induced by the polyelectrolyte chain. Our conductivity measurements reveal a critical aggregation concentration (cac) for CTASS micelle formation and SAXS profiles show the essentially less aggregation numbers comparing to them in CTAB micelles. Well above cac the ordinary micelles of CTAB are observed in the dilute regime when the concentration of SPB is extremely low. The values of apparent critical micelle concentration were fixed at a high concentration of the surfactant at the different latex content. In the more concentrated regimes (semi-dilute or concentrated) the increase of a surfactant fraction in the system leads to the irreversible coagulation, moreover the more concentrated solution the less stoichiometric ratio of charges we need to observe a coagulation. The influence of an ionic strength on the properties of the complex nanoparticles is also discussed. This research was supported by Marie Curie Research and Training Network POLYAMPHI “Self-Organized Nanostructures of Amphiphilic Copolymers”.

# INTERACTIONS OF FUNCTIONALIZED SILSESQUIOXANE-NANOPARTICLES WITH STAR-SHAPED POLY(ACRYLIC ACID) (PAA) AND MICELLES WITH PAA SHELL

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We present the complex formation between highly functionalized water-soluble silsesquioxane-nanoparticles with star-shaped polyacrylic acid (PAA) and well defined micelles of poly(n-butyl acrylate)-block-poly(acrylic acid) (PnBA-b-PAA). Complex formation may occur in our system by specific intermolecular interactions, such as hydrogen-bonding, acid-base interactions, and oppositely charged ionic interactions to grant for the constitution of a new type of stimuli-responsive polymer/silica nanocomposites [1]. The synthesis of the nanoparticles with a diameter of 3 nm is reported [2] as well as their labeling with a fluorescent dye utilized for Fluorescence Correlation Spectroscopy (FCS) studies. Complex formation and its dependence on pH and ionic strength are studied by Dynamic Light Scattering (DLS) titrations, potentiometry, conductometry, and 2D-NMR techniques. FCS and cryogenic Transmissions Electron Microscopy (cryo-TEM) sustain the formation of a novel class of water soluble organic/inorganic nano-hybrids.

[1] Mori, H.; Mueller, A. H. E.; Klee, J. E. Journal of the American Chemical Society 2003, 125, (13), 3712.
[2] Mori, H.; Lanzendoerfer, M. G.; Mueller, A. H. E.; Klee, J. E. Macromolecules 2004, 37, (14), 5228.

# HYBRID PARTICLES OF POLYSTYRENE AND CHITOSAN

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The complex formation between chitosan (CH), a polycation under acid conditions, and sodium dodecylsulfate (SDS), an anionic surfactant was studied at pH 4 by surface tension measurements. For the concentration of 0.1 g/L of CH, the critical aggregation concentration (cac) was found at SDS 0.10 mmol/L, while the critical micellar concentration (cmc) of pure SDS was G for the system SDS/CH amounted determined as 8.0 mmol/L. The reduction in -to 10.9 kJ/mol, indicating that the interactions between CH and SDS are favorable. Then complexes of SDS/CH were used as emulsion polymerization sites for styrene in the presence of potassium persulfate. The polymerization condition chosen was that corresponding to the cac. PS/CH hybrid particles 20) nm and mean zeta potential of –28 mV. PS presented mean diameter of (380 particles obtained by conventional emulsion polymerization in SDS often present mean zeta potential of –65 mV. Therefore, mean zeta potential of –28 mV indicates that hydrophilic CH chains are probably attached to the particle surface, increasing the surface potential. Dispersions of PS/CH were stable in the ionic strength of NaCl 2.0 mol/L during two months. The outstanding colloidal stability was attributed to the presence of a hydrated CH layer around the particles. The present procedure brings the advantage of synthesizing and stabilizing particles with functional groups on the surface in a one-step method using very small amounts of surfactant, a friendly condition for the environment. These polysaccharide-modified polymeric particles can be convenient substrates for adsorption of biomolecules, such as enzymes, lectins and antibodies.

# ELECTRO-OPTICS OF COLLOID/POLYELECTROLYTE COMPLEXES

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The adsorption of sodium poly(4-styrene sulfonate) (NaPSS) with different molecular weight (32, 70, 150, 350 and 1000 kDa) on weakly oppositely charged FeOOH particles is studied by electric light scattering method and microelectrophoresis [1]. Overcharging of the particle surface is realized in all cases with increasing NaPSS concentration. This causes stabilization of the suspensions against flocculation. The degree of surface charge overcompensation does not depend on the polyelectrolyte chain length. Hydrodynamic thickness of each layer is calculated from the change in the rotary diffusion coefficient of a single particle due to the NaPSS adsorption. It increases from 4.0 to 18.5 nm with increasing polyelectrolyte molecular weight. This means that "loops" and "tails" appear in the adsorbed layer, being longer for the polymers with longer polymer chain. The fraction of condensed Na+ counterions on the adsorbed NaPSS is calculated according to the theory of Sens and Joanny [2]. It agrees well with the fraction of condensed counterions on nonadsorbed NaPSS. This means that the condensed counterions are not released from the NaPSS chain after its adsorption onto weakly charged FeOOH particle. Polarization of condensed Na+ counterions along the chains of the adsorbed (highly charged) NaPSS is found to be responsible for creation of an additional electro-optical effect in suspensions stabilized by NaPSS adsorption. The relaxation frequency of this effect is found to depend on the polyelectrolyte molecular weight. The experimentally obtained values of the effect relaxation agree well with a theoretical prediction for polarization of condensed counterions along a free NaPSS chain [3]. The number of the adsorbed NaPSS chains is estimated also assuming counterion condensation and semiquantative agreement is found with the results obtained from the electrical polarizability of the polymer-coated particle.

[1] V. Milkova, Ts. Radeva, J. Colloid Interface Sci. in press.
[2] P. Sens, J.-F. Joanny, Phys. Rev. Lett. 84 (2000) 4862.
[3] G. Schwarz, J. Phys. Chem. 66 (1962) 2636.

# POLYELECTROLYTE COMPLEX FORMATION BETWEEN CATIONIC NANOGEL AND STRONG POLYANION

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The polyelectrolyte complex formation of a strong polyanion with positively charged nanogels was studied as a function of the polyion-nanogel mixing ratio (Rm) based on moles of anions vs cations under different concentrations (Cs in mol/L) of KCl. We used a polyampholytic nanogel consisting of lightly crosslinked terpolymer chains of N-isopropylacrylamide, acrylic acid and 1-vinylimidazole under an acidic condition (pH ~ 3) at which the gel particle has positive charges. Potassium poly(vinyl alcohol) sulfate (KPVS) was used as a strong polyanion. It has become apparent that there is a critical mixing ratio (Cmr) at which both size and molar mass of the complexed gel particles abruptly increase. The value of Cmr at a low Cs ($< 0.01$) was observed at Rm around unity. At Rm < Cmr the molar mass of the complex agreed with that of one gel particle with the calculated amount of the bound polyanions, indicating the formation of an "intra-particle" polyelectrolyte- nanogel complex upon "stoichiometric charge neutralization." At Rm > Cmr, the aggregation of the intra-particle complex takes place to form an "inter-particle" complex. During the process of the intra-particle complex formation, both hydrodynamic radius (Rh) and radius gyration (Rg) were found to decrease with the increase of Rm, demonstrating the gel collapse due to the complexation. Another important feature of our complexation system was that the polyelectrolyte exchange reaction takes place between the KPVS-bound nanogel complex formed at Rm = 1 and the uncomplexed free cationic nanogel. This was well supported by the following results: (i) Electrophoretic light scattering (ELS) measurements at 25 °C showed the positive but not zero mobility for the KPVS-nanogel complex at Rm = 1. (ii) This was the case when ELS was performed at 45 °C at which the gel particle had been in a fully collapsed state due to the hydrophobic interaction between the NIPA residues. (iii) The size (Rh and Rg) of the KPVS-nanogel complex increased upon addition of poly(diallyldimethylammonium chloride) (as a polysalt). (iv) There were few changes in Rh and Rg when a slight amount ($Cs < 0.02$) of KCl was added. (v) The further addition of KCl caused the aggregation at $Cs \sim 0.04$ but the dissolution at $Cs > 0.2$, as observed in water solutions of polyampholytes.

# THE INFLUENCE OF POLYION STOICHIOMETRY ON COUNTERION MOBILITY AND DIFFUSION IN POLYELECTROLYTE COMPLEXES: A 23NA NMR STUDY.

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Binary polyion complexes (‘duplexes’) are prepared from poly(styrene sulfonate sodium salt) (PSS) and poly(diallyl dimethylammonium chloride) (PDADMAC) by titration from dilute solutions with varying anion/cation monomer ratio. Concentrated complexes are formed after dialysis of the excess salt by lyophilisation and rehydration. 23Na NMR signals result in a Na content, which is constant for net positive complexes and increasing with polyanion fraction for net negative complexes, implying that no Na is required to neutralise the net positive complex. The polymer density shows a minimum for the neutral complex and is asymmetric, since net negative complexes yield much higher network densities. Counterion mobility is studied in dependence on polyion stoichiometry by 23Na relaxation rates R1 and R2 and Pulsed Field Gradient (PFG)-NMR diffusion coefficients. For net positive complexes relaxation rates are similar to those of free Na in solution, and diffusion coefficients are large, indicating that Na is not bound to the complex. However, with increasing anion fraction as the neutral complex is approached, diffusion coefficients are slightly increasing, which is attributed to the decrease in polymer network density. For net negative complexes, diffusion coefficients are significantly lowered, and relaxation rates are strongly increased, both indicating an immobilisation of Na ions due to binding to non-compensated polyanion charges. The 23Na mobility is continuously decreasing with increasing polyanion fraction, since polycation charges compensation the polyanion are replaced by 23Na. In conclusion, the combination of relaxation rates and diffusion coefficients provides details about the complex structure and its charge compensation, since diffusion coefficients depend on both counterion binding and matrix effects, while relaxation rates depend on counterion rotational mobility and thus on association to binding sites only.

# REINFORCEMENT EFFECT IN ROD/COIL IONOMER-BLENDS

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Molecularly reinforced composites of rod-like and flexible coil macromolecules have several advantages over macroscopic fiber reinforced materials. The problem of insufficient fiber-matrix adhesion vanishes in such polymer-polymer blends and, in principle. high modulus polymer/polymer composites should be easier to realize due to the facile increase in the aspect ratio (length l to diameter d ratio) of the reinforcing filler [1]. The usual problem of the tendency to form phase separated blends [2] can be overcome in polymer/polymer ionomer blends by ionogenic acidic/basic functional groups in the polymer components [3]. Here we report on the investigation of polyelectrolyte composites of sulfonated polyphenylenes with alkyl side chains representing the reinforcer component, and poly(ethyl acrylate-co-4-vinyl pyridine) (P(PEA-co-4VP) as matrix material. Copolymers (P(PPSH-co-MPSH) containing p-linked (PPSH) and meta-linked phenylene units (MPSH) were obtained by employing mixtures of 2,5- and 2,4-dibromobenzene-p-sulfonates in the Suzuki-polycondensation with bis(boronic acid ester); the all-meta linked polymer PMPSH is obtained correspondingly by only employing the 2,4-dibromo substituted building block [4]. The experimentally determined Young modulus of 24.8 wt.-% PMPSH containing blends was surprisingly high and increased from below 1 MPa of the pure matrix polymer to about 50 MPa of the ionomer blend. Compared to earlier work with the stiffer poly(p-phenylenes) (PPPSH) as reinforcer (moduli of the ionomer blend of 250 to 370 Mpa, cf. [5]), the employing of the broken rod component PMPSH leads to a lower modulus increase. However, the reinforcement factor is still much higher as compared to ionomer blends of sulfonated polystyrene (matrix) and rod-like poly(para-pyridylene/phenylene-ethinylene) (about 8 MPa) or coil-like poly(meta-pyridylene/phenylene-ethinylene) (only about 0.3 MPa) [6]. The experimental data infer that the reinforcement factor may be attributed to two different parameters: the shape of the reinforcer polymer filler that can be described by the fuzzy cylinder model [5], and by multifunctional crosslinking due to the counterion condensation. Ongoing work addresses the investigation of the contribution of the two parameters to the reinforcing effect.

[1] J.L. Kardos, J. Raisoni, Polym. Eng. Sci. 15, (1975) 183
[2] P. J. Flory, Macromolecules 11, (1978) 1138
[3] C. D. Eisenbach, J. Hofmann, A. Göldel, J. Noolandi, A. Ch. Shi, Macromolecules 32, (1999) 1463
[4] C. Eggert, Diplomarbeit, Univ. Stuttgart (2005)
[5] C.D. Eisenbach, A. Datko, A. Bayer, Polymer 46, (2005) 6614
[6] D. Winter, C.D. Eisenbach, Polymer 45, (2004) 2507

# INFLUENCE OF HYDROPHOBIC PARTS OF POLYELECTROLYTES ON STRUCTURE AND SHAPE OF POLYELECTROLYTE COMPLEXES

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In the last decades colloidal nanoparticles have received considerable attention because of their high potential for applications on many different fields as in industry, biotechnology and medicine. Special types of nanoparticles are colloidal polyelectrolyte complexes (PECs), which can be form by strong electrostatic interactions between oppositely charged polyelectrolytes (PEL). In a certain scope it is very simple to create specific properties as colloidal stability, particle size, charge excess or hydrophoby. By the choice of PELs with specific properties we can affect the stability and hydrophoby of PECs. Properties as particle size, particle size distribution and charge excess of a PEC dispersion are influenced by the mixing conditions and mixing ratios of polyanion to polycation (n-/n+). Recent works of our group deal with the influence of hydrophobic parts of PELs on the structure formation during formation of PECs. Alternating maleic acid copolymers with comonomers of different hydrophoby (ethene, isobutene, styrene) were modified anionic as well as cationic. The obtained structure unit PELs have equal length of backbone chain and equal charge density. The complex formation was made by simple mixing of the oppositely charged PEL solutions with a dosing pump. Tested mixing conditions were: a) starting solution: polycation b) starting solution: polyanion Different methods were used for characterization of complex properties. Stability of PEC dispersion was estimate by nephelometric turbidity measurements. The charge excess of PECs was determined by PEL-titration. Information about particle size and particle size distribution was obtained by dynamic light scattering. AFM provides images to the shape of formed PEC particles and informative basis to their densities. The studies show a strong dependence of colloidal stability as well as particle size distribution and the shape of the nanoparticles on hydrophoby of the PELs, which were used for complex formation.

