

E 13

Annual Report 2009

Physik-Department E13 Lehrstuhl für Funktionelle Materialien Technische Universität München



Prof. Dr. Winfried Petry Chair of Functional Materials Physik-Department E13

Deputy chairman for Prof. Dr. Petry: Prof. Dr. Peter Müller-Buschbaum

Physik-Department E13 Technische Universität München James-Franck-Straße 1 85747 Garching

Secretaries: Petra Douglas Susanna Fink

Tel.: +49(0)89 289 12452 Fax: +49(0)89 289 12473

Email: peter.mueller-buschbaum@ph.tum.de petra.douglas@ph.tum.de http://www.e13.ph.tum.de

Editor: Dr. Ezzeldin Metwalli

Cover-page picture:

2D GISAXS scattering patterns of bare and of covered structured silicon substrates. The substrates were structured via photolithography and reactive ion etching prior the coating with a conducting polymer blend film. The structures are equidistant channels with a width and a gapping of $2\mu m$. The depth of the channels is varied. For the polymer coating a blend of M3EH-PPV and F8BT is chosen, which shows good application possibilities for organic electronics such as organic solar cells (OSC) or organic light emitting diodes (OLED). All scattering images show a prominent palm-like structure except the small 2D image on the left side, which is measured at the uncoated channel sample with a depth of 150 nm. In comparison the central image results from a channeled substrate coated with the polymer film. In the upper images the etching depth was varied from 220 nm (left) to 350 nm (right) and the coating remained constant. It can be seen that the palm structure is inverted for deeper channels.

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Preface

It is a great pleasure to present in the name of the staff of E13 the annual report for the year 2009, which provides an overview on our teaching, research, and development activities. Our research activities are focused on functional materials and cover a broad range from soft matter physics to developments in methods and instrumentation. We examine the physical fundamentals of material properties using scattering methods (neutrons-, x-ray and light scattering). The general goal of our research is to explain the functional characteristics of soft condensed matter from the knowledge of the microscopic dynamics and structure.

In 2009, the chair activities covered the specific areas of water-based polymer systems, thin polymer films, polymer films for application in photovoltaics, polymer-hybrid systems, biopolymers, alloys and methodological and instrumental developments. The research activities related with organic photovoltaics had largely increased, which was based on an increase in manpower dedicated to this field of research and was accompanied with an extension of instrumental capabilities. These in-house experiments available in the E13 laboratories complemented the lively activities at large scale facilities, comprising synchrotron radiation and neutron scattering experiments. Moreover, the developments in methods and instrumentation extended to the large scale facilities: Both, the instrument TOF-TOF at the research reactor FRM-II was operated and upgraded and the development of micro-beam grazing incidence small angle x-ray scattering (μ GISAXS) was continued at the MINAXS instrument at PETRA III in Hamburg. We realized the development of μ GISAXS in combination with in-situ imaging ellipsometry.

In 2009, the chair E13 comprised 7 fellows, 27 PhD students, 8 diploma students, 5 master students, 3 bachelor students, 10 student assistants and 12 administrative and technical staff members. Also, we are delighted to appoint Dr. Ezzeldin Metwalli Ali to head the X-ray lab.

In general, all E13 members were very active at conferences and workshops, participating with talks and posters. Moreover, important conferences were organized by E13 members: In March the Nobel laureate Prof. Peter Grünberg was giving a lecture at the 33rd Edgar-Lüscher Seminar on information technology. A dedicated international GISAS conference was organized as a satellite conference to the XIV SAS conference in Oxford (UK) by Stephan V. Roth, Rainer Gehrke, Ralf Röhlsberger and Peter Müller-Buschbaum at DESY in Hamburg in September 2009. This year, Prof. Dr. Papadakis acted again as a women's representative of the Physics Department. Regarding teaching activities of E13, we offered general physics lectures for students of mechanical engineering (Müller-Buschbaum) and for teachers at colleges BT / ET / MT / EI (Papadakis) as well as specialized lectures such as "Neutron scattering and complementary methods" (Petry/Unruh), "Polymer physics" (Müller-Buschbaum/Papadakis) and "Nanostructured soft materials" (Müller-Buschbaum/Metwalli).

This annual report comprises a selection of the different research topics and projects carried out in the individual groups of E13. It highlights the engaged and successful research activities and collaborations with other groups and large scale facilities. I wish all E13 members a fruitful continuation and a successful year 2010.

Peter Müller-Buschbaum

March 2010

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1 Water based polymer systems



1.1 Brillouin light scattering study of mechanical properties of the thermoresponsive polymer PNIPAM

J. Wiedersich, A. Meier-Koll, P. Müller-Buschbaum

Poly(N-isopropyl acrylamide) (PNIPAM) is a thermo-responsive polymer that has a volume phase transition at the lower critical solution temperature (LCST) near 33 °C. Below the LCST the polymer incorporates water molecules into its network. At higher temperatures the polymer network collapses and shrinks to a smaller volume as compared to the swollen state. However, a comprehensive study on the mechanical properties of gelated PNIPAM solutions is still missing.



Figure 1.1:

left: Brillouin spectra of different PNIPAM concentrations at a temperature of $\theta = 20$ °C. From bottom to top the selected concentrations are 0 (pure water), 10%, 20%, 30%, 50%. The left side of the spectra shows conventional Lorentzian fits to the data, the right side shows fits with the memory ansatz. **right:** Brillouin spectra of a PNIPAM concentration of 20% at increasing temperature. From bottom to top the selected temperatures are 15 °C, 25 °C, 31 °C, 32 °C, and 40 °C. The spectra below the LCST (one Brillouin line) are fitted with the memory ansatz; at temperatures above LCST two simple Lorentzian fits yield the peak positions.

In the present investigation we study the viscoelastic behavior of aqueous PNIPAM solutions and gels at different polymer concentrations and temperatures below and above LCST with Brillouin light scattering. Samples were prepared by solving the appropriate amount of polymer with deionized water in quartz glass vials. Directly after preparation the vials were sealed. The samples were thoroughly equillibrated before beeing transfered to the thermostatically controlled environment of the experiment. Brillouin light scattering was performed with a six-pass tandem Fabry-Perot interferometer (Sandercock). As light source we used a Nd:Vanadate laser operating at a wavelength of 532.3 nm and delivering about 50 mW at the sample position. The polarized component of the scattered light was observed in near backscattering geometry (VV). The left panel of Fig. 1.1 shows examples of Brillouin spectra at a temperature of 20 °C and for different concentrations. Starting with pure water at the bottom, an increase of PNIPAM concentration leads to a significant broadening of the Brillouin lines and to a shift to higher frequencies. The right panel of Fig. 1.1 shows a similar set of a sample with certain PNIPAM concentration as the temperature is increased. At temperatures below the LCST, a single Brillouin line is observed. Above the LCST the sample becomes turbid (the signal decreases dramatically as seen by the signal-to-noise) and two sets of Brillouin lines are observed. Due to multiple scattering the lines are smeared out towards lower frequency, while they decrease more quickly at higher frequencies. For this temperature region, we don't perform a detailed line shape analysis, but just determine the positions of the two peaks.

We tried fitting the data with a conventional Lorentzian line shape (left fits) as well as with a memory ansatz (right fits). The memory ansatz leads to a spectrum that is given by

$$I(\omega) = \frac{I_0 \left[\gamma_0 + m''(\omega)\right]}{\left[\omega^2 - \omega_0^2 + \omega m'(\omega)\right]^2 + \left[\omega\gamma_0 + \omega m''(\omega)\right]^2}; \qquad m(\omega) = (\Delta^2/\omega) \cdot \left[(1 - i\omega\tau)^{-\beta} - 1\right],$$

where we use the Cole-Davidson function as the memory kernel $m(\omega)$. For the memory ansatz we kept $\gamma_0 = 0 \text{ GHz}$, $\tau = 1 \cdot 10^{-12} \text{ s}$ and $\beta = 1.0$. Therefore we have the same number of fitting parameters, namely I_0 , ω_0 and Δ , as for the Lorentzian fits. The memory ansatz generally leads to a better fitting than the Lorentz function (cf. Fig. 1.1).



Figure 1.2:

left: Plot of temperature and concentration dependent Brillouin position. Data below the bifurcation at LCST are fit with the memory ansatz; for the turbid region above LCST just the postions of both Brillouin peaks are fitted. **right:** Plot of Brillouin width, however, for the turbid region above LCST, the width of the Brillouin peaks is not determined (multiple scattering).

Figure 1.2 displays the results of our curve fitting. For water and low PNIPAM concentrations, the Brillouin frequency increases with temperature. At a concentration of about 20 - 25% a crossover to the opposite behaviour is observed: The sound velocity decreases with increasing temperature.

Above the LCST we observe a two phase behaviour with one sound velocity close to the value of pure water, and a significantly higher velocity in the second phase.

The damping of sound within the gel generally increases with increasing PNIPAM concentration and on lowering the temperature.

1.2 Volume phase transition of poly(styrene-b-(N-isopropylacrylamide)) block copolymer in water

A. Meier-Koll, J. Adelsberger, A. Sepe, A. Golosova, P. Busch, C.M. Papadakis, P. Müller-Buschbaum

Thermoresponsive hydrogels show a strong volume change which is exhibited when the material is heated above the lower critical solution temperature (LCST). Below the LCST water molecules bond the hydrophilic functional groups in the polymer. The polymeric network is soaked up with water and is therefore swollen. As the temperature is increased above the LCST the entropy is also increased. Water molecules are now hindered to bind to the polymer and are released from the network. As a consequence the polymeric network shrinks and manifests in a macroscopic volume phase transition. Due to this volume phase transition these material class has attracted great interest for use in applications like sensors, actuators and drug delivery systems. Among other polymeric hydrogels poly(N-isopropylacrylamide) (PNIPAM) is the most prominent representative of this material class. Its LCST is about 32 °C. Since the response times of hydrogels depend on the size of the gel, in the recent years efforts have been undertaken to create hydrogels build-up with micron-sized functional units. Diblock copolymers where one block is thermoresponsive and the other one is hydrophobic are one of the most simple realizations of these functional units.

Following this idea, we investigated the volume phase transition the hydrogel formed by poly(styrene-b-(N-isopropylacrylamide)) diblock copolymer in water. Above its critical micelle concentration (0.028 mg/ml) [1], the polymer forms core shell micelles. In the present example the core is build up by the PS while PNIPAM forms an inhomogeneous corona around the core. The shape of the corona depends strongly on the solvent quality for the PNIPAM which changes dramatically as the temperature crosses the LCST. A quantitative core shell model with an algebraic decay of the polymer concentration in the corona has been developed by Förster and coworkers [2]. In this model the exponent of the algebraic decay α is closely related to the Flory Exponent ν_{Flory} , which reflects the solved quality, by $\alpha + 1/\nu_{Flory} = 3$.

In the present investigation we focus on the temperature dependence of the shape of the particles and the structure of the gel below LCST as well the kinetics of the volume collapse above LCST. The sample was prepared by mixing 30 wt% polymer with D_2O .





a) SANS intensity profiles shown in double-logarithmic representation for different temperatures. Temperatures from bottom to top: 10, 20, 26, 27, 28, 32, 35 °C. Solid lines are fits to the core shell model. Curves are shifted for clarity. b) Temperature dependence of radii extracted from fits shown in a. Hard sphere radius (squares) from Percus-Yevick structure factor, outer micelle radius (circles) and core radius (diamonds) from core shell form factor.

In order to extract these information we performed temperature and time resolved small angle neutron scattering (SANS) experiments at KWS2 instrument of the JCNS at FRM2. The instrument was operated with neutrons of 7 Å wavelength and a sample-detector distances with 1.7 and 7.7 m. Fig. 1.3.a shows SANS profiles for temperature resolved measurements below and above the LCST. Far below the 27 °C the profiles exhibit a strong correlation peak near 0.2 /nm. As the temperature increases the correlation peak becomes less pronounced and at 27 °C it nearly disappears. Simultaneous the strong forward scattering appears which originates from the creation of phase boundaries between water-rich and polymer-rich domains. When the temperature becomes higher than 27 °C the correlation peak reappears at higher scattering vectors, suggesting that the micelles arrange at shorter interparticle distances. More detailed information are extracted from fitting the data with the previously considered core shell form factor and the Percus-Yevick structure factor and as far as necessary with a Porod scattering law. Fig. 1.3.b displays the Percus-Yevick hard sphere radius, the radius of the micelle corona and the core of the micelle. It shows that the collapse transition is stretched over a broad temperature range from 27 to 30 °C. The onset of the phase transition is manifest by the sudden increase of the distance between the micelle from 32 to 50 nm. This indicates that the micelles immediately start coagulate to clusters, while their outer diameter changes continuously over the transition range from 22 down to 12 nm. After completing the collapse transition the micelles arrange in cluster with interparticles distances of 20 nm.



Figure 1.4:

a) Exponente for the algebraic decay of polymer profile in the corona depending on temperture. b) Temporal evolution of the volume deswelling ratio after a temperature quench from 26 to 31 °C over whole measurement time. The inset shows early values of the deswelling ratio in logarthmic representation. In both graph the contineous curves are fits of an exponetial model. Data points, which strongly deviate from the model are not considered in the fit.

In fig. 1.4.a the temperature dependence exponent α is shown. Its drop from approximately 1 to 0 corresponds to the change of water from a theta solvent to bad solvent were the water is completely release and the corona forms a compact homogeneous shell. Fig. 1.4.b shows the evolution of the deswelling ratio obtained from a temperature quench of the sample from 26 to 31 °C. The kinetics of the volume deswelling can be modeled with an exponential Ansatz [3]. The extracted response time is in the range of 2.3 s.

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1.3 Structure and dynamics of thermo-responsive block copolymer hydrogels

J. Adelsberger, A. Jain, A. Kulkarni, A. Bivigou Koumba¹, A. Laschewsky¹, P. Müller-Buschbaum, C. M. Papadakis

¹ Potsdam Universität, Institut für Chemie, Potsdam-Golm, Germany

Thermo-responsive polymers have received increasing attention as they respond with a strong volume change to a small change of temperature across the lower critical solution temperature (LCST). They are of great interest for medical applications as well as for controllable nanoporous membranes [1]. A widely used LCST polymer is poly(N-isopropyl acrylamide) (PNIPAM) which has an LCST at 32 $^{\circ}$ C.

We investigate triblock copolymers which have two short hydrophobic polystyrene (PS) endblocks and a longer hydrophilic PNIPAM middleblock. In aqueous solution, they form flowerlike core-shell micelles or, above the critical gel concentration micellar hydrogels. If they are heated up to the LCST, the PNIPAM block becomes hydrophobic and releases water from the micellar shell, which consequently collapses. This volume change is reversible.

In order to determine the structure of the polymeric hydrogels, we use small-angle neutron scattering (SANS) [2]. For the investigation of the PNIPAM chain dynamics in the swollen and collapsed state, neutron spin echo (NSE) spectroscopy has proved to be a powerful method [3,4]. For SANS and NSE experiments, solutions of a polymer with 387 PNIPAM monomers and 10 fully deuterated PS monomers at each end (M = 46000 g/mol) were prepared in D₂O. Only the micellar shells are visible in this experiment, because D₂O has the same scattering length density as the deuterated PS blocks.



Figure 1.5:

Temperature-resolved SANS curves from a solution with 170 mg/ml at 20 °C (squares), 31 °C (circles), 32 °C (triangles up), 33 °C (triangles down), 40 °C (diamonds) together with the fitting curves. (b) Resulting core radius (filled circles), shell radius (open triangles) and effective radius (filled triangles) above and below the LCST (dashed line).

Using SANS, we could characterize the micelles in detail (figure 1.5a). As expected, the radius of the PS core does not change at the LCST, whereas the micellar shell collapses strongly at the LCST (see figure 1.5b). The correlation peak is shifted to higher *q*-values above the LCST, as the micelles become smaller and pack closely together due to their increased hydrophobicity. Moreover, the collapsed micelles form large clusters, as evident from strong forward scattering which follows approximately a Porod law, thus the clusters are compact objects (see figure 1.5a).



Figure 1.6: a) Intermediate scattering functions S(q,t)/S(q,0) for 50 mg/ml (circles), 200 mg/ml (triangles up) and 300 mg/ml (triangles down) b) Temperature dependence of the diffusion coefficient of the segmental dynamics for 50 mg/ml (circles), 200 mg/ml (triangles up) and 300 mg/ml (triangles down)

We measured the intermediate scattering function S(q,t)/S(q,0) of a solution of the same triblock copolymer in D₂O as a function of concentration (figure 1.6a). The obtained data were fitted with a double exponential decay:

$$S(q,t)/S(q,0) = A_{fast} \exp(-\Gamma_{internal}t) + (1 - A_{fast}) \exp(-\Gamma_{micelle}t)$$
(1.1)

In the above equation, A_{fast} denotes the amplitude of the fast decay due to internal dynamics. $\Gamma_{internal} = D_{internal} q^2$ and $\Gamma_{micelle} = D_{micelle} q^2$ are the decay constants of the fast and slow mode. Using the Stokes-Einstein equation, we determined the diffusion coefficient of the segmental dynamics, $D_{internal}$, and the micellar diffusion coefficient, $D_{micelle}$ (figure 1.6b). Below the LCST the segmental dynamics are slowed down with increasing polymer concentration. This is most likely due to the increased overlap of the micellar shells. Moreover, $D_{internal}$ increases abruptly at the LCST. We attribute this unexpected finding to the selective detection of those PNIPAM segments which stick out from the collapsed shells. Their movement is relatively unhindered, since most other PNIPAM segments are immobilized in the collapsed shells. The combination of SANS and NSE thus leads to a detailed understanding of the collapse of the micelles, the behavior of the micellar gel and the dynamics of the thermo-responsive block. The project is funded by DFG within the priority program "Intelligent hydrogels".

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1.4 Gold coated end-capped PNIPAM thin films

W. Wang, G. Kaune, J. Perlich², C. M. Papadakis, A. M. Bivigou Koumba¹, A. Laschewsky¹, K. Schlage², R. Röhlsberger², S. V. Roth², R. Cubitt³, P. Müller-Buschbaum

¹ Potsdam Universität, Inst. Chemie, Potsdam-Golm, Germany

- ² HASYLAB at DESY, Hamburg, Germany
- ³ ILL, Grenoble, France

Environmentally responsive polymers have been widely studied over the last decades. Among the thermoresponsive polymers poly(N-isopropylacrylamide) (PNIPAM) in water exhibits a phase transition at a lower critical solution temperature (LCST) of 32 °C, which has been investigated by a variety of experimental techniques in dilute and concentrated solutions. In particular, thin films allow for advanced applications such as thermoresponsive surfaces, miniaturized sensor systems and nano-switches. Whereas thermoresponsive surfaces make use of a change in the wetting properties, triggered by a change in temperature, miniaturized sensor systems and nano-switches are based on the change in hydrogel film thickness, because the surface area is fixed [1]. A simplified thin film sensor and nano-switch will consist of the active (sensor) layer and a metal top-layer. The active layer contains PNIPAM. In the present investigation *n*-butyltrithiocarbonate end-capped poly(*N*-isopropylacrylamide), denoted nbc-PNIPAM and a gold top-layer are used. Central aim of this work is to probe the swelling and switching kinetics of such gold coated nbc-PNIPAM films.

The initial dry nbc-PNIPAM films with a thickness of 39 ± 0.1 nm were prepared by spin coating from a 1,4-dioxane solution at room temperature on pre-cleaned Si wafer. In a second step the top gold layer was added by sputter deposition. The deposition rate was set to 0.43 nm/min. The final, nominal gold layer thicknesses after deposition were 0.4 and 5 nm, respectively. The neutron scattering experiments were carried out at the D17 reflectometer of ILL, Grenoble, in time-of-flight(TOF) mode. The initial dry, gold coated nbc-PNIPAM film of the desired gold layer thickness was mounted in a custom-made vapor chamber in air, thermostated to 23 °C and investigated. To prepare a swollen and equilibrated film for the temperature jump experiment, the vapor chamber was evacuated, and the water reservoir of the vapor chamber was filled with D₂O to install a saturated D₂O atmosphere. After the film reaching equilibrium of swelling water vapor atmosphere (230 min), to initiate the temperature jump from 23 to 40 °C, the set up was thermostated to 40 °C and investigated with in-situ neutron reflectivity (time = 0). A rate of 3.1 °C/min for increasing the temperature in the set-up was applied.

A detailed analysis of the kinetics of the temperature jump is achieved by fitting the individual neutron reflectivity curves. In these fits the bilayer sample is modeled with a main nbc-PNIPAM layer and a second gold-rich top-layer in agreement with the findings from the static samples. Figure 1.7 shows the result getting from these fits.

The temperature increase in the bilayer sample is shown in figure 1.7a. After 110 s the LCST of 29 °C is reached (marked by the dashed line). The response of the thick gold layer film is presented in figure 1.7b and 1.7c. Because the gold layer contains 77 vol% gold, it remains unchanged during the temperature jump and is not displayed in figure 1.7. The nbc-PNIPAM film (main layer) below the thick gold layer reacts with a decrease of its water content from 38 to 24 vol%. This is accompanied by a decrease in the relative film thickness d/d_{dry} from 1.27 to 1.10. The characteristic time constant for this water release is 280 s. However, surprisingly this decrease is followed by a slight relaxation back to higher water content and larger film thickness (27 vol% and 1.13). The time constant of this relaxation is larger with 900 s. Therefore, the temperature jump causes the nbc-PNIPAM film to collapse and afterwards slowly rearrange into a different structure. In the relaxation a small amount of the surrounding water is uptaken again and correspondingly the film relaxes to a larger film thickness as compared to the collapse.





Switching kinetics from 23 to 40 °C followed by neutron reflectivity: (a) temperature increases as a function of time in the film. Volume percentage of water (D₂O) in the main layer of the film is shown as a function of time (b) for the thick and (e) the thin gold layer. Time dependent change of the film thickness *d* normalized by the initial dry film thickness d_{dry} (c) for the thick and (f) the thin gold layer. Volume percentage of water in the top layer of the film is shown as a function of time (d) for the thin gold layer. LCST of the nbc-PNIPAM film is reached at a time marked by the dash line in all images.

The solid lines in figure 1.7 are model fits based on the gel swelling and shrinking model by Li and Tanaka [2]. In this model swelling and shrinking follows first-order kinetics and is not considered to be a pure diffusion process. Despite the initial stages of the temperature jump experiment reported here, the observed behavior can be explained within this model by assuming a first fast shrinkage process followed by a second (small) slow re-swelling process. The initial stages will be influenced by the passing of the LCST and thus are not expected to match to such a simple model approach.

Comparing now the thick gold layer film behavior (top row images in figure 1.7) with the one of the thin gold layer (bottom row images in figure 1.7) some differences are obvious. In contrast to the thick film, for the thin gold film, the gold layer itself (top layer) changes its water content (see figure 1.7d). This is caused by the small gold volume (21.6 vol%) of this layer, which means that most part of the layer is nbc-PNIPAM as well. The full film, main (nbc-PNIPAM) and top (gold and nbc-PNIPAM) part exhibit the same two step characteristics as seen for the sample with a thick gold layer as well. However, the time constants are different. The nbc-PNIPAM film reacts much faster, with a time constant of 190 s, as compared to the sample with a thick gold layer on top. In the sample with a thin gold layer the top part reacts even faster with a time constant of 120 s. The relaxation processes behave oppositely and relaxation takes 1800 and 1330 s for main and top layer of the thin gold layer sample, respectively. Due to the interaction with the gold in the top layer part a large amount of water is incorporated (48 vol%) before the temperature jump. The release is very strong and finally only 15 vol% is left. The nbc-PNIPAM layer behaves quite similar to the one with more gold on top and reduces its amount of water from 34 to 23 vol%. In the change of the relative film thickness d/d_{dry} the values reduce from 1.28 to 1.13 which is as well equal to the observation on the thick gold layer sample. However, the two step process is not visible and the change in relative film thickness appears to be a simple release.

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1.5 Characterization of thin hydrogel films based on PMDEGA

Q. Zhong, A. Laschewsky¹, P. Müller-Buschbaum

¹ Potsdam Universität, Inst. Chemie, Potsdam-Golm, Germany

Stimuli-responsive hydrogels exhibit interesting properties which attract increasing attention due to a large variety of applications, as drug delivery system [1], substrates for cell culture [2] and valves to control liquid transfer [3]. The novel thermo-responsive homopolymer poly(monomethoxy diethyleneglycol acrylate) (PMDEGA) exhibits a higher lower critical solution temperature (LCST) as compared to the frequently investigated thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM). PNIPAM has a LCST closed to room temperature, which will limit its use. For example, in some tropical countries as the average temperature is really high, there will be no use of PNIPAM in these areas. But PMDEGA has a higher LCST than PNIPAM, which could be an interesting alternative to the use of PNIPAM. In addition, to create an internal ordering in the hydrogel film of PMDEGA, the homopolymer is replaced by a PMDEGA based tri-block copolymer with polystyrene end-block, P(S-b-MDEGA-b-S).

The homogeneous films of PMDEGA and P(S-b-MDEGA-b-S) are prepared by spin-coating on silicon wafer. The solutions used for spin-coating are prepared by 1,4-dioxane with six different concentrations, varied from 1 mg/mL to 15 mg/mL. X-ray reflectivity measurement are performed to determine the film thicknesses. The data and fitted curves of PMDEGA (left) and P(S-b-MDEGA-b-S) (right) films are shown in Fig. 1.8a. The dots represent the measured data, while the solid line show the fitted curves done by Parratt32 software. All fitted curves agree well to the data. From bottom to the top, the film thickness is increasing from 1.7 nm to 82.5 nm (PMDEGA) and 6 nm to 82.4 nm (P(S-b-MDEGA-b-S)). Fig. 1.8b is obtained by plotting the thickness as a function of the concentration. From Fig. 1.8b, it can be seen that the concentrations of both PMDEGA and P(S-b-MDEGA-b-S) solutions show a linear relationship with the thickness. Thus in the solutions no chain overlap occurs and we have an easy way of controlling the film thickness by changing the polymer concentration of the solution. Because the



Figure 1.8:

(a) X-Ray reflectivity curves of the PMDEGA (left) and P(S-*b*-MDEGA-*b*-S) (right) polymer films. The black curves are the measured data, while the red ones are the fitting curves done by Parratt32 software. (b) Film thickness *d* plotted as a function of the PMDEGA (left) and P(S-*b*-MDEGA-*b*-S) (right) concentration of the dioxane solution. The solid line is a linear fit.

