

## CPP 11: POSTERS Amphiphilic Systems

Time: Tuesday 14:00–16:30

Location: P3

CPP 11.1 Tue 14:00 P3

**Micellization of PAO-PEO Diblock Copolymers** — MICHAEL STRÖBL, ●GERALD JOHANNES SCHNEIDER, JÖRG STELLBRINK, JÜRGEN ALLGAIER, and DIETER RICHTER — Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich

If amphiphilic diblock copolymers are dissolved in aqueous solutions micelles may be formed. The dependency of the shape from the interfacial tension between micelle and solvent has not been understood to any great extent and thus the investigation is of great importance for basic research. Existing applications further enhance the interest. For example active pharmaceutical ingredients which can be imbedded within the micelles and then selectively released at a particular place in a human body open a broad field of applications.

In order to investigate the dependency of the shape from the surface tension poly(alkyleneoxide)-poly(ethyleneoxide)-blockcopolymers, which were only recently synthesized [1], are very suitable. In aqueous solutions these samples form micelles whereas the geometry depends on the surface tension, and therefore on the length of the hydrophobic alkyleneoxide-block. In our contribution findings of SANS experiments are presented. The results of the surface tension measurements are compared to existing theories.

[1] J. Allgaier, S. Willbold, T. H. Chang, *Macromolecules*, 40, 518-525, 2007.

CPP 11.2 Tue 14:00 P3

**Multilamellare Vesikel untersucht mit Neutronenkleinwinkelstreuung** — ●HENRICH FRIELINGHAUS — Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, 85747 Garching, Germany

Es wurde ein Modell entwickelt, um die Kleinwinkelstreuung von Multilamellaren Vesikeln zu beschreiben. Bei den größten Längenskalen beschreibt das Guinier-Verhalten die Streuung. Ein erstes Potenzgesetz ist mit der Kompaktheit der Vesikel verknüpft. Für viele Schalen erscheint das Vesikel kompakter und ein Porod-Verhalten wird vorhergesagt, während für wenige Schalen die 2-dimensionale Struktur der Schalen dominiert. Alle Exponenten zwischen 2 und 4 sind im Prinzip möglich, so daß damit die Schalenzahl durch die Kompaktheit bestimmt werden kann. Bei noch kleineren Längenskalen wird ein Korrelationspeak vorhergesagt, der die regelmäßigen Abstände der Schalen beschreibt. Bei noch kleineren Längenskalen dominiert die 2-dimensionale Struktur der individuellen Schalen. Zudem wurden Fluktuationen der Schalenzentren betrachtet. Hierdurch wird der Korrelationspeak in Schärfe und Position verändert, und die Kompaktheit (bzw. deren Exponent) verringert. Dies liegt daran, daß mit diesen Fluktuationen die Struktur offener erscheint und der dominierende Schalenabstand wächst. Erste Ergebnisse zu Polymer-basierten Vesikeln werden vorgestellt.

CPP 11.3 Tue 14:00 P3

**Structure, dynamics and kinetics of thermoresponsive block-copolymer gels** — ●JOSEPH ADELSBERGER<sup>1</sup>, ANDREAS MEIER-KOLL<sup>1</sup>, WEINAN WANG<sup>1</sup>, THOMAS HELLWEG<sup>2</sup>, ACHILLE M. BIVIGOU KOUMBA<sup>3</sup>, ANDRÉ LASCHEWSKY<sup>3</sup>, PETER MÜLLER-BUSCHBAUM<sup>1</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>TU München, Physik-Department E13, Garching — <sup>2</sup>Universität Bayreuth, Physikalische Chemie I — <sup>3</sup>Universität Potsdam, Institut für Chemie

Thermoresponsive polymer gels display strong changes in volume when heated above the lower critical solution temperature (LCST). We investigate triblock copolymers consisting of two hydrophobic polystyrene (PS) end blocks and a hydrophilic poly-(N-isopropyl-acrylamide) (PNIPAM) middle block. In aqueous solution they form core-shell-micelles or micellar networks. The structure of the micelles and their correlation is determined using SANS and dynamic light scattering [1]. The micellar radius shows a sudden decrease at the LCST. Above the LCST the collapsed micelles form clusters. Water is released and the formerly hydrophilic shell shrinks. The results are compared to the ones of diblock copolymers [2]. Neutron spin-echo spectroscopy is used to study the segmental dynamics of the hydrophilic block. Below the LCST the averaged diffusion coefficient of the PNIPAM block is unchanged. Time resolved SANS allowed us to investigate the kinetics of structural changes induced by fast heating above the LCST.