# STABLE POLYELECTROLYTE COMPLEX DISPERSIONS BASED ON IONIC/NONIONIC RANDOM COPOLYMERS OF AMPS

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In recent years considerable efforts have been devoted to the preparation of interpolyelectrolyte complexes as colloidal dispersions because of their widespread applications in chemical engineering, pharmaceutical and biological areas. The most important parameters for their applications are the polymer concentrations, the size of nanoparticles and their storage stability. In this paper we focused on the formation of interpolyelectrolyte complexes as colloidal dispersions by electrostatic interaction between three ionic/nonionic random copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) with either t-butyl acrylamide (TBA) or methyl methacrylate (MM), and two complementary polymers, poly(diallyldimethylammonium chloride) (PDADMAC) and an ionene type polycation, containing 95 mol % N,N-dimethyl-2-hydroxypropyleneammonium chloride repeat units (PCA5), in a wide range of ratio between charges. The effect of preparation conditions, such as the polyelectrolyte structure, the mixing order and the titrant addition rate on the complex dispersions turbidity, z-averaged particle sizes and polydispersity indices were studied in detail. The role of different preparation parameters on the storage colloidal stability are also discussed.

[1] Buchhammer, H.-M.; Petzold, G.; Lunkwitz, K. Langmuir 1999, 15, 4306.
[2] Buchhammer, H.-M.; Mende, M; Oelmann, M. Colloids Surf. A 2003, 218, 151.
[3] Schwarz, S.; Dragan, E. S. Macromol. Symp. 2004, 210, 185.
[4] Dragan, S.; Schwarz, S. J Polym Sci: Part A: Polym Chem 2004, 42, 2495.
[5] Dragan, S., Schwarz, S. J Polym Sci: Part A: Polym Chem 2004, 42, 5244.
[6] Dragan, E. S., Mihai, M., Schwarz, S. Colloids Surf. A, in press

# POLYELECTROLYTE COMPLEX NANOPARTICLES MADE FROM CATIONIC SURFACTANTS AND POLY(MALEIC ACID-CO-PROPENE)

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Polyelectrolyte-complex particles with attractive properties for potential applications (1) can be tailored by controlling the interaction between oppositely charged polyelectrolytes (2) as well as between a polyelectrolyte and an oppositely charged surfactant molecule. In this work, the interactions between cationic surfactants and poly (maleic acid-co-propene) were investigated. The results show that the investigation of dynamic surface tensions using the bubble pressure tensiometry (SITA online) provides useful information for characterizing aqueous solutions of surfactant-polyelectrolyte mixtures. The changes in the surface activity due to the influence of polyanion at constant surfactant concentration will be discussed. The complexes differ in charge, size, and particle size distribution, depending on the charge ratio of individual components in the mixture (i.e. n-/n+). A clear influence of time on the complex formation in dependence on the composition of the mixture can be demonstrated, especially with N-Dodecylpyridiniumchloride (DDPY) as surfactant. By mixing equimolar amounts of both components: after complex preparation - “free” surfactant (not bound to polymer) is in the mixture; during the next days complexes “rearrange" and the shape of "dynamic surface tension curve" changes. With excess of polyanion: all added surfactant is bound rapidly to the polymer forming a stable and highly surface active complex.

[1] G. Petzold, S. Schwarz; Separation and Purification, 2006, in press
[2] Mende, M. ; Buchhammer, H.-M. ; Schwarz, S. ; Petzold, G. ; Jaeger, W.; Macromolecular Symposia 211 (2004). – S. 121-133

# ELECTROSTATIC SELF-ASSEMBLY OF POLY (N-ISOPROPYL-ACRYLAMIDE)- BLOCK-POLY(ACRYLIC ACID) AND OPPOSITELY CHARGED SURFACTANT

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During the past decade, there has been a widespread interest for the design and synthesis of a new polymer-based colloidal particles of high stability in aqueous solutions. Among these particles, colloidal complexes have emerged as a new type of microstructure with potential applications in drug delivery, and gene delivery. Colloidal complexes result from self-assembly between polyelectrolyte-neutral diblock copolymers and oppositely charged species. An interesting combination of a block copolymer is double- hydrophilic block copolymers in which one of the hydrophilic blocks is thermoresponsive, i. e., undergoes a transition from soluble to insoluble in water. When passing through the critical temperature, one of the hydrophilic block collapses, thus creating hydrophobic microdomains in analogy to polymeric surfactant. Or applying the thermal stimulus in the other direction, the aggregate formed by such block copolymers are dissociated. Poly(N-isopropylacrylamide) (PNIPA) is well known for its thermosensitive properties, exhibiting lower critical solution temperature (LCST) type phase behaviour in water. The block copolymer is the key feature of the electrostatic self-assembly. The overall size and the stability of the colloid depend on the nature of the electrostatic charges, on the molecular weight, and on the flexibility of the chains. In the present study, we investigate the structure and the stability of the colloidal complexes made from poly(N-isopropylacrylamide)-block-poly(acrylic acid) (PNIPAM-b-PAA) as anionic-neutral diblock copolymer and dodecyltrimethylammonium brobide (DTAB) as oppositely charged surfactant. Using light, X-ray scattering experiments, PNIPAM-b-PAA associates DTAB into colloidal complexes which have a core-shell microstructure. The core is consisted of densely packed surfactant micelles, presumably connected by the poly(acrylic acid) chains. The outer part of the complex is a corona formed by the PNIPAM. For all systems, we found that the critical charge ratio $Z_c = [S]/(n[P])$ above which the formation of hierarchical structures take place. Here, [S] and [P] are the molar concentration of surfactant and polymer, respectively, and n is the number of charged monomers in the polyelectrolyte block. The thermosensitive properties of the colloidal complexes over a wide range of experimental conditions will also be discussed.

[1] J. -F. Berret, et al., Eur. Phys. J. E, vol. 9, 301 (2002)
[2] J. -F. Berret, et al., J. Phys. Chem, B, vol. 107, 8111 (2003)
[3] J. -F. Berret, et al., Macromolecules, vol. 37, 4922 (2004)

# TRANSITIONS OF NANOSTRUCTURES OF DNA-CATIONIC SURFACTANT COMPLEXES IN THE AQUEOUS NACL SOLUTIONS

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Nanostructures of complexes of DNA with single chain surfactant of octadecyltrimethylammonium (OTA) and double chain surfactant of didodecyldimethylammonium (DDA) in the aqueous NaCl solution at concentration, Cs from 0 to 600 mM were studied using small-angle-scattering techniques (SAXS). SAXS profiles of the DNA-OTA complex show two SAXS peaks with a spacing ratio of 1:3^(1/2) in the solution at Cs below 150 mM and three peaks with a spacing ratio of 1:3^(1/2):2 at Cs above 250 mM. The contents of Na and Cl ions in the complexes evaluated from the atomic absorbance of Na and the potentiometry of Cl revealed the 1:1 complex for the DNA-OTA and 1:1.25 complex for the DNA-DDA. Molar ratios of Na and Cl ions to an ionic unit of DNA molecule containing in the DNA-OTA complex equilibrated with the solution at Cs below 100 mM were much less than 0.1 while they increased with NaCl concentration at Cs above 200 mM. The DNA-OTA complex at Cs above 260 mM exhibited an endothermic peak in the DSC measurements and the others not. The endothermic transition is due to the order-disorder transition of alkyl chains in the rod-like micelles of OTA. A transition of nanostructure accompanied with the endothermic transition was also observed. The change from the spheroid micelle to the rod-like micelle in the DNA-OTA complex with an increase in Cs can explain the results mentioned above. The experimental studies on the complexes of DNA with cetylpyridinium (CP) and Dodecylpyridinium (DP) surfactant in the aqueous NaCl solution will be also presented.

# CONVECTIONAL, SEDIMENTATION AND DRYING DISSIPATIVE STRUCTURES OF COLLOIDAL SUSPENSIONS

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Convectional, sedimentation and drying dissipative structural patterns formed in the course of drying aqueous and ethanol suspensions of colloidal silica spheres (100 nm to 1000 nm in diameter) were studied in a glass dish, a polystyrene dish and a watch glass. In ethanol suspensions, vigorous cell convectional flow was observed with the naked eyes, and the patterns changed dynamically with time. Broad ring like sedimentation patterns were observed in the suspension state just before the suspension was dried up, and the principal macroscopic patterns of the drying patterns were also broad ring, though the colorful and fine microscopic structures were observed from the optical microscopy. In aqueous suspensions, the broad ring patterns are formed within a short time in suspension state by the convectional flow of water and colloidal spheres. The sedimentary spheres always move by the convectional flow of water, and the broad ring patterns became sharp with time. Broad ring and microscopic ! fine structures are formed in the solidification processes on the bases of the convectional and sedimentation patterns. Especially, in a watch glass the sedimentary spheres were clarified to move toward upper and outer edge along the inclined cell wall by the cell convection and hence the patterns are formed by the balancing between the outside movement and the downward sedimentation of the spheres. Drying patterns show very fine microscopic patterns in addition of the macroscopic broad ring, etc. Synchronous cooperative interactions between the salt and colloidal spheres.

# STRUCTURAL PROPERTIES OF POLYELECTROLYTE / CHARGED SURFACTANT COMPLEXES.

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Interactions of polyelectrolytes (PE) with oppositely charged surfactants have received a large attention during the recent years. Complexation between the two species is key mechanism often found in various fields such as cosmetics, detergents, pharmaceutical, biology. In the absence of charged surfactant, the structure of flexible PE in good solvent mainly depends on the long-range electrostatic interactions. Due to electrostatic repulsions, the PE conformation is highly stretched. The scattered intensity from a PE solution displays a broad maximum at a scattering vector q* which scales as c^1/2 in the semidilute regime [1,2]. In the case of hydrophobic PE, the average conformation and the dispersion state of polyions are now determined by the interplay between electrostatic and hydrophobic interactions. Apparition of new phases have been evidenced through changes in the prefactor and the exponent of the scaling law describing the c-dependence of q* [3,4]. The average conformation of polyions can now be pictured as a pearl necklace. It is noticeable that most of the experiments on both hydrophilic and hydrophobic PE have been mainly performed by considering hydrophilic counterions. The hydrophobic character of the counterions has however never been investigated except in the limiting case of highly hydrophobic charged surfactants leading to PE - micelles complexation. In the present study, we are concerned with the role of the surfactant counterions when gradually increasing their hydrophobic character. Investigation has been performed by small angle X ray and neutron scattering and cryo-TEM microscopy. We used alkyltrimethylammonium (CH3-(CH2)n-N+-(CH3)3) of various alkyl lengths (n=0, 5 and 11) as counterion and fully sulfonated polystyrene (PSS-) as macroion. All the experiments have been performed in salt-free conditions and different polymer concentrations. Results for the low hydrophobic counterions will be presented. New interactions may appear, even without any formation of surfactant aggregates. It is thus intriguer to known whether this “annealed hydrophobicity” may modify the structure of the PE solutions as it is observed for chemically modified macroions (“quenched hydrophobic macroions”). Furthermore, the structure of PE - micelles complexes will also be shown for high hydrophobic counterions and a simple structural model will be proposed.

[1] Cotton et al, J. Phys. (France) Lett. 37 (1976) L-75; Nierlich et al, J. Phys. (France) 40 (1979) 701
[2] de Gennes et al, J. Phys. (France) 37 (1976) 1461; Hayter et al, J. Phys. (France) Lett. 41 (1980) L-451
[3] Essafi et al, J. Phys. II (France) 5 (1995) 1269; Waigh et al, Macromolecules 34 (2001) 1973
[4] Dobrynin et al, Macromolecules 32 (1999) 915

# STIMULI-SENSITIVE POLYELECTROLYTE COMPLEXES

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It is well known that the interaction between oppositely charged polyelectrolytes in water leads to the formation of polyelectrolyte complexes (PEC). However the formation of PEC in concentrated mixtures is less understood than the low concentration systems. In our laboratory, we are studying the influence of the polycation charge density on complexation in concentrated systems (20 % w/w), and their decomplexation process under semi-dilute condition (2 % w/w) in the presence of external stimuli, such as pH and ionic strength. Insoluble PECs were prepared from high molecular weight polyanions and a family of polycations, the Poly(vinylpyrrolidone–co–quaternized vinylimidazole) P(VP(x-1)–QVI(x)), where x is varied between 0 and 1. The influence of the polycation charge density (x) on complexation and decomplexation was investigated by phase equilibrium analysis and rheological methods. The degree of decomplexation as a function of pH could be determined by viscosity measurements using semi-dilute solutions. For acrylic acid based polyanions it was found that decomplexation is promoted by increasing pH and ionic strength with a maximum viscosity of the decomplexed species at intermediate pH. This viscosity maximum can be controlled by the charge density of the polycation used. Further increase in pH results in a decrease of viscosity, due to screening effects of the counter-ions. At neutral pH, the mixture containing lower charge density polycations ($x < 0.5$) gave higher viscosity values compared to decomplexed samples where the polycation was fully charged, suggesting a higher degree of decomplexation. Rheology data suggest that decomplexation is almost complete for $x < 0.4$ under semi-dilute conditions with little influence of the polycation composition on the polyanion chain conformation. In extension to this work, ultrasound velocity measurements is currently carried out to understand the kinetics of the complexation and decomplexation processes.