LCST is an important property of temperature-sensitive hydrogels, white light interferrometry is used to measure the LCST behavior of both PMDEGA and P(S-*b*-MDEGA-*b*-S) films. Fig. 1.9a shows the temperature-dependent changes of the film thickness measured for one selected P(S-*b*-MDEGA-*b*-S) film exposed to saturated water vapor. The film thickness increases when temperature increase from 23 °C to 32 °C. This unusual phenomenon may be caused by a change of the vapor pressure, which increases inside the sample chamber when the temperature is increased. At a higher vapor pressure more water molecules are available and the hydrogel films will swell better. In order to verify this temperature dependence, 5 sodium chloride solutions with different concentrations were prepared, and the saturated vapor pressure are increased

from 2380 Pa (saturated sodium chloride solution) to 3169 Pa (pure water). The swelling behavior of P(S-*b*-MDEGA-*b*-S) films exposed to these five sodium chloride solutions and pure water is measured (see Fig. 1.9b). It is obvious that the lower vapor pressure will decrease





(a) Temperature-dependent changes of the film thickness measured for P(S-*b*-MDEGA-*b*-S) film exposed to saturated water vapor. (b) Swelling behavior of P(S-*b*-MDEGA-*b*-S) films measured with pure water and five sodium chloride solution. (c) Ratio of the swollen and dry thickness plotted as a function of the saturated vapor pressure.

the final swollen thickness, the maximum ratio of the swollen and dry thickness decrease from 2.13 (pure water) to 1.06 (saturated sodium chloride solution). Plotting the ratio as a function of the saturated vapor pressure, Fig. 1.9c is obtained. From this observation it is clear, that P(S-*b*-MDEGA-*b*-S) films are very sensitive to the total vapor pressure. Even a little decrease of the vapor pressure can cause a large drop of the swollen film thickness. Fig. 1.10a shows the measured LCST behavior of PMDEGA (50 nm, left) and P(S-*b*-MDEGA-*b*-S) (52nm, right) films. Both of them show a broad transition region when compared to the frequently investigated thermoresponsive polymer PNIPAM. The introduction of polystyrene end-blocks only slightly increase the LCST by 1 °C. In first derivatives $\delta d/\delta T$ plotted as a function of temperature, the transition temperature of both polymer films are visible (see Fig. 1.10b). The transition temperatures of PMDEGA and P(S-*b*-MDEGA-*b*-S) are 38 °C and 39 °C, respectively.



Figure 1.10:

(a) LCST behavior of PMDEGA (50 nm, left) and P(S-*b*-MDEGA-*b*-S) (52nm, right) films exposed to water vapor. (b) The first derivative $\delta d/\delta T$ plotted as a function of temperature.

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2 Thin polymer films



2.1 Flow of droplets on inclined surfaces

D. Magerl, V. Körstgens, P. Müller-Buschbaum

Theoretical simulations and predictions have stated that the flow of very small droplets on surfaces differs significantly from that of normal day drops e.g. raindrops on a windshield [1]. Our goal is to find experimental proof to this phenomenon. Therefore we investigated two different liquids i.e. water and toluene on inclined silicon wafers with different surface preparation. The theory predicts that the movement of a droplet on a surface under an external body force (in our experiment: gravity) is a combination of slipping and rolling as shown in Fig.2.1a. The slipping is a collective movement of all particles in the droplet in the same direction. The droplet shape and the relative position of all particles within the droplet are unaffected and therefore the friction at the substrate has a strong influence on the velocity. Contrarily the rolling motion is a rotation around the center of mass of the droplet and close to the surface there is no movement relative to it. However the particles inside the droplet have to move relatively to each other and the velocity is influenced by dissipation in the volume. The dissipation is higher the more the droplet differs from the spherical shape as it is shown in Fig.2.1b for the distortion at the surface. Thus the velocity of small droplets with large contact angles is dominated by friction at the substrate while the velocity of droplets with smaller contact angles is dominated by dissipation in the volume.



Figure 2.1:

a) Schematic drawing of a droplet. Movement is a combination of rolling and sliding. b) Velocity field inside a droplet. The inset represents the viscous energy dissipation per unit volume of fluid as a function of the height. (both from [1])

In the experiment the volume or contact area of a droplet have to be determined as well as its velocity on an incline. Therefore we built a chamber that can be tilted in such a way that the surface is either horizontal or in a well defined angle, see Fig.2.2c. We deposit a droplet on the horizontal surface with a pipette and measure its contact area with a camera. Then the whole chamber is tilted and the droplet starts to run down the incline as shown in Fig.2.2a+b. A second camera makes a movie of the flowing droplet after it moved a few millimeters from its starting point to make sure that the droplet runs down with a constant velocity. From the single images of this movie and their timestamps we can determine the velocity of the droplet. In order to prevent the liquid from evaporating the chamber is closed and vials filled with the according liquid are put inside to generate a saturated atmosphere inside the chamber.

We used different liquids as well as different cleaning methods for the substrate to change the surface energy. Toluene on an acid cleaned silicon surface showed a linear increase in velocity with the volume while toluene on a basic cleaned substrate showed a linear increase with the



Figure 2.2:

a) Chamber before tilting. Deposition of droplet and measurement of contact area with camera 1. b) Chamber after tilting, droplet is moving, measurement of velocity with camera 2. c) Photograph of the chamber. On the left is camera 2. A glass can be slid to open and close the small hole through which the droplet is deposited. The incline is at 60°. Filled vials are behind the incline.

contact area as shown in Fig.2.3a+b. From this result we conclude that the former experiment is in the regime where dissipation in the volume is the dominant factor for the movement of the droplet and the latter is in a regime where friction at the substrate dominates. However in both cases the droplets deformed significantly from the circular shape. Therefore a comparison with the simulations and theoretical predictions should be considered with care. Moreover, we performed measurements with toluene on an acid cleaned wafer that was treated with HMDS (hexamethyldisilazane) for 24 hours after cleaning to increase the contact angle on it [2]. The droplets on silicon pieces with this treatment keep their shape and are better suited for comparison. Measurements are shown in Fig.2.3c.



Figure 2.3:

Velocity of the droplet plotted against its area, the solid lines are fits to the data. a) Toluene on basic cleaned silicon substrate (angle: 10°). b) Toluene on acid cleaned silicon substrate (angle: 10°). c) Toluene on acid cleaned substrate with HMDS treatment (angle: 60°).

The experiments on surfaces without HMDS treatment were conducted with a tilting angle of 10°. After switching to the HMDS treated surface a higher force is needed to let the droplets start to roll down so the angle was changed to 60°. Thus the velocity is much higher than in the previous experiments but the droplet sizes could be reduced as well. For this measurement the increase is almost linear with the area like for the basic cleaned surfaces which is due to the higher contact angle than in the acid cleaned case without HMDS treatment and therefore fits nicely to simulations.

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2.2 Periodic nanostructures of colloidal thin films via wetting and evaporation

S.V. Roth¹, A. Rothkirch¹, T. Autenrieth¹, R. Gehrke¹, T. Wroblewski¹, M.C. Burghammer², C. Riekel², L. Schulz³, R. Hengstler⁴, P. Müller-Buschbaum

- ¹ HASYLAB at DESY, Hamburg, Germany
- ² ESRF, Grenoble, France
- ³ Université de Fribourg, Fribourg, Switzerland
- ⁴ AREVA NP GmbH, Erlangen, Germany

The fundamental understanding of wetting and flow behavior of nanoparticle and (bio)polymeric solutions and blends on solid substrates is crucial for their application in many technological fields, e.g. optical coatings, or data storage applications. During solution casting, the nanostructuring takes place at the triple phase contact line air-solution-substrate [1] (see 2.4a) for an optical micrograph) and involves complex hydrodynamic processes. In our approach here we used a combinatorial high-throughput approach to investigate a solution cast gradient consisting of colloidal gold nanoparticles on top of a silicon substrate by means of a 300nm-sized X-ray in combination with grazing incidence small-angle x-ray scattering (nanoGISAXS) [2].



Figure 2.4:

a) Optical micrograph of the triple phase contact line. D denotes the droplet, W the wetting region. b) Results of the unsupervised classificiation. A banded structure for $y > 400 \ \mu m$ in the wetting region is clearly visible. c) Quantitative analysis of the most-prominent length scales ξ in the scanned region. Black: Manual analysis; red: likelihood-based evaluation of the most-prominent length scales ξ ; Blue: occurence of maxima in ξ based on a stip-slick-model. d) Typical nanoGISAXS pattern in the wetting region.

To apply unsupervised classification, we divided the data set into classes based on the Euclidean distance as similarity measure. To initialize the iterative clustering, we have chosen randomly selected out-of-plane (oop) scans $I(q_y)$. Assuming six potential classes j = 1...6, we discriminated the logarithm of the intensity $\ln(I(q_y))$ by

$$\sigma_j^2 = \sum_{q_y} \left[\ln(I_y(q_y)) - \ln(I_j(q_y)) \right]^2,$$
(2.1)

with $I_y(q_y)$, -0.3 nm⁻¹ $\leq q_y \leq$ 2.9 nm⁻¹, denoting the oop-scan at position y.

At each iteration step, the oop-scans are assigned to the class having the largest similarity, i.e. smallest σ_j . Then, new mean class representations (mean oop-scans) are calculated. The iteration is repeated, until none of the mean oop-scans changes significantly. This leads to the clustering in 2.4b).

For manual quantitative analysis, we based the next step on the division into classes obtained from unsupervised classification. For each eighth oop-scan the structure and morphology of the domains was extracted, using

$$I(q_{y}) = M(q_{y}) + SF(q_{y}) + PFF(q_{y}),$$
(2.2)

where $M(q_y)$ denotes the Gaussian resolution function for the beam, $SF(q_y)$ an experimental Lorentzian structure factor

$$SF(q_y) \propto \frac{1}{1 + 4 \cdot ((q_y - q_{max})/\omega)^2},$$
 (2.3)

with ω its width. $PFF(q_y)$ is the particle form factor for spheres with a nominal diameter of 5 nm. This allows for extracting the most-prominent in-plane length scale ξ via $\xi = 2\pi/q_{max}$. The result of the manual analysis is shown in fig. 2.4c) as diamond symbols.

For further analysis, we used supervised classification. As can be seen from fig. 2.4c), we may use ξ to divide the manually analyzed data into three classes with different ξ :

- class 1 $y < 300 \ \mu m$ with $\xi_1 = 60 \ nm$
- class 2 480 μ m < y < 600 μ m with ξ_2 = 350 nm
- class 3 $y \ge 1000 \ \mu m$ with $\xi_3 = 240 \ nm$

Class representations were averaged, and the slopes of the averaged $I(q_y)$ in two different q_y regions were evaluated to represent each class *i*=1,2,3. For any remaining oop scan we used the likelihood $P_{i=1,2,3}(y)$ [3] for belonging to one of the three classes defined above to calculate an average $\xi_L(y)$ via

$$\xi_L(y) = P_1(y) \cdot \xi_1 + P_2(y) \cdot \xi_2 + P_3(y) \cdot \xi_3.$$
(2.4)

This leads to the red symbols in fig. 2.4c). In 2.4d) we display a typical nanoGISAXS pattern showing the nanostructure in the wetting region.

In summary, we applied classification methods to analyze scanning nanoGISAXS data of a dried colloidal solution droplet. The manual as well as the classification results agree, with the latter revealing structural transitions from a frozen colloidal solution to a well-defined domain nanostructure of the order of 100 nm outside the optical rim of the droplet, see fig. 2.4c). The periodic change in the nanostructure along the wetting region can be explained by a simplified stick-slip model. The blue lines in fig 2.4c) indicate maxima in ξ , agreeing excellently with the results from classification.

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2.3 Structures of monodisperse polystyrene nanospheres on a rough solid support

V. Körstgens, J. Wiedersich, R. Meier, J. Perlich¹, S.V. Roth¹, R. Gehrke¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

The new developed combination of the surface sensitive scattering method grazing incidence small angle x-ray scattering (GISAXS) and imaging ellipsometry offers a wide range of possibilities for static and kinetic measurements [1]. With the use of a mircosized beam local structure information is obtained and subsequent stepwise movement of the sample perpendicular to the sample surface allows for the investigation of structural gradients in the sample. With scanning μ GISAXS the structure of a dried droplet of monodisperse polystyrene nanosphere aqueous dispersion is investigated. The rough substrate is established by dewetting of a thin film of the diblock copolymer poly(styrene-*b*-methyl methacrylate).



Figure 2.5:

Dried colloidal drop of nanosphere dispersion **a** Sketch of the top view of the dried drop. The yellow background represents the dewetted polymer structure. The circularly shaped object has a pronounced rim (pictured in brown). The arrow marks the size and direction of the incident x-ray beam. The box in dashed lines indicates the section pictured in b. **b** optical micrograph (image composed using two foci); 1 mm x 0.75 mm **c** measurements of the Δ and Ψ map of the dewetted polymer structure obtained with imaging ellipsometry and resulting thickness map.

The imaging ellipsometer SPEM, a single wavelength (532 nm) instrument, of Nanofilm Technologie GmbH was installed at the beamline BW4 at HASYLAB (DESY, Hamburg). The concept of the combined instrument is that the sample is placed horizontally (xy plane) on the alignment stage of the ellipsometer. After ellipsometric alignment and measurement with a lateral resolution of 1 μ m the desired incidence angle for the x-ray beam is set by tilting the whole ellipsometer. The orientation of the sample with respect to the laser beam is not affected by this procedure. In the performed experiment, the sample-to-detector distance was set to 2.089 m and a beamsize of 24 μ m x 42 μ m focused on the sample position was used. First a single μ GISAXS measurement on the dried colloidal drop was performed with an incident

angle of 0.510° . The x-ray beam was set to hit the circular shaped object in the center. The footprint of the beam was smaller than the diameter of the inner part of the droplet as sketched in figure 2.5a. The 2d detector pattern obtained results from a superposition of the GISAXS with an additional SAXS signal. The SAXS signal is centered around the direct beam (including refraction effects). Its presence is due to the x-ray beam's transmission through the pronounced rim of the colloidal drop. In normal thin film samples such an additional SAXS signal is not visible in the GISAXS geometry. To suppress the SAXS contribution of the rim and to get structural information about the inner part of the colloidal droplet the rim was then removed in beam direction. With this modified sample a scanning GISAXS measurement was performed with a step size of 500 μ m covering 4 mm. At each position of this GISAXS scan conducted with the ellipsometer stage, the ellipsometric alignment was checked and Δ and Ψ maps were recorded. The goniometer positions were corrected if necessary to ensure the incident angle of 0.51° selected for the GISAXS experiment.



Figure 2.6:

Scanning experiment **a** Δ map recorded with ellipsometer at positions from the center, **b** corresponding 2d GISAXS patterns

In figure 2.6 the scanning experiment is illustrated with the Δ maps (figure 2.6a) and the corresponding 2d GISAXS scattering patterns (figure 2.6b) for every second step beginning in the center outward to the rim and further to the outside of the colloidal drop. Oscillations in the bright and dark areas in the Δ map indicate variations in height. The Δ -maps in the central part, (denoted with position 0 mm, 1 mm and 2 mm, respectively in figure 2.6a) show the cracks of the nanosphere layer. The surface of the rim results in a speckle pattern (denoted with position 3 mm in figure 2.6a), whereas outside the droplet the island pattern of the dewetted diblock polymer is observable (denoted with position 4 mm in figure 2.6a). In the 2d scattering pattern for the position in the center of the drop (denoted with position 0 mm in figure 2.6b) there is a clear reduction of the SAXS contribution to the overall scattering signal. As the rim perpendicular to the beam direction has been removed a clearer GISAXS pattern of the central part of the drop is achieved. In the position where the x-ray beam hits the rim (marked with 3 mm in figure 2.6b) the scattering pattern is dominated by the SAXS signal as ring shaped intensity is centered around the direct and the specular beam. At the outside of the colloidal drop the scattering signal is equal to the GISAXS pattern of the dewetted polymer on silicon substrate as measured individually with a control sample without deposited colloidal particles (marked with 4 mm in figure 2.6b).

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2.4 Advanced sample preparation for density and viscosity measurements of polybutadiene melts at the polymer-solid interface

E.T. Hoppe, D. Magerl, C.M. Papadakis

The properties of a polymer melt close to a solid interface may be significantly altered compared to the bulk, e.g. the chain conformations and the density [1]. This has implications on the stability of coatings, e.g. in medical implants, in chip fabrication, for the application of glues or inks, and the stability of composites of polymers with nanoparticles. However, not only the structural changes near a solid interface are of importance, but also the dynamics, i.e. the local mechanical properties.

The goal of the project is to achieve an improved understanding of the interphase of a polymersolid contact by correlating the mass density, i.e. the polymer structure, with the local viscosity, i.e. the polymer dynamics, near the solid interface. At this we have chosen 1,4polybutadiene (PB) as a model system with a broad range of molar masses from 4,200 g/mol to 2,200,000 g/mol.

The interphase viscosity will be determined using interface-sensitive fluorescence correlation spectroscopy (FCS) where the interphase near the substrate will be selectively illuminated. At this we will use total internal reflection (TIR) excitation. The mass density profile of PB near the substrate will be determined with high-resolution neutron reflectometry (NR). However, these two experimental techniques have different physical requirements on the substrates.

For TIR-FCS, on the one hand, the substrate has to be transparent in a wavelength range from 400 nm to 650 nm with a high refractive index. For these reasons, heavy flint glass is chosen as substrates for TIR-FCS. For NR, on the other hand, the substrate has to be transparent for neutrons, highly homogeneous and flat. To make use of the whole neutron beam cross section, the sample substrate should have a surface area of 6×6 cm. The substrate thickness should be at least 3 mm to enable a beam injection through the side of the substrate onto the solid-polymer interface. This allows an investigation of the polymer interphase without being restricted by reflections from silicon and the silicon oxide layer. In order to obtain surface properties comparable to those of heavy flint glass, a 200 nm silicon oxide layer is created on the silicon surface by dry thermal oxidation. The oxide layer thickness as well as the RMS roughness are determined by white light interferometry and x-ray reflectometry (Fig. 2.7 a).



Figure 2.7:

a) X-ray reflectivity curve of a 200 nm silicon oxide layer on silicon. 20 \times 20 μ m AFM height image of b) silicon oxide having a RMS roughness of σ =0.4 nm and c) triethoxysilyl modified 1,2-PB coated silicon oxide having a σ of 1.3 nm

To vary the interaction between the polymer and the solid, the surface is subsequently altered by *hydrophilic* acid treatment, a layer of *hydrophobic* octadecyldimethylmethoxysilane (ODMS), *fluorophilic* perfluorinated silane (HFTDTS) or *neutral* triethoxysilyl modified 1,2-polybutadiene to the silicon oxide surface. AFM images (Fig. 2.7 b&c) indicate that the surfaces of silicon oxide and of a silanized surface are flat with RMS roughness of 0.4 nm or 1.3 nm, respectively.

Contact angle measurements of water on the silanized substrates (Fig. 2.8) show large differences (0-116°) indicating vastly different surface potentials. Therefore qualitatively different PB-solid interactions are expected.



Figure 2.8:

Contact angles of water drops with a volume of 1μ L on a) acid treated silicon oxide b) perfluorinated silane c) ODMS d) triethoxysilyl modified 1,2-polybutadiene

PB films were prepared on top of those surfaces and were verified for homogenity with grazingincidence small-angle x-ray scattering at BW4 beamline at HASYLAB at DESY as evidenced by the pronounced correlated roughness oscillations (Fig.2.9).



Figure 2.9: 2D GISAXS image of a 65 nm thick PB (55,000 g/mol) film on acid treated silicon oxide.

In summary, we have prepared large well-defined substrates for TIR-FCS and NR measurements with comparable surface interaction components by applying different monolayers of covalently bonded silane to the substrates.

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2.5 Near-surface composition profiles of pressure sensitive adhesive films

A. Diethert, P. Müller-Buschbaum

Pressure sensitive adhesives (PSAs) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers. Typically, two or three different monomers are combined in the statistical copolymer to balance the different requests of the PSA [1-4]. The adhesive properties of the PSA films are mainly determined by surface-near regions. However, detailed information about surface structures of such adhesive films is still missing.

In the presented work we compare the behavior of two different statistical copolymers consisting of two different types of monomers. The sticky monomer ethylhexyl acrylate (EHA) is the majority component of both. It is copolymerized with a harder, glassy monomer which is methylmeth acrylate (MMA) for the first copolymer and styrene (S) for the second one. The ratios are 80% EHA : 20% MMA and 90% EHA : 10% S, respectively. Since the glass transition temperature of PEHA is $-65^{\circ}C$ the systems are very mobile.

The PSA films were prepared with solution casting on pre-cleaned glass substrates under ambient conditions. During drying, the films are protected by a cubic box of approximately 30 cm. From a naive point of view, one would have expected homogenous films which are characterized by the average monomer composition but we always detect an enrichment of one type of monomer at the sample surface.

To investigate the surface structure, we probed the density profile perpendicular to the PSA surface using x-ray reflectivity (XRR). This method has many advantages: it gives a resolution in the Angstroem-regime, the whole refractive index profile can be extracted out of one measurement, it is non-destructive, no special sample preparation is required and one gets averaged information over the whole illuminated sample area. The XRR measurements were performed with a Siemens D5000 diffractometer using a wavelength of 1.54 Å. For the data analysis we used Parratt32, a simulation tool for neutron and x-ray reflectivity.



Figure 2.10:

a) x-ray reflectivity data and fits in Fresnel-normalized representation of the statistical copolymer with 80% EHA and 20% MMA and b) the corresponding refractive index profiles.

Figure 2.10 a shows reflectivity curves of the statistical copolymer with 80% EHA and 20% MMA, also referred to as P(EHA-stat-20MMA), in the so-called Fresnel-normalized representation, which is beneficial for thin enrichment layers. The curve plotted in blue color represents a freshly prepared sample (see sample age within the figure) and the curve plotted in green

color shows data from a samples which was stored for almost one year at room temperature conditions. The red solid lines are the fits to the data. Figures 2.10 b shows the corresponding refractive index profiles where z = 0 denotes the sample surface. The black solid lines are positioned at the values of the refractive indices of the corresponding homopolymers related to the involved copolymers.

For both sample ages, we find an oscillating refractive index profile, and thus an oscillating composition profile, in the near-surface region. Homogeneous bulk material, which is characterized by the averaged refractive index of both materials, is reached in a depth of about z = 1000 Å.

For the freshly prepared sample, there is a strong enrichment of PMMA at the polymer-air interface, which is followed by a second, weaker PMMA-enriched zone in a depth of z = 65 Å. Underneath, we find a PEHA-dominated region which is most pronounced at z = 150 Å and then converges towards homogeneous bulk material. For $0 \le z \le 150$ Å the aged sample shows an almost inverted behavior. The PMMA-enrichment peak is shifted to z = 45 Å and PEHA is enriched at the surface. This behavior can be explained by the tendency to minimize the surface tension of the film. The corresponding values [5, 6] are $\gamma_{\text{PEHA}} = 30$ mN/m and $\gamma_{\text{PMMA}} = 38.5$ mN/m and so, the material with the lower surface tension enriches at the surface.



Figure 2.11:

a) x-ray reflectivity data and fits in Fresnel-normalized reprezentation of the statistical copolymer with 90% EHA and 10% S and b) the corresponding refractive index profiles.

Figure 2.11 shows the corresponding data for P(EHA-stat-S). In contrast to P(EHA-stat-MMA), there is an ab initio enrichment of the majority component PEHA which is followed by a layer of PS at z = 60 Å. The enrichment of PEHA is preserved due to the lower surface tension of PEHA compared to PS. During aging, the intensity of the PS-peak decreases and a PEHA-dominated region between z = 120 Å and 700 Å arises.

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2.6 Detection of the surface energy of PSA films by contact angle measurement

A. K. Sommer, A. Diethert, P. Müller-Buschbaum

Forming bonds with pressure sensitive adhesives (PSA) can be activated by applying pressure and there is no need for extra usage of solvent, water or heat. The external pressure applied on the PSA surface determines the so-called tack value. Thus there is a wide range of application of PSAs: they are designed for permanent or removable gluing and can support big loads, which is particularly interesting for applications in industry. A wide range of PSAs is built up of statistical copolymers, which include two or three different types of monomers with variable properties.

In the presented work, the copolymers contain two monomers, statistically distributed along the polymer chain in the proportion of 10 to 90%: in all probes the 90% component is poly(ethyl hexylacrylate) (PEHA), which is sticky and due to its low glass transition temperature rather soft. The PSA should have good adhesion to the substrate, however too strong shearing and flowing within the film should be avoided. Therefore for the 10% component a harder, glassy monomer is chosen. The 10% components used in the investigated films are poly(methyl methacrylate) (PMMA) and poly(maleic acid anhydride) (PMAA).

To fabricate the samples the copolymers are dissolved in toluene and then 1 ml of the solvent is casted onto a microscope slide (26×76 mm). In order to control the humidity the casting process is executed in an exsiccator (SCHOTT, DURAN) filled with silica gel. Thus an almost completely dry environment can be guaranteed. After 24h the solvent has evaporated and the dry sample has a thickness of $50 \ \mu m$ which is confirmed by weight measurement.

An important parameter for the characterization of PSAs is the surface tension as it has great influence on the adhesive properties. This parameter can be determined by surface angle measurements. The results give information about the structure and chemistry of the PSA in its surface region.



Figure 2.12:

Contact angle as a function of time for 4 different liquid drops on a P(EHA-stat-MMA) film

In the performed experiments four different liquids with varying polarity are used: ethylene glycol (dispersive and polar contribution to the surface energy: $\gamma_d = 29 \text{ mN/m}$, $\gamma_p = 19 \text{ mN/m}$), diiodomethane ($\gamma_d = 47.4 \text{ mN/m}$, $\gamma_p = 2,6 \text{ mN/m}$), water ($\gamma_d = 19.9 \text{ mN/m}$, $\gamma_p = 52.2 \text{ mN/m}$) and paraffin oil ($\gamma = 29.5 \text{ mN/m}$) being purely dispersive.

A droplet of $0, 3\mu l$ (diiodomethane, ethylene glycol, water) or $1\mu l$ (paraffin oil) is placed onto the polymer film and recorded with a "uEye" camera for about 80s (12 times for each liquid). In each picture the contact angle is fitted with the "SCA20" software from "Dataphysics" as a function of time by assuming an elliptical contour of the droplet. As the liquid evaporates it is not possible to directly measure the equilibrium contact angle Θ_f . Thus to obtain Θ_f the curves are fitted with the function

$$\frac{\Theta(t)}{\Theta_f} = 1 + (\frac{180^{\circ}}{\Theta_f} - 1) \exp\left(-k * (t - t_0)^n\right)$$
(2.5)

where the parameters k, n, t_0 and Θ_f are varied. This is similar to a mathematical approach reported in [1]. For very long measuring times the contact angle approaches Θ_f , at t = 0 the contact angle is 180°. The obtained contact angles for the four different liquids are represented as colored lines in Fig. 2.12 for P(EHA-stat-MMA). The black solid lines are the fits to the data using the function mentioned above. The averaged Θ_f for the different liquids are shown in the respective figures.



