CPP 4: Focus: Structure and Dynamics of Responsive Hydrogels II

Time: Monday 14:00–16:15 Location: H37

Invited Talk CPP 4.1 Mon 14:00 H37

Current mechanistic and experimental views on the heat-induced phase transition of aqueous poly(N-isopropylacrylamide) solutions. — •Francoise Winnik — Faculty of Pharmacy and Department of Chemistry, University of Montreal, Montreal, QC Canada

Poly(N-isopropylacrylamide) (PNIPAM) is highly soluble in cold water, but it becomes insoluble as its solution temperature exceeds 32 oC, the lower critical solution temperature (LCST) or cloud point (TCP). This phase transition is governed by the cooperative dehydration of PNIPAM chains and concomitant collapse of individual chains from hydrated coils into hydrophobic globules, which associate to form larger mesoglobules. Recent fundamental and experimental investigations aimed at understanding the physics of the coil-to-globule transition in PNIPAM solutions will be presented with emphasis on the effect of polymer architecture and of additives. [1]

[1] F. Tanaka et al. Phys. Rev.Lett. (2008)101,028302; X.P. Qiu, et al. Macromolecules (2007) 40. 7069.

CPP 4.2 Mon 14:30 H37

Molecular simulation study of the volume transition of hydrogels — •Jonathan Walter[1], Viktor Ermatchkov[1], Jadran Vrabec[2], and Hans Hasse[1] — [1]Laboratory of Engineering Thermodynamics, University of Kaiserslautern, 67663 Kaiserslautern, Germany — [2]Thermodynamics and Energy Technology, University of Paderborn, 33098 Paderborn, Germany

Hydrogels are three-dimensional networks of hydrophilic polymers. The swelling behaviour, one of their most interesting properties, is determined by their network properties and the external conditions. The volume transition of hydrogels mainly depends on the nature of the polymer backbone and the solvent. The cross-linker usually only has a minor influence. This allows studying the volume transition of hydrogel by simulations of the computationally much less expensive polymer strand + solvent system. The volume transition of the hydrogel then corresponds to the change of the polymer strand between its collapsed form in a poor solvent and its stretched form in a good solvent. Here, the swelling and collapsing of Poly(N-isopropylacrylamide) is studied by molecular dynamics simulation on the basis of transferable all-atom and united-atom force fields using explicit solvent models from different literature sources. This work focuses on the influence of the temperature and solvent composition on the volume transition of the hydrogel. It is shown that the molecular simulations allow qualitative predictions of the swelling behaviour observed in experiments.

CPP 4.3 Mon 14:45 H37

Thermodynamics of aqueous solutions containing N-isopropyl acrylamide hydrogels — •Viktor Ermatchkov, Luciana Ninni Schäfer, and Gerd Maurer — Laboratory of Engineering Thermodynamics (LTD), Department of Mechanical and Process Engineering, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

Applications of hydrogels are based on their physico-chemical properties, among which the swelling behavior is one of the most important. The development of models for a reliable description of the phase equilibrium in systems containing hydrogels requires quantitative experimental data on the swelling behavior of well-characterized hydrogels.

In previous work, the phase equilibrium and swelling properties of some synthetic hydrogels was determined and quantitatively described by combining expressions for the Gibbs energy of an aqueous solution of polymers and for the Helmholtz energy of an elastic network. The hydrogels consisted of a single nonionic monomer N-isopropyl acrylamide (NIPAAm) as well as of mixtures of NIPAAm and anionic comonomer (sodium methacrylate). In the current work these investigations are extended to other (NIPAAm)-hydrogels, in particular to hydrogels with two ionic comonomers of different charges (2-Acryloylamino-2-methylpropane-1-sulfonic acid and N-[3-(dimethylamino)propyl]-2-methylprop-2-enamide) and to hydrogels containing also a zwitterionic comonomer (3-(dimethyl{3-[(2-methylacryloyl)amino]propyl}ammonio)propane-1-sulfonate).

New experimental results for the swelling of such hydrogels in aqueous solutions as well as model extensions are presented.