# AFM AND ITC STUDIES OF XANTHAN-CHITOSAN COMPLEXATION: INFLUENCE OF POLYANION AND POLYCATION CHAIN LENGTH

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We have previously shown that xanthan can be compacted to yield well-defined complexes similar to those observed for DNA [1]. To further understand the polyelectrolyte complexation process and its driving force, the interaction between xanthan and chitosan was studied by isothermal titration calorimetry (ITC) for two different MWs of xanthan. Chitosans with different degree of polymerisation, ranging from a trimer to a high DP chitosan, were employed. ITC experiments typically are carried out at higher concentrations than those used when polyelectrolyte complexes of toroidal and rod-like shapes are formed. The study therefore also included AFM studies of the final ITC mixture. The complexation between xanthan and chitosan was found to be an entropically driven process. Furthermore, even though the trimer chitosan interacted with xanthan in what can be described as a one-site process, not all charges were involved in the complexation process when the equilibrium level was reached. When the chain length of chitosan was increased, increasingly complicated titration curves where observed, while AFM imaging revealed the formation of more structured complexes.

[1] Maurstad G, Danielsen S, Stokke BT: J. Phys. Chem. B, 2003, 32: 8172-8180

# COALESCENCE OF CARDIOLIPIN VESICLES INDUCED BY ANTIPHOSPHOLIPID ANTIBODIES

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We observed that anti-cardiolipin antibodies (ACA) may induce the coalescence (adhesion) of negatively charged giant unilamellar phospholipid vesicles containing cardiolipin (GUV). This effect is achieved without the binding of ACA into the membrane since it was previously found that such binding requires apolipoprotein H. In order to better understand the above experimental result a theoretical model was constructed. In the model the shape of ACA is considered as globular, while the effective charge distribution within ACA molecules is described by two equal positive charges (e), separated by a distance l. The electrolyte solution with ACA molecules is sandwiched between two large, planar surfaces (representing two opposed lipid bilayers of GUV), each carrying a uniform negative surface charge density. The non-local Poisson-Boltzmann theory for the model ACA molecules is introduced. The orientational restrictions of ACA molecules in the vicinity of the charged hard surfaces are considered. It is obtained that the two negatively charged surfaces experience attractive force due to intra-molecular correlations of multipolar ACA molecules between them. It is indicated that such attraction is common in blood plasma involving negatively charged fragments (vesicles) of membranes of apoptotic cells, low density lipoproteins and platelet microparticles and therefore play an important role in formation of blood clots.

# HYDROPHOBIC AND ELECTROSTATIC INTERACTION IN AQUEOUS SOLUTIONS OF POLYELECTROLYTE - SURFACTANT

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Aqueous solutions of a mixture of polyelectrolytes with surfactants are widely used in a variety of industrial applications. The study of interaction between the same and oppositely charged polyelectrolytes and surfactants is of fundamental importance. Polycation - polyanion complexes (PK - PA ) and polyelectrolyte - surfactant complexes (PSC) were investigated with respect to their hydrophilic - hydrophobic interactions with water. This work presents a study of relaxation of surface tension of aqueous solutions PK- PA and PSC at different concentrations, molar ratio of polyanion to polycation (n-/n+) and temperatures. Viscosity and also sizes of particles and their diffusion coefficients were measured by Photon correlation spectroscopy. Our measurements show that hydrophobic and electrostatic interactions lead to formation of PK-PA and PSC aggregates. Micellization of solutions influences the formation of these aggregates.

# NANOSTRUCTURED ORGANIC/INORGANIC MATERIALS VIA POLYMER-TEMPLATED SOL-GEL AND INORGANIC SYNTHESES

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Phase-separated morphologies of acid- and ion-functionalized PS-co-[soft block (ethylene/butylene or isobutylene)]-co-PS block copolymers (BCP) and perfluorosulfonate ionomers can act as templates for sol-gel polymerizations of inorganic alkoxides and organo-alkoxysilanes and other inorganic metal oxide syntheses resulting in nanostructured organic/inorganic hybrids. Precursor monomers or ions diffuse to the polar phase where reactions culminate in metal oxide quasi-networks or nanocrystals. In addition to using pre-formed polymers, organic/inorganic nanocomposites can be formulated in a way such that all molecular building blocks are present in co-miscible precursor solutions so that the resultant materials are self-assembled. While nanocomposite morphologies can mimic those of the template, new frustrated morphologies can be induced. It will be shown how these inorganic modifications influence the mechanical, viscoelastic, thermal and permeation properties of the host polymer. Also, the modified BCPs and poly(ethylene-ran-methacrylic acid) copolymers were exposed to iron and iron/cobalt chloride solutions and subsequent in situ reactions were affected to produce dispersed nanoparticles such that the nanocomposites have magnetic properties. Projected applications of these materials will be briefly discussed.

# DENDRIMER TEMPLATED CALCIUM ALGINATE NANOPARTICLES FOR ANTICANCER DRUG DELIVERY

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Addition of calcium chloride solution to a dilute sodium alginate solution leads to the formation of fibrous structures. However, in presence of polyamidoamine dendrimer uniform, monodisperse, nanoparticles are formed. These nanoparticles are loaded with doxorubicin. The nanoparticles are characterised by atomic force microscopy and transmission electron microscopy. They were also characterised for size and zeta potential and fluorescence characteristics. We show that the particles are < 100 nm uniform sized, negatively charged and are formed due to the condensation of alginate by dendrimer folled by Calcium mediated complexation of free negative charges. The particle size and charge vary with change in dendrimer/alginate and alginate/calcium stoichiometry respectively. The drug binds to alginate and a typical UV and fluorescence characteristics suggests that the formation of J-aggregates of doxorubicin takes place in the nanoparticles. A simple electrostatic complexation method is reported for making nanoparticles for anticancer drug delivery.

# CHAIN STRATIFICATION IN POLYELECTROLYTE MULTILAYERS

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The polyelectrolyte stratification in multilayers consisting of poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) is investigated by linear dichroism. The UV-absorption of Polystyrene sufonate has a transition dipole moment which is aligned along the long axis of the styrene sulfonate monomer. Polarized absorption spectroscopy is used to determine the average orientations of the transition dipole moments μtr. Films prepared from 1 M KCl solution at low temperatures show a preferential orientation of the side groups parallel to the substrate. At high deposition temperature, with neutron reflectivity pronounced layer interpenetration is found. On a molecular level, the side group orientation is random.

# EVIDENCE OF NANOPARTICLE AGGREGATION IN POLYELECTROLYTE MULTILAYERS

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Negatively charged silver nanoparticles are adsorbed onto surfaces functionalized with poly (ethylene imine). If poly (allylamine hydrochloride) from solutions containing high salt concentrations is adsorbed on top of the nanoparticle monolayer, the appearance of a second absorbance peak indicates formation of nanoparticle aggregates. AFM as well as spectroscopy with polarized light under variation of the angle of incidence show that the aggregates are three-dimensional. UV-Vis spectroscopy indicates that adsorption of additional polyelectrolyte layers compresses the nanoparticle aggregates. We conclude that adsorbing polyelectrolytes exert lateral forces onto the nanoparticles leading to aggregation. Conditions for polyelectrolyte multilayer buildup avoiding nanoparticle aggregation are explored.

# SWELLING KINETICS AND STRUCTURAL CHANGES OF POLYELECTROLYTE MULTILAYERS IN CONTACT WITH AQUEOUS SOLUTION AND WATER VAPOR

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The sequential layer-by-layer adsorption of polyanions and polycations to build poly¬electrolyte multilayers has triggered enormous interest in their potential uses in a wide range of fields, from photonic to pharmaceutical applications. This is due to the ease of preparation, the possibility to control film thickness with Angstrom precision and because the macroscopic properties can be influenced by the chemical composition of the polymers [1]. The detailed mechanism of film formation and the manipulation of the films by external means are current topics of active research. Experimental studies have shown that the main driving force for the assembly of multilayer films is the electrostatic attraction between the oppositely charged polyelectrolyte chains and the concomitant release of counter ions. We have found that a minimum charge density of ca. 60 % of the fully charged chains is necessary for obtaining stable films [2]. We will show that the conformation of the solvent swollen films - prior to drying - is determined by the initial adsorption conditions [3], but can be altered ex-situ by exposure to a liquid phase of very high ionic strength. Recently, it has been observed that the swelling depends on outermost layer [4,5]. The water uptake of the outer layers is more pronounced, which leads to the assumption, that they are more loosely packed than the inner layers near the template [5]. A neutron reflectivity study of this effect in addition indicated the existence of two kinds of water, bound with different strength within the films. Beside an unexpected two-step kinetics of swelling, the reflectivity curves of the layers against vacuum before and after re-hydration in D2O vapor did not agree. It was only after subsequent re-hydration in saturated H2O vapor that the initial and final reflectivity curves against vacuum superimposed. We will discuss our findings in the context of polyion complex formation, interdigitation and film imperfections.

[1] G. Decher, Science 277, 1232 (1997)
[2] R. Steitz, W. Jaeger, R. v. Klitzing, Langmuir 17, 4471 (2001)
[3] R. Steitz, V. Leiner, R. Siebrecht, R. v. Klitzing, Colloids Surfaces A 163, 63 (2000)
[4] B. Schwarz, M. Schönhoff, Langmuir 18, 2964 (2002)
[5] J. E. Wong, F. Rehfeldt, P. Hänni, M. Tanaka, R. v. Klitzing, Macromolecules, 37, 7285 (2004)

# CONDUCTIVITY SPECTRA OF POLYELECTROLYTE MULTILAYERS

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Consisting of ionic moieties and providing mechanically very stable material in ultrathin films on the nanometer scale, polyelectrolyte multilayers are potential candidates as ion conductive membranes for battery applications. For this purpose, the transport properties of small ionic components, such as the counterions is of interest. We investigate here the frequency-dependent conductivity of polyelectrolyte multilayers with the aim of understanding ion transport mechanisms. Multilayers of poly(styrene sulfonate sodium salt) (PSS) and poly(allylamine hydrochloride) (PAH) are prepared on glass slides coated with an indium tin oxide (ITO) electrode. Conductivity spectra are taken in a sandwich geometry on typically several 100 layers. The upper electrode is structured to reduce the probability of short circuits and to allow reproducibility tests. At low frequencies (< 100 Hz) polarization effects dominate the spectra, while in the kHz range a DC plateau is found, and at higher frequencies the conductivity is sharply increasing with frequency. The value of dc conductivity depends mainly on the state of hydration of the multilayers, where conductivity is decreasing with increasing drying time after preparation. With increasing temperature, the conductivity is first decreasing, and then strongly increasing, which can be attributed to a superposition of the influences of drying and of an activation of the ion transport.

# PORE SIZE DISTRIBUTIONS IN POLYELECTROLYTE MULTILAYERS EXTRACTED FROM AN NMR CRYOPOROMETRY STUDY OF WATER MELTING

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The permeability and the porosity of polyelectrolyte multilayers are properties of major interest, as they are crucial for applications in encapsulation, controlled release, and membrane separation. Here, we approach the topic with cryoporometry, a technique well established in inorganic porous materials: The freezing point of water in nanoscopic pores is reduced as compared to bulk water. The Gibbs-Thompson relation gives the shift of the melting temperature in dependence on pore size, such that pore size distributions can be extracted from melting curves.

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. 1H NMR experiments are performed on concentrated dispersions of multilayer-coated colloids on silica particles. The 1H signal of water, determined in a Hahn echo is monitored in a temperature range between –80 °C and room temperature, where it is increasing with increasing temperature. In a Hahn echo, it is the spin-spin relaxation rate and thus the motional correlation time, which determines the signal. A theoretical model, assuming a log-normal distribution of water motional correlation times is employed to fit the data.

Three different modes of pore sizes can be extracted, which are centered around about 1 nm, 2 nm and ≥5 nm. The 2 nm mode can be attributed to pores present in the silica particles, as demonstrated by reference experiments on uncoated particles. The mode at ≥5 nm is most probably due to inter-particle water or hydration water of the terminating layer.

Finally, the mode at 1 nm is attributed to pores in the multilayers. This value agrees well with data obtained by other authors, who recently performed permeation experiments (Liu and Bruening 2004, Jin and Tieke 2005) and found cut-off values of the order of 1 nm for the size of permeating molecules. It is interesting to note this agreement, since the methods monitor porosity in completely different ways: While our experiment is an average over all pores, for permeation only paths interconnecting sufficiently large pores are relevant. The agreement can be understood as proof of a very homogeneous nanostructure of polyelectrolyte multilayers.

# PH DEPENDENCE AND PROTEIN SELECTIVITY OF WEAK POLYELECTROLYTE MULTILAYERS STUDIED BY IN-SITU ATR-FTIR SPECTROSCOPY

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The selective interaction between polyelectrolyte multilayers (PEM) consecutively adsorbed from poly(ethyleneimine) (PEI) and poly(acrylic acid) (PAC) and a binary mixture containing concanavalin A (COA) and lysozyme (LYZ) based on electrostatic interaction is reported. The composition and structure of the PEM and the uptake of proteins were analysed by in-situ attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy and the morphology and thickness were characterized by atomic force microscopy (AFM) and ellipsometry. The PEM dissociation degree and charge state and the protein adsorption was shown to be highly dependent on the outermost layer type and the pH in solution. High protein uptake was obtained under electrostatically attractive conditions. This was used to bind selectively one protein from a binary mixture of LYZ/COA. In detail it could be demonstrated, that six layered PEM-6 at pH = 7.3 showed a preferential sorption of positively charged LYZ, while at PEM-5 and pH = 7.3 negatively charged COA could be selectively bound. No protein sorption from the binary mixture was observed for PEM-6 at pH = 4.0, when the PAC outermost layer was neutral, as well as for positively charged PEM-5 at pH = 4.0, when both COA and LYZ were positively charged. Furthermore, from factor analysis of the spectral data the higher selectivity was found for PEM-5 compared to PEM-6. Increasing the ionic strength revealed a drastic decrease in the selectivity of both PEM. Evidence was found, that the proteins were predominantly bound at the surface and to a minor extent in the bulk phase of PEM. These results suggest possible application fields of PEI/PAC multilayer assemblies related to the preparative separation of binary and multicomponent protein mixtures (biofluids, food) as well as to the design of selective protein resistant surfaces.