Figure 2.13: Owen/Wendt diagrams for a) P(EHA-stat-MMA) and b) P(EHA-stat-MAA)

By applying the Owens/Wendt theory [2] the surface energy of the polymer film can be calculated. This theory basically divides the surface energy γ into two components: surface energy due to dispersive interaction γ_d and polar interaction γ_p . The resulting principle equation is

$$\frac{(1+\cos(\theta))\gamma}{2\sqrt{\gamma_d}} = \sqrt{\gamma_d^{\text{polymer}}} + \sqrt{\gamma_p^{\text{polymer}}}\sqrt{\frac{\gamma}{\gamma_d} - 1}.$$
(2.6)

Fig. 2.13 a shows the so-called Owens/Wendt plots for P(EHA-stat-MMA) and Fig. 2.13 b P(EHA-stat-MAA) in which $\sqrt{\gamma_p^{\text{Polymer}}}$ is the slope and $\sqrt{\gamma_d^{\text{Polymer}}}$ the intercept of the fitted linear equation.

The literature values of the surface energies are $\gamma^{\text{PEHA}} = 30 \text{ mN/m}$, $\gamma^{\text{PMMA}} = 38.5 \text{ mN/m}$ and $\gamma^{\text{PMAA}} = 74.7 \text{ mN/m}$. For both PSA films the surface energy is higher than the value of PEHA. For P(EHA-stat-MMA) the value is very similar to the surface tension of PMMA originating from an enrichment layer of PMMA in the near-surface region. As the surface energy does not completely coincide with the PMMA value, it can be assumed that there is also a small amount of PEHA near the surface. The surface energy measured for P(EHA-stat-MAA) is very close to that of PEHA regarding the big difference between γ^{PEHA} and γ^{PMAA} . As a consequence the surface region is dominated by PEHA.

To control and extend the results obtained by contact angle measurements the samples will also be analyzed with x-ray reflectometry since further information about the composition normal to the surface can be collected. Additionally, the influence of the film composition on the mechanical properties will be investigated with mechanical tack experiments.

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2.7 Interface induced morphology transition in tri-block copolymer films swollen with low molecular weight homopolymer

P. Müller-Buschbaum, L. Schulz¹, E. Metwalli, J.-F. Moulin², R. Cubitt³

- ¹ Université de Fribourg, Fribourg, Switzerland
- ² GKSS-Forschungszentrum, Geesthacht, Germany
- ³ ILL, Grenoble, France

Of particular interest is the use of an additive to alter the morphology and mechanical properties of linear block copolymers to overcome the normally required tailored synthesis of applicationspecific copolymer molecules. The characteristics of a microphase-ordered block copolymer can be systematically modified through physical blending with either a (non)preferential solvent, a parent homopolymer or a second copolymer. The addition of homopolymer molecules to a microphase-ordered block copolymer either swells the host micro-domains or induces a morphological transformation to a nanostructure with a different interfacial curvature. In contrast to AB-type di-block copolymer/homopolymer blends, the addition of a mid-block-associating homopolymer to an ordered ABA-type tri-block copolymer is expected to have a far more significant effect on the properties and phase behavior of the resulting copolymer/homopolymer blend due to a decrease in the fraction of bridged mid-blocks. The molecular weight of added homopolymer in relation to that of the compatible copolymer block, and the composition of the blend expressed in terms of the homopolymer mass percent turned out to be important parameters. Miscibility is usually retained in such blends if the ratio of molecular weight of the added homopolymer to the molecular weight of the compatible block and the added amount of homopolymer are relatively small. An increase in either or both of these quantities ultimately induces macrophase separation at equilibrium.



Figure 2.14:

Two dimensional scattering patterns recorded in the GISANS measurements (for an incident angle $\alpha_i < \alpha_c$) for the three different surface treatments, from top to bottom: (a-c) acid-cleaning, (d-f) base-cleaning and (g-i) PS-brush. In the left column (a, d, g) 0.1, in the middle column (b, e, h) 0.2 and in the right column (c, f, i) 0.5 V% PSd was added to the triblock copolymer. The intensity is shown with a logarithmic color coding. Taken from [4]

As compared to bulk morphologies, in thin films the interaction with the confining asymmetric wall (substrate and air interface) typically complicates the behavior and can result in modification of the morphologies. Usually preferential wetting of one of the blocks at an interface leads to a parallel orientation of the micro-domains, and when the thickness of the film is incommensurate with the lamellar (or cylindrical/spherical) period, quantization of the film thickness takes place by the formation of terraces. In tri-block copolymer films in addition to a comparable behavior of surface induced ordering deviations from the bulk structure were reported: The wall interaction can introduce a change in characteristic spacing, such as shrinkage or stretching of the domain spacing [1, 2] or it can cause morphology transitions.

Experimental difficulties in selectively addressing such buried interfaces, meaning the structure of the copolymer at the substrate, were overcome by the use of grazing incidence small angle neutron scattering (GISANS). Fig. 2.14 shows selected GISANS data for different surface energies [1, 2]. Three different chemical treatments of the silicon substrates have been applied to achieve a neutral, mid-block and end-block selective wall and detect the corresponding changes in the short-ranged part of the interface potential to the structure and morphology of the blend films [1-4].



Figure 2.15:

Lateral spacing L_S of the triblock copolymer at the interface as a function of the added amount of PSd PS for the samples after acid-cleaning (triangles), base-cleaning (squares) and the PS-brush surface (spheres). The dashed line shows the spacing with added homopolymer picturing the contraction upon addition of PSd. Taken from [4].

Within this investigation we apply GISANS to probe the effect of blending an ABA-type triblock copolymer with a B-type homopolymer in bulky films, thereby addressing the area of thick films. In comparison to the volume structure inside the films the interface structure is characterized as a function of three different short-ranged interactions installed with different surface treatments [3]. The nano-structure due to micro-phase separation of the tri-block copolymer is measured. Morphological transitions in the interface structure are observed, which have no counter part in the film volume (see fig. 2.15) [4].

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2.8 Kinetics of structural changes in thin block copolymer films during thermal treatment

A. Sepe, Z. Di, D. Posselt¹, J. Perlich², D. M. Smilgies³, M. A. Singh⁴, C. M. Papadakis

- ¹ Roskilde University, Department of Science, IMFUFA, Roskilde Denmark
- ² HASYLAB at DESY, Hamburg
- ³ Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA
- ⁴ Queen's University, Department of Physics, Kingston, Ontario, Canada

Thin, nanostructured block copolymer films find a number of applications, especially as templates for anorganic materials, which may be used as optical elements or data storage devices [1]. For this reason, it is necessary to promote defect-free structures. Spin-coating is often used to prepare films because it is a fast and easy technique and results in homogeneous thin films, but the fast self-assembly introduces defects and multi-domain structures. Therefore, thermal annealing has frequently been applied in order to improve the long-range order [2]. Annealing temperature is a key parameter because it influences both, the interface tension and the polymer mobility.

We have studied thin films from lamellar poly(styrene-b-butadiene) diblock copolymers (P(S*b*-B)), initially having the perpendicular lamellar orientation [3]. The influence of thermal treatment was investigated by means of in-situ grazing-incidence small-angle X-ray scattering (GISAXS) and ex-situ atomic force microscopy (AFM). In the P(S-b-B) system, the glass transition temperature T_q of PB is -80 ° C, i.e. PB is mobile at room temperature (RT), whereas for PS, T_q is 102 ° C, i.e. PS is in the immobile, glassy state at RT. To investigate the role of mobility for the annealing process, we have systematically varied the annealing temperature between 60 ° C and 120 °C. A symmetric P(S-b-B) diblock copolymer, having a molar mass of 216 kg/mol and an initial lamellar thickness of 80 nm, was spin-coated from toluene solution onto Si wafers, then dried in vacuum for 1 day at RT, resulting in a film thickness of 150 nm. The structural properties were studied by means of GISAXS experiments, using a heatable sample chamber flushed with N_2 . The experiments were carried out at beamline BW4, HASYLAB at DESY. We have performed GISAXS measurements during thermal annealing of P(S-b-B) (Fig. 2.16a). Thermal treatment below 100 ° C does not alter the straight diffuse Bragg rods (DBRs), i.e. the perpendicular orientation is unchanged. Upon thermal treatment above $100 \degree C$, the DBRs are less well-defined, i.e. the perpendicular orientation is destabilized. At the annealing temperature, bending of the DBRs is observed at 60 $^{\circ}$ C – 100 $^{\circ}$ C. After cooling down, the DBRs reappear, the process is thus reversible. In contrast, for an annealing temperature of 120 $^{\circ}$ C (i.e. above T_q of PS), the DBRs disappear during annealing and they do not reappear upon cooling down to room temperature. This is confirmed by AFM (Fig. 2.16b), where no lamellar structure can be discerned any longer after annealing at 120 °C.

We conclude that the processes during thermal treatment of lamellar diblock copolymer films are greatly dependent on treatment temperature. In particular, the highest glass transition temperature of the two blocks plays an important role. Thermal annealing below the T_g of the PS block results mainly in a flattening of the film surface and a decrease of the lamellar thickness, whereas above, severe changes of the orientational distribution of the lamellar structure are observed.

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Figure 2.16:

a) GISAXS images of P(S-*b*-B) before \blacktriangle , during \blacktriangleleft and after \checkmark thermal treatment at 60 ° C, 80 ° C, 100 ° C and 120 ° C respectively. Right panel: corresponding lateral intensity profiles along the stripes marked in the 2D images. b) AFM images (3x3 μm^2) of an as prepared film and after thermal treatment at 60 ° C, 100 ° C and 120 ° C and subsequent cooling down, respectively.

2.9 Induced orientational order in diblock copolymer thin films via directional solvent vapor-flow

E. Metwalli, J. Perlich, W. Wang, A. Diethert, S.V. Roth, C.M. Papadakis, S.V. Roth¹, Peter Müller-Buschbaumm

¹ HASYLAB at DESY, Hamburg, Germany

The chemically distinct and immiscible polymer blocks of the diblock copolymers (DBCs) selfassemble during the microphase separation into ordered patterns on a scale of nanometers. An expedient tunability of the size, shape, and periodicity of the microphase-separated domains is achieved by manipulating the DBCs' molecular characteristics. A fine control over long-range ordering of the microdomain structures allows the fabrication of integrated micro- and nanosystems with a high degree of complexity and functionality. So far, several techniques have been successful in achieving an enhanced morphology long-range alignment of DBCs by precisely localizing the nano sized domains; these have included chemical and topographical patterned surfaces as well as external fields, viz., surface, mechanical, electric, and solvent evaporation. In the present investigation, we perform a novel type of solvent treatment of the spin-coated cylinder forming composition of DBCs to achieve highly ordered nanopatterns, based on the solvent vapor flowing parallel to the polymer film. We used polystyrene-block-polyethylene oxide DBCs films, denoted P(S-b-EO), with a total number average molecular weight M_n = 26.5 kg/mol, and a weight ratio of 75:25 (PS:PEO).



Figure 2.17:

AFM images of the P(S-b-EO) film with 65 nm thickness after benzene vapor treatment without (a) and with vapor-flow (b, c, and d) at speed of 0.2 m/s. (b) highly oriented parallel cylinders are formed upon vapor-flow shearing.

The powder polymer was initially dissolved in benzene at different concentrations and used for the coating step. The pre-cleaned silicon substrates were coated using the spin coating method (2500 rpm, 30 s). The polymer films were solvent-annealed inside a chamber under a controlled benzene vapor pressure. During the annealing process, vapor-flow was allowed to continuously
pass over the sample in one direction inside a hood. Characterization of the microstructure, surface morphology and thicknesses of the DBC films was carried out with X-ray reflectometry (XR), scanning electron microscopy (SEM), atomic force microscopy (AFM), and optical microscopy. Also, both grazing-incidence X-ray diffraction (GIXRD) and small-angle scattering (GISAXS) were used to investigate the structure of the vapor-flow annealled polymer film.



Figure 2.18:

GISAXS 2d patterns of DBC thin film (left) without and (right) with applied vapor-flow: A second order rod-like peak at the position 2q* in the GISAXS pattern (right) confirms the highly oriented cylinder morphology being aligned parallel with respect to the surface plane upon directional benzene vapor-flow.

For an intermediate value of the film thickness (65 nm), a partially crystalline polymer film with terrace patterns containing finger-like crystalline domains is observed as revealed from the realspace AFM characterization (Fig. 2.17). Polystyrene domains sandwiched between crystalline PEO domains in P(S-b-EO) are observed in areas between the large non-regular crystalline domains of the polymer film after the benzene vapor treatment. The film morphology of the parallel cylinders to the surface plane was reproducibly prepared. An important observation in the current study is the formation of highly oriented cylinder morphology (Fig. 2.17b) via vaporflow treatment of the polymer film during the annealing process. A poweder like oriented parallel cylinders of the same sample are observed when the vapor-flow was off (Fig. 2.17b). The morphologies with and without the vapor-flow in an unsealed vapor annealing set-up were fully reproducible. The GISAXS patterns for the polymer films with and without the vapor-flow shearing are presented in Fig. 2.18. A lateral spacing (31 nm) between the two neighboring PEO cylinders is observed irrespective of the vapor-flow. However, a highly orientated parallel cylinders are obtained and porved from both the AFM image (Fig. 2.17a) and the second higher order scattering rod in the GISAXS pattern (Fig. 2.18b). The enhancment of aligment in the vapor flow is attributed to a vapor-flow induced shearing effect on the polymer film. The semicrystalline PEO block forms cylinders that initiate a growth rate with a favorable perpendicular orientation of the PEO crystals with respect to the cylinder axis. Such highly ordered nanostructured polymer films are essential for some applications such as templates for metal nanopatterning [1,2].

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2.10 Structural changes of thin block copolymer films in selective solvent vapor

Z. Di, C. M. Papadakis, D. Posselt¹, D.-M. Smilgies²

- ¹ Roskilde University, Department of Sciences, IMFUFA, Roskilde, Denmark
- ² Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA

Thin block copolymer films are promising candidates for a variety of applications, such as the preparation of nanoporous films, nanostructured templates, photonic crystals and biosensors [1]. Long-range order can, for instance, be achieved by solvent vapor treatment with subsequent drying. However, the molecular mechanisms and mesoscopic rearrangements involved in solvent annealing are still largely unexplored.

The thin film geometry allowed us to study the processes during vapor treatment in great detail [2-4]. Using in-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS) with 2D detection, structural changes parallel to the lamellar interface can be distinguished from those along the film normal. We addressed the question on which time scale long-range order is achieved, and how this process is related to the increase of polymer mobility at the glass transition of the blocks and to the decrease of the interfacial tension upon uptake of solvent.





GISAXS images of the P(S-*b*-B) thin film during treatment with saturated CHX vapor at the treatment times given in the figures.

A thin film of lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) diblock copolymers having a molar mass of 22.1 kg/mol, an initial lamellar thickness of 18.9 nm and a film thickness of 97 nm was investigated [4]. The film was treated with saturated vapor of cyclohexane (CHX), which is a good solvent for PB and a theta solvent for PS, i.e. it is slightly selective for PB.

In-situ grazing-incidence small-angle X-ray scattering (GISAXS) was carried out at beamline D1 at the Cornell High Energy Synchrotron Source (CHESS). The time resolution was a few seconds.

The GISAXS image of the as-prepared sample (Fig. 2.19) shows both, weak diffuse Bragg sheets (DBSs) along the film normal, q_z , and diffuse Debye-Scherrer rings (DDSRs), indicating the presence of lamellae having their interfaces parallel to the substrate surface as well as randomly oriented lamellae. During vapor treatment, the GISAXS images change drastically and reveal the presence of a transient state with improved long-range order and eventual disordering of the film (Fig. 2.19). Especially at 7.5-13.5 min after the start, the DDSR vanishes partly, and well-pronounced DBSs appear. For times longer than 13.5 min, a broad DDSR appears. We conclude that, temporarily, a state with higher order appears, which, however, becomes disordered upon prolonged vapor treatment. The film thickness during vapor treatment was determined from the period of the intensity oscillations in the DDSRs [5]. From the ratio of the initial and the actual film thickness, the polymer volume fraction during vapor treatment, ϕ , could be determined to decrease from 1.0 to 0.55.

Knowledge of ϕ allowed us to estimate the times at which the glass transition and the orderto-disorder (ODT) transition take place. Since the glass transition temperature, T_g , of PB is very low (-89 °C), we only need to consider the decrease of T_g of PS. Using the Kelley-Bueche equation [6], we estimate that T_g (PS) reaches room temperature when $\phi < 0.9$, which is the case after 3.5 min of vapor treatment. Thus, already shortly after the start of the treatment, the polymers are sufficiently mobile for long-range order re-arrangements. Vapor uptake, however, also decreases the effective interfacial tension between the two blocks, which eventually results in crossing of the ODT and disordering. Assuming that the interaction energy between PS and PB scales with ϕ , we have estimated that the ODT occurs at $\phi \approx 0.6$ which is the case after 20 min of vapor treatment. We conclude that first, the polymers become mobile and only later the mesostructure vanishes. In-between these times, achievement of higher long-range order with a more well-defined lamellar orientation is possible. These findings are summarized in Fig. 2.20.



Figure 2.20:

Sketch of the structure of the asprepared sample (a), the transient state of improved long-range order (b) and the final, disordered state (c). The different shades of gray indicate the PS and PB parts of the lamellae. For clarity, only a few lamellar domains are shown. The substrate is marked by dashes.

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2.11 Structural changes in a lamellar block copolymer thin film during solvent vapor treatment below saturated pressure

Z. Di, C. M. Papadakis, D. Posselt¹, D.-M. Smilgies²

- ¹ Roskilde University, Department of Sciences, IMFUFA, Roskilde, Denmark
- ² Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA

Thin film of block copolymers represent an interesting class of materials, mainly due to their potential to self-assemble into highly regular structures of mesoscopic dimension [1]. Treatment with solvent vapor is a promising means for block copolymer thin film equilibration, i.e. an efficient way to improve the long-range order. Our previous studies [2] reveal that, in lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) films, prolonged solvent vapor treatment indeed improves the long-range order, however, eventually leads to disordering of the block copolymer. In the present work, we carried out vapor treatment with a vapor pressure *below saturation* such that the sample maintains the lamellar morphology throughout. We focus on three aspects: (i) the gradient of swelling from the film surface to the substrate, (ii) the influence of the solvent selectivity on the swelling of the two parts of the lamellae, and (iii) the formation of additional lamellae.

We have studied a thin film of P(S-*b*-B) with a molar mass of 28.0 kg/mol and a lamellar thickness, $D_{\text{lam}} = 22.5$ nm. The initial film thickness was 376 nm. The solvent used for the vapor treatment was cyclohexane (CHX) which is a good solvent for PB and a theta solvent for PS, i.e. it is slightly selective for PB. Liquid CHX is injected into the cell, and the solvent vapor pressure is controlled by a gas flow through the sample cell. The film thickness was measured in-situ using a white-light interferometer. The structural changes were monitored using in-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS) at beamline D1 at CHESS, Cornell University.



Figure 2.21:

(a) Swelling curve of the P(S*b*-B) thin film in CHX together with GISAXS images acquired at the treatment times indicated by the arrows. The film normal is vertical. (b) The degree of swelling of the film thickness (blue curve) and of the lamellar thickness (red dots) as a function of treatment time. (c) Schematics of the restructuring of the lamellar stack during vapor treatment. Only the uppermost and lowermost lamellae are shown. The substrate is hatched.

The GISAXS image of the as-prepared film displays 1st and 3rd order diffuse Bragg sheets (DBSs) along the film normal (each order has two branches, figure 2.21a). This reflects that the lamellae are mainly parallel to the film surface and that the PS and the PB parts of the lamellae are equally thick. During the treatment with CHX vapor, the film continuously swells from 376 nm to 511 nm, and both, the intensity and position of the DBSs change drastically: During the first minute, the higher-order DBSs vanish, i.e. the correlation of the lamellar interfaces is

weakened. After 3-4 min, 2nd and 3rd order DBSs re-appear, indicating (i) an improved correlation of the lamellar interfaces and (ii) asymmetric swelling. The latter is due to the selectivity of CHX for PB resulting in a higher degree of swelling for the PB part of the lamellae. After ~ 10 min of vapor treatment, the scattering does not change any longer, i.e. a new equilibrium state is reached.

Careful inspection of the positions of the 1st and 3rd order DBSs shows that, during the first few minutes of vapor treatment, their ratio does not match the one expected for a stack of equally thick lamellae. We conclude that D_{lam} displays a gradient from the film surface (where the lamellae are more swollen than on average) to the substrate surface (where they are less swollen than on average). This gradient is evident because the as-prepared film is relatively thick, thus the solvent vapor needs time to swell the entire film equally.

The lamellar thickness D_{lam} as obtained from the position of the 1st order DBS behaves differently from the film thickness as a function of treatment time (Fig. 2.21b). Initially, D_{lam} increases faster than the film thickness, i.e. the uptake of solvent results mainly in swelling along the lamellar normal. The discrepancy is due to the fact that mainly the upper (more swollen) lamellae contribute to the average position of the 1st order DBSs. After ~ 0.6 min of treatment, the swelling of the lamellae abruptly slows down, which we attribute to the glass transition of the PS domain: After having taken up a sufficient amount of CHX, PS goes from the glassy to the liquid state, and the block copolymers become significantly more mobile. The two blocks can now assume more coiled molecular conformations, which are entropically favored when solvent is present [3]. These result in an increased interfacial area per copolymer and in a lower D_{lam} than for pure uniaxial swelling. After ~ 1.3 min, the lamellae de-swell strongly. We have observed this effect before [2], and have attributed it to high interfacial demand which makes it impossible to accomodate all copolymers at a certain lamellar interface. Thus, additional lamellae are formed, and the blocks can relax to their new (coiled) equilibrium conformation with a lower D_{lam} than in the as-prepared state. Eventually, D_{lam} levels off after ~ 4 min of treatment, i.e. a new equilibrium state is reached.

We have witnessed complex structural changes in a P(S-*b*-B) diblock copolymer thin film during treatment with CHX vapor below saturation vapor pressure (Fig. 2.21c). Both the finite diffusivity of the solvent in the polymer film, its selectivity towards the PB block and the glass transition temperature of the PS block were found to be important parameters. Uneven and asymmetric swelling as well as the formation of additional lamellae were observed.

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3 Polymer films for applications in photovoltaics



3.1 Crystallinity of P3OT in thin polymer films

S. M. Prams, M. A. Ruderer, P. Müller-Buschbaum

Like many polymers the conductive polymer poly(3-octylthiophene-2,5-diyl) (P3OT) is counted among the semi-crystalline materials. This means P3OT includes regions in which the polymer chains order in a crystalline way. These regions are usually surrounded by amorphous regions without crystalline ordered structure. In conductive polymer devices crystallinity is of special interest since it has influence on its conductivity. The orientation of the crystalline phases can for instance lead to anisotropic conductivity [1].

Thin films consisting of P3OT were prepared by spin-coating from tetradytrofuran (THF) solution on pre-cleaned glass substrates. According to a previously ascertained linear correlation between film thickness and polymer concentration of the solution, the used concentration of 10 g/l leads to a film thickness of 120 nm. For exploration of the influence of thermal treatment, films were annealed at 130 °C for 15 minutes on a hot plate under vacuum conditions and quenched to room temperature.

To examine the crystallinity of the P3OT films grazing incidence wide angle x-ray scattering (GIWAXS) was used. Placed at a distance of 123 mm behind the sample, the detector covers an angular region from 0° to 35° . This setup allows the detection of structures in the nm- and sub-nm-region. The scattering experiments were performed at the beamline BW4 at HASYLAB in Hamburg.

The analysis of the scattering images is accomplished by sector integrals perpendicular (vertical) and parallel (horizontal) to the substrate surface. The integrals are compared with each other in two different ways.

Fig 3.1a shows the comparison of vertical and horizontal integrals of the same polymer film, like indicated by the pictograms. The top graphs (I) and (II) pertain to the annealed film, the bottom graphs (III) and (IV) to the unannealed film. All of the graphs displayed show intensity maxima caused by crystalline structures within the films. The (100), (200) and (300) maxima can be assigned to the same structural length named "*a*". The (100) is the main maximum of this structural length. (200) and (300) are higher order peaks. Consequently their values of *q* are twice ($q_{(200)} = 5.1 \text{ nm}^{-1}$) and three times ($q_{(300)} = 7.7 \text{ nm}^{-1}$) higher than $q_{(100)} = 2.5 \text{ nm}^{-1}$ respectively. Via the formula $a = \frac{2\pi h}{q}$, with the crystallographic indice h = 1 the value of a = 2.5 nm can be calculated from the (100) peak . The (010) peak corresponds to a structure size b = 0.4 nm oriented perpendicular to a [2, 3].

Although the structures a and b are perpendicular to each other within each crystalline region, the orientation of the different crystalline regions has an angular distribution. For the unannealed film the intensity of the (100) maximum is higher in vertical direction while the intensity of the (010) maximum is equal in horizontal and vertical direction. The corresponding comparison for the annealed film shows almost equal intensities for the (100) maximum in both directions. In vertical direction the intensity of the (010) maximum is higher than in horizontal direction.

The direct comparison of the annealed and unannealed films in vertical direction (Fig 3.1b, top), shows a shift towards higher values of q for the (100), (200), (300) and (010) maxima in the graphs of the annealed film. This corresponds to a 9 % shrinkage of the structures a and b in real space.

For the annealed film the (100) maximum is less intense and broadened. In Fig 3.1c a region



Figure 3.1:

Sector integrals from GIWAXS scattering images. a) Direct comparison of horizontal (I/III) vs. vertical (II/IV) sectors for annealed polymer films (top) and unannealed films (bottom). b) Direct comparison of annealed (V/VII) vs. unannealed (VI/VIII) films in vertical (top) and horizontal direction (bottom). Graphs (I) and (II), (III) and (IV), (V) and (VI), as well as (VII) and (VIII) are shifted by the same value respectively. c) Zoom of the (100) maximum region of the vertical sector integrals of b).

with a small slope can be found around the position of the (100) maximum of the unannealed film. The intensity of the (010) maximum is enhanced in the annealed film with respect to the unannealed one.

The horizontal graphs (Fig 3.1b, bottom) show a shift of the maxima toward higher values of q as well. In contrast to the vertical graph, the intensity of the (100) due to annealing and the intensity of the (010) maximum decreases.

In summary, the examined polymer films show crystalline features even without post production annealing. The relatively simple molecular structure of the P3OT monomer presumably promotes the formation of crystalline ordered regions in the film.

In the annealed film the structure a is more strongly oriented in horizontal direction than it is for the unannealed film. Inversely the structure b is oriented stronger in vertical direction. These observations lead to the conclusion that the predominant orientation of the crystalline regions changes due to the annealing.