[1] A. Jain, C. M. Papadakis et al., *Macromol. Symp.*, submitted

[2] K. Troll, C. M. Papadakis et al., *Colloid Polym. Sci.*, 286 (2008),

1079-1092

CPP 11.4 Tue 14:00 P3

**Phase Separation Kinetics under Continuous Cooling: Shape matters** — ●DORIS VOLLMER, MIKA KOBAYASHI, GUENTER AUERNHAMMER, and YUMINO HAYASE — MPI for Polymer Research, Mainz

The dynamics of phase separation strongly depends on the thermal protocol, for example, whether phase separation is induced by a single quench from a one-phase to a two-phase region, or slow continuous ramping. In the latter case, qualitatively new features can arise, like oscillations in the turbidity and the apparent heat capacity. Oscillatory phase separation has been observed in several systems, as different as microemulsions, polymer solutions, and even in binary mixtures of olive oil and methanol. Material exchange is achieved through the macroscopic interface between both coexisting phases. To investigate the effect of the interfacial area on the phase transition kinetics we modified the area per unit volume using samples of different geometry, i.e. cylindrical and dog-bone shaped cells. As a model system we studied the phase separation of microemulsions and methanol and hexane under continuous cooling. In the dog-bone shaped cells the oscillation period exceeds those in cylindrical ones at cooling rates of a few K/h. The different dependence on the cooling rate indicates that the phase separation kinetics is either determined by volume dominated nucleation (fast cooling) or interface induced droplet formation (slow cooling).

CPP 11.5 Tue 14:00 P3

**Phase Separation Dynamics in (Pseudo)Binary Mixtures** — ●EBIE M. SAM, GUENTER K. AUERNHAMMER, YUMINO HAYASE, and DORIS VOLLMER — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

We investigated the phase separation dynamics in a pseudo-binary mixture of C4E1 and water, doped with a few percent of decane. The system phase separates under heating, as it crosses the binodal. Cooling rates of 1-20 K/h were used. We used sample cells with a diameter of 15cm and a height of around 1 cm, resulting in an aspect ratio of approx 15. Video microscopy of scattered light was utilized to track the dynamics of the phase separation. A temperature gradient was induced, with the upper side hotter. Patterns, whose sizes are comparable to the cell-thickness, were observed just after the initial clouding. Due to the sign of the temperature gradient their origin cannot be attributed to the Rayleigh-Benard convection. Possibly these patterns could be formed by the latent heat during the droplet-formation in the system. This is sufficient to induce a convective flow. A similar explanation could be given to the patterns we observed in the methanol-hexane binary system, which phase separates under cooling.

CPP 11.6 Tue 14:00 P3

**Collapse behavior of thermosensitive poly(2-oxazoline) copolymers** — STEPHAN SALZINGER<sup>1</sup>, STEPHAN HUBER<sup>1</sup>, RAINER JORDAN<sup>1</sup>, and ●CHRISTINE M. PAPADAKIS<sup>2</sup> — <sup>1</sup>TU München, Department Chemie, Garching — <sup>2</sup>TU München, Physikdepartment E13, Garching

The poly(2-oxazoline) (POx) system offers the possibility to tune the water-solubility in a wide range. Moreover, using 2-isopropyl (iPr) or n-propyl (nPr) as a side group results in a thermo-sensitive polymer with a lower critical solution temperature (LCST). Along with a number of architectures (homo-, gradient or block copolymers), a large variety of polysoaps can be created [1].

We have investigated the LCST behavior of iPrOx or nPrOx homopolymers as well as their gradient copolymers with n-nonyl-2-oxazoline (NOx) in aqueous solution. The LCST and the molecular aggregation behavior were investigated using single molecule as well as ensemble characterization techniques (fluorescence correlation spectroscopy (FCS), turbidimetry and scattering techniques).

[1] R. Jordan, C. M. Papadakis, et al., *Colloid Polym. Sci.* **282**, 833 (2004); *Macromol. Chem. Phys.* **208**, 1402 (2007); *Colloid Polym. Sci.* **285**, 491 (2007); *Macromol. Chem. Phys.* **209**, 2248, (2008).