M. Müller, B. Keßler, N. Houbenov, K. Bohata, Z. Pientka, E. Brynda, Biomacromolecules 7 (4), 1285-1294, 2006

# PREPARATION OF MONOMODAL POLYELECTROLYTE COMPLEX NANOPARTICLES BY CONSECUTIVE CENTRIFUGATION

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We report on the refinement of anionic and cationic nanoparticles of nonstoichometric polyelectrolyte complexes (PEC) by consecutive centrifugation, which was studied by dynamic light scattering (DLS), atomic force microscopy (AFM), colloid titration and infrared spectroscopy (IR). PEC dispersions were prepared by mixing polycations like PDADMAC and polyanions like copolymers of maleic acid (PMA-X) or poly(styrenesulfonate) (PSS) at the monomolar mixing ratio of n-/n+ = 1.50 (anionic PEC) and 0.66 (cationic PEC), respectively, and defined polymer concentrations. The particle size (Rh), titrable charge amount and IR spectra were determined in the original state, after first centrifugation and after second centrifugation of the dispersions. Freshly prepared PEC dispersions contained excess polyelectrolyte, small primary complexes and aggregated PEC particles. Consecutive centrifugation of freshly prepared PEC dispersions resulted in the separation of these compounds and the formation of monomodal PEC particles sizing around 100 nm found by DLS. These results were supported by AFM measurements on the respective dispersions deposited on glass plates. Anionic PEC-1.50 particles tended to adopt slightly smaller sizes (~90 nm) in comparison to cationic PEC-0.66 ones (~110 nm). IR spectroscopy showed changes in the environment of the carboxylate groups of maleic acid copolymers by consecutive centrifugation. We assume, that the obtained low polydispersity is due to an accelerated colloid ripening process due to Ostwald and the high macroscopic stability is due to repulsive electrostatic interparticle interactions and attractive hydrophobic intraparticle interaction. These monomodal PEC particles might be projected as latex analogues or nanocarriers for drugs and proteins.

M. Müller, B. Keßler, S. Richter, Langmuir, 21(15), 7044-7051 (2005)
W. Ouyang, M. Müller, Macromol. Bioscience (2006, submitted)

# MOLECULAR MOBILITY AND TRANSPORT IN POLYMER MEMBRANES AND POLYELECTROLYTE MULTILAYERS

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Polyelectrolyte multilayers from layer-by-layer deposition of oppositely charged polyelectrolytes are applied as membranes. They can be tailored in surface charge, charge density and hydrophobicity for efficient separation, selective adsorption and antifouling. In many separation and transport processes pore sizes are crutial. Diffusion-time dependent measurement of the diffusion coefficient by PFG NMR of probe molecules yields the average pore size. The result for water in porous poly(amide) membranes corresponds very well to that determined from scanning electron microscopy. However, in multilayers from poly (ethylene imine) and poly(acrylic acid) effects of restricted diffusion are found as well, while no static pores are found in the electron micrographs. Restrictions in the apparent diffusion result from specific interaction between probe molecules and the polymers. The later fact becomes evident in the investigation of the diffusion of alcohol-water mixtures, where the diffusion behavior of water and alcohol differs. A more detailed picture is derived from the average propagator calculated from the diffusion decay. The propagator describes the probability of displacements of the probe molecule during the observation time. Chemical shift resolution in the diffusion experiments permits the simultaneous investigation of different probe molecules in a mixture. While there is a strong diffusion-time dependence for pure propanole, there is no diffusion-time dependence for the propagator of propanole in a propanole-water mixture in the polyelectrolyte multilayer. Since there are no static pores or channels in the multilayers, transport through multilayers is coupled to the mobility in the polymers which form “breathing pores”. These are formed in the polymers in interaction with the small molecules. The mobility of the polymers is investigated using solid-state relaxation NMR, where detection via 13C provides site- specific resolution. The broad distribution of relaxation times is best handled by a numeric inversion of the Laplace transform which results in a pseudo two-dimensional plot. Proton T1rho appears to be most suited for the investigation of polymer mobility in the kilohertz range of rates, which is most relevant for the transport processes.

# ELECTRO-OPTICS OF POLYELECTROLYTE MULTILAYERS ON NANOPARTICLES

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The layer-by-layer growth of multilayer assemblies of two oppositely charged polymers is investigated using electric light scattering. The electro-optical technique provides with respect to the classical electrophoresis a complementary way to obtain useful information on the electric surface properties (permanent and induced dipole moments) of colloidal particles in the presence of a surrounding polymer layer. The effective hydrodynamic thickness of the adsorbed layer can also be determined, following the time decay of the electro-optical effect before and after deposition of each layer, Using electro-optics, multilayer films on ellipsoidal FeOOH particles are investigated at low ionic strength, with emphasis on the effect of polyelectrolyte charge density and chain length on the film thickness and electrical polarizability of the polymer-coated particles. In contrast with the electrophoretic mobility, the electrical polarizability increases with increasing number of the adsorbed layers. In the linear growth regime, the polarizability increases similarly to the film thickness. This means that the electro-optical effect results from polarization of ions belonging only to the last-adsorbed layer. The technique also gives a molecular-weight dependence of both the magnitude and the relaxation frequency of the electro-optical effect. Lower frequency of the effect relaxation is found for the films ending with highly charged polyelectrolyte in comparison to the films ending with weakly charged polymer. This is attributed to polarization of condensed counterions along the chains of the last-adsorbed highly charged polyelectrolyte. In all cases, independence of the counterion dynamics of the layer number is obtained, which leads to the conclusion that the electrical properties of the last-adsorbed layer govern the behavior of the whole multilayer film. Although incorporation of condensed small ions into the film bulk seems probable in some films, their participation in creation of the electro-optical effect is found negligible. The experimental data collected in this work allow us to conclude that the electro-optics can be effectively used for studies in situ of formation and electrical properties of polyelectrolyte multilayers.

[1] Ts. Radeva, V. Milkova, I. Petkanchin, Colloids Surf. A, 240 (2004) 27.
[2] Ts. Radeva, V. Milkova, I. Petkanchin, J. Colloid Interface Sci., 279 (2004) 351.
[3] Ts. Radeva, K. Kamburova, I. Petkanchin, J. Colloid Interface Sci., in press.

# INTEGRATION OF FLAT FREESTANDING POLYELECTROLYTE MULTILAYER MEMBRANES IN LARGER SCALE STRUCTURES

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Ultrathin, semi-permeable membranes are not only essential in natural systems (membranes of cells or organelles) but they are also important for applications (separation, filtering) in miniaturized devices. Membranes, integrated as diffusion barriers or filters in micron scale devices need to fulfill equivalent requirements as the natural systems, in particular mechanical stability and functionality (e.g. permeability), while being only tens of nm in thickness to allow fast diffusion times. Promising candidates for such membranes are polyelectrolyte multilayers, which were found to be mechanically stable, and variable in functionality. We have developed a method that allows us to couple $mm^2$ areas of defect free film with thicknesses down to 50 nm to structured surfaces and to avoid crumpling of the membrane. We could again use this technique to produce arrays of micron size. The freestanding membrane is a diffusion barrier for high molecular weight molecules, while small molecules can pass through the membrane and thus allows us to sense solution properties [1]. Recently the usage of dried freestanding polyelectrolyte membranes as highly sensitive mechanical sensors was presented [2].We have shown that also osmotic pressures lead to membrane deflection. That could be described quantitatively.

[1] M. Nolte, B. Schoeler, C. S. Peyratout, D. G. Kurth, A. Fery, Adv. Mater. 2005, 17, 1665.
[2] C. Y. Jiang, S. Markutsya, Y. Pikus, V. V. Tsukruk, Nat. Mater. 2004, 3, 721.

# SURFACE MODIFICATION OF WOOD FIBRES BY ADSORPTION OF POLYELECTROLYTE MULTILAYERS

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The technique of building polyelectrolyte multilayers (PEM) on solid substrates has been developing during the last decade [1, 2]. This relatively new technique shows potential as a new way of engineering any surface, such as modifying the surface properties of wood fibres. In the present investigation, PEMs consisting of poly-dimethyldiallylammoniomchloride (PDADMAC) and polystyrene sulfonate (PSS), as well as hydrogen bonded PEMs of Poly ethylene oxide (PEO) and Poly Acrylic Acid (PAA), have been built on silicon oxide surfaces, using stagnation Point Adsorption Reflectometry (SPAR), and on wood fibres. Furthermore the adsorbed amount of PDADMAC and PSS to the fibres has been measured by nitrogen and sulphur analysis respectively. The results show that there is a PEM build up on the fibres. Paper testing of sheets prepared from fibres treated by PDADMAC/PSS or PEO/PAA PEM demonstrates an increase in the Tensile Index and the stress at break in the order of 100 %, when about 10 layers have been adsorbed. Special fibre treatment has been performed according to a novel method where a single fibre is partly covered by a PEM using a Dynamic Contact Angle Analyser (DCA). This technique makes it possible to study the wetability of the modified surface according to the Wilhelmy technique [3]. Fibres treated by PDADMAC/PSS show a significantly more hydrophobic surface when the fibre was treated by PDADMAC in the outermost layer, compared to PSS. Also treatment of individual fibres by Poly Allyl Amine (PAH) and PAA has been conducted; demonstrating similar results to PDADMAC/PSS, i.e. adsorption of PAH in the outermost layer gives a more hydrophobic fibre. For the treatment of fibres with PAH/PAA at pH 7.5/3.5 the PAH treatment results in a advancing contact angle of ~100 degrees whereas PAA results in a advancing contact angle of 40 degrees. The treated and the non-treated parts of the fibres treated by PDADMAC/PSS, have also been analysed using Environmental Scanning Electron Microscope (ESEM).

[1] G. Decher, Science 277 (1997) 1232

[2] Mulitlayer Thin Films, ed. G. Decher and J.B. Schlenoff. 2003, New York/Weinhem: Wiley-VCH. 524.

[3] J.H. Klungness, Tappi Journal 64 (1981) 65

# CHARACTERIZATION OF THICK POLYELECTROLYTE MULTILAYERS AND THEIR GROWTH PROCESSES ON A QUARTZ CRYSTAL RESONATOR

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In the the layer-by-layer (LbL) deposition of alternate cationic and anionic polyelectrolytes, a quartz crystal resonator (QCR) is already an indispensable instrument for determining the mass, the growth mechanism and the viscoelastic properties of the polymer film. With thin layers the interpretation of experimental data from a resonator is straightforward and even under liquid the classical Sauerbrey equation with proper corrections can be used for determining the areal mass density of the layer. However, as the layer grows, the error in the mass measurement increases which is often erroneously attributed to the influence of the viscoelasticity of the polymer. Finally at a certain point of growing thickness the resonance frequency changes direction and starts to increase, indicating apparent mass decrease according to the Sauerbrey equation. This point is called an acoustic film resonance where the layer thickness has achieved the quarter-wavelength of the transverse acoustic wave. In the present work we discuss the theory of thick layers on a QCR where the thickness considerably exceeds the acoustic film resonance, extending far beyond the Sauerbrey validity range. By plotting the measured surface acoustic impedance of a growing film as an Argand diagram in the complex plane, we obtain a spiral. The shape of this "impedance spiral" depends on the acoustic loss angle of the layer material and regularity of the growth process. The location of the spiral pole, its convergence point, in the complex plane gives directly the bulk acoustic impedance of the layer material in suitable conditions. By fitting the experimental data to the theoretical spiral it is possible to estimate the viscoelastic parameters of the layer material. The growth process in the layer-by-layer technique of preparing polyelectrolyte multilayers is known to be either linear or exponential or their combination. The different growth processes are shown on the impedance spiral as different distributions of data points. The changes in the growth mechanism and the formation of new, elastically different phases can be monitored on a QCR by using appropriate calculation procedures. Three well-known polyelectrolyte multilayer systems were chosen for demonstrating the method of spirals: poly (L-lysine)-hyaluronate, chitosan-hyaluronate, and poly-(diallyldimethylammonium)-polystyrenesulfonate.

# POLYSACCHARIDE HYBRID MULTILAYER FILMS

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Hyaluronan (HA) and chitosan (CHI) are biocompatible, nontoxic and highly hydrated polysaccharides that have many promising applications in tissue engineering, joint lubrication and controlled release of drug molecules etc. These polyelectrolytes can be also used for deposition of stable polymer films using layer by layer method. Current polyelectrolyte system adopts an exponential buildup regime when deposited in 0.15 M NaCl. The buildup regime can be fine-tuned by changing the ionic strength of the solution. (1) We have deposited hybrid multilayer films by co-depositing synthetic polyelectrolyte layers of poly (acrylic acid) (PAA) and poly (allylamine hydrochloride) (PAH) inside the HA/CHI films in order to study the effect of the synthetic blending material on the stiffness and the buildup mechanism of these biocompatible films. The films are deposited by a fully automated layer-by-layer machine. On the characterization of elastic properties of the films we have utilized self-made quartz crystal impedance measurement system that is capable of measuring acoustic film resonance on a thickness shear mode resonator.(2)

[1] Richert,L.; Lavalle, P.; Payan, E.; Shu, X.Z.; Prestwich, G. D.; Stoltz, J.-F.; Schaaf, P.; Voegel, J.-C.; Picart, C. Langmuir 2004, 20, 448-458

[2] Kankare, J.; Loikas, K.; Salomäki, M. Anal. Chem. 2006, 78, 1875-1882

# LAYER-BY-LAYER ASSEMBLED FILMS AND ION SEPARATION MEMBRANES BASED ON 18-AZACROWN-6 AND ANIONIC POLYELECTROLYTES

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The preparation and the characteristic properties of new layer-by-layer (LbL) assembled ultrathin films of 1,4,7,10,13,16-hexaazacyclododecane (hexacyclen, 18-azacrown-6) and polystyrenesulfonate (PSS) or polyvinylsulfate (PVS) are reported. The films were prepared upon alternating adsorption of the cationic and anionic compounds from aqueous solution onto charged substrates. The influence of the pH on the film formation is discussed. Detailed studies on 18- azacrown-6/PSS-films indicate two linear growth regimes at pH-values of about 1.7 and 6.0 [1]. Since 18-azacrown-6 is known to be an anion receptor, the use of the LbL-assemblies as ion separation membranes was tested. It was found that 18-azacrown-6/PVS films are excellently suited for separation of mono- and divalent anions. Separation factors chloride/sulfate of 110, and chloride/sulfite of 1420 were found, if the membranes were exposed to copper acetate before use. The effect of the copper acetate treatment and the origin of the unusually high separation factors are discussed. Studies of ion rejection under nanofiltration conditions are also reported. At a transmembrane pressure of 20 bar, 93.5 percent of the chloride ions and 96.2 percent of the sulfate ions are rejected.