The shrinkage of the crystalline structures can be explained by a structural optimization caused from reorientations of the side groups as well as by residual THF molecules leaving the polymer film during the annealing [4].

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3.2 Analysis of solvent residuals in thin films of conducting polymers

M. Schindler, R. Meier, M. A. Ruderer, P. Müller-Buschbaum

Since conducting polymers show widespread application possibilities, e.g. in organic solar cells and organic field effect transistors, it is a serious concern to investigate long-time stability and aging. Aging can be enhanced due to remaining solvent embedded in the polymer matrix of thin films. Remaining solvent affects the mobility of the polymers and results in an ongoing change of the microstructure, which is accompanied by changes in the electrical performance.

One of our goals is to investigate the remaining solvent in thin conducting polymer films with neutron reflectivity (NR), utilizing the contrast between protonated and deuterated solvents. Perlich et al. [1] reported a significant enrichment of solvent at the substrate/polymer interface in thin polystyrene films, still present after different annealing and storage conditions. We will use titanium with a scattering length density (SLD) of $-1.95 \cdot 10^{-6}A^{-2}$ for the substrate material instead of silicon with a much higher SLD of $2.07 \cdot 10^{-6}A^{-2}$. This increases the detectability of residual solvent in thin polymer films due to a prominent shift of the critical edge as shown in the inset of fig. 3.2. The shown simulation was calculated using the *Parrat* algorithm [2]. For the polymer in this simulation we used MEH-PPV with a SLD of $5.67 \cdot 10^{-7}A^{-2}$ and as solvent we took deuterated tetrahydrofuran (dTHF) with a SLD of $5.73 \cdot 10^{-6}A^{-2}$.



Figure 3.2:

Simulated neutron reflectivity curve of a MEH-PPV film with a thickness of 100 nm on a titanium substrate with different solvent contents of deuterated tetrahydrofuran (dTHF). Inset shows the difference between a silicon and a titanium substrate.

In Fig. 3.2 it can be seen that there is a significant difference in the shift of the critical edge due to the solvent residuals, as simulated for a solvent content of 5%, 10%, and 15%. Our goal is to verify this simulations in experiment at the instrument MIRA at the FRM2 in Garching.

In another approach we are also investigating thin films of polymer blends with scanning transmission x-ray microscopy (STXM) at the PolLux beamline at the Paul Scherrer Institute (PSI) in Switzerland. This beamline offers energies from 200 to 1400eV, which enables us to search for remaining solvent by using solvents containing oxygen and polymers without oxygen. The K-absorption edge of oxygen, which we are looking for in the transmission spectra, has an energy of 540eV and hence is clearly detectable in the energy range of the beamline. This limits the choice of solvents suitable for the STXM measurements to the solvents tetrahydrofuran (THF), cyclohexanone and dioxane, with ongoing search for alternatives. This

set-up allows us to get a spatially and quantitatively resolved distribution of remaining solvent in the thin polymer blend films.

For both described approaches the polymers are dissolved in organic solvents and spin-coated on acidic pre-cleaned titanium substrates for the NR measurements and on TEM-grids for the STXM measurements. For the neutron experiments we are going to use p-phenylenevinylne-based conductive polymers (MDMO-PPV, MEH-PPV, M3EH-PPV, and CN-PPV) and for the STXM measurements blends based on P3HT:PVK, F8BT:PVK, and F8BT:PVK.

For the STXM measurements we have already analyzed the film topology and composition of a polymer blend film based F8BT:PVK using optical and atomic force microscopy. For the 20nm resolution of the PolLux beamline a phase separation of the polymer blend in the region of $0.5\mu m$ to $10\mu m$ is desired in order to achieve a good and clear contrast between the homopolymer domains.



Figure 3.3: Optical and atomic force microscopy pictures of a F8BT and PVK blend.

Fig. 3.3 shows the phase separation of the polymer blend, clearly visible by the darker islands embedded in the brighter matrix. The inset depicts an AFM image of the phase at a total size of $15 \times 15 \mu m^2$. The phase separation has a broad distribution of the typical structure size, going from 1 μm up to 10 μm , and hence makes an investigation with the spatial resolution of the PolLux beamline possible.

For the future the nanostructures have to be optimized concerning their homogeneity and size and additional sophisticated polymer blends have to be investigated also using other solvents. This study allows us to get an insight into one possible effect of aging, which is still a very crucial problem concerning long time stability of organic solar cells.

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3.3 Modification of the electrical conductivity in conjugated polymer films

A. Nathan, M. A. Ruderer, R. Cubitt¹ and P. Müller-Buschbaum

¹ ILL, Grenoble, France

Conjugated polymers in thin film geometry are of great interest for various applications such as printed electronics, organic photovoltaics, organic light emitting diodes and organic field effect transistors. Therefore, the selective modification and control of the electrical conductivity of such polymers has special importance. Since long time, polyacetylene in particular attracted a lot of attention due to the possibility of changing its conductivity over several orders of magnitude by using doping [1]. The trans-structure of polyacetylene establishes a double degenerated ground state defining the precondition for the low conductivity which is already present at room temperature. According to the Peierl's transition, known from one-dimension metal systems, the ground state complies with a valence and conduction band separated by an energy gap, the Peierl's gap. Because the single and double bonds are mutually interchangeable along the polymer chain defects occur during polymerization. These defects can be described as so called neutral solitons which are stable and mobile along the polymer chain without any loss of energy. However, the process crucial for conductivity in polyacetylene is interchain hopping of the solitons. As neutral solitons do not transport charges these defects do not contribute to the conductivity of polyacetylene. To create charged solitons and therefore to increase the conductivity doping is necessary. Upon moderate doping strong electron-phonon coupling transfers the charges from the dopand, typically a halogen, to the polymer chain, stored in spinless solitons with charge $\pm e$ in comparison to the undoped situation. The dopand ions themselves are localized close to the defects and influence the overall conductivity process as well. At high level doping, bound states of solitons give rise to so called polarons, which cause a high conductivity.



Figure 3.4:

(a) UV/Vis measurement of absorbance. Undoped film (solid line) of a polyacetylene derivative and after 5 minutes in an iodine solution (dashed line). (b) Detailed view of the maxima of the absorbance curves.

There has been a fast progress in synthesizing conjugated polymers in recent years. Nevertheless little effort was expended to exceed or investigate with advanced techniques the results obtained by Chiang et al.[1] over three centuries ago. In this work we revisit thin films of newly developed polyacetylene derivatives in respect to different doping methods by applying advanced scattering techniques. The newly available polyacetylene derivatives offer the advantage of higher stability against oxidation and thus promise better processing conditions.

First experiments were conducted using a polyacetylene derivative dissolved in toluene. Glass substrates were cleaned for 15 minutes at $80 \,^{\circ}$ C in an acid solution within two hours before use. Then, in a box impermeable to light these films were processed over night through solution casting under atmospheric conditions. In our first doping procedure a solution of iodine in methanol was applied. All samples were put in a flat glass vessel filled with the iodine solution for doping, covered by another vessel to protect them from light. We removed the samples in intervals of 5 minutes and performed UV/Vis measurements subsequently.

As seen in Figure 3.4, the maxima in the UV/Vis measurement is shifted to shorter wavelength after doping in the iodine methanol solution. This higher separation between adjacent energy levels is mainly caused by a reduction of the conjugation length. Therefore the shift indicates a higher number of defects within the film. On the other hand the absorbance increases at the peak according to the expected improvement of conductivity. Especially the absorbance towards longer wavelengths gains through doping. This feature is due to an additional energy state of the charged solitons inducing the so-called mid-gap occurring at 0.65 - 0.75 eV [2]. The additional peak is not within the range of the measured wavelengths, but the shoulder of the increase can be seen clearly. For higher concentrations of doping the maximum absorbance decreases in favor of the mid-gap. Figure 3.5 shows this behavior of the maximum.



Figure 3.5: Maximum of absorbance depending on the doping time with iodine methanol solution

The applied doping method shows unfavorable effects, e.g. the film partly detaches from the substrate and possible swelling of the film. Furthermore residuals of the doping solution on the surface of the film might influence light absorption and conductivity measurements. Therefore the doping method will be improved and adjusted to the polymer. The dopand itself might be replaced in further investigations by bromine or FeClf₄⁻ [3].

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3.4 Thin photoactive polymer blend films on structured substrates: A GISAXS study

R. Meier, S. V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Thin conducting photoactive polymer films have become of great interest over the last decade. This is mainly due to their various possibilities of application in electronic devices such as organic solar cells (OSCs), organic light emitting devices (OLEDs) or organic field effect transistors (OFETs). They combine mechanical flexibility, optical adjustability and many more device design possibilities with production advantages such as solution processability and cheap manufacturing cost. But it has to mentioned that e.g. for the photovoltaic application there is still a lack of overall power conversion efficiency of the organic devices in comparison to the inorganic counterpart mostly based on silicon. The best reported polymer based solar cell has a power conversion efficiency of 1.2% for a lab device and therefore can not compete with the commercially based silicon solar cells (around 16%) [1]. Hence many ways are considered to improve the device characteristics. One of them is to increase light absorption and to control the crucial phase separation in the polymer films. The phase separation of the polymer blend has a desired length scale in the order of the estimated mean diffusion length of the generated excitons ($d_{diff} \approx 15 - 20nm$).

Our approach is to pre-structure the substrate and to coat it in a following step with a thin photoactive polymer film by spin coating. Due to the underlying structure the polymer film has an inhomogeneous film thickness. It can be shown that the phase separation of a polymer blend film depends not only on the degree of polymerization like it is predicted by the Flory-Huggins mean field approach but for thin films also strongly depends on the film thickness [2]. This can lead to a sophisticated inner film structure with a combination of areas on the sample with a phase separation on the nanoscale suited for charge carrier separation and parts with a larger phase separation interesting for charge carrier transport to the electrode.



Figure 3.6: 2D-scattering images of a structured silicon substrate (a) and the same substrate coated with a thin polymer blend film.

Hence, it is necessary to characterize the inner film structure of these polymer films. A promising approach is grazing incidence small angle X-ray scattering (GISAXS), which was performed at the BW4, DESY (Hamburg). Fig. 3.6 shows the 2-dimensional scattering images of a plane channel structured silicon substrate (a) and one coated with a polymer blend based on the two photoactive polymers F8BT and M3EH-PPV (b). For both samples the channel structure has a size of $2\mu m$, an equidistant periodicity of $4\mu m$ and an etched depth of 150nm. The structures are achieved using hard lithography with a positive Shipley S1805 photo-resist followed by reactive ion etching (RIE) with a gas mixture of SiF_6 and C_4F_8 .

The ring around the specular peak, which is hidden in both images behind the beam stop, results from the perfect order of the fabricated channels. Atomic force microscopy images also show a perfect shape of the channel structure and a constant etched depth over the whole sample. On the contrary scattering images of samples with an imperfect orientation do not show this ring shape.

The prominent *palm-like* structure of the coated sample (b) results from the transition from the sharp box-like shape of the uncoated channels to the more wavy surface topology of the coated sample with the polymer film on top of the textured substrate. In the detector cut of sample (b) (fig. 3.7) a clear peak at the position of the critical angle for the polymer ($\alpha_{crit} = 0.14^{\circ}$) can be detected and hence it is clear evidence for the existence of the polymer film and its influence on the scattering image. We assume that the palm structure is due to complex interferences from the wavy polymer film. Additional experiments with homopolymer films on structured substrate show similar palm structures as well. But by variation of the etched depth of the channels and hence a tuned wavy surface of the polymer film the palm structure is changed dramatically concerning its periodicity and orientation (upwards vs. downwards). In addition fig. 3.7 also shows the out-of-plane cuts for sample (b) taken at the critical angle of the polymer ($\alpha_f = 0.14^{\circ}$), at the maximum position of the detector cut ($\alpha_f = 0.17$), and at the critical angle of silicon ($\alpha_f = 0.2^{\circ}$). The inserted arrows highlight the evolvement of the palm like structure for increasing reflected angles.





Detector cut of sample (a) and (b) showing the peak at the critical angle of the polymer blend and out-of-plane cuts taken at different angles α_f for sample (b)

From the cuts shown in fig. 3.7 it can be seen that in order to extract the full information of the scattering images a 2-dimensional fitting is necessary. As a next step this has to be realized using the simulation software IsGISAXS [3]. Also optical absorption and reflection measurements of the textured and coated substrates have to be performed.

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3.5 Photophysics and photocurrent generation in polythiophene/polyfluorene copolymer blends

M. A. Ruderer, C. R. McNeill¹, A. Abrusci¹, I. Hwang¹, N. C. Greenham¹, P. Müller-Buschbaum

¹ University of Cambridge, Cavendish Laboratory, Cambridge, UK

In polymer photovoltaics two classes of solar cells are of major interest where the active layer is the main difference. On the one hand fullerene/polymer systems and on the other hand all-polymer combinations are the most investigated combinations. While for fullerene/polymer systems efficiencies of over 5 % are reported, one of the most promising all-polymer systems, poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole]-2',2"-diyl) (F8TBT)/poly((3-hexylthiophene) (P3HT), has shown efficiencies of nearly 2 %.[1] For both systems annealing is required to reach high device performance. In this study the evolution of photophysics and device performance of P3HT:F8TBT due to temperature treatment is investigated and combined with structural changes probed with grazing-incidence small-angle X-ray scattering (GISAXS).



Figure 3.8:

a) 2D GISAXS patterns of as-spun and annealed (100 °C, 140 °C, and 180 °C) P3HT:F8TBT films. The color code represents the scattering intensity. The specular reflection is shielded by a beam stop. b) Double logarithmic plot of the out-of-plane cuts of the GISAXS data taken at the critical q-value of F8TBT ($q_z = 0.52 \text{ nm}^{-1}$). The data (black triangles) are fitted (red solid lines) with the effective interface model. The dashed line represents the resolution limit. All curves are shifted along the y-axis for clarity.[3]

In Fig. 3.8 the GISAXS data of P3HT:F8TBT blend films as-spun and with different anneal temperatures are shown. The 2d scattering pattern (Fig. 3.8a) provide qualitative information on the inner structure of the investigated films. In vertical direction a special type of oscillations due to correlated roughness indicates the formation of a layered structure. The coarsening of lateral structures with increasing anneal temperature can directly be seen in the narrowing of the scattering signal in horizontal direction. To obtain a quantitative information out-of plane cuts were performed (Fig. 3.8b). The fitting of the data [2] reveals the evolution of a small length scale which is not present for in the as-spun film and increases from 25 nm at 100 °C to 150 nm for an annealing temperature of 180 °C. This structural length does not describe the size of an objects but the distances of objects and may correspond to the distance of small pure P3HT domains in an impure F8TBT matrix.

The device characteristics of P3HT:F8TBT solar cells are shown in Fig. 3.9. The cells are tested under simulated sunlight and the current-voltage characteristics are extracted (Fig. 3.9a). The devices show improvement of performance with an additional annealing step. 140 °C was found as the optimal annealing temperature to reach highest efficiencies. The open circuit voltage is increasing with annealing temperature and is attributed to the dark current. With an additional LiF layer acting as an hole blocking layer between the active layer and the top electrode the open circuit voltage is significantly increasing (black dashed line) and becomes anneal temperature independent. The spectral dependence of external quantum efficiency was measured under lower light intensities and also shows an optimal anneal temperature of 140 °C for P3HT:F8TBT devices (Fig. 3.9b). From the red-shift in the absorption spectrum and decrease of photoluminescence lifetime (not shown here) reordering of P3HT at 100 °C is already seen. Furthermore photocurrent spectroscopy studies aided with by optical modeling it is found that photocurrent is efficiently generated from both polymers in the blend. The relative contribution of both polymers is changing with annealing temperature.



Figure 3.9:

Variation in the device characteristics of xylene-processed P3HT:F8TBT photovoltaic devices with annealing. a) Current-voltage characteristics under simulated sunlight (100mW cm² AM1.5G). b) Spectral dependence of external quantum efficiency.[3]

Consequently, the rearrangement of P3HT on a molecular level is not sufficient enough to reach optimal device performance but additional phase separation is needed which for P3HT:F8TBT blend systems is optimal at 140 °C. Interestingly, the optimum performance is not found at a small structure size on the order of the exciton diffusion length. Thus while for exciton dissociation close intermixed morphology is advantageous, the separation of coulombically bound charge pairs at the polymer interface is in phase separated systems increased. An annealing process at 140 °C seems to balance this for P3HT:F8TBT systems.[3]

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3.6 Structuring of an electron-blocking PEDOT:PSS layer in organic solar cells

R. Meier, F. Markl, P. Müller-Buschbaum

Photoactive conducting polymers have shown great potential for future application in organic electronics such as Organic Solar Cells (OSCs). Power conversion efficiencies of up to 4.5% have already been reached for organic blend devices based on the p-type polymer P3HT and the n-type fullerene PCBM [1]. In order to compete with the silicon based inorganic solar cells the efficiency still has to be improved although they have many other design and production advantages such as optical adjustability, flexible design and solution processability.



Figure 3.10: Sketch of a flat organic solar cell and of a structured organic solar cell highlighting the idea of improved light absorption.

The design of such an organic solar cells is in general based on multiple stacked layers: a transparent and conducting bottom electrode, mainly ITO or FTO, is covered by an electron blocking PEDOT:PSS layer. On top of this the photoactive layer, in our case a heterojunction based on two conducting polymers, is spin-coated and finally a thin aluminum layer as the top-electrode is evaporated on top of the device. In order to improve the electronic characteristics we focus on the influence of the water solvable PEDOT:PSS layer. Our idea is to tune the surface of the electron-blocking layer in order to improve the light absorption by internal reflection.

In fig. 3.10 it can be seen that by spin-coating of a polymer layer on top of the pre-structured PEDOT:PSS layer a wavy film topography can be achieved. This film is covered by an aluminum layer, which acts as a diffuse light reflector for the penetrating light and hence allows a even thinner design of the organic solar cell. Also the increased electrode surface area results in better characteristics of the device.





The channel structure is achieved by a wet imprinting routine. Therefore the ITO substrate is covered with PEDOT:PPS-H₂O-solution and the imprinting master is pressed on the wet substrate with a defined force. After an overall drying time of 24h the master is removed and the inverted master structure remains on the substrate. As a master the channel structure of a CD and a DVD is used after removing their encapsulating layer mechanically.

The absorption spectra of an unstructured (sample (a)), a structured by CD (sample (b)), and by DVD (sample (c)) PEDOT:PSS layer is measured using an UV/Vis set-up (fig. 3.11).





Atomic force microscopy image of sample (b) coated with photoactive polymer blend film and corresponding profile cut showing the wavy surface topology.

The unstructured sample (a) shows no absorption peak whereas the structured samples (b) and (c) have prominent absorption maxima, which are as well dependent on the size of the imprinted structures. From sample (c) with a channel size of $d_{cd} = 0.7\mu m$ and a periodicity of $p_{cd} = 2.5\mu m$ the peak is shifted to shorter wavelengths for smaller structure sizes as seen for the DVD imprint ($d_{dvd} = 350nm$ and $p_{dvd} = 900nm$). It was already shown by N.Bonod et. al. that for lamellar metallic gratings it is possible to achieve full light absorption even independently of the incident polarization [2]. The reason for the light absorption of metallic gratings is the generation of surface plasmons. As in our case the metal is represented by a conducting polymer, we can expect similar absorption effects.





For the final device a photoactive polymer blend based on P3HT and F8BT was spin-coated on the channel structure. The expected smooth and wavy surface topology can be nicely seen at the atomic force microscopy image and its corresponding profile cut shown in fig. 3.12. The I-V-characteristics in fig. 3.13 show a quite promising improvement of the short circuit current and the power conversion efficiency. But it has to be stated that the used system is absolutely not optimized towards its device performance: There are better polymer blend systems already available and the increased PEDOT:PSS film thickness, which is due to the wet imprinting, also influences the electronic characteristics.

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3.7 Structured photoactive layers for improved light absorption in organic photovoltaics

H.-Y. Chiang, R. Meier, P. Müller-Buschbaum

Semi-conduction, photoactive polymers are the key for future renewable energy conversion approaches such as organic photovolatics. Despite a still smaller efficiency as compared to the conventional solid state photovoltaic devices, the improvements are dramatic over the last years. As a consequence, organic solar cells have already made the jump from basic research to a large scale commercial product offered by private industrial companies. This evolution shows the great potential of the field of organic photovoltaics for the future energy production. Mainly it is due to the advantages in production like flexible design, solution processability, and cheap manufacturing cost in comparison to their inorganic competitor. Instead of costly clean-room fabrication, the simple roll-to-roll printing was successfully used. Having access to flexible solar modules will introduce major changes in the global use of photovoltaic devices.

However, despite the big achievements in organic photovolatics, still fundamental understanding as well as further improvements in device performance are required.



Figure 3.14:

The upper figure represents an unstructured organic solar cell, whereas the lower one represents an organic solar cell with an structured photoactive layer. The sketched incoming light paths highlight the theoretical increased optical path length in the photoactive layer if it is structured.

Fig. 3.14 shows a general sketch of an organic solar cell. It consists of a multilayer stack from a transparent conducting substrate (ITO), a thin electron blocking layer (PEDOT:PSS), the photoactive layer, and a thin aluminum layer as the top electrode. By absorbing photons in the photoactive layer excitons are generated and separated. The resulting charges are transported to the bottom and top electrode producing a current. Our goal is to structure the organic cells by mechanical imprinting in order to increase the overall light absorption of the thin photoactive films by multiple light scattering and hence to allow an even thinner and more efficient design of the solar cells. A thinner design is necessary because of the high probability of the generated excitons to recombine before they can be separated to each electrode. This is due to their short diffusions lengths of $d_{diff} \approx 15 - 20nm$ and it is the main reason for the still comparable low power conversion efficiency of the organic solar cells.

In our study we focus on organic solar cells based on conducting polymer blends. First results have already been achieved for the imprinting of a channel like structure using a simple CD structure as a master. Therefore a thin polymer layer based on F8BT was spin coated on acidic pre-cleaned silicon substrate. The polymer was solved in toluene at a concentration of 10g/l. The imprinting results are strongly dependent on the temperature, the applied pressure, and the time. As it was shown by Cardozo et.al. a good imprint can be realized at a pressure of p = 24000 kPa, a temperature of T = 110 °C, and an imprinting time of t = 15 min for thin F8BT films [1]. In order not to harm the polymer film our first experiments were performed at a much less pressure of $p \approx 30$ kPa only. Fig. 3.15 shows the basic experimental set-up used for



the imprinting.

The glass transition temperature of F8BT is at $T_g = 130$ °C and hence can be easily reached without destroying the CD master made of polycarbonate. Before lifting off the master the samples are cooled down in order to avoid any defects coming from the still soft polymeric layer. As it can be seen from the optical microscope images in shown in fig. 3.16 the temperature has a strong influence on the imprinting of the F8BT layer. For sample (a) the temperature was set to T = 90 °C, for (b) T = 130 °C, and for (c) T = 160 °C. Sample (a) shows due to the low temperature no channel structure at all. The F8BT film was not soft enough to allow for structuring at the applied pressure. By increasing the temperature above the glass transition temperature of the photoactive polymer the channel structure evolves. However, still defects are present and further optimization is required. At too high temperatures (sample (c)) the CD master itself is affected and starts to soften. Hence no more channels can be produced by the used method.



Figure 3.16:

The optical microscope images with a size of $30 \ \mu \text{m} \times 23 \ \mu \text{m}$ show the results after imprinting at different temperatures. For sample (a) the temperature was set to $T = 90 \ ^{\circ}\text{C}$, sample (b) $T = 130 \ ^{\circ}\text{C}$, and sample (c) $T = 160 \ ^{\circ}\text{C}$. The channel structure evolves for temperatures above the T_g and vanishes for too high temperatures.

The study is still ongoing and future experiments are necessary to improve the area of the structure transfer and to investigate the influence of the temperature and the pressure on the imprint quality in more detail. Therefore also atomic force microscopy images are necessary. Finally complete devices have to be characterized concerning light absorption and reflection and their influence on the overall performance of the electrical characteristics.

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4 Polymer-hybrid systems



4.1 Controlling the morphology of thin titania films for applications in hybrid inorganic-organic solar cells

M. Rawolle, P. Lellig¹, M. Memesa¹, J. S. Gutmann^{1,2}, P. Müller-Buschbaum

- ¹ Max-Planck-Institut für Polymerforschung, Mainz, Germany
- ² Johannes Gutenberg-University, Mainz, Germany

Nanostructured thin films of titania have a variety of applications because of their physical properties, for example in catalysis or photovoltaics. For applications in photovoltaics a large surface area is desirable as the separation of charge only can take place at the interface between titania and the hole-conducting material, which can consist of a hole-conducting polymer or a dye in combination with an electrolyte as in the case of the Graetzel cell.[1] To trap as much light within the cell as possible a large absorption coefficient is desirable. A sponge structure with a pore size of a few tens of nanometers combined with pores with a larger diameter is a promising morphology for titania to meet these demands.



Figure 4.1:

GISAXS measurements of calcined titania films prepared with different mixing speeds: a) 2-dimensional scattering image for one sample. b) Out-of plane cuts at the position of the titania Yoneda peak for 9 different samples. c) Detector cuts in the region of the Yoneda peaks for the 9 different samples: a clear splitting between the Yoneda peaks of the silicon substrate and the titania can be observed. The cuts in b) and c) are shifted along the y-axis for illustrative purposes.

Therefore, we focus on the preparation of titania thin films with such a morphology spread out over surfaces with an area of a few square-centimeters. Block copolymers can be used in a 'good-poor solvent pair' induced phase separation process coupled with sol-gel chemistry to create structured titania films in a reproducible way. We use the amphiphilic diblock copolymer Poly(dimethyl siloxane)-block-methyl methacrylate poly(ethylene oxide) [PDMS-b- MA(PEO)] as templating agent.[2] The polymer is first dissolved in Tetrahydrofuran and 2-Propanol, which are good solvents for both the hydrophobic and the hydrophilic part of the copolymer. After complete dissolution hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP) are added in a well-defined way. HCl and TTIP are on the one hand the source for the sol-gel process, on the other hand they act as poor solvents for the hydrophobic part and therefore induce the phase separation which leads to the nanostructures in the film. Changing the mixing speed of the same weight fractions of all the components results in small changes in the morphology of the film which is prepared via spin-coating on pre-cleaned silicon substrates. In a final step the films are calcined at high temperatures either in air or in a nitrogen atmosphere. The amorphous titania should be converted to the crystalline form of anatase titania which is a semiconductor with a band gap in the ultraviolet. By calcination in air the polymer which determines the structure of the titania is combusted. In an atmosphere of inert gas the PDMS-block is converted into a ceramic of silica oxy-carbide (SiOC), which has a high dielectric constant and could be of use as blocking layer in a solar cell. The influence of the calcination temperature on the morphology and the crystallinity of the titania films is also under investigation.