CPP 11.7 Tue 14:00 P3

**Circular Dichroisms und Energietransfer bei molekularen Aggregaten** — JAN RODEN<sup>1</sup>, ●ALEXANDER EISFELD<sup>1</sup> und JOHN BRIGGS<sup>2</sup>

— <sup>1</sup>MPI-PKS Dresden, Finite Systems — <sup>2</sup>Uni Freiburg, Theoretische Quantendynamik

Amphiphile Cyanin Farbstoffe können supramolekulare Aggregate bilden [1]. Unter Verwendung der CES-Näherung (Coherent Exciton Scattering [2]), können experimentelle Aggregat-Spektren mit sehr guter Übereinstimmung direkt aus dem gemessenen Monomer-Spektrum berechnet werden [3]. Es lassen sich die verschiedenen Linienformen des blau verschobenen H-Bandes und des extrem schmalen, rot verschobenen J-Bandes auf einfache Weise erklären. Insbesondere erhalten wir den exponentiellen Abfall der langwelligen Flanke des J-Bandes (Urbach-Martienssen Regel) analytisch aus der Form des Monomer-Spektrums in diesem Energie-Bereich [4].

Neben der Absorption zeigt sich auch beim Circular Dichroismus eine gute Übereinstimmung zwischen Theorie und Experiment [4]. Des weiteren untersuchen wir den Einfluss von Vibrationen auf den Energietransfer in molekularen Aggregaten im Rahmen der CES Näherung. [1] S. Kirstein and S. Dähne, *Int. J. of Photoenergy* (2006), Article ID 20363

[2] J.S. Briggs, A. Herzenberg *J. Phys. B* 3, 1663 (1970)

[3] A. Eisfeld and J.S. Briggs, *Chem. Phys.* 324, 376 (2006)

[4] A. Eisfeld and J.S. Briggs, *Chem. Phys. Lett.* 446, 354 (2007)

[5] A. Eisfeld, R. Kniprath and J.S. Briggs, *J. Chem. Phys.* 126, 104904 (2007)

CPP 11.8 Tue 14:00 P3

**Aggregation of cationic surfactants with different counterions in the presence of poly(methacrylic acid)** — ●ALINA IOVESCU, DAN-FLORIN ANGHEL, SHUJI SAITO, ADRIANA BARAN, and GABRIELA STÎNGA — Department of Colloids, \*Ilie Murgulescu\* Institute of Physical Chemistry, Spl. Independentei 202, Bucharest, Romania

Counterions effect of a cationic surfactant upon its interaction with poly(methacrylic acid) (PMA) was investigated and compared with the analogous in poly(acrylic acid) (PAA) systems. Decylammonium (DeA+) with different counterions (Cl-, SCN-, acetate (Ac-) and butyrate (Bu-) were employed. The interaction critical concentrations, determined from surface tension measurements, were the critical aggregation concentration (cac or T1) at which the surfactants are abruptly

bound to the polymer chain in a micellar form (the primary aggregates), T2' at which the isolated primary aggregates on the polymer chain begin to contact with each other forming secondary aggregates, and T2 at which free micelles appear in equilibrium. For each counterion, T1 with PMA was higher than the respective T1 with PAA. In aqueous solution, PMA was compactly coiled up forming hydrophobic microdomains (HMD) in the chain. The surfactants were first bound to the HMD, and at T1 the free ones cooperatively formed primary aggregates on the other parts of PMA. Different from PAA systems, T1 with PMA was the sum of the surfactant amount bound to HMD and the ordinary cac. For both polymers, T1 raised in the order DeA-Ac < DeA-Bu < DeA-Cl < DeA-SCN, which was opposite to the order of the respective critical micellar concentration (cmc).

CPP 11.9 Tue 14:00 P3

**Wetting and surface tension dynamics of aqueous anionic surfactant/cationic polyelectrolyte mixture** — ●V. DUTSCHK<sup>1</sup>, R. SLAVCHOV<sup>1,2</sup>, B. RADOEV<sup>2</sup>, G. PETZOLD<sup>1</sup>, and B. BREITZKE<sup>3</sup> — <sup>1</sup>Leibniz Institute of Polymer Research Dresden, Germany — <sup>2</sup>Faculty of Chemistry, University of Sofia, Bulgaria — <sup>3</sup>Sasol Germany GmbH

It is well-known that the interaction between polyelectrolyte and surfactant starts at very low concentrations, therefore basic research is often carried out for low concentrations of surfactant solutions below the cmc.

Differences in the wetting kinetics depend on adsorption mechanisms. Modifying the highly hydrophobic polymer surfaces with solutions and mixtures allowed the conclusion that hydrophilisation of highly hydrophobic polymer surfaces occurs if modifying them with positively charged surfactant-polyelectrolyte mixtures (depending on the concentration of the both components). If the surfaces were modified with negatively charged mixtures, no change in the wettability of the Parafilm surface were observed. An essential conclusion is that the degree of wettability of a highly hydrophobic polymer surface with aqueous surfactant solutions and their mixtures can be assessed from the measurements of dynamic surface tensions. The corresponding isotherms of the surface tension and the contact angle show almost the same shape if the measuring points are recorded in non-equilibrium state at the same time.