[1] A. El Hashani, B. Tieke; J. Nanosci. Nanotechnol. 6 (2006), in press.

# POLYELECTROLYTE MULTILAYERS AS BIOMIMETIC SURFACE COATINGS

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Polyelectrolytes have been used for a broad variety of material modifications. Polyelectrolyte multilayers (PEMs) can be obtained by alternating adsorption of oppositely charged poly - electrolytes from aqueous solutions to a substrate[1-3]. This so called Layer-by-Layer (LbL) technique can be used to modify charged surfaces independently of their 3D structure or morphology. Process parameters such as the solution pH value, ionic strength, number of layers and type of polyion, etc. can be varied to control the chemical, morphological and mechanical properties of the coating. Most if not all components of the extracellular matrix (ECM) such as structural and adhesive proteins, growth factors and glycosaminoglycans (GAGs) are charged under certain conditions and hence applicable as polyelectrolytes. Therefore, the LbL technique is considered to be a useful method to obtain ECM-like structures on material surfaces and thus achieve control over adhesion, growth and differentiation of cells[4]. We utilized the polycations poly (ethylene imine) (PEI) and chitosan, and the polyanion heparin, a GAG with anticoagulant activity, to prepare PEMs. The assembly process was analysed by physicochemical methods to characterize wettability, surface charge, layer thickness/ mass change and topography. Applied methods were water contact angle and zeta-potential measurements, quartz crystal microbalance (QCM) and atomic force microscopy (AFM). It could be shown that the pH values of the polyelectrolyte solutions as well as the ionic strength have a strong influence on the process of multilayer formation. To investigate the biological properties of the coatings both the adsorption of the adhesive protein fibronectin (FN) and adhesion and proliferation of fibroblasts were investigated. It was found that more FN adsorbed on polycation terminated PEMs, which was accompanied by better cell attachment and proliferation. This was against our expectations because FN exhibits distinct binding domains for heparin. One probable cause for this effect is the electrostatic repulsion between the negatively charged heparin surface and FN, which results also in an impaired attachment of cells. In conclusion, the LbL technique is a versatile method to coat biomaterials for tissue engineering application as well as implants[4]. Further work is required to adjust the adsorption conditions to achieve a targeted interaction of multilayer components with adhesive proteins such as fibronectin.

[1] Decher G, Science 1997, 277: 1232
[2] Iler RJ, Colloid Interface Science 1966, 21: 569
[3] Decher G, Thin Solid Films 1992, 210: 831
[4] Groth T, Lendlein A, Angewandte Chemie, Internationale Edition 2004, 43: 926

# INFLUENCE OF SURFACE PROPERTIES ON LAYER BY LAYER ASSEMBLY OF MUCIN AND CHITOSAN FILMS

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Bovine submaxillary gland mucin (BSM) and chitosan were used to build layer by layer structures on silica and hydrophobized silica surfaces. One adsorption cycle comprised a mucin adsorption step followed by a chitosan adsorption step and the build-up was monitored using in situ ellipsometry to obtain time resolved values of the thickness and adsorbed amount of the film. We found that the adsorbed amount of the film increases approximately linearly with each adsorption cycle on hydrophobized silica whereas construction on silica was found not to be possible at the experimental conditions used. Due to the low amount adsorbed on silica in comparison with hydrophobized silica for the first mucin addition, we conclude that sufficient amount of the first mucin layer is crucial for the subsequent multilayer build-up. On hydrophobized silica we assume that the hydrophobic domains of the mucin interact with the surface ensuring substantial adsorption and firm attachment of this glycoprotein, whereas the affinity for hydrophilic surfaces is much lower.

Few studies have so far reported on the effects of surface properties on subsequent PEM build-up. Most studies on PEM involve surfaces that are pre-treated by e.g. highly charged polymers that readily adsorbs to create a highly charged positive or negative surface. In this respect hydrophobization of the substrate provides a different approach as a way of priming a surface for polyelectrolyte systems that involve amphiphilic polymers.

# COMPUTER SIMULATIONS OF DENDRIMERS WITH CHARGED TERMINAL GROUPS

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Structural properties of dendrimers with charged, monovalent terminal groups and counterions in an athermal solvent are studied by lattice Monte Carlo simulations using the cooperative motion algorithm as tossing scheme. The full Coulomb potential and the excluded volume interactions between pairs of ions and beads are taken explicitly into account with the reduced temperature T* as the main, variable parameter. In particular, the influence of variation of the latter on the mean effective charge per end-bead, total mean energy, mean-square radius of gyration, mean-square center-to-end-bead distance is analyzed and molecular weight dependencies of, are shown. The simulations indicate that condensation of counterions onto the end-beads occurs as T* is lowered. This effect is accompanied by relatively weak, gradual swelling and shrinking of the molecules. Furthermore, the local structure of the systems is also inspected by means of pair correlation functions that provide information on distributions of monomers, terminal groups and counterions in space. The simulations show that counterions penetrate the interior of the dendrimer, and due to condensation, there is a major increase in their concentration there as T* decreases. The change in size of the molecule is also reflected by the distributions of monomers and terminal groups.

# PROTEIN-LIKE IONIC NIPA/DMAPA-COPOLYMERS: SYNTHESIS, PROPERTIES AND TEMPERATURE-DEPENDENT SOLUTION BEHAVIOR AT VARIOUS PH VALUES

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Protein-like ionic copolymers of N-isopropylacrylamide (NIPA) and 3(N,N-dimethylamino) propylacrylamide (DMAPA) were synthesized through the redox-initiated free radical polymerization of the comonomers (initial molar ratio was 90:10) in aqueous media at pH ~6 (protonated form of DMAPA) and at pH ~10 (non-protonated form of DMAPA). The syntheses were carried out in two temperature regimes: either at 20 $^{o}$C (polymerization in homogeneous solution), or at 50 $^{o}$C (precipitation polymerization above the phase separation threshold). Final copolymers were purified with dialysis. According to NMR spectroscopy, the comonomer composition of the macromolecules was close to the initial one, i.e., around 90:10 (mol/mol), independently on the synthesis conditions. The temperature-dependent solution behavior of the NIPA/DMAPA-copolymers was studied with thermoturbidimetry method in aqueous media for the protonated (with HCl) and non-protonated (treated by NaOH and dialyzed) forms of the respective polyelectrolyte specimens. It was found that the non-protonated form of all copolymers exhibited solution behavior typical of the LCST-behavior of thermosensitive NIPA-homopolymers with the cloud points in the vicinity of 33-37 $^{o}$C. The salt forms of the copolymers showed certain differences. The copolymers in protonated form did not precipitate from the 2.5 mg/mL aqueous solutions at temperatures up to 70 $^{o}$C, at least. High-sensitivity DSC revealed a heat capacity peak with Tmax 35-36 $^{o}$C for the NIPA/DMAPA-copolymer synthesized at 50 $^{o}$C and pH 6, whereas no cooperative transitions were detected over the temperature range of 20-70 $^{o}$C for the copolymers synthesized at 20 $^{o}$C independently of pH values of polymerization medium (i.e., 6 and 10), as well as for the copolymer prepared at 50 $^{o}$C and pH 10. These results testified that the protonated form of NIPA/DMAPA-copolymer synthesized at 50 $^{o}$C and pH 6 can be classified as a “protein-like” copolymer [1]. A characteristic feature of the conformation of such copolymers is a core-shell structure of their macromolecules, where heteroblock chains are folded so that the blocks enriched with more hydrophobic units (NIPA in this case) form a dense core stabilized by hydrophobic interactions, and the blocks enriched with hydrophilic units (protonated DMAPA in this case) form loose shell, which is capable of preventing the polymer particles against the aggregation and subsequent heating-induced precipitation [2].

[1] Khokhlov A.R., Khalatur P.G. (1998) Physica A (Amsterdam) 249: 253.
[2] Lozinsky V.I. (2006) Adv.Polym.Sci. 196: 87.

# ION CONDENSATION TO SEMIFLEXIBLE POLYIONS

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It has been experimentally observed that trivalent ions are capable of promoting compaction of semi-flexible chains. In this work we perform Monte Carlo simulations on model systems with varying chain size and stiffness and evaluate the action of multivalent salt on the chain conformation. Longer chains tend to achieve relatively more compact conformations than shorter ones, with similar dimensions when collapsed for both short and long. The influence of contour length and intrinsic stiffness on the ion condensation process is studied by analysis of the ion-ion nearest-neighbor distribution. The method [1] does not involve any arbitrary parameters, being thus system independent, and can be used with most simulation techniques. It is observed that the trends followed by ion condensation are dependent on the concentration of the compacting agent. For low concentrations, ion condensation tends to decrease with increasing stiffness, for intermediate concentrations the effect of stiffness is not significant, but for high concentrations ion condensation increases with chain stiffness. In what concerns the effect of contour length, the general trend is an increase of the degree of ion condensation as the chain length increases, in accordance to experimental evidence.

[1] J.M.G. Sarraguca and A.A.C.C. Pais, Chem. Phys. Lett. 398, 140-145 (2004).

# COIL-GLOBULE COEXISTENCE IN DNA CHAINS

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The folding of biological macromolecules has always attracted much interest from the physical, chemical and biological points of view. Over the last decade, the particular case of DNA compaction by different agents has earned a special interest due to its importance in gene therapy. In this work we discuss different factors governing the compaction and coil-globule coexistence behavior of DNA. We initially analyse the role played by fluctuations in the degree of binding of an external compacting agent in the conformational behaviour of the chain backbone. The analysis relies both on Monte-Carlo simulation results and simple statistical approaches. Compacting agents of various binding characteristics are taken into consideration and the degree of charge neutralisation upon the chain is related to conformational indicators. Selected model systems comprising stiff chains in the presence of multivalent ions are employed to assess also intrinsic single-chain conformational fluctuation, in the presence of external agents but not resulting from differences in binding. It is shown that trends found for a variety of compacting agents, including the extension of the coil-globule coexistence regions, can be rationalised on the basis of this analysis.

# MOLECULAR DYNAMICS SIMULATIONS OF BRANCHED COMB-LIKE POLYELECTROLYTES IN SOLUTION

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We present recent results on conformational behaviour of comb-like branched polyelectrolytes. Using molecular dynamics simulations with explicit electrostatics, we study the effect of the degree of charging of the polymer and the chain architecture (branching density, length of branches) on the conformational behaviour. We compare the simulation data with theoretical predictions for amphiphilic graft copolymers, which we expect to be qualitatively similar.

# MOLECULAR DYNAMICS SIMULATION OF TIME-RESOLVED FLUORESCENCE ANISOTROPY DECAYS FROM LABELED POLYELECTROLYTES IN DILUTE SOLUTIONS

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Molecular dynamic simulations aimed at understanding the relationship between (i) conformational changes and dynamics of polyelectrolyte chains with increasing degree of ionization in solvents differing in thermodynamic quality and (ii) fluorescence anisotropy decays from pendant fluorophores attached to the chain were performed using the Langevin thermostat. The model is coarse grained, the solvated counterions are taken into account explicitly while the solvent is treated implicitly. The results of simulations were compared with our original (already published) data on linear poly(methacrylic acid) labeled by dansyl. The experimental and simulated data compare well at the semi-quantitative level. All simplifications used in the model are thoroughly discussed, mainly differences between the behaviors of quenched and annealed polyelectrolytes. The study shows that the time-resolved fluorescence anisotropy is a suitable tool for monitoring the conformational behavior of polyelectrolytes in bad solvents, but simultaneously it shows some complications and potential danger of misinterpretation of fluorescence data.

# MODIFICATION OF FUOSS EQUATION FOR VISCOSITY OF STRONG POLYELECTROLYTES

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Dependencies of reduced viscosity $(n-n0)/(n*Cp)$ of strong polyelectrolyte polydiallyldimethyl ammonium chloride (PDADMAC) on polymer concentration Cp in aqueous solutions of low-molecular electrolytes (NaCl, Na2SO4, K3[Fe(CN)6] were measured. The series of curves with anomaly concentration dependency of viscosity were received. Plot of $lg[(n-n0)/(n*Cp)]$ versus lgCp gives a family of parallel straight lines. As follows, it is possible to use the generalized Fuoss equation$(n-n0)/(n*Cp) =A(Cp)^{\sigma}+B$. Reduced viscosity of solutions containing low- and high-molecular electrolytes could be characterized by the only similarity parameter [1]: $(\lambda/R)^{3}=(4\pi*M/3Mo)(\lambda^{3})Cp*Na$, where $\lambda$ - the Debye length, R - average distance between macromolecular coils, M – molecular weight of polymer, Mo – molecular weight of monomer unit, Cp– polymer concentration, Na– Avogadro number. The similarity parameter could be presented in empiric form $(\lambda^{3})*Cp*Na= [(1+\sum pi*(zi^{2}))] (-3/2)/(Cp^{1/2})$ where pi- ratio of concentration i-typed ions to polymer concentration. Plot of $(n-n0)/(n*Cp)$ versus logarithm of the similarity parameter $ln[(1+\sum pi*(zi^{2}))]^{(-3/2)}/(Cp^{1/2})$ gives the only curve. It means that the suggested generalized Fuoss equation satisfactory describes the behavior of strong polyelectrolytes in salt solutions of different concentrations.