Information on the morphology in the volume of the film is gained from grazing incidence small angle X-ray scattering (GISAXS) at the HASYLAB beamline BW4 at DESY, Hamburg. Figure 4.1 shows results of the GISAXS measurements. The measurements are done with spin-coated titania films prepared with different mixing speeds. We observe no change in the size of the small pores in the sponge structure, as can be seen from the unchanged structure peak in 4.1 b), marked with an arrow. The structure peak corresponds to a structure of about 25nm. Structure information on the larger pores is hidden in the resolution of the setup with a sample-to-detector distance of about 2m. As can be seen from the detector cuts around the titania Yoneda peak in 4.1 c) the position of the titania Yoneda changes with the mixing speed. This change in position corresponds to a change in mass density and therefore a change in the overall porosity of the film. The same can be seen in the corresponding SEM measurements of the surface of the samples. SEM pictures of two different samples which correspond to the lowermost and the topmost cuts in 4.1 b) and c) respectively are shown in figure 4.2. Figures 4.2 b) and d) show that the size of the small pores in the sponge structure stays constant. In contrast the amount of large pores increases (see figure 4.2 a) and c)).



Figure 4.2:

SEM pictures of the sponge structure of titania: Subfigures a) and b) show images of the sample corresponding to the lowermost GISAXS cuts in figure 4.1, the SEM pictures of the sample corresponding to the topmost GISAXS cuts in 4.1 are shown in subfigure c) and d).

In addition the influence of different calcination temperatures was investigated regarding the morphology as well as the filling of the pores with grazing incidence small angle neutron scattering (GISANS) at the beamline KWS2 of the Juelich research center at FRM2, Munich.

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4.2 Hierarchically structured TiO₂ films prepared by polymer/colloidal templating

G. Kaune, M. Memesa¹, S. V. Roth², J. S. Gutmann¹, P. Müller-Buschbaum

- ¹ Max-Planck-Institut für Polymerforschung, Mainz, Germany
- ² HASYLAB at DESY, Hamburg, Germany

Structuring of titanium dioxide (TiO₂) thin films has attracted enormous interest in the past few years, since nanostructured TiO₂ shows outstanding properties and has widespread application potential e.g. in photovoltaics, catalysis and self-cleaning surfaces. Of particular interest is the introduction of hierarchical structures, where different structural levels provide a divided functionality of the film. In photovoltaic applications, a hierarchical pore structure promises improved power conversion characteristics: a mesopore structure is required for separation of the bound charge carriers generated by the trapped light, a macropore superstructure provides transport channels for the infiltration of the hole conducting material [1], and a structure on micrometer scale reduces surface reflection and improves light absorption [2].

A functional hierarchical structure was introduced in TiO_2 thin films by combining a solgel process with a diblock copolymer as structure directing agent and microsphere templating. Poly(dimethyl siloxane)-*block*-methyl methacrylat(ethylene oxide) (PDMS-*b*-MA(PEO)) was used as structure directing agent in the sol-gel process and poly(methyl methacrylate) (PMMA) microspheres with a diameter of 1 μ m acted as template for the micrometer-scale structure. For film preparation the PMMA microspheres were added to the sol-gel solution and the solution subsequently spin coated. The obtained nanocomposite films were either treated with actetic acid or calcined to remove the templating polymers and to bare the porous TiO₂ network.



Figure 4.3:

SEM images of an untreated nanocomposite film (p), a calcined film (c), an acetic acid treated film (s) and an acetic acid treated and calcined film (s + c). In the images with low magnification the arrangement of the macropores and the micrometer-sized holes is visible, the images with high magnification show a detailed view of the macropore and mesopore structure.

Figure 4.3 shows a comparison of the structures installed in the TiO₂ films together with the structure of an untreated nanocomposite film. Independently from the polymer extraction method a well-pronounced hierarchical pore structure is present in the films: (1) ordered mesopores arranged by the PDMS-*b*-MA(PEO) template with a diameter of 30 to 40 nm, (2) macropores resulting from a phase separation process during spin coating with a size of about 200 nm,

and (3) surface depressions with a diameter of 1 μ m left from the removed PMMA microspheres. In the calcined film, the macropores have a nearly circular shape and are separated from each other, whereas in the acetic acid treated film the pore shape is irregular with eroded edges. The size of the mesopores is significantly larger than the pore size usually achieved in mesoporous materials (≤ 10 nm, [3]) and thus opens the possibility for application of hole conducting materials with large molecular dimensions, e.g. conductive polymers with a high molecular weight.



Figure 4.4:

a) 2D GISAXS images and horizontal cuts taken at the position of the lateral maximum of the untreated nanocomposite film and the TiO₂ films. Solid lines are fits to the data to extract the preferred structural lengths Λ_1 and Λ_2 . b) Variation of Λ_1 (open circles) and Λ_2 (full squares) with preparation method. The size of the mesopores is increased in the calcined film compared to the acetic acid treated films.

The pore structure was further investigated with grazing incidence small-angle X-ray scattering (GISAXS). Figure 4.4 shows the measured scattering data together with the characteristic pore dimensions extracted from fits to the data. In the calcined film the size of the mesopores is larger than in the acetic acid treated film, indicating that calcination yields a higher film porosity than acetic acid treatment. This is corroborated by an analysis of the Yoneda peak positions: whereas the peak positions in the acetic acid and acetic acid treated and subsequently calcined films correspond to porosities of 72 % and 75 %, respectively, the porosity of the calcined film is 84 %. The data also show that calcination after acetic acid treatment does not further modify the pore size. In consequence, direct calcination is the preferable extraction method for preparation of films with large mesopores and a high porosity as they are required in hybid solar cells [4]. In summary, TiO₂ thin films were successfully structured on three different length scales. The application of this hierarchically structured films in a solar cell promises an increased efficiency compared to films consisting only of a mesopore structure due to the additional functionality provided by the macropores and the microstructure.

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4.3 Layer-by-layer fabrication of hierarchical structures in sol-gel templated thin titania films

J. Perlich, M. Memesa¹, J. S. Gutmann^{1,2}, P. Müller-Buschbaum

- ¹ Max-Planck-Institut für Polymerforschung, Mainz, Germany
- ² Johannes Gutenberg University, Mainz, Germany

Nanostructured titania thin films have gained great popularity in a variety of applications such as coatings, photocatalysis, gas sensing, and photovoltaics. For most of these applications a defined morphology of the titania nanostructures is crucial for the functionality and significantly influences the performance. The morphology determines the volume-to-surface ratio and hence the surface available for interfacial reactions. In order to increase the surface area by an increase of the total film thickness or to fabricate asymmetric films with multilayers of different structure sizes, layer-by-layer depositions via dip-coating are commonly applied. This yields an arrangement of a gradual multilayer ensemble consisting of individual layers with distinct morphologies.



Figure 4.5: Schematic representation of the multilayer approach (left). FESEM images with different magnifications after the final process in top view (right). The scale bar has a length of 1 μ m.

The presented investigation focuses on the preparation of hierarchical structures in an iterative layer-by-layer spin-coating approach as schematically presented in Fig. 4.5 [1]. The first layer of titania nanostructures with distinct size is prepared on top of the solid support. We use polystyrene-*block*-polyethyleneoxide (P(S-*b*-EO)) as the structure directing agent that is combined with a so-called good-poor solvent-pair-induced phase separation coupled with sol-gel chemistry. By adjusting the preparation conditions, a second layer yielding particles with decreased size is deposited on top of the preceding layer, hence resulting basically in a single layer of two superimposing hierarchical morphologies. Finally, particles with an again increased size are deposited. The entire ensemble of particles forms a system of hierarchical structures.

The structural investigation was performed with scanning electron microscopy (SEM) and complemented by grazing incidence small angle X-ray scattering (GISAXS). The surface sensitive GISAXS measurements were performed at the synchrotron beamline BW4 at HASYLAB using a moderate micro-focussed X-ray beam [2]. The final result of the preparation is imaged with FESEM. Fig. 4.5 shows the resulting titania morphology after the final preparation step. Titania granules of different size ranges are clearly identified. The overview image confirms a homogeneous spreading of the tailored structure. Further magnification reveals that the uppermost granules cover large amounts of small nanogranules (<100 nm) and very large granules (up to 1 μ m). The highest magnification also shows, that the large granules exhibit a nanostructured surface with structure sizes <10 nm. Hence several intrinsic structural level exists.

With GISAXS the nanogranules are addressed. Fig. 4.6a shows the 2D scattering patterns after the preparation steps I, II and III. The scattering pattern of step I shows a narrow intensity distribution in horizontal direction, thus a high contribution of scattered intensity with small q_y . Consequently, the characteristic lateral length scale Λ of the titania granules in the thin film is large. Following the scheme of Fig. 4.5, step II introduces much smaller nanogranules to the system and therefore, scattered intensity is expected at larger q_y . This can be clearly observed in the scattering pattern of step II by a broadening of the horizontal intensity distribution. Finally, introducing some granules in the mid-size range with preparation step III, the corresponding 2d scattering pattern indicates an increase of the scattering intensity in the mid-range q_y . This agrees nicely with the observed morphology in Fig. 4.5. For the quantitative analysis, line cuts in the horizontal direction from the 2D patterns are displayed in Fig. 4.6b. The cuts were performed at the critical angle of anatase titania. Characteristic lateral length scales Λ of the titania were modelled with form factors of the granules. A Lorentzian size distribution of Λ was assumed to account for statistical deviations from the mean size of the granules [3]. In the fit the experimentally determined resolution function was taken into account.



Figure 4.6:

(a) Composite image comprising GISAXS patterns after step I, II and III and (b) the corresponding horizontal line cuts from the 2D GISAXS intensity. The curves are shifted along the y-axis for clarity. The solid lines are fits to the data. The dashed line indicates the resolution limit. The two characteristic structural levels are marked with A and B.

After preparation step I, in addition to the unresolved micrometer size granules, a single most prominent characteristic lateral length A of 360 nm is extracted. The characteristic lateral length A corresponds to the mean granule size. The addition of much smaller granules in step II results in a second characteristic length B of approximately 90 nm. The characteristic length A remains unchanged. Finally, after again adding unresolved larger objects in step III, the characteristic length A and B both stay unchanged (indicated by the arrows in Fig. 4.6b). The extracted lengths fit nicely to the structural dimension observed with the FESEM images and prove that with additional spin-coating steps titania objects of desired size can be added without altering the size of the initially deposited ones.

In summary, the applied layer-by-layer spin-coating approach of sol-gel templated titania structures allows for a fabrication of hierarchical structures with multiple structural levels. GISAXS provides the information, that the once prepared structural levels are preserved throughout the complete three step process. Therefore subsequent calcination induces no morphological transition of the preceding structures. The results emphasize on the usage of such an approach on the superposition of even completely different morphologies, whereas tailoring is supplied by the selected sol-gel synthesis.

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4.4 Custom tailored titania nanostructures for application in hybrid photovoltaic systems

M. A. Niedermeier, P. Müller-Buschbaum

Titania thin film are commonly used in photovoltaics within dye-sensitized solar cells. These cells are typically composed of a transparent conducting oxide (TCO) on a glass substrate which serves as the front electrode and also as substrate for the porous titania film. The titania film is covered with a monolayer of dye (e.g. Ruthenium-complexes) which is followed by either an electrolyte containing I⁻ and I₃⁻ or more recently by p-type conductive polymers. The setup is terminated with a back electrode which can be for example platinum or gold.

The distinctive feature of this solar cell is the porous titania film. Since the absorption coefficient of the dye is too small, a monomolecular layer is not able to absorb sufficient sunlight. By using a porous instead of a bulk film the effective surface is increased by several orders of magnitude. This increase is directly transferred to the absorption of sunlight by the dye. Along this route, by tailoring an optimized morphology the overall efficiency of the solar cell can be largely increased.

By combining spin coating with the use of a sol gel processes we have a powerful tool to manufacture tailored nanostructured titania thin films. A diblock copolymer serves as a structure directing template to obtain nanocomposite films which are calcinated to obtain crystalline nanostructured titania thin films. The structuring of the diblock copolymer is achieved with a so-called good-poor solvent pair induced phase separation process. In his work, Cheng et al showed that by adjusting the weight fractions of the components a large variety of titania structures can be reproducibly fabricated [1]. This is very beneficial in a technological as well as a practical way as the same experimental setup is sufficient to produce all the different structures. We used two commercially available (Polymer Source Inc) diblock copolymers poly(styrene-block-ethylene oxide) (PS-b-PEO) with molecular masses of 25400 g/mol and 21000 g/mol, respectively. The respective molecular weights of the polystyrene and polyethylene oxide blocks were PS: 19000 g/mol, PEO: 6400 g/mol and PS: 16000 g/mol, PEO: 5000 g/mol. 1,4 Dioxan was used as good solvent for both polymer blocks and 37% HCl was used as bad solvent for the PS block. Titanium tetraisopropoxide (TTIP) was used as the sol gel precursor. From here on the two diblock copolymers will be referred to as PS-b-PEO-(25400) and PS-b-PEO-(21000).

Cheng used the PS-b-PEO-(25400) for his researches and his ternary phase diagram. The influence on the morphology of the new polymer's slightly different molecular weight and different weight ratios of the two blocks have been investigated with field emission scanning electron microscopy (FESEM) measurements.

sol gel process	w_{dioxan}	w_{HCl}	w_{TTIP}
Ι	0.92	0.04	0.04
II	0.935	0.015	0.05

Table: Weight fractions of the sol gel components.

The table shows the weight fractions for the sol gel processes I and II. Figure 4.7 shows two FESEM pictures from sol gel process I using PS-b-PEO-(25400) (a) and PS-b-PEO-(21000) (b). It can clearly be seen that the two different polymers don't produce the same structures despite the same weight fractions having been used. The PS-b-PEO-(25400) produces granulas ranging averagely from sizes of about 1 μ m to sizes down to 200 nm.

Additionally nanowires and nanowire aggregates with widths of less than 50 nm and lengths of several 100 nm ranging up more than 1 μ m can be distinguished. The PS-b-PEO-(21000) also



Figure 4.7:

FESEM images of the structures obtained after sol gel process I using (a) the PS-b-PEO-(25400) and (b) the PS-b-PEO-(21000) in top view. The scale bar in each image corresponds to a length of 500 nm.

shows granulas with sizes of similar range. However, the nanowire and nanowire aggregates can not be found. Instead small granulas and agglomerated granulas with sizes less than 50 nm are found all over the sample, covering partially the large granulas as well as the whole space in between.



Figure 4.8:

FESEM images of the structures obtained after sol gel process II using (a) the PS-b-PEO-(25400) and (b) the PS-b-PEO-(21000) in top view. The scale bar in each image corresponds to a length of 500 nm.

Figure 4.8 shows two FESEM pictures from sol gel process II using the (a) PS-b-PEO-(25400) and (b) the PS-b-PEO-(21000). Again a significant difference in the structure can be seen. The sol gel process using the PS-b-PEO-(25400) resulted in a densely packed nanodoughnut-shaped structure with diameters ranging from 1 μ m to less than 50 nm. Mreover, the nanodoughnuts are stacked on top of each other. The nanodoughnut structure is only rarely found on the sample with the PS-b-PEO-(21000). Here, the prominent structure are nanogranulas which range from 1 μ m down to 200 nm. It is also observable that those granulas are less densely packed. Just like observed in figure 4.7 (b) again very small nanogranulas mixed with occasional nanodoughnuts is observed at the sol gel process II.

Only from those first experiments we can conclude that even a slight change in polymer weight as well as a change in the weight fractions of the two blocks seriously affects the morphology of the obtained nanostructures. This pictures the sensitivity of the sol-gel rout to the used experimental conditions and put serious constraints to the reproducible use of block copolymers a structure directing agents.

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4.5 Controlled embedding of semiconducting nanoparticles in a conducting polymer template

M. A. Ruderer, P. Müller-Buschbaum

Conjugated polymers have shown to be interesting candidates for organic photovoltaics due to their high absorption coefficient, mechanical flexibility, easy processibility and low cost. Furthermore the possibility to tune the properties of these polymers makes a broad application feasible. Nevertheless there are stringent constraints in the morphology of the active layer due to the short exciton diffusion length (in the order of 10 nm), i.e. charge carrier separation has to occur in this length scale. Due to the improved charge carrier separation at interfaces a two component system is required. The main approach is the blending of two conjugated polymers. But while polymer blends tend to form structure sizes in the range of hundred nanometers [1], one promising approach are conjugated block copolymers which generate nanostructures in the desired range due to micro-phase separation. Besides using an all polymer system for photovoltaic applications so called hybrid systems combine properties of both, organic and inorganic systems. In such systems the structured inorganic component is typically used as a template for the organic component, e.g. a conjugated polymer.[2] Our approach uses a diblock copolymer with a rod like conjugated part and a coil like standard block as the template to control the embedding of inorganic nanoparticles.[3]

As a template thin films made of the rod-coil like diblock copolymer poly(p-phenylene-bstyrene) (P(PP-b-S)) are used whereas the rod like part is the conducting one. In equilibrium rod-coil like polymers form so called supramolecular structures due to micro-phase separation with a typical length scale in the order of 10 nm. Depending on the block ratio lamella, hexagonal etc. structures are formed. The thin films are prepared via spin coating from polymer solution which forms smooth films but in a non-equilibrium state. To reach equilibrium a subsequent annealing step, such as thermal or solvent treatments, is required. Besides annealing also the solvent has shown influence on the resulting structure (Fig. 4.9). In the case of toluene micelles of 19 nm diameters are already found in solution and transferred to the substrate. The subsequent thermal annealing has no influence on the micellar structure.[4] If THF is used as the solvent homogenous films are created. While thermal annealing generates a perforated surface, solvent annealing results in a smooth one. The inner structure of the smooth P(PP-b-S) films



Figure 4.9:

AFM images of P(PP-b-S) films prepared via spin coating from toluene (a) and THF (b,c) with subsequent thermal (a) or solvent (b,c) annealing. The color code is adjusted for each image separately.

made from THF with a following solvent treatment step where investigated with grazing incidence small angle X-ray scattering (GISAXS). Fig. 4.10 shows the 2d-scattering data (a) and the corresponding simulation with IsGISAXS (b). For the simulation a model consisting of cylinders of PPP embedded in a homogenous film of PS was used. The cylinders have a diameter of 10 nm and a height of 79 nm. For the distribution of the cylinders a one dimensional paracrystal with a mean distance of 16 nm was applied. That means that a nanostructured films of conducting cylinders in a amorphous styrene environment with a length scale which are favorable for photovoltaic applications were created.

As the second component titania nanoparticles with a catechol functionalization were embedded in the P(PP-b-S) films. Therefore the nanoparticles are dissolved in THF and mixed with



Figure 4.10:

a) 2d-scattering data of the GISAXS measurement of a P(PP-b-S) film made from THF with subsequent solvent treatment. b) The corresponding IsGISAXS simulation. For both images the same color code was used. c) Out-of-plane cuts of P(PP-b-S) films with embedded titania nanoparticles. The nanoparticle ratio is increasing form bottom (0 %) to top (20 %). The black arrow highlights the structure factor of the block copolymer and the red arrow marks the form factor of the embedded nanoparticles.

the polymer solution in different ratios up to 20 %. The resulting films were investigated with GISAXS. To extract lateral length scales from the 2d scattering pattern horizontal cuts, so called out-of-plane cuts, are carried out (Fig. 4.10c). The pure block copolymer film shows one feature (black arrow) which corresponds to a length scale of 16 nm and describes the distance between the cylinders as described above. With increasing nanoparticle ratio this feature gets less pronounced which means a decreasing contrast between the two polymers. Consequently, the titania nanoparticle balance the refractive index of the two polymers. As titania has an higher refractive index than both polymers the nanoparticles embed preferentially in the phase of the polymer with the lower refractive index, polystyrene in this case. Furthermore, with increasing nanoparticle content the marked structure factor shifts slightly to smaller q_y positions which means to higher length scales. Due to embedding of nanoparticles the polystyrene phase is swollen and the distance of the PPP cylinders is increasing. The second evolving feature in the out of plane cut (red arrow) corresponds to the form factor of the spherical nanoparticles.[5] In summary, homogeneous thin films of the conducting block copolymer P(PP-b-S) were prepared via spin coating. Micro-phase separation investigated with GISAXS was obtained by a solvent treatment step. The resulting length scale of 16 nm is favorable for photovoltaic applications. In a further step it was shown that titania nanoparticles preferentially embed in the polystyrene phase and therefore in the non-conducting part of the polymer. Consequently a conducting system with two separated conducting components was created.

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4.6 Possibility of magnetoelastic effects in magnetic nanoparticle diblockcopolymer nanostructures

L. Schulz¹, A. Omran, W. Schirmacher², B. Russ³, S. Vallopilly⁴, P. Böni³, W. Petry, P. Müller-Buschbaum

- ¹ Université de Fribourg, Fribourg, Switzerland
- ² also at Institut für Physik, Universität Mainz, Germany
- ³ TU Müchen, Phys.-Dept. E21, Garching, Germany
- ⁴ LENS, Indiana University Cyclotron Facility, Bloomington, IN, USA

Magnetic properties of nanoparticle systems are of great interest because, firstly, they form model systems for understanding the mechanism of disordered magnetism and, secondly, they have wide technological applications ranging from data storage including high-frequency loss-free switching over medical applications to the creation of new materials.

The magnetization as a function of an applied field of thin composite films, consisting of polystyrene-coated γ -Fe₂O₃ (maghemite) nanoparticles embedded into polystyrene-block-polyisoprene (PS-b-I) copolymer films have been measured The magnetization data show typical features of anisotropic super-paramagnets including a hysteresis at low temperatures and blocking phenomena. However, the data cannot be reconciled with the unmodified Stoner-Wohlfarth-Neel theory. Applying an appropriate generalization find evidence for either an elastic torque being exerted on the nanoparticles by the field or a broad distribution of anisotropy constants.



Figure 4.11:

Left: Calculated hysteresis curves for different elasticity parameters. Red dashes: $\gamma = K/3G$ =0 (Stoner-Wohlfarth theory), green lines (inwards) $\gamma = 0.5$, 1.0, 1.5, 2.0. Symbols: measured data of the 45 % sample at T = 2 K.

Right: Low-temperature curves for anisotropy spread compared to the elastic torque model and experimental data at 2 K

The left part of Fig. 4.11 shows the data at 2 K together with theoretical curves assuming in addition to a nonvanishing magnetoelastic anisotropy K and random orientation the existence of an elastic twist due to a torque exerted by the field. The control parameter is the ratio $\gamma = K/3G$ of the anisotropy and the shear modulus G, ranging between 0 and 2. One could take the good agreement with the data for $\gamma \approx 1$ as evidence for the presence of the elastic mechanism. As the bulk value for the magnetocrystalline anisotopy of maghemite is $K = 4.7 \cdot 10^3 \text{ Jm}^{-3}$ we see that we are dealing with values of a shear modulus G of the order of kPa. This is an extremely low value in comparison with typical shear moduli of macroscopic elastic materials.



Figure 4.12:

Left: Measured hysteresis curves at several temperatures. Insert: measured remanence (symbols) vs. theory (line).

Right: Calculated curves at the same temperatures. Insert: measured coercivity (symbols) vs. theory (line).

However, as the nanoparticles are loosely packed inside the PS pockets, and because the shear stiffness of our films is at the borderline of yielding, we consider such a value to be still realistic. However, we also found an alternative approach for explaining the low-temperature magnetization behavior. It is based on including a spread in the anisotropy constant K that could possibly arise from shape and surface effects. We make an ansatz with a normal distribution, characterized by an average value K_0 and a witdth δ_K . We find that the low-temperature magnetization curve can be also reproduced (with $\delta_K = 0.4K_0$) and the resulting curve agrees to the one obtained in the elastic torque model (Right part of Fig. 4.11)

The temperature dependence in the torque model was calculated by ackowledging the polydispersity of the particles measured by the out-of phase AC susceptibility. We obtained a lognormal distribution with relative width of 0.8. For each temperature particles larger than the blocking volume $V_B = 25k_BT/K$, are blocked and are assumed to act in the same way as at low temperatures. the "mobile" particles with $V > V_B$ are treated by standard equilibrium thermodynamics.

In order to obtain the correct switching behavior for decreasing h < 0, we realized that the activation barrier is lowered by a reversed field. In the two parts of Fig. 4.12 we compare the calculated finite-temperature magnetization curves with our measured ones between 2K and 100K. We see that we obtain rather good agreement. A striking feature is that the slope near H = 0, which from a naive point of view should obey a Curie law, becomes temperature independent as a combined result of the polydispersivity and the elastic effect.

Fig. 4.12 also shows a comparison of the measured remanence and the calculated one as a function of temperature obtained by evaluating the magnetization of blocked particles at h = 0. The theoretical coercivity values could only be extracted from numerical calculations and agree well with the experimental data (Fig. 4.12).

4.7 Direct polymer grafting on carbon nanotubes by means of SIPGP

A. A. Golosova¹, S. S. Funari², P. Lindner³, R. Jordan^{1,4}, C. M. Papdakis

- ¹ TU München, Department Chemie, Garching, Germany
- ² HASYLAB at DESY, Hamburg, Germany
- ³ ILL, Grenoble, France
- ⁴ TU Dresden, Department Chemie, Dresden, Germany

The aim of the project is to develop novel nanocomposites of block copolymers and functionalized carbon nanotubes (CNTs). A well-known problem when exploiting CNTs as active fillers in polymer matrix, is their poor dispersion ability and compatibility. Due to the effective van der Waals attraction, CNTs form large clusters and agglomerates, which behave differently from individual CNTs [1]. Chemical modification of CNTs is an elegant way to tune their surface properties and to improve the dispersion ability [2]. Moreover, grafting the polymers to the CNTs' framework proved to be more attractive compared to the modification with small molecules or chemical groups, since long polymer chains can help to unbundle the CNTs and to prevent their subsequent self-agglomeration.

To form stable polymer grafts from vinyl monomers, we use self-initiated photografting and photopolymerization (SIPGP) [3], which, to our knowledge, has not been reported yet for the modification of CNTs (Fig. 4.13). The easy and non-destructive procedure is found to be successful for the functionalization of single- (SW) and multi-walled (MW) CNTs with polystyrene (PS) (SWPS, MWPS) and poly(4-vinylpyridine).



Figure 4.13: Modification of CNTs with polystyrene grafts

Using Raman spectroscopy, after the modification we found a high conversion of sp^2 -hybridized carbons into sp^3 state, which can be estimated by the increase of intensity of the disorder mode (D-band) relative to the G-band which is due to the graphitic structure (Fig. 4.14). This means the polymers are covalently bound to the CNT framework and not just physically adsorbed. The longer the polymerization time, the higher the grafting density and length of the polymer grafts, which is confirmed by Raman spectroscopy and thermo-gravimetric analysis (Fig. 4.14, Table 1).