CPP 4.4 Mon 15:00 H37

Free volume and swelling in thin films of poly(N-isopropylacrylamide) end-capped with n-butyltrithiocarbonate — •Stephan Harms[1], Klaus Rätzke[1], Franz Faupel[1], Werner Egger[2], Luca Ravelli[2], André Laschewsky[3], Weinan Wang[4], and Peter Müller-Buschbaum[4] — [1]CAU Kiel, Institut für Materialwissenschaft - Materialverbunde — [2]Universität der Bundeswehr München — [3]Potsdam Universität, Inst. Chemie — [4]TU München, Physik-Department LS E13

Thin hydrogel films of poly(N-isopropylacrylamid) end-capped with n-butyltriocarbonate (nbc-PNIPAM) show a thickness dependent swelling behavior, i.e. the thinner the films, the more they can swell, normalized to the respective thickness [1]. A tentative explanation is centered on differences in free volume. As the o-Ps lifetime is a generally accepted measure for the average free volume, positron annihilation lifetime spectroscopy as function of energy is performed to obtain depth profiles of the free volume of nbc-PNIPAM films with thicknesses from 40 to 200 nm. The results clearly show higher o-Ps lifetimes and hence higher free volume for thinner films. Results are discussed with respect to free volume and mobility influences on sorption and swelling behavior.

[1] Wang W., Troll K., Kaune G., Metwalli E., Ruderer M., Skrabania K., Laschewsky A., Roth S.V., Papadakis C.M., Müller-Buschbaum P.; Macromolecules 2008, 41, 3209

CPP 4.5 Mon 15:15 H37

Crosslinking and Patterning of Sensitive Polymers with Electron Beam Lithography: Sensoric Application — •Claudia Kaiser[1], Ingolf Moench[2], and Karl-Friedrich Arndt[1] — [1]Physical Chemistry of Polymers, Department of Chemistry, TU Dresden, 01062 Dresden, Germany — [2]Leibniz-Institute for Solid State and Materials Research Dresden, Germany

Sensitive hydrogels provide an excellent basis for various industrial applications due to their ability to change conformation in response to even a little change in environmental conditions (e.g. temperature, concentration of a second component or pH). Examples are optoelectronics, fluidics or pharmaceutics. A further possibility offers the integration in sensor systems. Miniaturization of hydrogel patterns is a basic requirement for application in microsystems. Thus, latest researches are engaged in the synthesis and characterization of hydrogel structures in the μm and 100 nm scale. The aim of our work is to give an overview about the possibilities to pattern several stimuli-sensitive polymers with electron beam lithography. We present results concerning synthesis, structuring parameters, attained dimensions, and the retained sensitivity by measuring property changes. To show the variability of the technique we investigate the polymers hydroxypropylcellulose, PNIPAM, P4VP, pluronic F127, and PVA/PAA-blend. For different application, e.g. to monitor the swelling-/deswelling-process by measurement of corresponding signals it could be useful to functionalize the polymer layer by filling. Therefore, the polymer layers become filled with different nanoparticles.

CPP 4.6 Mon 15:30 H37

Structure and response of pNIPAM microgels loaded with gold particles under thermal and optical stimuli — •Adrian Carl and Regine von Klitzing — Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin

Gold particles as well as pNIPAM microgels have been studied separately over the last decade. We studied the changes in thermal and optical responsivity of several composite particles compared to the properties of separate materials. Gold nanospheres and nanorods (AuNPs) were synthesised in the presence of pNIPAM microgels which contain different amounts of charged comonomers.

The influence of the gold particle shape and particle number on the swelling behaviour was studied by DLS measurements at two different wavelengths to investigate possible surface plasmon resonance effects. In order to obtain information about the distribution of the AuNPs inside of the microgel network, AFM, TEM and SAXS measurements were applied. During the phase transition of the microgels from swollen to collapsed state in the temperature range of 30-40°C (depending on the comonomers used), a wide broadening of the SPR-band in the UV-VIS spectra indicated a strong reversible interaction of the AuNPs.

The optical responsivity was further examined by turbidity measurements and a 2-laser DLS apparatus.

[1] Karg, M. Pastoriza-Santos, I. Rodriguez-Gonzalez, B.; von Klitzing, R. Wellert, S. Hellweg, T. Langmuir 2008, 24, 6300-6306

[2] Eustis, S. El-Sayed, M. A. Chem. Soc. Rev. 2006, 35, 209-217

Invited Talk CPP 4.7 Mon 15:45 H37

Swelling, structure and hybrid microgel particles — •Antonio Fernandez-Barbero — Department of Applied Physics, University of Almería, 04120-Almería, Spain

Different aspects about the swelling of individual microgel particles are revised: thermodynamics, microscopic structure, colloidal aggregation, solvent confinement,..., as well as discontinuous transitions. The structure of dense colloidal suspensions containing microgel particles will be discussed. Finally, the properties of different material are combined to design and fabricate hybrid particles with modulated response.