[1] Suleimenov I.E., Budtova T.V., Shapenova E.M., Belnikevich N.G., Bekturov E.A. A Generalized form of the Fuoss law for viscosity of polyelectrolytes in salt solutions of complex composition // High molecular compounds, A, 2005, 47, № 10, P. 1841–1853

# MICROCALORIMETRIC STUDY OF THE PROTONATION AND COMPLEXATION OF THE POLYMERIC AMINES LPEI, BPEI AND LPPI

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The properties of the weak polyelectrolytes LPEI (linear polyethyleneimine), BPEI (branched polyethyleneimine), LPPI (linear polypropyleneimine) and for comparison TETREN (1,4,7,10,13-penataza-tridecane) have been studied mainly by potentiometric titrations. However for a detailed understanding of the acid-base and complexation reactions of these reactions in solution the thermodynamic functions H, S and G have to be known. Even so there are only a small number of micro calorimetric studies of polyelectrolyte solutions in literature. Therefore we carried out potentiometric and calorimetric titrations of hydrochloric form of the polymeric amines LPEI, BPEI, LPPI and for comparison of the linear pentamine TETREN (1,4,7,10,13-penataza-tridecane) at 25 °C and 65 °C. A comparison of the titration curves shows the influence of the structure on the properties of the polyamines in solution. In addition titrations of the protonated polyamines in presence of varying amounts of $Cu^{2+}$ are reported and the thermodynamic functions G and S for the binding of $Cu^{2+}$ deduced.

# CHARGE DENSITY EFFECT ON THE ELECTROLYTIC CONDUCTIVITY BEHAVIOR OF SOME CATIONIC POLYSACCHARIDE SOLUTIONS

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The charge density effect on the electrolyte conductivity behavior of some cationic polysaccharides in water and water/methanol mixture was studied. The polyelectrolytes investigated with pendent quaternary ammonium salt groups, N-alkyl-N, N- dimethyl-2-hydroxypropyleneammonium chloride, have been synthesized by chemical modification of dextran samples [1]. This new class of polyelectrolytes has various linear charge density parameters, located below and above the critical threshold value of counterions condensation = 1 (linear charge density = 0.25-3.18). The results were analysed within the Manning's theory [2, 3]. The conductometric measurements show the next aspects: a) For all cationic polyssacharides, the equivalent conductivity values increase with dilution over the almost entire concentration range; b) The values of equivalent conductivity decrease with increasing! charge density irrespective of the its value position, below and above 1; c)The interaction parameters, fc, were found to depend on both the polymer concentration and the charge density; d) Lower experimental values for the equivalent conductivity and the interaction parameter than the theoretical ones have been noticed. This could be assigned to various conformations of the chains which could lead to greater values of charge density than those calculated from the chemical structure of the chain supposed to be in a rod-like conformation. It seems that Manning‘s model can not describe the conductometric behavior of these kind of cationic polysaccharides.

[1] Nichifor, M.; Lopes, S.; Bastos, M.; Lopes, A. J. Phys. Chem. B 2004, 108, 16463.
[2] Manning, G. S. J. Chem. Phys. 1969, 51, 924.
[3] Manning, G. S. J. Phys. Chem. 1975, 79, 262.

# RHEOLOGICAL BEHAVIOR OF SOME CATIONIC POLYELECTROLYTE SOLUTIONS

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Polyelectrolyte solution properties are influenced by many factors related to the characteristics of the polyelectrolyte chains (chemical structure of the monomer unit, the chain length, the charge density, polyelectrolyte concentration, length and content of hydrophobic groups), counterion nature (size and valence) and medium properties (pH, temperature and dielectric constant) [1, 2] . This work centers on the effects of polyelectrolyte concentration and temperature on the rheological behavior of some polyelectrolytes in aqueous solution both in the presence or absence of low molar mass electrolyte, NaCl. Polymers under study are cationic polyelectrolytes with quaternary ammonium groups, N,N-dimethyl-2-hydroxypropyleneammonium chloride, located along the main chain, with or without nonpolar side chain (PCA5 and PCA5D1, respectively). They were synthesized by condensation polymerization of epichlorohydrin (ECH) with dimethylamine (DMA), N,N-dimethyl-1,3-diaminopropane (DMDAP) – polymer type PCA5, and primary amine with nonpolar chain, decyloxypropylamine - polymer type PCA5D1, according to the method presented in detail elsewhere [3, 4 ]. The rheological measurements were performed by using a CVO Rheometer with parallel plate geometry (60 mm diameter) and thermal control by Peltier effect. Dynamic shear oscillation measurements at small strains are carried out in the frequency range of 0.01 – 100 rad/s. The experimental data show that complex viscosity, storage (G') and loss (G") moduli are sensitive to polymer concentration and the salt presence. The temperature effect becomes more important at temperature C. values higher than 50.

[1] Förster, S., and Schmidt, M. 1995, Adv. Polym. Sci., 120, 51.
[2] Wandrey, C., and Hunkeler, D. 2002, Study of Polyion Counterion Interaction by Electrochemical Methods, Tripathy, S. K., Kumar, J. and Nalwa, H. S. (Ed.), American Scientific Publisher, 147.
[3] Dragan, S., and Ghimici, L. 1991, Angew. Makromol. Chem., 192, 199.
[4] Dragan, S.; Ghimici, L. Bull. Inst. Pol. Iasi 1998 XLIV, 109.

# ORGANIC – INORGANIC COMPOSITES BY INTERACTIONS IN AQUEOUS SOLUTIONS

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The paper presents two ways for obtaining organic-inorganic composites by the interactions of hydroxyapatite precursors in polymeric aqueous solutions. The first method consists in interactions between two aqueous solutions: the diammonium hydrogen phosphate and the calcium nitrate tetrahydrate, directly in an aqueous solution of calcium atelocollagenate. In contrast with the classical techniques, the precipitate has not been submitted to calcinations in order to complete the crystallization. The maintaining in suspension state, in the medium of dispersion, makes the crystalline aggregates maintained at a metastable form. The second method is a precipitation of the same precursors into an aqueous solution of maleic copolymer. The maleic polyelectrolyte plays an important role in inhibiting crystal growth. The use of the synthetic polyelectrolytes as modulators of crystallization was studied [1, 2] and the results determined us to further research this property in hydroxyapatite formation. The influence of polyelectrolytes regarding the interaction between calcium and phosphate ions was studied by potentiometric/ conductometric/ turbidimetric titration. The nanoparticles of hydroxyapatite were characterized by FTIR spectroscopy, X-ray diffraction and scanning electron microscopy.

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[1] K.P. Klepetsanis, P.G. Koutsoukos, G.C. Chitanu, A. Carpov, The inhibition of calcium carbonate formation by copolymers containing maleic acid, chapter in Solution Properties and Application of Water Soluble Polymers, edited by Z. Amjad, ACS Symposium Series, New York, Plenum Press, chap. 10, 117-130, 1998.

[2] R.M. Piticescu, G.C. Chitanu. M.L. Popescu, W. Lojkowski, A. Opalinska, T. Strachowski, Annals of Transplantation, 9 (1A), 20-25, 2004.

# TITRATION OF POLYAMPHOLYTES. A DIELECTRIC DISCONTINUITY ISSUE.

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The charging processes as well as the discrete unit charge distribution at the surface of spherical polyampholytes (macroions) were studied by computer modeling. Using a grand canonical Monte Carlo method and a Tanford and Kirkwood approach to describe the interaction potentials between explicit discrete ampholytic charging sites, the effects of the Coulomb interactions, the polyampholyte/solution interface dielectric discontinuity, the solution ionic strength and the surface site distributions were investigated. In particular, homogeneous, heterogeneous and patch site distributions were considered in order to reproduce the titrating site distribution at the solid/solution interface of some macroions. We demonstrate that the charging process of polyampholyte is controlled by the subtle balance between Coulomb interactions, the solution ionic strength effect and the dielectric breakdown through the solid-liquid interface. Results show also that the site distribution plays a crucial role on the charging process: In patch site distributions, charges accumulate at the perimeter of each patch due to finite size effects. When comparisons between homogeneous and heterogeneous distributions are made, three different charging mechanisms are obtained. To bridge the gap between modeling and experiments, titration curves for pyrogenic silica nanoparticles were calculated and compared with experimental data obtained at different ionic concentrations. A remarkably good agreement was found.

# POLYELECTROLYTE COMPLEXES INVESTIGATED BY PFG NMR

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Pulsed-field gradient NMR is a versatile tool for the determination of the diffusion coefficient of molecules in solution. The spectral resolution provided by NMR permits the identification of the moving species, which is utilized for the simultaneous study of polyelectrolyte and counterion or polycation and polyanion in the formation of polyelectrolyte complexes. In order to handle the distribution of diffusion coefficients resulting from the molecular weight distribution, a numeric inverse Laplace transform has been applied [1]. Organic counterions are investigated simultaneously with the polyelectrolyte. From a comparison of the diffusion coefficients of the counterion with the polyelectrolyte to the solution of the free counterion, the fraction of bound / condensed counterions is determined. Due to the electrostatic repulsion of the charges along the chain polyelectrolytes adopt a more extended conformation than uncharged polymers. Upon the addition of salt the charges are screened and the polyelectrolyte adopts a more compact conformation [2]. Due to the higher affinity effect is stronger for bivalent counterions. The addition of an oppositely charged polyelectrolyte maybe seen as a multivalent counterion as demonstrated with Poly(styrene sulfonate) (PSS) to poly(diallyldimethylammonium chloride) (PDADMAC), where the hydrodynamic size of the primary complex formed is significantly smaller that that of the free PDADMAC.

[1] http://www.macdiarmid.ac.nz/nmr/development/2dlaplace.html
[2] Ute Böhme, Ulrich Scheler, Macromolecular Symposia, 184, (2002), p. 349

# SYNTHESIS AND CHARACTERIZATION OF RIGID-ROD POLYELECTROLYTES IN AQUEOUS SOLUTION BY PFG NMR

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One important issue in polyelectrolyte research is the counterion condensation and the determination of the effective charge in aqueous solution. In particular the counterion condensation is not yet fully understood. The aim of this work was to contribute to the understanding of the behaviour of polyelectrolytes in solution with focus on the counterion condensation. For that purpose rigid polyelectrolytes based on aromatic polyamides bearing one sulfonic acid group at each aromatic unit (sulfonated Kevlar) have been synthesized. The rigidity of the polymer backbone reduces the variances of chain mobility, thus leading to a more simple system (conformational degree of freedom). Fully sulfonated polyaramides were successfully prepared by the so-called Yamazaki method [1] using sulfoterephthalic acid or sulfoisophthalic acid and 2,5-diamino benzene sulfonic acid as monomers. The reaction was carried out in pyridine in the presence of triphenyl phosphite and lithium chloride. The polyelectrolytes were obtained as pyridinium salts. The pyridinium counterion enabled us to study the mobility of both the polyelectrolyte chains and the low-molecular weight counterion, thus allowing to study the counterion condensation. GPC measurements (solvent: DMAc/H2O/LiCl; MW standard: polyvinylpyrrolidone) gave molecular weights as high as 44,000 g/mol (Mw) and 28,000 g/mol (Mn), while viscosity measurements, carried out in conc. sulfuric acid, suggested molecular weights of only 4,400 g/mol (calc. based on the Mark-Houwink equation for Kevlar). PFG NMR permits the determination of the diffusion coefficient of the polymer and the counterion simultaneously. Because of the fast exchange between condensed and free pyridine an average diffusion coefficient is determined, showing that one third of the counterions is condensed. From a combination of PFG NMR and electrophoresis NMR the effective charge of the polyelectrolyte is determined [3, 4]. From this charge and the fact, that one third of the counterions is condensed a degree of polymerization of 20 (Mn ca. 8000 g/mol) has been determined.

[1] N. Yamazaki, M. Matsumoto, F. Higashi, J. Polym. Sci., Polym. Chem. Ed. 13 (1975), 1373.
[2] Y. Oishi, M. Kakimoto, Y. Imai, Macromolecules 22 (1988), 547
[3] U. Scheler, in H.S. Nalva (ed.) 'Handbook of Polyelectrolytes and their applications', American Scientific Publishers (2002)
[4] Ute Böhme, Ulrich Scheler, Colloids and Surfaces A, 222, (2003), 35

# SAXS STUDIES ON LOCAL CONFORMATIONS OF IONIC AND NONIONIC POLYPEPTIDES IN SOLUTIONS

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As is well known, the conformations of a polypeptide chain in the helical state (H-state) or the helix-to-coil transition state (H/C-state) have attracted much attention in relation to conformations of proteins. Poly(L-glutamic acid) (PLGA) exhibits the conformational transition between H- and C-states by changing pH of the solution. Numerous studies were done on the conformations of PLGA in H- and H/C states [1], but studies on the conformation in C-state are so limited [2]. We have undertaken the study by small-angle X-ray scattering(SAXS) to see how the local structure of PLGA-salt in C-state is affected by the species of counter-ions. In the presence of counterions $Li^+$, $Na^+$ and $TMA^+$ (tetramethylammonium), PLGA-salt behaves [3] as a wormlike chain having persistence length of 6-8. In the presence of counterions $Ba^{++}$ and $Ca^{++}$, on the other hand, the conformations become more compact than a wormlike chain and would rather be represented by a swollen network-structure. This might suggest the presence of something like intra- and inter-molecular cross-linking between counterions of di-ionic-valence and carboxylic groups. In the presence of $Mg^{++}$, however, the conformation of PLGA-salt was better represented by a wormlike chain. The particle scattering function $P(\theta)$ was theoretically derived [4-6] for the broken-rodlike (BR) chain model, consisting of several rods alternatively joined by flexible random coils. $P(\theta)$ for the BR chain model was applied to compare averaged number of residues per helical sequence for partially ionized poly(sodium L-glutamate) (Na-PLGA) in added-salt aqueous solution and nonionized poly(L-glutamic acid) (PLGA) in N-methylacetamide, both in a helical state. As a result, it was shown [7] that in the latter molecule is approximately tenfold larger than that in the former one, in consistence with the suggestion of Holtzer et al. [8]. As is well established, poly(β-benzyl L-aspartate) (PBLA) undergoes the helix-to-coil transition [9] in chloroform-dichloroacetic acid mixture and in m-cresol and its cooperativity parameter is remarkably smaller than in the former solvent than in the latter. In order to see how such a difference of cooperativity parameter is reflected in , the SAXS curves for PBLA were registered as a function of temperature. The analysis is in progress.