Raman spectroscopy of the SW CNTs: native (dots), modified with PS after 1 day of polymerization (dashed line) and 3 days of polymerization (solid line)

Atomic force microscopy (AFM) was used as a method of the morphological analysis of the native and modified CNTs, drop-cast onto mica from dilute suspensions of the CNTs in toluene.
	1 day polym	3 days polym
SWPS	9	15
MWPS	16	30





Figure 4.15:

AFM images of MW CNTs: native (a) and modified with PS after 1 day of polymerization (b) (c)

We observe an efficient deagglomeration of the CNTs after the modification, while their length is preserved, which means that the modification procedure is efficient and does not destroy the CNTs (Fig. 4.15).

SANS experiments were performed at D11 at ILL in order to study the effect of modification on the dimensions and aggregation behavior of the CNTs in solutions. Using different solvents, like deuterated toluene (d-toluene) on the one hand and low molecular weight polystyrene or a mixture of deuterated and protonated toluene on the other hand, we could highlight the PS shell or the CNTs themselves, respectively. The scattering intensity I(q) of the CNTs dispersed in PS exhibits a power law exponent between -2 and -3 over a broad q range independent of the level of functionalization of the CNTs (Fig. 4.16a). Thus, the dominant structures in the suspension of CNTs in PS are clusters of the nanotubes. Unbundling is not possible because of the high viscosity of PS. In contrast, a power law with a slope -1 is observed in the scattering curves from the modified CNTs dispersed in d-toluene (Fig. 4.16b,c), which is characteristic of rods. Though cluster formation in the d-toluene is still observed, CNTs (or small clusters of them) can be considered to be flexible on large scales (which is confirmed by the AFM images) and stiff on short length scales.



Figure 4.16: SANS on native and modified CNTs dispersed in PS (a) and d-toluene (b,c)

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4.8 Real time GISAXS investigation of cobalt metal deposition onto a polymer template

E. Metwalli, V. Körstgens, K. Schlage¹, S. Couet¹, G. Kaune, R. Meier, S.V. Roth¹, R. Röhlsberger¹, and P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Magnetic nanoparticles in an insulating matrix, such as a polymer matrix, have recently attracted tremendous interest due to the unique physical and chemical properties of the nanosized metal/polymer composites. A good control over the size, shape and spacing between nanostructured metal dispersed in a 3D polymer film matrix afford an opportunity to tune and optimize the magnetic response of the surface in a magnetic field. Many routes are used to fabricate magnetic metal polymer composites. Physical sputtering of cobalt (Co) atoms and plasma polymerization of a hydrocarbon monomer have been previously used to fabricate a uniform dispersion of metallic Co in a hydrocarbon film [1]. In the present report we used the sputtering technique [2, 3] to investigate the deposition of Co metal onto the cylindrical morphology of a polystyrene-block-polyethyleneoxide P(S-b-EO) diblock copolymer thin film. Utilizing a portable DC magnetron sputtering deposition system mounted at the beamline, grazing incidence small-angle X-ray scattering (GISAXS) is employed to investigate the in situ real time formation and growth of Co nanostructures on the polymer film. The GISAXS measurements were carried out at beamline BW4 of DORIS III storage ring [4, 5] at HASYLAB (DESY, Hamburg). The sample inside the sputtering chamber was placed horizontally (xy plane) and at an incidence angle $\alpha_i = 0.5^\circ$ by tilting the whole sputtering chamber with respect to the incidence X-ray beam using a goniometer. The incidence angle is well above the critical angle of both, the polymer film and the substrate ($\alpha_{c(PS)} = 0.154^\circ$, $\alpha_{c(PEO)} = 0.161^\circ$, $\alpha_{c(Si)} = 0.22^\circ$). Therefore, the Yoneda peaks of both materials and the specular peak are well separated on the 2D detector. The GISAXS 2D images were collect on a noise-free high resolution Pilatus-100k detector. The detector allows high time-resolution of 1 second. In 30 min we have collected 1800 images of the metal/polymer composite while Co is deposited on the polymer film in a real time mode. Due to limited dimension (487×195 pixels) of the Pilatus detector two identical measurements are performed to cover the full scattering image, in the first measurement the detector longer axis (195 pixel) is aligned parallel the sample surface (q_y direction) and in the second measurement the detector is rotated by 90° to orient the long detector axis in the q_z direction. The 2D GISAXS images (one second time scans) are shown in Fig. 4.17. The 2D image (Fig. 4.17a of the Co-free thin P(S-b-EO) copolymer film shows two intensity maxima (white arrow), on both sides of the specular beam stop, that originate from the interference of the PS-domains intercalated between two cylindrical crystalline PEO domains. This interference effect arises because the PS domains are separated by a preferential nearest neighbors (center-to-center) distance, D of 31 nm. The 2D intensity images of the Co metal/polymer composites are shown in Fig. 4.17b-r. As the amount of deposited Co increases (up to 200 s deposition time), the intensity of prominent rod scattering peak and an additional second order peak at 2q* appears in the scattering images (Fig. 4.17b-c). The latter rod scattering peaks gradually grow in intensity along the q_z axis (Fig. 4.17b-c). No additional characteristic scattering peaks are observed for the Co particles on the q_y direction. These results prove an extreme selectivity of the Co atoms on the PS domains as indicated by the increase of the scattering intensity of the characteristic polymer structural peaks.

With increasing the amount of Co at deposition time larger than 200 second, a broad diffuse scattering grows outwards (Fig. 4.171d-r) at the plane of incidence (at $q_y=0$). The continuous broad scattering in the 2d images indicates a non-specific deposition of the Co on the polymer film. A transition from selective to non-selective Co deposition starts at deposition time of about 200 s. Co atoms are non-specifically grows on the polymer template and due to high X-ray scattering cross section of the Co atom, an increase of a broad diffuse scattering that merge



Figure 4.17:

Composite image showing 2D GISAXS scattering patterns of (a) microphaseseparated P(S-b-EO) copolymer thin film, (b-r) after 1800 repetitions of one-second deposition at a rate of 0.4 nm/min of Co onto the polymer film. An image every 100 s Co deposition time is shown. A specular beamstop is used to shield the high intensity specular reflection peak. The white arrows indicate the rod scattering intensity maxima along the q_y direction. Note that the sample is placed upside down due to the sputtering chamber geometry. The composite image (b-r) every 100 s deposition time shows the development of a second order rod scattering peak and an enhanced intensity of the rod scattering pattern. Unspecific broad diffuse scattering starts to develop outwards from the X-ray plane of incidence at deposition time of 300s (image d) and indicates an initial continuous metal layer formation

into the characteristic rod peaks indicates the formation of a pseudo monolayer of Co metal on the polymer film. The same experiment is again repeated but the Pilatus detector was rotated by 90° so that a larger area of the detector is along the q_z direction. From the second set of images (not shown) an initial modulation peak along q_z appears after 500 s and indicates the formation of a continuous uniform Co layer. With increasing the deposition time, the number of modulation peaks along the q_z increases while the spacing distance decreases with growing the Co uniform film thickness. As a conclusion, the in situ real time GISAXS investigation is critical for understanding how the arrangements of Co metal correlates with the structure of copolymer domains within the film and opens new possibilities for the investigation of metal-polymer interactions. Our results indicate that Co atoms are deposited in registry with the polymer morphology up to a critical concentration. Upon further increase of the Co concentration, the deposition is not any more specific to the PS domains and instead a continuous metal layer is formed.

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5 Biopolymers



5.1 Pico- to nanosecond dynamics in phospholipid membranes

S. Busch, C. Smuda¹, L. C. Pardo Soto², and T. Unruh

- ¹ Eidgenössische Technische Hochschule Zürich, Switzerland
- ² Universitat Politècnica de Catalunya, Spain

Emulsifiers are of big importance in everyday life, whenever mixtures of oil and water have to be stabilized. One example from food industry is the emulsifier soy bean lecithin which one can find in every chocolate. It keeps the cacao oil from separating from the rest, keeping the chocolate homogeneously brown. Whilst this is more of cosmetic importance, there are also use cases where the emulsifier is important for the function – such as in parenteral nutrition.

The importance of emulsifiers in pharmaceutical applications is growing rapidly. The majority of newly synthesized drugs is not water soluble. Therefore, the well-known pharmaceutical forms as intravenous injections cannot be applied without big harm to the patient. One of the most promising ways to make these substances available to medicine is to prepare them as emulsions or suspensions, consisting of tiny lipophilic parts surrounded by the emulsifier in water.

Emulsions contain a liquid oil phase. They are easily produced but have the disadvantage to release the incorporated drug on a short time scale. This issue can be overcome by using suspensions which contain a solid oil phase, retaining the drug better. In order to mix the drug with the oily support medium, one produces an emulsion at elevated temperatures which is then cooled below the temperature where the nanoparticles crystallize and become solid.

This step is critical because the surface of the particles increases suddenly and is not completely covered by the emulsifier any more. During this stage, the particles can aggregate and form gels – which is not acceptable for a medical application. It seems natural that the mobility of the emulsifier is connected to its ability to quickly cover the particles again.

One of the most promising candidates for emulsifiers are phospholipid membranes. In fact, they are not only interesting from this application point of view but also because they are one of the most fundamental constituents of cells, building up the cell wall. The cell wall has to be both, solid and liquid at the same time – a barrier for nutrients and poisonous substances, allowing simultaneously the motion and interaction of membrane-bound proteins.

The molecular motion of phospholipids had in fact been a puzzle already for a long time: the motions seen with macroscopic techniques such as fluorescence microscopy were up to a factor 100 slower than the ones one had observed with microscopic techniques as neutron scattering. This means that there must be a transition from the fast to the slow motion between the two observed time scales.

The image of this transition which had been accepted for a long time was the one of a fast motion of the phospholipid molecule between its neighbours, trapped in a "cage" of those. On longer time (and length) scales, one would observe a different motion, namely the one caused by some rare escape events of the molecule from this cage. As this would not happen often, the resulting motion would be slower.

This view was challenged recently, when molecular dynamics (MD) simulations of such large systems became feasible for longer times. In these simulations, the escape from the cage of neighbours was not observed. Instead, the molecules seemed to perform collective motions in rapidly assembling and disassembling patches, exhibiting a flow-like behaviour on short time scales.

We have therefore studied the dynamics of the stabilizing phospholipid DMPC with and without a variety of additives using quasielastic neutron scattering. This has been done with much improved instrumentation compared to the original works on the time-of-flight neutron spectrometer TOFTOF at the FRM II. Quasielastic neutron scattering employs a neutron beam with a well-defined energy. The sample is then interacting with the neutrons, changing both, direction and velocity of the neutron during this interaction. If the atoms in the sample do not move, they do not exchange energy with the neutrons – their energy after the interaction is the same as the one before. If the atoms in the sample are moving, they can give small "kicks" to the neutrons and vice versa: the energy distribution of the neutrons after the interaction is broadened. The width of the energy distribution is directly connected to the speed of the motions in the sample.

One parameter which can be varied between experiments is the interaction time between neutron and sample. A fundamental relation in Quantum Dynamics, Heisenberg's uncertainty principle, links this interaction time directly with the precision with which the neutron beam was prepared before the sample: the smaller the energy distribution of the neutrons that impinge on the sample, the longer is their interaction time with the sample. It is therefore possible to study both, short (pico-) and long (nanosecond) timescales by varying the energy distribution of the neutrons.

The data are compatible with the old measurements – assuming diffusion as transport mechanism yields a much too fast motion compared to the macroscopic values. However, assuming a flow-like motion, the data can be just as well (or better) described. The data are therefore completely compatible with the simulation and suggest that also the old data sets, if re-evaluated, would be in agreement with this new view of the long-range motion in phospholipid membranes, making the assumption of escaping the cages unnecessary.

This result is not only important for the fundamental understanding of the diffusion mechanism in phospholipid membranes. From this point, one can go further and study the influence of different co-stabilizers on the dynamics of the phospholipid. We have done so using a variety of additives – which do not show any influence on the dynamics of the membrane. The only exception has been Cholesterol which strongly reduces the mobility.

A decrease of the mobility after addition of cholesterol has also been observed with other methods and is thought to be connected to the formation of so-called lipid rafts which could host some groups of proteins which can by this means be grouped into functional units.



Figure 5.1:

A possible scenario for a crystallizing emulsion stabilized with phospholipid molecules. Left: An Emulsion droplet with stabilizing molecules. The droplet is surrounded by a complete monolayer and some surplus material. Middle: When decreasing the temperature, the droplet becomes solid and changes its form drastically. The surface increases and is not completely covered by the stabilizer any more. Right: After some time, the stabilizing molecules have re-arranged themselves such that the particle is completely covered again.

5.2 Influence of film morphology on the swelling of thin casein films

E. Metwalli, R. Gebhardt¹, V. Körstgens, R. Cubitt², U. Kulozik¹, P. Müller-Buschbaum

- ¹ TU München, Chair for Food Process Engineering and Dairy Technology, Freising-Weihnstephan, Germany
- ² ILL, Grenoble, France

Casein micelles in milk form unique bio-colloids from calcium, phosphate, and proteins. Due to their binding ability, casein micelles for non-food applications include coatings, adhesives, paints, textile fabrics and cosmetics. Four main types of proteins are involved in the casein micelle: α_{1s} -casein (38 %), α_{2s} -casein (10 %), β -casein (36 %) and κ -casein (13%), which form hydrated casein micelles about 100 nm in size [1]. Various models [2] have been proposed to describe the casein micelle structure including coat-core, sub-micelle, and the internal structure. Casein-associated water molecules are divided into different classes based on the method used to study the system. In general, for dairy protein systems, they are classified [3] as (1) structural water, i.e., water molecules directly involved in the stabilization of the protein structure; (2) hydration water, which refers to a monolayer of water molecules that is dynamically oriented and exhibits restricted motion due to a significant decrease in the translational and rotational modes of motion caused by macromolecular-water interactions; and (3) hydrodynamic hydration water, which is transported with the protein during diffusion in an aqueous solution. GISANS technique provides a better way to make detailed investigations of the hydration water. A dry casein film format together with the surface sensitive technique GISANS is an interesting



Figure 5.2:

Line cuts along the surface normal (q_z cuts) of the GISANS 2d intensity, measured at 30°C for 1 min up to 60 min swelling time, show a well pronounced Yoneda peak. A shift of the peak position towards higher q_z values is observed for time up to 11 min.

approach to probe the casein protein water hydration when compared with solution-based techniques such as SAXS or NMR. Our previous investigation [4] on water uptake of native casein protein films by the time-resolved GISANS indicated that the water content reaches an equilibrium after about 10 min and the native micelle (100 nm in size) exists in coexistence with smaller objects, called mini-micelles (15 nm). Such mini-micelles are detectable due to progressive formation of high contrast D₂O outer shell on these small objects. As the temperature of water vapor treatment increases, an aggregation of the mini-micelles in size up to 180 nm is formed.





Within the present work this systematic study has been further extended to explore different casein protein film morphologies. Changing the casein film morphology is achieved by varying the equilibrated size distributions of the micelles in solution using EDTA, then, casein protein is deposited on solid silicon support by spin coating method. Despite, the Ca²⁺ ions are removed by EDTA the casein protein is chemically similar to native one, but, the internal structure is different. In-situ GISANS was employed to investigate the structure of Ca-free casein films as a function of D₂O uptake at different temperatures. The one minute GISANS scans indicated an equilibrated structure is again achieved after <10 min (see Fig. 5.2). Preliminary data analysis indicates that the small objects (15-20 nm) in the Ca-free casein protein film are clearly discriminated at $q_y = 0.26 \text{ nm}^{-1}$ (see Fig. 5.3) with much less number of the large micelles (>100 nm). Upon water uptake at higher temperatures possible aggregation of the so called mini-micelles in water-vapor is indicated by an increase of the overall the intensity at low q_y values. Both data on native and Ca-free casein protein film are complementary and will be used to draw a clear picture of the role of water hydration layer in coexistence and aggregation of both the large and mini- casein micelles.

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5.3 Structural changes of casein micelles in rennin gradient films

R. Gebhardt¹, U. Kulozik¹, M. Burghammer², C. Riekel², P. Müller-Buschbaum

- ¹ TU München, Chair for Food Process Engineering and Dairy Technology, Freising-Weihnstephan, Germany
- ² ESRF, Grenoble, France

We investigated the effect of rennin on the micelle structure and microstructure of casein films with micro-beam grazing incidence small angle X-ray scattering (μ GISAXS) and optical microscopy. The main enzyme of the rennin extract, the protease chymosine, splits the polypeptide chain of κ -casein, which induces coagulation of the casein micelles. In order to investigate the enzymatic reaction we followed two approaches.

First, we prepared a casein film consisting of casein micelles and a superimposed rennin gradient. The concentration of rennin within the gradient varied by four orders of magnitude. Using micro-beam grazing incidence small angle X-ray scattering we determined the sizes of casein micelles and colloidal calcium phosphate particles as a function of rennin concentration within the gradient film.





Mean sizes *D* for casein micelles (dots), the smaller casein component (rectangles) and colloidal calcium phosphate particles at varying rennin concentration; figure taken from [1].

We showed that the size of the casein micelles decreases with increasing rennin concentration while the size of the colloidal calcium phosphate clusters remains constant. In accordance with a first-order enzyme reaction mechanism, we could describe the rennin-induced decay of the micellar sizes by an exponential function. In addition, we observed two distinct film morphologies at high and low rennin concentration using optical microscopy. At intermediate rennin concentration we found a two-phase surface structure in which both film morphologies coexisted.

Second, we performed a μ GISAXS scan to investigate changes on the multi-level structure of casein micelles that occur after deposition of a droplet of rennin on a casein film. We found that the diffusion of the droplet into the film led to an increased surface roughness and a formation of islands due to the concentration gradient of rennin. We could quantify the concentration profile of rennin due to the diffusion process since the altered surface morphology resulted in a significant variation of the GISAXS pattern, more precisely in the occurrence of a second Yoneda peak. This second Yoneda peak showed a strong dependence and a compensatory effect with respect to the original one. Thus, we could determine a diffusion constant *D* for rennin in a casein film by evaluating the variation of the Yoneda peak intensity as a function of the diffusion time *t*.

Compared to the untreated film, no change in mean size of the micelle components (casein micelles, substructure and colloidal calcium phosphate) could be detected within the rennin droplet area. In contrast, a broadening of their corresponding size distributions became evident.



Figure 5.5:

Calculated size distributions for casein micelles (mean size 120 nm), for the casein micelle substructure (mean size: 12 nm) and for colloidal calcium phosphate particles (mean size: 1 nm) measure in the untreated (solid line) and rennin treated film area (dashed line); figure taken from [2].

The experimental results can be explained assuming that only surface near casein micelles become solvated and enzymatic treated after rennin droplet deposition. The remaining casein micelles kept their native structure and size within the casein film.

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6 Alloys



6.1 Phonon properties of Ni-Mn-Ga shape memory alloys in martensite and austenite phases

S. Ener, J. Neuhaus, K. Hradil¹, R. Mole, P. Link, W. Petry

¹ Georg-August-Universität Göttingen, Institut für Physikalische Chemie, Göttingen, Germany

Shape memory alloys exhibit a shape recovery of a given sample after mechanical deformation by cycling through a structural phase transition. In magnetic shape memory (MSM) materials it is possible to obtain a shape memory effect by applying an external magnetic field instead of changing the temperature. These smart materials are suited for technical applications like actuators as they can achieve fast shape changes. Elongations up to 10% even at frequencies up to several kHz were observed in an off-stoichiometric Ni₂MnGa Heusler alloy [1].



Figure 6.1:

Phonon dispersion of $Ni_{49}Mn_{32}Ga_{19}$ of the high temperature austenite $L2_1$ phase. The scatters are the experimental values, the solid lines represents calculations with a BvK model (work in progress).

We investigated the vibrational properties of Ni-Mn-Ga alloys with two different compositions. Small changes in composition allow to adapt the crystallographic and magnetic phase transition temperatures for future technical applications. To understand the physical origins of the phase transitions we investigated the phonon dispersion of the high temperature austenite as well as the low temperature martensite (5-layer modulated) phase for an off-stoichiometric Ni₄₉Mn₃₂Ga₁₉ alloy. The temperature dependence of the phonon modes of the TA₂ branch were also investigated in a stoichiometric Ni₂MnGa sample. The phonon measurements were carried out on the three axes spectrometers PUMA (thermal neutrons) and PANDA (cold neutrons) at the FRM II.

Fig. 6.1 shows the dispersion of the high temperature L2₁ phase at 373 K. The phonon measurements were taken along the high symmetry directions [$\xi\xi\xi$], [ξ 00] and [$\xi\xi$ 0]. The most striking feature in the austenite phase is the anomalous phonon softening in the TA₂ phonon branch near ξ =0.3. Fig.6.2 shows the temperature dependence of the modes near this anomaly. For the stoichiometric sample a change in the anomalous softening occurs near the Curie temperature. Below the structural transition temperature (austenite to pre-martensite 3M phase) the phonon frequencies are increasing again (Fig.6.2a). The correspondence of the Curie and structural phase transition temperature to the change of the phonon behaviour, however, is not precise. For the off-stoichiometric sample the behaviour looks similar (Fig.6.2b), but the change in the dynamical behaviour does not at all follow the magnetic transition as it has been reported in literature for similar alloys [2].

The off-stoichiometric Ni₄₉Mn₃₂Ga₁₉ alloy transforms to an orthorhombic 5-layer modulated martensite phase below the structural transition temperature. The high symmetry directions





 $[\xi\xi\xi]$, $[00\xi]$, $[\xi00]$, $[\xi\xi0]$ and $[0\xi\xi]$ were measured with the instrument PUMA at room temperature (Fig.6.3a). No particular softening in the TA₂[$\xi\xi0$] phonon branch was observed, the entire branch stiffens on cooling. Compared to the austenite phase additional low energy excitations of the modulated structure appeared (Fig.6.3b). At very high frequencies another optical branch showed up which has not been observed in the austenite phase. Further analysis will provide thermodynamical properties like vibrational entropy and comparison to known [3] and ongoing first principle calculations.



Figure 6.3:

(a) Phonon dispersion of $Ni_{49}Mn_{32}Ga_{19}$ in the 5M structure at room temperature. The solid lines are for eye guide. (b) Iso-intensity plot of the low energy excitations.

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6.2 Irradiation induced creep and growth of zirconium-based alloys for PWR guide tubes

R. M. Hengstler

Zirconium-based alloys have been used as nuclear power reactor core internals for decades, due to their low thermal neutron cross section, their mechanical stability and low chemical interaction that minimizes corrosion and hydrogen uptake with subsequent material embrittlement. Pressurized water reactor ("PWR") guide tubes made of zirconium-based alloys as a polycrystal with anisotropic hcp lattice structure show creep and growth under neutron irradiation. These dimensional changes result in length changes of the fuel assemblies as a whole that are acceptable in certain limits but should be minimized. The microstructural processes in the material during neutron irradiation depend on various parameters like internal and external stress, temperature, neutron flux and dose and are currently not sufficiently understood. Further investigation of the microstructural material changes by neutron irradiation could improve the behavior prediction for new fuel assembly designs where operational experience is lacking, e.g. for EPR. Since in-pile experiments in PWR environments need a long period of time, are very cost extensive and limit the number of specimens, ion irradiation as a method for neutron damage simulation in guide tube materials is being studied in the context of a PhD thesis in cooperation with AREVA NP GmbH, Erlangen. The specimens are not necessarily activated by ion irradiation which could provide a very cost effective method for the study of irradiationinduced creep and growth.

It has been reported by several authors that, under certain experimental conditions, ion irradiation can be used to create the same irradiation damage as neutrons [1]. In Zr-based alloys, the expected damaged microstructure contains vacancy and interstitial loops of specific size and density distributions and lattice orientation. These structures can be directly observed by transmission electron microscopy ("TEM") and indirectly by material analysis techniques that are sensitive towards lattice defects, such as positron spectroscopy or X-ray microbeam diffraction. Thus, as a first step towards a parameter study of Zr-based alloys under ion irradiation, ion irradiation under different experimental conditions with subsequent post irradiation examination was conducted in 2009 to find the best experimental parameters for the neutron damage simulation.

Several ion accelerator beamtimes have been conducted at the MLL tandem accelerator and the tandem accelerator of the Max-Planck-Institute for Plasmaphysics with irradiation temperature and dose corresponding to typical PWR environments. Zr-90 was used as projectile to avoid chemical interaction between projectile and target.

As compared to neutrons, ion irradiation leads to an inhomogeneous damage profile in the target with a damage peak of about 1 μ m thickness in a depth of several μ m at the used experimental conditions. That geometry requires special preparation techniques to cut a TEM lamella with a typical thickness of 50 nm out of the damage peak region. Standard focussed ion beam cutting can be used to reach the damage peak region but leads to heavy irradiation damage by the beam; that damage has been minimized by adjustments of beam current and ion energy and tests with subsequent ion milling. The heating of the TEM samples under the electron beam during examination at certain conditions favors the formation of a zirconium oxide layer on the lamella's surface. These artefacts have to be avoided to ensure that the microctructure examined under the TEM is the structure created by the ion irradiation and not influenced or altered by the preparation techniques. Therefore, several alternative mechanical or chemical preparation methods are being tested at the moment.

A first indirect microstructural analysis of Zr-alloy specimens irradiated to low ion fluences of $5 \cdot 10^{13} \text{ cm}^{-2}$ to $1 \cdot 10^{14} \text{ cm}^{-2}$ at room temperature has been conducted by positron Doppler spec-

troscopy at the FRM II's NEPOMUC facility. The analysis shows a good distinction between unirradiated and irradiated regions and gives a clear depth dependence of the s-parameter, a measure for the defect density, as predicted by theory and simulation calculations by the TRIM Monte Carlo code [2]. The s-parameter in the irradiated area is more than 5% higher than in the unirradiated region (see figure below).

Further and more detailed damage analysis by positron spectroscopy is planned for 2010, as well as X-ray microbeam analysis and extended TEM investigations.



Figure 6.4: Depth dependence of the defect density in Zr-irradiated Zry

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7 Methodological and instrumental developments



7.1 In situ characterization of polymer nanostructures with a new developed combination of GISAXS and imaging ellipsometry

V. Körstgens, J. Wiedersich, R. Meier, J. Perlich¹, S.V. Roth¹, R. Gehrke¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

In a new method we expand the possibilities of the surface sensitive scattering method grazing incidence small angle x-ray scattering (GISAXS), by the integration of imaging ellipsometry [1]. GISAXS allows the investigation of nanostructures with high statistical relevance, and probes not only surface structures but also buried structures. As both methods, imaging ellipsometry and GISAXS, offer the opportunity for in-situ measurements, the full advantage of the combination of GISAXS and imaging ellipsometry arises for kinetic studies where the influence of external parameters like temperature, gas pressure, pH or ion concentration on the morphology is followed. Correspondingly, processes can be investigated simultaneously with the two independent methods GISAXS and imaging ellipsometry.



Figure 7.1: Ellipsometer installation at GISAXS beamline BW4 with accentuation of some functional parts pictured.

The imaging ellipsometer SPEM, a single wavelength (532 nm) instrument, of Nanofilm Technologie GmbH, was installed at the beamline BW4 at HASYLAB (DESY, Hamburg) as shown in figure 7.1. The concept of the combined instrument is that the sample is placed horizontally (xy plane) on the alignment stage of the ellipsometer. After ellipsometric alignment and measurement with a lateral resolution of 1 μ m the desired incidence angle for the x-ray beam is set by tilting the whole ellipsometer including the laser arm and the detector arm using a 2-circle segment. The orientation of the sample with respect to the laser beam is not affected by this procedure. In the performed experiment, the sample-to-detector distance was set to 2.089 m and a beamsize of 24 μ m x 42 μ m focused on the sample position was used. Most of the x-ray flight path was covered with evacuated flight tubes except for the sample position to freely move the imaging ellipsometer. Once the sample was aligned correctly on the ellipsometer, ellipsometric measurements were possible, independent of any operational x-ray scattering experiment. The changing of the angle of incidence of the x-ray beam has no influence on the ellipsometer measurements since the ellipsometer is moved always as a whole in the x-ray beam. A singular calibration of the instrument is necessary to ensure that the laser beam and the x-ray beam cross each other at one known point on the sample surface. That means one has to match the central position in the field of view of the ellipsometer when the sample surface is in focus with the position where the x-ray beam hits the surface. For a first coarse adjustment thin films of polymer material especially sensitive to x-ray radiation damage turned out to be very suitable because it was possible to directly follow the foot print of the x-ray beam in the ellipsometer images during any movements. In a second step a higher precision in the calibration procedure was achieved with the use of lithographic channel structures. Due to the channel structures it was possible to correct for small deviations in the y-position and to precisely align the 90° angle arrangement between x-ray and laser beam installed. In the GISAXS experiment the scattering patterns are strongly influenced if the x-ray beam does not hit the lithographic channel structure in parallel. An alignment precision of better than 0.01° was achieved.



Figure 7.2:

In situ experiment of a drying droplet of nanosphere dispersion a) optical images recorded with ellipsometer b) 2D GISAXS pattern with starting time of data acquisition, <0 denotes the substrate before droplet deposition.

One investigated example application is the ordering of polystyrene nanospheres. The drying of a drop of monodisperse polystyrene nanosphere dispersion on a rough substrate is followed in situ. The rough substrate is established by dewetting of a thin film of a diblock copolymer. The height of individual islands of the dewetted structure was determined as 120 ± 30 nm with imaging ellipsometry. In figure 7.2a the images of the substrate before droplet deposition (<0s) and at various times after droplet deposition captured with the ellipsometer are shown. The corresponding 2d scattering patterns are shown in figure 7.2b denoted with the time when data acquisition was started. With droplet deposition the surface of the drop is vaguely pictured on the optical image and the corresponding scattering intensity is very low in comparison to the substrate before droplet deposition. Due to the distinct curvature of the droplet in the first 1000 s of the drying process a grazing incidence condition is not fulfilled for the x-ray beam hitting the surface of the drop. Only weak intensity is displayed on the detector because the large droplet volume absorbs strongly the transmitting x-ray beam. With further evaporation of the dispersant water the thinning of the liquid layer with dispersed nanospheres can be followed by the appearance of Fizeau fringes in the images taken with the ellipsometer (figure 7.2a; 1320) s). The corresponding scattering pattern shows an increasing intensity close to the direct beam. With further thinning the layer is translucent and the island structure of the substrate is visible on the images taken with the ellipsometer (figure 7.2a; 1650 s). The ordering of nanospheres is evident not before 1980 s, when the scattering pattern evolves (figure 7.2a: 1980 s). The experiment shows that only after solvent evaporation the typical scattering pattern with a SAXS signal superimposed by the GISAXS signal does built up.

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7.2 Selected activities of the HEU-MEU group at FRM II in 2009

H. Breitkreutz, R. Jungwirth, W. Schmid, S. Dirndorfer, W. Petry

In 2009, the HEU-MEU group at FRM II continued its activities to develop a new fuel for FRM II, on the theoretical as well as on the experimental side. In the following, an overview of the major activities of the group is given.

7.2.1 Heavy ion irradiation of several kinds of UMo/Al samples (R. Jungwirth)

Disperse UMo/Al is a candidate for the new fuel of FRM II. Up to now, this fuel suffers from strong irradiation induced diffusion processes during in-pile irradiation. Si seems to suppress the formation of the undesired interdiffusion layer (IDL) forming during in-pile irradiation of UMo/Al dispersion test fuel plates. It has been found that adding Si to the Al matrix of this fuel results in the formation of a Si-rich diffusion layer (SiRDL) covering the UMo particles. This layer obviously forms during the production process before irradiation. It is therefore of great interest to find the minimal Si content that has to be added to the Al matrix to obtain a sufficiently thick and homogeneous Si-rich layer coating the UMo particles.

We examined three different UMo/Al,Si miniplates with an Al matrix containing 2wt% Si (alloyed AlSi powder) as well as 5wt% and 7wt% Si (Al+Si blended powder). These samples had been produced by conventional hot rolling by AREVA-CERCA. A Si rich layer has formed around each UMo particle in the 5wt% and 7wt% Si case. In contrast, no Si rich layer has been found in the 2wt%Si case (compare Fig. 7.3).





Further more we examined the development of the IDL formed through a heavy ion irradiation

test which took place at the MLL tandem accelerator in Garching/Germany.

It has been found that the SiRDL is attacked by the radiation induced diffusion layer. The SiRDL does therefore not by itself protect the UMo particle from the growth of an IDL during heavy ion irradiation since the SiRDL is dissolved inside the IDL (compare Fig. 7.4). The degree of decomposition is dose-dependent. When the SiRDL has been completely dissolved, a normal UMo/Al diffusion occurs in case there is no Si particle nearby. In case that a Si particle is in close contact to UMo, the resulting IDL is Si rich. Furthermore, the thickness of the IDL is significantly reduced in case that the UMo particle and the Si particle are in contact.



Figure 7.4:

IDL (red arrow) growth around UMo particles protected by a SiRDL into two steps. Details of the transversal cross section of the heavy ion irradiated part of the UMo/AlSi7 miniplate. An IDL has formed according to the penetration depth of the heavy ions. A SiRDL is visible around the UMo particle (green arrows). A-The two UMo particles located at the sample surfaces are surrounded by first a SiRDL and then an IDL. Area taken at the periphery of the irradiated zone i.e. where the final fluency is lower. B: In the upper part of UMo particle embedded in the Al matrix, the SiRDL has been dissolved by the IDL formed during heavy ion irradiation. The IDL is directly in contact with the UMo particle core. C: A standard UMo/Al interaction occurs and the shape of the UMo particle indicates clearly that UMo has been consumed in the interaction.

7.2.2 Sputtering of monolithic UMo folis (W. Schmid)

The fuel development group is investigating DC magnetron sputtering as an alternative technique for UMo fuel plate production. We want to use sputtering for the two steps necessary to produce reactor fuel plates from UMo, which is the manufacturing full size monolithic UMo fuel foils on the one side as well as surrounding UMo fuel foils with diffusion preventive layers and cladding layers on the other side.

The sputtering process offers two advantages in comparison to the existing thermo-mechanical fuel processing techniques: First, sputtering allows to grow perfect layers from any desired material on any substrate in any size. This means, that monolithic full size foils and blank sheets from any given UMo alloy can be produced in one single processing step and that a given UMo foil produced by sputtering or another processing technique can be surrounded with a layer of any other material in just one further step, be it as a diffusion preventive barrier or as a cladding. Thus sputtering develops fuel plate production from the existing very extensive, error-prone and multi-step processes to a simple two-step process. Second, sputter-deposited layers offer the advantage to have a very good, in the optimal case even the maximum physically possible adhesion to each other if the process is prepared properly.

Therefore material combinations can be realized that cannot be produced with conventional techniques as welding. This means, that the bonding of sputter deposited fuel, diffusion barrier and cladding layers to each other does not occur as a possible production problem at all, as sputtering automatically guarantees a good adhesion.



Figure 7.5: Schematic view of the tabletop sputtering device.

On laboratory scale the sputtering technique provides the opportunity to quickly produce a large number of tailored high quality samples for experiments or even a small number of tailored high quality full-size fuel plates for irradiation tests and further examinations. This is the primary aim of our efforts. The applicability of sputtering to industrial scale fuel plate production seems promising but certainly needs further development and is not examined by our group.

Over the last two years we built up two DC magnetron sputtering assemblies: a small tabletop setup for the production of samples with a size up to $100 \text{ mm} \times 100 \text{ mm}$ as well as a full-size plant for the fabrication of plates sized $700 \text{ mm} \times 65 \text{ mm}$, which is a common dimension for a large test plate. Both assemblies have successfully been operated in the past with surrogate materials and the processes of full size foil production as well as cladding respectively barrier layer deposition have successfully been shown.

In mid 2009 the operation of the tabletop setup was changed from the test phase with surrogate materials to the standard operational phase with UMo. A large number of monoand multilayered samples from DU-8wt.%Mo (DU: depleted uranium) and other materials have been produced since then: samples of $10 \text{ mm } \times 10 \text{ mm}$ size and several micrometers thickness for irradiation tests and microscopy, samples of $25 \text{ mm } \times 25 \text{ mm}$ size and 10-20micrometers thickness for tensile and shearing tests as well as samples of $100 \text{ mm } \times 100 \text{ mm}$ in size and one to 150 micrometers thickness for manufacturing, irradiation and thermal annealing tests. Most of the samples were produced for the fuel development group at FRM





II, but we also provided samples for SCK-CEN (Belgium), TRIUMF (Canada) and CEA (France).

Examinations of the produced samples show, that sputtered DU-8wt.%Mo is in the desired tetragonal γ -phase after the sputtering process, and the composition of the material does not change during the sputtering process within the errors of measurement. Both questions are crucial for the utilization of sputtering as fuel processing technique and will be further investigated by more precise measurements.

In 2008 and 2009 the full-size sputtering plant was mounted inside a glove box to enable an operation under inert atmosphere. The glove box guarantees, that the quantity of present oxygen and water during the production of foils, barrier layers or cladding and even during handling of the material is always below 1 ppm, which results in a nearly complete elimination of oxidation and oxide layer formation in all process steps. The glove box with the full-size plant was installed in a radioisotope laboratory in 2009 and received the approval for operation with radioactive materials by the Technical Supervisory Association (TÜV) and the Bayerisches Staatsministerium für Umwelt und Gesundheit in November 2009. The standard operational phase started in December 2009. First plate production is expected in the first quarter of 2010.

7.2.3 Tensile tests on monolithic samples (S. Dirndorfer)

Another possible candidate for the new fuel is the monolithic form of UMo, again with 8 wt.% molybdenum. As new techniques are necessary to fabricate this fuel, the bond strength of the monolithic fuel plates to the cladding and / or the diffusion barrier is an aspect of worldwide studies and to date relatively unknown. The bond strength is considered to be a plausible indicator for the quality of the mechanical contact. At FRM II monolithic specimens are produced by technique of sputtering. To get more information about bond strength of sputtered fuel plates, sputtered specimens have been subjected to tensile test which were executed according to ASTM C633 designation as far as possible.

Using tensile tests the bond strength of the following material combinations have been exam-

ined: U-Mo / cladding, U-Mo / diffusion barrier and diffusion barrier / cladding.

Double layer foils, consisting of uranium-molybdenum alloy with 8 wt.% Mo (DU-8Mo) as fuel surrogate, AlFeNi or Al 6061 as cladding and Ti, Bi, Zr or Zry-4 as diffusion barrier material have been used. They have been produced by sputtering or hot rolling. Beforehand the behaviour of the bonding agent used to mount the specimens onto the specimen holders has also been examined. Figure 7.7 shows two bonded specimen holders.



Figure 7.7:

Two bonded specimen holders. In later experiments, the sample will be bonded to the specimen holders by the adhesive on both sides.

Preparation of specimen holders was done in the following way: A cleaning of the specimen holders, grit blasting, in-depth cleaning after sandblasting by using an ultrasonic bath with acetone are good adjusted processes which delivered a high bond strength of the bonding agent.

Before bonding the two specimen holders that shall be sticked together, had to be cleaned with acetone and by using a fluffree cloth. The bonding agent is placed onto the cleaned surface and dispensed by a spatula. If specimen should be tested it had to be placed onto surface with bonding agent. The other specimen holder which is also coated with bonding agent has been placed onto the first one by using a prismatic pair (something like V-blocks to stabilise specimen holders during tempering process and avoid slipping). They also ensure that the two holders were sticked together without any offset. A vise or an equal fixing tool holds the prismatic pair together during tempering process.

Tensile tests have been executed with Zwick Roell Z100 a standard machine for tensile testing (see figure 7.8).

As bonding agent EP-15 from Masterbond Inc. has been used and it showed a bond strength of (70.03 \pm 4.96) MPa at optimised parameters. A breakdown of results on different tempering parameters is shown in figure 7.9. The parameters differ only slightly, so that the overall value



Figure 7.8: Tensile testing machine

with error quoted above has been generated for these measurements. The bond strength of this bonding agent will serve as basis for all later measurements.



Figure 7.9: Results for bonding agent

7.2.4 Coupled 3D neutronic thermohydraulic calculations (H. Breitkreutz)

With the increasing demand for 3-dimensional results with high spatial resolution in nuclear reactor physics for neutronic as well as for thermohydraulic calculations, it was necessary to develop a coupled code system to satisfy these needs also for compact core research reactors. In a first step, results for the typical fuel plate and its attached cooling channel in the core of FRM

II were regarded.

The objective was to use the latest versions of state-of-the-art codes for neutronics and computational fluid dynamics (CFD) and combine them in a way that they automatically exchange data and produce highly detailed steady-state solutions for both neutronic and thermohydraulic questions. No changes should be required to the used codes at all, but only additions that can easily be ported to newer versions of the codes when they become available. Due to computational limitations on the thermohydraulic side, separate models had to be set up for the Monte Carlo (MC) simulation and the CFD calculation. The CFD model takes advantage from the cylindrical symmetry of the FRM II core and therefore includes only a small extract from the MC model. Especially the CFD model was constructed to include every detail of the real geometry in order to resemble the flow as close as possible. By solving the Navier-Stokes equations, it was possible to resolve yet unknown details of the flow in the cooling channels of the compact core.

The neutronic calculations were carried out with the latest version (2.7B) of MCNPX, a widely used Monte Carlo code. All necessary particles including delayed gammas were included in the simulations to get the distribution of the energy deposition as accurate as possible. A cylindrical mesh with 13.200 cells was superimposed on the geometry of the core to define a grid for this. Because of the cylindrical symmetry of the model, the distribution could be assumed to be equal for all 113 plates. Several million particles were simulated to reduce the statistical error to less than 3% for all of these cells.



Figure 7.10: Induced turbulences after the comb that fixes the fuel plates.

For the thermohydraulic calculations, a model of one fuel plate and a cooling channel was set-up in ANSYS CFX, a commercial 3d-CFD code. A mesh consisting of more than half a million nodes was used for the subsequent calculations with conjugate heat transfer. A Perland FORTRAN interface was developed to import results from MCNPX into CFX. The SST (Shear Stress Transport) turbulence model, a combination of the k- ω - and the k- ϵ -model proved reasonable for the turbulence modeling in the cooling channels. As only one fuel plate was regarded, appropriate periodic boundary conditions were set for the plate, so that the current model can be considered representative for the FRM II. The influence of the installations in the D₂O tank was averaged in order to maintain the cylindrical symmetry.

Results from CFX were evaluated with a set of Perl-scripts. The resulting heat distribution in the fuel plate was averaged in 64 cells for each fuel and cladding. The heat distribution was reimported into MCNPX to account for different material temperatures by means of stochastic interpolation with a square root-weighting between material libraries for different temperatures that were precompiled using NJOY. This way, the heat distribution is included in the setup of the fuel plates in further neutronic calculations and temperature effects on neutronics are properly taken into account.



Figure 7.11: Temperature profile on the surface of the fuel plate.

Final convergence was achieved after only two cycles, which could be expected regarding the comparably low temperatures in compact cores. For FRM II, all critical values like maximum temperature, temperature distribution, heat flux, pressure drop and others are in very good agreement with those calculated previously with classical techniques, but provide a much larger variety of details, especially concerning flow properties. For example, the effect of combs that fix the fuel plates and induced turbulences at the inlet and at the end of the fuel plates can now be quantified in-depth. In addition, the temperature and pressure distribution in the flow is now known to a very high degree.

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7.3 Effect of macroscopic relaxation on residual stress analysis by diffraction methods

J. Repper, M. Hofmann, C. Krempaszky², B. Regener², E. Berhuber³, W. Petry, E. Werner⁴

- ¹ TU München, Christian-Doppler-Labor für Werkstoffmechanik von Hochleistungslegierungen, Garching, Germany
- $^2~$ Böhler Schmiedetechnik GmbH & Co
 KG, Kapfenberg, Austria
- ³ TU München, Lehrstuhl für Werkstoffkunde und Werkstoffmechanik, Garching, Germany

Residual stresses can be distinguished into three types differing in the spatial extension of the stress fields. Microscopic stresses are either volume-averaged over several grains (type II stresses) or localized within a grain (type III stresses). Macroscopic stresses (type I stresses), on the other hand, vary over a length scale which is comparable to the macroscopic dimensions of the component. These stresses are correlated to the service life time of a component. Compressive type I stresses near the surface, for example, can reduce the accumulation of microcracks resulting in a gain in life time. In contrast, tensile type I stresses may lead to a reduction of strength and toughness due to spontaneous cracking. Diffraction methods allow the residual stress distribution to be determined non-destructively even deep inside the bulk material. Especially with neutron diffraction large penetration depths may be reached. Nevertheless, in diffraction experiments always a mixture of macroscopic stresses and microscopic residual stresses (mainly type II stresses) is detected. In diffraction experiments the macroscopic stresses are determined by comparison of the interference line position of a Bragg reflection of a strained sample and the interference line position of the same Bragg reflection of a macrostress free reference sample. Therefore, one of the basic assumptions in macroscopic residual stress analysis by diffraction methods is the identity of the microscopic stress state in the strained component and in the macrostress free reference sample, otherwise spurious residual stresses will be determined. Hence, the production of the reference sample usual extracted from the strained component is assumed to have no influence on the microscopic stress state in the material. The influence of the macroscopic stress relaxation during the extraction process on the microscopic stress state was investigated at a disc consisting of the high temperature Nickel-base superalloy IN 718 with a thickness of approx. 18.5 mm and an original diameter of approx. 100 mm. The disc was forged at 990 °C with a soaking time of 65 min. The forging procedure results in a high degree of plastic deformation within the sample material. It was cooled down to room temperature by water quenching to ensure high macroscopic residual stress gradients within the disc. This cooling process is expected to suppress the precipitation of additional phases within the matrix phase and the material can be treated as single phase material. The residual stress state in the center of the disc was unloaded by a reduction of the diameter of the parent disc (R = 50 mm) by electrical discharge machining to R = 2 mm figure 7.12. The neutron measurements to determine the residual stress states in the samples were carried out at the materials science neutron diffractometer STRESS-SPEC at the neutron source FRM II [1]. The strains in the three principal directions x_1 , x_2 and x_3 were measured. The Bragg reflection of the γ {311} lattice planes of the matrix phase can be found at $2\theta \approx 91.3^{\circ}$ for a wavelength of $\lambda = 1.556$ Å. The gauge volume was adapted to 3x3x3mm³ to ensure good counting statistics. Throughthickness scans were performed with 11 measurement points along the center axis of the disc. The sample with R = 2 mm is free of macroscopic stresses and hence it is used as reference sample.

The residual stress distribution of the parent disc (R = 50 mm) determined experimentally using the scattering angles measured for the R = 2 mm sample as reference values is shown in figure 7.13. The results are compared to the macroscopic residual stress distributions calculated



Figure 7.12:

Photography of the disc after the experiment. The disc radii was reduced stepwise by electrical discharge machining. The results for the discs with radii of 10 and 20 mm are discussed elsewhere

by a FE-model. There are significant differences between the simulated residual stress distribution and the experimentally determined stresses, as asymmetries and quantitative differences in the stress values. In contrast to the simulated stresses the experimental data shows non vanishing axial stresses and thus contradicts clearly the mechanical equilibrium (the axial stresses must vanish in the middle of the disc for negligible free edge effects). These discrepancies can be explained by not taking into account the changed microscopic residual stress state resulting from the relaxation of the stresses during the extraction of the sample with R = 2 mm from the uncut disc (R = 50 mm). The cutting process relaxes load large enough to induce local plastic deformation. Then, macroscopic unloading results in an elastic straining (e.g. at the grain boundaries) of grains adjacent to plastically deformed regions. These strains result in microscopic (type II) residual stresses [2,3,4]. The level of these stresses varies locally in the material because it is governed by the elastic and/or plastic anisotropy of individual grains. Variations in the degree of predeformation of different material regions owing to locally differing quenching conditions result also in non-uniform microstress distributions across the thickness of the sample (responsible for the asymmetries in the experimentally determined stress distributions in figure 7.13). The grains in highly stressed regions may have already yielded, whereas other regions contain mainly elastically strained grains. In addition, different stress gradients in the initial stress state of the parent disc may transfer larger load to surrounding material areas during unloading. The microscopic stresses reach stress levels of about +100 MPa, which is approximately 25% of the maximum initial stress amplitude.



Figure 7.13:

Residual stress distributions in the three principal directions x_1 (squares), x_2 (circles) and x_3 (triangles) across the thickness of the parent disc. The dashed lines on both sides of the graphs mark the upper and bottom surfaces of the disc. The experimental results (open symbols) are compared with the macroscopic stresses calculated by a FE-model simulation (filled symbols).

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7.4 Raman and inelastic neutron scattering study of niobium-phosphate glass for Raman gain applications

T. Unruh, W. Schirmacher¹, B. Schmid¹, A. Schulte², Y. Guo², T. Cardinal³

- ¹ Universität Mainz, Institut für Physik, Germany
- ² University of Central Florida, Department of Physics and College of Optics & Photonics-CREOL, Orlando, USA
- ³ ICMCB, CNRS, University of Bordeaux, Pessac Cedex, France

Raman gain materials are used in so called Raman gain amplifiers for broadband amplification in data transmission via optical fibers. Nowadays, the data transmission rate in optical fibers is about 2.5-10 Gbit/s. However, the transmission in a single fiber cannot be increased much above 160 Gbit/s. To overcome this limitation wavelength and time division multiplexing methods, respectively, have been developed. By these methods, multiple data streams are transported by a single fiber in parallel using a broad band of wavelengths. In this way several Tbit/s could be transmitted by a single fiber. Respecting that an optical cable may consist of a large number of independent single fibers, it can be speculated that in the future data storage and processing will be much more speed-limited than data transmission. Nevertheless, the transport of information over long distances is accompanied by serious losses of signal intensity even when using highest quality fibers. For the new data transmission technology the development of broad band amplifiers is, therefore, essential.



Figure 7.14:

Color plot of the scattering function $S(Q, \omega)$ of glassy $(Nb_2O_5)_{40} \cdot (NaPO_3)_{60}$ as measured by INS. The data was collected at the TOFTOF spectrometer (FRM II) using an incident neutron wavelength of 2.8 Å. The broad 'Boson peak', increasing in intensity with increasing momentum transfer $\hbar Q$, is clearly visible on both sides of the elastic line ($\hbar \omega = 0$).

Promising candidates for this purpose are Raman gain amplifiers which already have an usable continuous amplification range of more than 20 THz. These amplifiers are based on stimulated Raman scattering: A strong pump laser with a frequency ω_p close to ω_s of the signal beam is coupled into the data transmitting fiber. Raman scattering stimulated by the signal beam increases the signal intensity (Raman gain). The energy difference $\hbar(\omega_p - \omega_s)$ is absorbed by vibrational modes of the medium. It has been demonstrated for Tellurite glasses by Stegeman and coworkers that Raman gain for optical applications is strongly correlated to the cross-section for spontaneous Raman scattering [1]. Raman spectra of such glasses exhibit a strongly pronounced scattering intensity at small energy transfers which is essential to obtain a broad frequency range

of excitations needed for Raman gain applications. A similar feature in corresponding inelastic neutron scattering (INS) spectra is known as 'Boson peak' (cf. Fig 7.14). While the neutron data yields the density-of-states the Raman data is in addition to that determined by elasto-optic effects. To separate both contributions the vibrational properties of binary niobium-phosphate glasses (NP-glasses), a promising candidate for Raman gain with a particular broad frequency range, were additionally studied by inelastic neutron scattering at the time-of-flight spectrometer TOFTOF [2,3].

On the basis of these INS and corresponding Raman data we were successful to separate the vibrational properties and elasto-optic effects using a new theory of Raman scattering [4]. In this theory a model with fluctuating elastic constants (local disorder) is used for the calculation of Raman scattering. The longitudinal and transversal dynamic susceptibilities were calculated using self-consistent Born approximation assuming spatial fluctuations of the shear modulus [5]. The scattering function for neutrons can be derived via the vibrational density of states calculated from the dynamic susceptibilities.

This theory was used to simultaneously fit the neutron and Raman spectrum derived from measurements of the niobium-phosphate glass $(Nb_2O_5)_{40} \cdot (NaPO_3)_{60}$. The results of this fit are depicted in Fig. 7.15. It is clearly visible that the shape of the peak function is different in the



Figure 7.15:

Fit of the theory (cf. text) to the experimental INS (left) and Raman data (right) of glassy $(Nb_2O_5)_{40} \cdot (NaPO_3)_{60}$.

Raman and neutron case. Nevertheless, the experimental data is well described by the theory. It shall be noted here again: The theory assumes that excess intensity in the low energy range for Raman scattering is caused by the disorder of the elasto-optic constants whereas the vibrational density of states is detected by neutrons. It has, therefore, be confirmed that the origin of the 'Boson peak' in neutron spectra is different to the reason for the enhanced low energy intensity measured by Raman scattering. This conclusion could further be supported by our observation that when increasing the Nb₂O₅ concentration of the glass the 'Boson peak' intensity decreases but the corresponding Raman intensity increases. This effect could hardly be explained if the origin of both features is the same.