[1] Y. Muroga, H. Tagawa et al., Macromolecules, 21 (1988) 2756.
[2] R.B. Hawkins, A. Holtzer, Macromolecules, 5 (1972) 294.
[3] S. Shimizu, Y. Muroga et al., in preparation.
[4] Y. Muroga, Macromolecules, 21 (1988) 2751.
[5] Y. Muroga, Macromolecules, 25 (1992) 3385.
[6] Y. Muroga, Macromolecules, 25 (1992) 6063.
[7] Y. Muroga, Biopolymers, 54 (2000) 58.
[8] D.K. Schiffer, A. Holtzer, Biopolymers, 13 (1974) 853.
[9] Y. Hayashi, A.Teramoto et al., Biopolymers, 8(1969) 403.

# SAXS STUDIES ON CONFORMATIONS OF POLYELECTROLYTES AND BIOPOLYMERS IN SOLUTIONS

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Small-angle X-ray scattering (SAXS) studies were undertaken to analyse the conformations of polyelectrolytes and biopolymers in solutions and following results were obtained: (1) Poly(sodium methacrylate) PNaMA and poly(sodium ethacrylate) PNaEA have both hydrophilic and hydrophobic side-groups and show pH-induced conformational transition between compact- form at low charge-density and extended-form at high charge-density. The analysis by SAXS has clarified [1-2] that the structures of their extended-coiled forms are similar and equally represented by a wormlike chain, but the architectures of their compact forms are different from each other. The compact form of PNaMA is still represented by a wormlike chain in a theta-medium, whereas that of PNaEA is represented by swollen network-structure. (2) The scattering function $P(\theta)$ representing a detail in the helical-form and random-coiled-form of a polypeptide chain in solution was analytically derived [3] in order to study its local conformation. $P(\theta)$ for helices of various types are characterized by a maximum in scattering-vector corresponding to Bragg spacing of 3-5A, whereas $P(\theta)$ for random-coils has no such maximum. Comparison of the extant data [4] of poly(L-glutamic acid) and poly(L-lysine) in solution with the calculated $P(\theta)$ shows that the helical structures in both polypeptide chains are of the 3.6/13-helix (α-helix) rather than 3.0/10 type. (3) As is well known, the structures of cucumber green mottle mosaic virus (CGMMV) and tobacco mosaic virus (TMV) are similarly constructed with a single RNA chain, CGMMV-RNA and TMV-RNA, respectively and coat proteins, but the biological activity of CGMMV tends to fade at a lower temperature than TMV when the temperature is raised. The analysis of the SAXS data has clarified [5-6] that the local structure of CGMMV-RNA more easily collapses with increasing temperature, compared with TMV-RNA. This result suggests that the lower thermal stability of CGMMV might be due to more vulnerable structures of CGMMV-RNA.

[1] Y. Muroga, T. Yoshida, S. Kawaguchi, Biophys. Chem., 81 (1999) 45-57.
[2] Y. Muroga, S. Iida, S. Shimizu, H.Ikake, K. Kurita, Biophys. Chem., 110 (2004) 49-58.
[3] Y. Muroga, Biopolymers, 59 (2001) 320-329.
[4] A.I. Grigoryev, L.A. Volkova, O.B.Ptitsyn, FEBS Lett. 14 (1971) 189-191.
[5] Y. Muroga, Y. Sano, H. Tagawa, et.al., Biophys. Chem., 83 (1999) 197-209.
[6] Y. Muroga, Y. Sano, H. Tagawa, in preparation.

# LCST TYPE OF PHASE SEPARATION IN AQUEOUS MIXTURE OF POLYELECTROLYTES

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In our previous study, phase separation behavior in aqueous mixture of different polyelectorolytes having equal charge densities and like charges has been investigated as functions of total concentration and ratio of mixture. The phase separation behavior was a normal upper critical solution temperature (UCST) type, though the compatibility between different polyelectorolytes was relatively good [1]. The good compatibility between different polyelectorolytes having equal charge densities and like charges is attributed to the identity of electrostatic interactions between the same and different molecules. Accordingly, it is expected that the compatibility will be poorer if the charges of different polyelectorolytes become unequal. This is the motivation of this study. In the present study, phase separation behavior in aqueous mixture of different polyelectorolytes having like charges has been investigated as functions of concentration and charge density. When the charge densities of both polyelectorolytes were equally high, the phase separation behavior was UCST type as was described above. As was expected, with decreasing the charge density of one polyelectorolyte keeping the charge density of another polyelectrolyte unchanged, the compatibility between different polyelectorolytes became poorer. However, when the charge density of one polyelectorolyte was lowered below a certain value, the phase separation behavior suddenly changed from the UCST type to a lower critical solution temperature (LCST) type. Possible mechanism, which drives the present LCST type phase separation, will be discussed.

[1] K. Nishida, M. Shibata, T. Kanaya and K. Kaji, Polymer 42 (2001) 1501.

# SIMULATION OF MICELLE FORMATION BY STAR DIBLOCK COPOLYMERS WITH POLYELECTROLYTE BLOCK

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Coarse-grained computer simulations of star block copolymers were carried out to study complex structure formation in water solutions. Four-armed star diblock copolymers where inner block is hydrophobic and the outer block is hydrophilic weak polyelectrolyte were considered. The system was simulated with monovalent counterions in salt-free solution and in presence of salt. The process of micelles formation and their morphology was followed. The system was considered as a model for PMMA-b-PAA star copolymers in aqueous solution which self-assemble into spherical and wormlike micelles at certain external conditions and chemical structure. The results of simulation were compared with theoretical predictions for this system using mean-field theory for diblock copolymers with one neural and one polyelectrolyte block in dilute aqueous solution in the salt dominance regime.

# RHEOLOGICAL PROPERTIES OF ASSOCIATIVE POLYELECTROLYTE STAR POLYMERS

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Rheological properties of a 4-armed amphiphilic star polymer in aqueous solutions were studied. The arms of the polymer consist of diblock polymers of poly(acrylic acid) (PAA) attached to the central core and short block of polystyrene (PS) as end-capping block. The weak polyelectrolyte, PAA, makes the polymer water soluble, while the short hydrophobic PS chains act as stickers, giving the polymer associative properties. The viscoelastic properties of the aqueous solutions were studied with respect to polymer concentration, pH, ionic strength and temperature.

# QUENCHED HYDROPHOBIC POLYELECTROLYTES: COMBINED SMALL-ANGLE NEUTRON AND X-RAY SCATTERING STUDIES

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The structure of aqueous solutions of highly charged hydrophobic polyelectrolytes was investigated using high-resolution small-angle neutron and X-ray scattering. The choice of one technique rather than another was driven by the contrast between the solvent (H20 and/or D2O) and the species (macroions and/or counterions) we want to look at. Various architectures of sulfonated polystyrene macroions with distinct sulfonation rates as well as distinct counterions were considered. We will present results that show strong evidence for the existence of pearl-necklace conformations with dense charged aggregates connected by stretched chain parts. Precisely, the X-ray scattering functions display a maximum of intramolecular origin at high q values . In the hydrophobic case, this maximum is characteristic of hollow spheres formed by condensed counterions around the hydrophobic aggregates. The sizes of these spheres are in agreement with those extracted from the macroion form factor measured through neutron scattering, by considering this time full spheres. Such pearl-necklace conformations have been predicted on the basis of scaling arguments for polyelectrolytes under poor solvent conditions [1,2] and have been earlier suggested by low-resolution small-angle X-ray scattering studies [3,4]. They were also confirmed by molecular dynamics and Monte Carlo simulations using the full Coulomb interaction with explicite counterions [5-7]. They result from the balance between the tendency to precipitate, the electrostatic repulsion and the entropic degrees of freedom. It was however suggested that fluctuations should impose a severe obstacle in observing these pearl-necklace structures [6]. Here, we are more concerned with quenched polyelectrolytes and the non-sulfonated sequences may form microdomains. The resulting shape could therefore be similar, though the physical case is not the one theory was made for.

[1] Dobrynin A.V., Rubinstein M., Obukhov S. Macromolecules 1996, 29, 2974
[2] Dobrynin A.V., Rubinstein M. Macromolecules 2001, 34, 1964
[3] Essafi W., Lafuma F., Williams C.E. J. Phys. II 1995, 5, 1269; Eur. Phys. J. B 1999, 9, 261
[4] Baigl D., Ober R., Qu D., Fery A., Williams C.E. Europhys. Lett. 2003, 62, 588
[5] Micka U., Holm C., Kremer K. Langmuir 1999, 15, 4033
[6] Limbach H.J., Holm C. J. Phys. Chem. B 2003, 107, 8041
[7] Uyaver S., Seidel C. J. Phys. Chem. B 2004, 108, 18804

# THE IMPORTANCE OF HYDRODYNAMIC EFFECTS IN POLYELECTROLYTE ELECTROPHORESIS

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We investigate the electrophoretic mobility of polyelectrolytes in free solution under the influence of an applied DC electric field via coarse-grained molecular dynamics. The simulation method uses an implicit solvent model with an effective dielectric permittivity, but includes both long range hydrodynamic and full electrostatic interactions. The simulation results are compared to various sets of experimental data and to static and dynamic simulations disregarding hydrodynamic interactions. We investigate the influence on chain confirmations and the corresponding counterion distribution around the chain which changes the electrophoretic mobility significantly.

# A MODEL POLYELECTROLYTE SYSTEM WITH HIERARCHICAL SELF-ASSEMBLY: IMPORTANCE OF COUNTERION VALENCY.

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Hydrophobically modified poly-para-phenylene molecules provide an ideal model system for studying aggregation of like-charged polyelectrolytes. We have studied self-organization in such systems with counterions of different valency via computer simulations. These molecules exhibit a hierarchical organization ranging from individual cylindrical micelles to aggregates of these micelles. As the valency of the counterions is increased the repulsive interactions among self-assembled bundles of PPPs are replaced with attractive interactions. This leads to the observation of much larger aggregates as confirmed via light scattering experiments as well as our computer simulations.

# POLYELECTROLYTE BEHAVIOR OF SELF-ASSEMBLED GUANOSINE AGGREGATES

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Guanosine is the DNA nucleotide, which consists of the guanine base and the sugar-phosphate moiety. Dissociation of the phosphate group in aqueous solutions makes the DNA double helix a strong polyelectrolyte with 2 negative charges per 0.34 nm. Guanosine molecules have the ability to form even more complex, four-fold, helices. They can form from guanine-rich DNA strands and have a sugar-phosphate backbone (quadruplex DNA). Alternatively, single guanosine molecules self-assemble into long supramolecular aggregates without any vertical bonding. The basic building unit is the same in both cases: four guanosine molecules assemble by hydrogen bonds (Hoogsteen bonding) into a cyclic array called the G-quartet. The disk-shaped quartets have a strong tendency for stacking into long cylindrical aggregates due to attractive pi-pi interactions between the guanine bases. Depending on the pH-value of the solution, a G-quartet can have 4 to 8 negative charges. Stacking of the quartets thus produces a highly charged polyion with a linear charge density of 4 – 8 negative charges per 0.34 nm. We have studied solution dynamics of self-assembled deoxyguanosine 5'-monophosphate by dynamic light scattering (DLS). Usually two diffusive modes were observed. The slower mode is present in the whole concentration range. It arises probably from the diffusion of large globular clusters and is not related to self-assembly. Similar slow DLS modes have been reported in a variety of polyelectrolyte solutions. The faster DLS mode is assigned to the diffusion of self-assembled guanosine aggregates and is not observed for concentrations below 4 wt %. It's appearance is correlated with the appearance of additional resonance lines in 31P NMR spectra due to G-quartet stacking. The diffusion coefficient of the fast DLS mode shows a typical polyelectrolyte behavior: it increases with increasing guanosine concentration until a saturation value is reached in the semidilute regime [1]. Such behavior can be described by the Coupled Mode Theory [2] when counterion condensation is taken into account. The addition of salt (KCl) results in a very complex solution dynamics due to a competition between potassium-promoted self-assembly and screening effects [3].

[1] L. Spindler et al., Eur. Phys. J. E 7, 95-102 (2002).
[2] K.S. Schmitz, An Introduction to Dynamic Light Scattering by Macromolecules (Academic Press, 1990).
[3] L. Spindler et al., Eur. Phys. J. E 13, 27 (2004).

# DIFFUSION AND SEGMENTAL DYNAMICS OF DOUBLE-STRANDED DNA

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Diffusion and segmental dynamics of the double-stranded lambda-phage DNA polymer are quantitatively studied over the transition range from stiff to semiflexible chains by means of fluorescence correlation spectroscopy. Investigation of fluorescence fluctuations of single-end fluorescently labeled monodisperse DNA fragments unambiguously shows that double-stranded DNA in the length range of 100−20000 base pairs behaves as a semiflexible polymer with dynamics largely determined by hydrodynamic interactions.

# ELECTROSTATICS OF DNA AND OF DNA-PROTEIN COMPLEXES

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We will present some recent results of the theory of DNA-DNA electrostatic interactions [1-6]. Based on this theory, we will a) describe the force-distance curves in dense DNA hexagonal assemgly [2], b) introduce the electrostatic mechanism of recognition of homologous DNAs [3,4], c) determine the degree of torsional deformations of DNA backbones induced by DNA-DNA electrostatic interactions in dense assemblies [4], d) consider the pattern of DNA azimuthal frustrations on hexagonal lattice, e) discuss the effects of DNA helical non-ideality on DNA melting behavior in dense DNA aggregates [5], f) analyze the formation and growth of DNA toroidal condensates [6]. Comparison with experimental data for each of these phenomena will be presented. We will also show the results of the theory of complex formation of DNA with oppositely charged spherical and cyindrical particles [7]. We will consider an electrostatic model of DNA conformational transition at elevated salt concentrations [8]. We will discuss electrostatic interactions of nucleosome core particles based on statistics of their azumuthal frustrations in nucleosomal bilayers [9]. In the end, we will present some results of a new model of DNA-protein electrostatic recognition based on the principle of adjustment and complementarity of their charge patterns and discuss its implications on (facilitated) diffusion of proteins along DNA during their search for binding sites on DNA [10].

[1] A.A. Kornyshev and S. Leikin, J. Chem. Phys. 107, 3656 (1997); 108, 7035(E) (1998).
[2] A.G. Cherstvy, A.A. Kornyshev, and S. Leikin, J. Phys. Chem. B, 107, 13362 (2002).
[3] A.A. Kornyshev and S. Leikin, Phys. Rev. Lett., 86, 3666 (2001)
[4] A.G. Cherstvy, A.A. Kornyshev, and S. Leikin, J. Phys. Chem. B, 108, 6508 (2004).
[5] A.G. Cherstvy and A.A. Kornyshev, J. Phys. Chem. B, 109, 13024 (2005).
[6] A.G. Cherstvy, J. Physics: Cond. Matter, 17, 1363 (2005).
[7] A.G. Cherstvy and R. G. Winkler, J. Chem. Phys., 120, 9394 (2004).
[8] A.G. Cherstvy, J. Chem. Phys. 123, 116101 (2005).
[9] A.G. Cherstvy and R. Everaers, work in preparation
[10] A.G. Cherstvy, A.A. Kornyshev, and A. Wynveen, work in preparation.

# MESOSCALE SIMULATIONS OF POLYELECTROLYTES IN AN ELECTRIC FIELD

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Polyelectrolytes play an essential role in nature as well as in technical applications and the understanding of their properties has been a challenging task for scientists from a number of different research areas. In theoretical physics, analytical theories and computer simulation techniques have been developed in order to elucidate their structure and dynamics. Due to a rapid growth of available computer power, nowadays even complex fluids such as dilute or semidilute polymer solutions, colloidal suspensions, and biological macromolecules can be studied by computer simulations. The dynamics of these systems is strongly affected or even dominated by hydrodynamic interactions. In our mesoscale computer simulations, we study the dynamics of a polyelectrolyte in dilute solution. The polymer is comprised of N charged monomers which are surrounded by oppositely charged counterions such that the whole system is electrically neutral. Additionally, an external electric field is applied. The polyelectrolyte bonds are described by a harmonic potential and the excluded volume interaction is taken into account by a purely repulsive Lennard-Jones potential. Since it is not necessary to know the microscopic details of the solvent dynamics in order to get the correct hydrodynamic behavior on the length scale of the polyelectrolyte, the solvent is described by the MPC (multi-particle collision dynamics) algorithm [1,2], which provides a simplified and coarse-grained description of the solvent. We systematically vary the polymer length, the interaction strength, and the strength of the external field and study the conformational and dynamical properties of the system. In particular, results will be presented for the mobility of the polyelectrolyte and the counterions. The dynamics of the solvent will be discussed in the light of a possible screening of hydrodynamic interactions. Moreover, the results will be compared to simulations without hydrodynamic interactions.

[1] A. Malevanets and R. Kapral, J. Chem. Phys. 110, 8605 (1999)
[2] A. Malevanets and R. Kapral, J. Chem. Phys. 112, 7260 (2000)

# COMPUTER SIMULATION OF OLIGOPEPTIDE DIMERISATION.

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Short peptides aggregate in solution into large supramolecular aggregates resembling the structure of amyloid fibrils in Alzheimer disease. The aggregation depends on the protonation state of two amino acids Arg and Glu in the peptide. At pH below approx. 5 the Glu is negatively charged making the peptide neutral. At pH above 5 Glu is neutral resulting in net positive charge of the peptide. At pH below 5 the formation of fibrils is experimentally observed to be much faster compared to pH above 5 (1,2). In the present work the dimer formation is studied by means of molecular dynamics simulations for the two different protonation states. The aggregation is characterised by the potential of mean force (PMF) between the centres of mass of the two peptides. The minimum and the local extrema of the PMF are related to the free energy of binding and to the kinetics of the reaction respectively. The influence of the protonation states of Glu on the P MF is rationalised and the implications for the formation of larger aggregates are discussed.

[1] A.Aggeli,N Boden, C.Fishwick, Euro.Phys.J. B17,499-513 (2000)
[2] A.Aggeli,N Boden JACS 125, 9619-9628 (2003)

# ELECTROSTATIC SELF-ASSEMBLY: POLYELECTROLYTES AS NANOTEMPLATES AND BUILDING BLOCKS FOR SUPRAMOLECULAR STRUCTURES

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We investigate the formation of structures based on polyelectrolytes, polymers that carry many ionic groups. In "electrostatic nanotemplating", inorganic counterions allow to create well-defined organic-inorganic hybrid structures. The self-assembly of macroions with organic counterions can yield defined supramolecular structures. Macroions of varying architecture, such as linear flexible polyelectrolytes, rodlike polyelectrolytes, dendrimers and microgels are used as model polyelectrolytes. Polyelectrolytes in solution show special phenomena in viscosity or diffusion. Although polyelectrolytes are widely found in nature and used in a variety of applications, their behavior is not yet completely understood. Experimental results indicate that the behavior of polyelectrolyte solutions is to a large extend caused by intermolecular interactions mediated by counterions. In "electrostatic nanotemplating" polyelectrolytes of a certain architecture attracting oppositely charged metal ions in solution serve as a precursor. In a second step, noble metal or semiconductor nanocrystals are formed by chemical reaction of the precursor ions, e.g. gold counterions are reduced to metallic gold. The polyelectrolyte influences the growth of the inorganic crystal. Hybrid particles are investigated by electron microscopy and scattering methods. It is shown that the approach can be used for different polyelectrolytes from microgels to rodlike polyelectrolyte micelles and differences in mechanisms will be discussed. We further take advantage of the macroion-counterion interaction to connect multiple macroions into larger structures. By this "electrostatic self-assembly" with organic counterions, the structure formation not only depends on macroion/counterion ratio but also significantly on the positions of the charged groups at multivalent counterions. We find that it is possible to build defined aggregates of different architectures by the assembly of stiff, multivalent organic counterions with polyelectrolytes of certain architectures. While no classical surfactants with hydrophobic tails are used to induce self-assembly, electrostatic interaction in addition to geometric factors plays a major role in these systems. In summary, the interaction of polyelectrolytes and counterions and its potential use for the controlled design of structures will be discussed.

Antonietti, M.; Gröhn, F.; Angew. Chem Int. Eng. Ed. 1997, 36, 2080.
Gröhn, F.; Bauer,; Amis, E.J.; Macromolecules, 2000, 33, 6042.
Gröhn, F.; Bauer, B.J.; Amis, E.J.; Macromolecules, 2001, 34, 2179.
Gröhn, F.; Bauer, B.J.; Amis, E.J.; Macromolecules, 2002, 35, 4852.
Melinger, J.S., Kleiman, V.D., McMorrow, D., Gröhn, F., Bauer, B.J., Amis, E.J; J. Phys. Chem. A 107(18) 3424-3431,2003.

# SURFACTANT AND POLYELECTROLYTE COADSORPTION ON SELECTIVE SURFACES

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The co-adsorption of a cationic polyelectrolyte and an anionic surfactant on silica and glass surfaces were investigated using various spectroscopic and surface force measurements. The particular system dealt with in this investigation is selective since the polyelectrolyte does adsorb to the surface in the absence of surfactant, whereas the surfactant does not adsorb in the absence of polyelectrolyte. It is found that the total adsorbed mass is highest when the surfactant and polyelectrolyte form complexes in bulk solution that are close to the charge neutralization point. The interactions forces between polyelectrolyte-coated surfaces, i.e., in the absence of surfactant, are dominated by long-range electrostatic double-layer forces. However, the layers formed by co-adsorption from solutions containing both polyelectrolyte and surfactant generate long-range forces of electrosteric nature. The adhesive interactions correlate to the bulk behavior of the components in the system. The final state of the adsorbed layer in terms of the history of the system will be presented together with the conditions for formation of long-lived trapped adsorption states from mixed polymer-surfactant solutions.

# PROPERTY RELATIONS IN AMPHOTERIC POLYMERS IN FIBER APPLICATIONS

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We have synthesized amphoteric terpolymers aiming to enhance the value of forest-derived fiber resources. We observed superior gains in fiber performance following treatment with polyampholytes of various molecular mass, charge density and degree of blockiness. We used bulk phase and interfacial analyses, including streaming potential, piezoelectric sensing, atomic force microscopy and surface spectroscopies to understand the effect of independent physicochemical variables including solution pH, ionic strength and the presence of other polymeric additives such as poly-aluminum chloride (PAC). Remarkably, the strength gains were achieved without the usual negative consequences associated with other charged polymers, e.g. increased fiber flocculation, poor dewatering characteristics, and unstable colloidal charge in the aqueous system. The results obtained are being used to develop a conceptual model of how polyampholytes adsorb onto cellulosic fibers and how they contribute to inter-fiber bonding, providing a basis for developing the next generation of higher-performing strength additives.

# A SIMPLE ROUTE TO SURFACTANT FREE STIMULI SENSITIVE MICROGEL DISPERSIONS AND THEIR APPLICATIONS IN FLUID LOSS CONTROL

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Polyelectrolyte and polyampholyte systems which are sensitive to external stimuli such as pH and ionic strength undergo volume phase transitions due to the application of such stimuli. These gel particles can be in or between one of two states; swollen or collapsed. The transition between these states can be used as a "switch" to change the rheological properties of a suspension. The resulting colloidal stimuli sensitive suspensions have a wide range of applications such as drug delivery systems. There is also significant interest in filtration and oil field applications. Here we introduce a very simple but surfactant free method to produce responsive microgel particles with tailored particle sizes. Large hydrogel blocks of poly methacrylic acid (pMAA), poly 2-(dimethylamino) ethyl methacrylate (pDMEMA) and a copolymer (p(MAA-co-DMEMA)) all with varying crosslinking densities were synthesized via free radical polymerisation. These hydrogel blocks were cut using a high shear mechanical cutting technique to form a microgel suspension. The resulting suspensions were characterised using light scattering and rheological measurements. The hydrogel particles with low crosslinking density were shown to have the greatest effect on the viscosity of the dispersions. pH, volume fraction and ionic strength were shown to dramatically influence the viscosity of the systems. In order to study the applicability of such hydrogel dispersions to control fluid loss the filtration behaviour of the resulting suspensions were investigated by the filtration through a bed of modified glass beads under pressure.

[1] B.R. Saunders and B. Vincent, Adv Colloid Interface Sci, 80 (1999), 1.
[2] R. Pelton, Adv Colloid Interface Sci, 85 (2000), 1.
[3] K. Ogawa, A. Nakayama and E. Kokufuta, Langmuir, 19, (2003) 3178.
[4] S. Ito, K. Ogawa, H. Suzuki, B. Wang, R. Yoshida and E. Kokufutu, Langmuir, 15 (1999), 4289.
[5] R.N. Sydney, New Scientist, 2496 (2005), 26.
[6] F. G. Donnan, Chemical Reviews,1 (1924), 73.

# NOVEL PH RESPONSIVE POLYACRYLAMIDE (MICRO)GELS CONTAINING DISULPHIDE LINKAGES

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The advancement of hydrogel technology has led to the development of various types of novel crosslinking methods, which exhibit a wide range of stimuli-responsive behaviour. When compared to conventional stimuli responsive gels i.e. gels that are responsive because of their main chain, such gels offer the opportunity of making otherwise unresponsive gels responsive. Such responses might include programmed degradation or reversible mechanical behaviour. Here we present the synthesis of novel pH responsive polyacrylamide hydrogels. The mechanical properties of the hydrogel and the rheological behaviour of microgel suspensions were investigated. The motivation for the work was to study the sharp variation in viscosity that is observed when the pH of a microgel solution is changed, and the effect of pH changes on the elastic modulus of the bulk gel. pH responsive polyacrylamide based microgels have not yet been reported in the literature. Pure polyacrylamide gels do not exhibit any pH dependent behaviour. Previous studies on disulphide crosslinked gels, that are pH sensitive, have utilized polymers that were pH sensitive (1-4). This particular combination of pH sensitive crosslinker and insensitive backbone creates a good opportunity to study the contribution of the crosslinker separate from mainchain responses to pH changes.

[1] Lee H, Park T G, Reduction/Oxidation Induced Cleavable/Crosslinkable Temperature Sensitive Hydrogel Network Containing Disulphide Linkages, Polymer J. 20 (1998) 976-980

[2] Bromberg, L, Temechenko, M, Alakov, V, Hatton, TA, Kinetics of Swelling of Polyether-Modified Poly(acrylic acid) Microgels with Permanent and Degradable Cross-Links, Langmuir 21 (2005) 1590-1598

[3] Hiratani H, Alvarez-Lorenzo C, Chuang J, Yu A, Grosberg, Tanaka T, Effect of Reversible Cross-Linker, N,N-Bis(acryloyl)cystamine on Calcium Ion Adsorption by Imprinted Gels, Langmuir 17 (2001) 4431-4436

[4] Chiu HC, Wang CH, Synthesis of Temperature/pH Sensitive Hydrogels containing Disulphide Linkages as Cross-Links and Their Characterization, Polymer J. 32 (2000) 574-582

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