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8 Teaching and conferences

8.1 Lectures, seminars and lab courses

Spring semester 2009

Prof. Dr. Peter Müller-Buschbaum, *Experimentalphysik 2 für Maschinenwesen* Prof. Dr. Peter Müller-Buschbaum, *Seminar über Struktur und Dynamik kondensierter Materie* Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine Papadakis, *Seminar über spezielle Probleme der weichen Materie* Prof. Dr. Christine M. Papadakis, *Angewandte Physik: Polymerphysik 2*

Prof. Dr. Christine M. Papadakis, *Experimentalphysik 2 für LB* (EI/BT/MT)

Prof. Dr. Peter Müller-Buschbaum, Dr. Ezzeldin Metwalli Ali, Nanostructured Soft Materials 2

Prof. Dr. Winfried Petry, Dr. Tobias Unruh, Neutronenstreuung und komplementäre Methoden II

Fall semester 2009/20010

Prof. Dr. Peter Müller-Buschbaum, Physik 1 für Maschinenwesen
Prof. Dr. Peter Müller-Buschbaum, Angewandte Physik: Polymerphysik 1
Prof. Dr. Peter Müller-Buschbaum, Seminar über Struktur und Dynamik kondensierter Materie
Prof. Dr. Peter Müller-Buschbaum, Seminar über spezielle Probleme der weichen Materie
Prof. Dr. Peter Müller-Buschbaum, Dr. Ezzeldin Metwalli Ali Nanostructured Soft Materials 1
Prof. Dr. Winfried Petry, Dr. Tobias Unruh, Neutronenstreuung und komplementäre Methoden I

Lab courses 2009

Statische und dynamische Lichtstreuung (Biophysikalisches Praktikum) Theoretische und praktische Einführung in AFM (Fortgeschrittenenpraktikum) Thermische Analyse (Fortgeschrittenenpraktikum) Neutronenstreuung am FRM II (Fortgeschrittenenpraktikum) JCNS Laboratory Course - Neutron Scattering (Forschungspraktikum)

8.2 Conferences

GISAS 2009 Satellite Conference of SAS2009 Sep 20-23 2009, DESY Hamburg



Conference topics:

- BioGISAS
- Polymer Soft matter
- GISANS
- Nanocomposites in 2D
- New methods & Instrumentation, Detectors
- Magnetic thin films
- Coherence application in GISAS
- Growth kinetics in 2D
- Modelling, simulation & data analysis

Organizing committee: S.V. Roth, R. Röhlsberger, R. Gehrke (HASYLAB) and P. Müller-Buschbaum (TU München)
Lüscher Lectures – Informationstechnologie am Gymnasium Zwiesel Mar 27-29 2009

33. Edgar - Lüscher - Seminar

am Gymnasium Zwiesel Freitag, 27. März 2009, bis Sonntag, 29. März 2009



Thema: Informationstechnologie

Schirmherr:

Prof. Dr. Dr. h.c. mult. Wolfgang Herrmann, Präsident der TU München

Veranstalter:

Ltd. OStD Klaus Drauschke, Ministerialbeauftragter für die Gymnasien in Niederbayern; TU München

Wissenschaftliche Leitung:

Prof. Dr. Walter Schirmacher, TU München Prof. Dr. Winfried Petry, TU München



Lüscher Lectures – Geophysik Bay. Lehrerfortbildungsakademie in Dillingen (Donau) 14 - 16 Oct 2009

Leitung: StDWerner Ettinger / Prof. Dr. Walter Schirmacher Schulart: Alle Schularten Zielgruppe: Lehrkräfte Lehrgangsort: Dillingen

9 Publications, talks and funding

9.1 Publications

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- H. Breitkreutz, A. Röhrmoser, W. Petry 3-dimensional coupled neutronic and thermohydraulic calculations for a compact core combining MCNPX and CFX
 Proceedings of ANIMMA 2009, Marseille (2009)
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- S.V. Roth, M. Kuhlmann, H. Walter, A. Snigirev, I. Snigireva, B. Legeler, C. Schroer, M. Burghammer, C. Riekel, P. Müller-Buschbaum Colloidal silver nanoparticle gradient layer prepared by drying between two walls of different wettability
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- W. Wang, E. Metwalli, J. Perlich, C. M. Papadakis, R. Cubitt, P. Müller-Buschbaum Cyclic switching of water storage in thin block copolymer films containing poly(Nisopropylacrylamide) Macromolecules 42, 9041-9051 (2009)
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9.2 Talks

- J. Adelsberger *The dynamics of thermosensitive micellar hydrogels as studied using neutron spin-echo spec- troscopy* Colloquium "Analytik von Hydrogelen", Karlsruhe, 7 – 8 Apr 2009
- J. Adelsberger, A. Meier-Koll, W. Wang, T. Hellweg, O. Holderer, P. Busch, V. Pipich, A. M. Bivigou Koumba, A. Laschewsky, P. Müller-Buschbaum, C. M. Papadakis Structure and dynamics of thermoresponsive blockcopolymer gels
 FRM II Users' Meeting, Garching, 25 May 2009

- J. Adelsberger Structure and dynamics of thermoresponsive blockcopolymer gels DPG SPP 1259 "Intelligente Hydrogele" Colloquium, Dortmund, 22 – 23 Sep 2009
- H. Breitkreutz, F.M. Wagner, W. Petry *Physical and Medical Aspects of the Fast Neutron Beam MEDAPP at FRM II* **YRM-NCT 2009, Mainz**
- Z. Di, C.M. Papadakis, D. Posselt, D.-M. Smilgies Structural changes in thin block copolymer films during vapor treatment DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- Z. Di

Structural rearrangement in a lamellar block copolymer thin film during solvent vapor treatment 1st International Conference on Nanostructured Materials and Nanocomposites, Kottayam, India, 6 – 8 Apr 2009

• Z. Di

Structural rearrangement in a lamellar block copolymer thin film during solvent vapor treatment 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009

- A. Diethert, S. V. Roth, P. Müller-Buschbaum Surface enrichment layers in pressure sensitive adhesive films DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- A. Diethert, P. Müller-Buschbaum Surface-near composition profiles of pressure sensitive adhesive films
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- S. Ener, T. Mehaddene, J. Neuhaus, W. Petry Lattice dynamics in ferromagnetic shape memory alloys
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- S. Ener, J. Neuhaus, W. Petry, K. Hradil, P. Link, R. Mole Lattice dynamics in ferromagnetic shape memory alloys SPP 1239, Focus Meeting, Bonn, 30 Oct 2009
- A. Golosova, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- A. Golosova, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* IGSSE Meeting, Burg Raithenhaslach, 18 – 19 Jun 2009
- A. Golosova, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes* Seminar at Chemistry Department, Garching, 7 Sep 2009
- A. Golosova, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* International Conference on Carbon Based Nanocomposites CNTComp09, Hamburg, 20 – 23 Sep 2009

- R. M. Hengstler *Fuel development for nuclear research and power reactors* Neutrons in Science and Industry, Garching, 8 Jun 2009
- E.T. Hoppe, C.M. Papadakis
 Polymer interphase properties at the polymer-solid interface 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 18 May 2009
- R. Ivanova, C.M. Papadakis, T.B. Bonné, T. Komenda, K. Lüdtke, K. Mortensen, P.K. Pranzas, R. Jordan
 Self-assembly and multi-compartment micellar hydrogel formation of amphiphilic di- and triblock copolymers containing fluorophilic blocks
 JCNS 2009, Tutzing, 5 8 Oct 2009
- R. Jungwirth, H. Breitkreutz, W. Petry, A. Röhrmoser Optimization of the Si content in UMo-Al Si RERTR 2009, Beijing, China, 1 – 5 Nov 2009
- G. Kaune, M. A. Ruderer, E. Metwalli, R. Meier, W. Wang, S. Couet, K. Schlage, R. Röhlsberger, S. V. Roth, P. Müller-Buschbaum Growth of metal thin films on conductive polymer surfaces DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- G. Kaune
 *GISANS study of sponge-like TiO*₂ *structures for photovoltaic applications* 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 18 Jun 2009
- G. Kaune, M. A. Ruderer, E. Metwalli, R. Meier, W. Wang, S. Couet, K. Schlage, R. Röhlsberger, S. V. Roth, P. Müller-Buschbaum In-situ GISAXS study of gold film growth on a conductive polymer film SAS09, Oxford, UK 13 – 18 Sep 2009
- G. Kaune, M. A. Ruderer, E. Metwalli, R. Meier, W. Wang, S. Couet, K. Schlage, R. Röhlsberger, S. V. Roth, P. Müller-Buschbaum In-situ GISAXS study of gold film growth on a conductive polymer film GISAS 2009, Hamburg, 20 – 23 Sep 2009
- G. Kaune, P. Lellig, J. Perlich, M. Rawolle, M. Miedermeier, M. Memesa, J. S. Gutmann, P. Müller-Buschbaum Inorganic-organic hybrid films with integrated function Arbeitskreistreffen SPP 1181, Darmstadt, 9 Dec 2009
- V. Körstgens, R. Meier, J. Wiedersich, J. Perlich, S. V. Roth, P. Müller-Buschbaum Combination of μGISAXS and imaging ellipsometry - a new versatile instrument for the surface sensitive investigation of polymer films
 DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
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- A. Lennaers, S. Van de Berghe, F. Charollais, P. Lemoine, C. Jarousse, A. Röhrmoser, W. Petry *Microstructural analysis of ground UMo fuel with and without Si added to the matrix, irradiated to high burn up* RERTR 2009, Beijing, China, 1 – 5 Nov 2009
- D. Magerl, V. Körstgens, P. Müller-Buschbaum Movement of microliter and submicroliter droplets on inclined surfaces
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- R. Meier, M. A. Ruderer, G. Kaune, J. Perlich, R. Georgii, P. Müller-Buschbaum *Neutron reflectivity on conducting polymer films* 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- A. Meier-Koll, J. Adelsberger, A. Golosova, P. Busch, V. Pipich, C.M. Papadakis, P. Müller-Buschbaum Spinodal decomposition of PNIPAM based hydrogels as probed with SANS 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- E. Metwalli, J.-F. Moulin, J. Perlich, W. Wang, A. Diethert, S.V. Roth, Peter Müller-Buschbaum
 Progressive selective gold deposition from a flowing stream of solution onto a polymer template
 HASYLAB Users' Meeting, Satellite Meeting, Hamburg, 29 Jan 2009
- E. Metwalli, J.-F. Moulin, J. Perlich, A. Diethert, W. Wang, S.V. Roth, C.M. Papadakis, P. Müller-Buschbaum
 Promoting selective gold immobilization onto polymer nanotemplates using solution flow-stream technique DPG Frühjahrstagung, Dresden, 22 27 Mar 2009
- E. Metwalli, J.-F. Moulin, R. Gebhardt, V. Körstgens, R. Cubitt, A. Tolkach, U. Kulozik, P. Müller-Buschbaum
 Hydration behavior of casein micelles in thin film geometry: A GISANS study
 DPG Frühjahrstagung, Dresden, 22 27 Mar 2009
- E. Metwalli, J.-F. Moulin, M. Rauscher, G. Kaune, M.A. Ruderer, M. Haese-Seiller, R. Kampmann, P. Müller-Buschbaum Structural investigation of block copolymer thin films using TOF-GISANS
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- E. Metwalli, J.-F. Moulin, J. Perlich, A. Diethert, W. Wang, S.V. Roth, C.M. Papadakis, P. Müller-Buschbaum *Guiding metal nanoparticles onto a polymer template using a flow-stream technique* Euro AFM Forum, Garching, 1 – 3 Jul 2009
- E. Metwalli, J.-F. Moulin, R. Gebhardt, V. Körstgens, R. Cubitt, A. Tolkach, U. Kulozik, P. Müller-Buschbaum
 Hydration behavior of casein micelles in thin film geometry: A GISANS study
 Invited Talk, Heinrich-Heine-Universität, Düsseldorf, 16 Jul 2009

- E. Metwalli, J.-F. Moulin, J. Perlich, A. Diethert, W. Wang, S.V. Roth, C.M. Papadakis, P. Müller-Buschbaum Guiding metal nanoparticles onto a polymer template using a flow-stream technique DFG SPP 1164 Nano- & Microfluidics Workshop, Bad Honnef, 29 – 31 Jul 2009
- E. Metwalli, K. Schlage, V. Körstgens, S. Couet, R. Meier, G. Kaune, S.V. Roth, R. Röhlsberger, P. Müller-Buschbaum Real time GISAXS study of magnetic nanoparticle assemblies on polymer templates Nanoworkshop 2009, Prague, Czech Republic, 2 – 4 Sep 2009
- E. Metwalli, J.-F. Moulin, M. Rauscher, P. Müller-Buschbaum Structual studies on the interfaces of block copolymer thin films using TOF-GISANS JCNS 2009, Tutzing, 5 – 8 Oct 2009
- P. Müller-Buschbaum Report of the HASYLAB User Committe (HUC) - report 2008 HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- P. Müller-Buschbaum Grazing incidence small neutron angle scattering - an advanced characterization technique for structured polymer films Scattering Weekend, Erlangen, 21-22 Feb 2009
- P. Müller-Buschbaum User support at DESY - a users view
 PNI Begutachtung Photonen, Hamburg, 16 Mar 2009
- P. Müller-Buschbaum, L. Schulz, E. Metwalli, J.-F. Moulin, R. Cubitt Lateral structures of buried interfaces in A-B-A-type block polymer films DPG Frühjahrstagung, Dresden, 22-27 Mar 2009
- P. Müller-Buschbaum
 Characterization of thin polymer films by grazing-incidence small-angle x-ray scattering EMRS 2009, Strasbourg, France, 8 12 Jun 2009
- P. Müller-Buschbaum, L. Schulz, E. Metwalli, J.-F. Moulin, R.Cubitt Lateral structures of buried interfaces as probed with GISANS
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- P. Müller-Buschbaum, E. Metwalli, R. Gebhardt, A. Tolkach, U. Kulozik *Thin casein films as prepared by spin-coating: Influence of film thickness, pH and calcium concen tration* Euro AFM Forum 2009, Garching, 1 – 3 Jul 2009
- P. Müller-Buschbaum, G. Kaune, M.A. Ruderer, E. Metwalli, R. Meier, W. Wang, S. Couet, K. Schlage, R. Röhlsberger, S. V. Roth *Growth of metal thin films on conductive polymer surfaces* Nanoworkshop 2009, Prague, Czech Republic, 2-4 Sep 2009
- P. Müller-Buschbaum, G. Kaune, E. Metwalli, J.-F. Moulin, M. Haese-Seiller, R. Kampmann Polymer nanostructures at buried interfaces probed with time-of flight grazing incidence small angle neutron scattering SAS09, Oxford, UK, 13 – 18 Sep 2009

- P. Müller-Buschbaum, S.V. Roth, E. Metwalli, J.-F. Moulin, R. Cubitt *Modeling grazing incidence small angle x-ray and neutron scattering data* Workshop "Off-spec 2009", Feldafing, 27-29 Sep 2009
- P. Müller-Buschbaum, M.A.Ruderer, E. Metwalli, J.-F. Moulin, R. Cubitt Lateral structures of buried interfaces as probed with GISANS JCNS 2009, Tutzing, 5 – 8 Oct 2009
- P. Müller-Buschbaum
 Functional materials based on polymer- and hybrid-nanostructures
 Physikalisches Kolloquium der Universität Giessen, Giessen, 2 Nov 2009
- P. Müller-Buschbaum Bringing GISAXS to the field of polymers - how all started Ehrenkolloquium anlässlich des 60. Geburstages von Manfred Stamm, Dresden, 6 Nov 2009
- P. Müller-Buschbaum Functional materials based on polymer- and hybrid-nanostructures Workshop "Partnership for Soft Condensed Matter (PSCM)", Grenoble, France, 16-18 Dec 2009
- J. Neuhaus, W. Petry Magnetic, magnetoelastic and dynamical properties of martensitic Heusler alloys: Phonon spectra SPP 1239-Klausur, Duisburg, 16 Feb 2009
- J. Neuhaus

Neutrons for science and industry, the instrumentation of the FRM II 14th International Seminar on Neutron Scattering Investigation in Condensed Matter, Poznan, Poland, 15 May 2009

- J. Neuhaus Material science with neutrons in Garching DAAD Delegationsreise, MIFI, Moscow, Russia, 6 Nov 2009
- C.M. Papadakis Structural changes of block copolymer thin films in solvent vapor - time-resolved GISAXS HASYLAB Users' Meeting, Satellite Workshop, Hamburg, 29 Jan 2009
- C.M. Papadakis *Strukturierte Polymersysteme*
 DFG-Rundgespräch Weiche Materie, Bad Honnef, 25 – 27 Feb 2009
- C.M. Papadakis, J. Adelsberger, A. Jain, A. Kulkarni, K. Troll, W. Wang, A.M. Bivigou Koumba, A. Laschewsky, P. Müller-Buschbaum *Micellar solutions and hydrogels from temperature-responsive, amphiphilic block copolymers.* 1st International Conference on Nanostructured Materials and Nanocomposites, Kottayam, India, 6 – 8 Apr 2009
- C.M. Papadakis Structural Changes of Block Copolymer Thin Films in Solvent Vapor Universität Ulm, 22 Apr 2009

- C.M. Papadakis Neutron and X-ray Reflectometry - A Tutorial
 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- C.M. Papadakis, P. Černoch, P. Štěpánek, D.-M. Smilgies, S.V. Roth Formation of lateral structures in diblock copolymer films by vapor treatment GISAS 2009, Hamburg, 20 – 23 Sep 2009
- C.M. Papadakis, J. Adelsberger, A. Kulkarni, A. Jain, A. Meier-Koll, W. Wang, A.M. Bivigou-Koumba, A. Laschewsky, T. Hellweg, P. Müller-Buschbaum Structure and dynamics of self-assembled thermoresponsive polymer gels based on poly(N-isopropylacrylamide) of different architechture MRS Fall Meeting 2009, Boston, USA, 30 Nov – 4 Dec 2009
- W. Petry Die Forschungs-Neutronenquelle Heinz Maier-Leibnitz Areva Erlangen, 3 Mar 2009
- W. Petry

Vom Wackeln der Atome und der Schönheit der Neutronen Vortrag anlässlich der Feierlichkeiten zur Emeritierung von Prof. Gero Vogl, TU Wien, Austria, 2 Jul 2009

- W. Petry. J. Neuhaus, t. Mehaddene. S. Ener Dynamics of ferromagnetic shape memory alloys in the austenite and martensite phase DYPROSO 2009, Antwerpen, 13 – 17 Sep 2009
- W. Petry *Multiple purpose research reactors for the 21st century* IGORR 2009, Beijing, China, 27 – 31 Oct 2009
- W. van Renterghem, A. Leenaers, S. van den Berghe, M.-C. Anselmet, F. Charollais, P. Lemoine, W. Petry *Transmission electron microscopy investigation of irradiated atomised and ground U(Mo) dispersion fuel, with or without Si added to the matrix.*RERTR 2009, Beijing, China, 1 5 Nov 2009
- J. Repper, M. Hofmann, R. Schneider, H.-G. Brokmeier Materials science by neutron diffraction FEMaS Workshop, Lisbon, Portugal, 12 – 15 Jan 2009
- J. Repper, C. Krempaszky, M. Hofmann, E.Werner, W. Petry Macroscopic stress relaxation in complex high performance alloys TMS2009 138th Annual Meeting & Exhibition, San Francisco, California, USA, 15 – 19 Feb 2009
- J. Repper, M. Hofmann, C. Krempaszky Intergranular and interphase microstresses by neutron diffraction MECA SENS V, Tokyo, Japan, 10 – 12 Nov 2009
- A. Röhrmoser, W. Fries, H. Gerstenberg, P. Jüttner, C. Müller, I. Neuhaus, W. Petry Neutronic evaluation of target irradiation at FRM II for Mo-99 supply IGORR 2009, Beijing, China, 27 – 31 Oct 2009

- S.V. Roth, G. Herzog, A. Buffet, S. Couet, R. Gehrke, R. Röhlsberger, A. Rothkirch, K. Schlage, W. Wurth, G. Kaune, V. Körstgens, R. Meier, E. Metwalli, P. Müller-Buschbaum *Designed polymer-metal nanocomposites: On the use of colloidal polymer templates* DPG Frühjahrstagung, Dresden, 22-27 Mar 2009
- M. A. Ruderer *A neutron study of photoactive rod-coil diblock copolymer films* Complete Winter School, Antholz, Italy, 13 – 16 Mar 2009
- M. A. Ruderer, R. Meier, J. Perlich, G. Kaune, R. Cubitt, M. Haese-Seiler, R. Kampmann, P. Müller-Buschbaum Electronic materials with variable conductivities via block copolymer-homopolymer blend films 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 – 18 Jun 2009
- M. A. Ruderer, R. Meier, P. Müller-Buschbaum Enhanced light harvesting in semiconducting nanoparticle/polymer composites Nanoworkshop 2009, Prague, Czech Republic, 2 – 4 Sep 2009
- T. Unruh, C. Smuda, S. Busch, O. Holderer, W. Häußler *Diffusive motions in molecular liquids* Invited talk, Institut für Festkörperforschung (IFF), Jülich, 8 Jan 2009
- T. Unruh, C. Smuda, S. Busch Diffusive motions in molecular liquids Invited talk, 9th International Conference on Quasielastic Neutron Scattering, PSI, Villigen, Switzerland, 10 – 13 Feb 2009
- T. Unruh, C. Smuda, S. Busch, G. Gemmecker Molecular motions in liquid medium-chain n-alkanes
 DPG Frühjahrstagung, Dresden, 25 – 27 Mar 2009
- T. Unruh *Research at the time-of-flight spectrometer TOFTOF at the FRM II* Invited talk, Helmholtz Zentrum Berlin, Berlin, 16 Apr 2009
- T. Unruh *Quasielastic neutron scattering at FRM II: The method, the instruments and applications in pharmacy and biology* Invited talk, BIONyX Workshop, Barcelona, Spain, 22 May 2009
- T. Unruh, W. Schirmacher, B. Schmid, A. Schulte, Y. Guo, T. Cardinal Raman and inelastic neutron scattering study of niobium-phosphate glass for Raman gain application Invited talk, 6th International Discussion Meeting on Relaxations in Complex Systems, Rome, Italy, 30 Aug – 5 Sep 2009
- F.M. Wagner, B. Loeper, Th. Bücherl, H. Breitkreutz, W. Petry *Use of fission radiation in life sciences and materials characterisation* RRFM 2009, Wien, Austria, 22 23 Mar 2009
- F.M. Wagner, H. Breitkreutz, T. Bücherl, B. Loeper-Kabasakal, W. Petry Use of fission radiation in life sciences and materials characterisation ANIMMA 2009, Marseille, France, 2 – 7 Jun 2009

- F.M. Wagner, H. Breitkreutz, T. Bücherl, B. Loeper-Kabasakal, W. Petry *The Beam of Fission Neutrons at FRM II and its Application in Medicine, Biology, and Materials Characterisation* ANIMMA 2009, Marseille, France, 2 – 7 Jun 2009
- W. Wang, K. Troll, G. Kaune, E. Metwalli, M. Ruderer, K. Skrabania, A. Laschewsky, S. V. Roth, C. M. Papadakis, P. Müller-Buschbaum *Temperature dependent swelling and switching kinetics of gold coated end-capped PNIPAM thin films* DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- W. Wang Swelling of thin PNIPAM films as probed with neutron reflectivity Colloquium "Analytik von Hydrogelen", Karlsruhe, 7 – 8 Apr 2009
- W. Wang, P. Müller-Buschbaum Structure and kinetic of thin stimuli-responsive hydrogel films based on amphiphilic diblock copolymers
 DPG SPP 1259 "Intelligente Hydrogele" Kolloquium, Dortmund, 22 – 23 Sep 2009
- E. Welcomme, H. Palancher, C. Sabathier, Ph. Martin, J. Allenou, F. Charollais, M.C. Anselmet, C. Valot, P. Lemoine, R. Tucoulou, C. Jarousse, L. Beck, R. Jungwirth, W. Petry *Heavy ion irradiation of UMo7/Al fuel: methodological approach* RRFM 2009, Wien, Austria, 22–23 Mar 2009
- J. Wiedersich, A. Diethert, P. Müller-Buschbaum, W. Petry Brillouin spectroscopy on thin polymer films
 DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- Q. Zhong, W. Wang, E. Metwalli, A. M. Bivigou-Koumba1, A. Laschewsky, C.M. Papadakis, M. Haese-Seiller, R. Kampmann, P. Müller-Buschbaum *Structure characterization of hydrogel film based on pMDEGA* 4th FRM II Workshop on Neutron Scattering, Burg Rothenfels, 15 18 Jun 2009

9.3 Posters

- J. Adelsberger, A. Meier-Koll, W. Wang, T. Hellweg, A.M. Bivigou Koumba, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis *Structure, dynamics and kinetics of thermoresponsive block copolymer gels* HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- J. Adelsberger, A. Meier-Koll, W. Wang, A. Golosova, S. Funari, P. Busch, O. Holderer, V. Pipich, A.M. Bivigou Koumba, A. Laschewsky, T. Hellweg, P. Müller-Buschbaum, C.M. Papadakis
 Structure, dynamics and kinetics of thermoresponsive block copolymer gels
 DPG Frühjahrstagung, Dresden, 22 27 Mar 2009
- J. Adelsberger, A. Meier-Koll, W. Wang, A. Golosova, S. Funari, P. Busch, O. Holderer, V. Pipich, A.M. Bivigou Koumba, A. Laschewsky, T. Hellweg, P. Müller-Buschbaum, C.M. Papadakis
 Structure, dynamics and kinetics of thermoresponsive blockcopolymer gels
 Frontiers in Polymer Science, Mainz, 7 9 Jun 2009

- J. Adelsberger, A. Kulkarni, A. Jain, A. Meier-Koll, W. Wang, A. Golosova, A. M. Bivigou Koumba, A. Laschewsky, T. Hellweg, O. Holderer, P. Busch, V. Pipich, P. Müller-Buschbaum, C. M. Papadakis Structure and dynamics of poly(N-isopropylacrylamide)-based thermoresponsive triblock copolymer gels JCNS 2009, Tutzing, 5 – 8 Oct 2009
- D.W. Breiby, P.T.K. Chin, J.W. Andreasen, K.A. Grimsrud, Z. Di, R.A.J. Janssen Biaxially oriented CdSe nanorods NanoMat 2009, Lillehammer, Norway, 15-19 Jun 2009
- H. Breitkreutz, A. Röhrmoser, W. Petry 3-Dimensional neutronic and thermohydraulic calculations for FRM II: the X² program system ANIMMA 2009, Marseille, France, 2 – 7 Jun 2009
- H. Breitkreutz, A. Röhrmoser, W. Petry 3-Dimensional Coupled Neutronic and Thermohydraulic Calculations for a Compact Core Combining MCNPX and CFX ANIMMA 2009, Marseille, France, 2 – 7 Jun 2009
- Z. Di, D.-M. Smilgies, D. Posselt, A. Timmann, C.M. Papadakis Structural rearrangements in lamellar block copolymer thin films during solvent vapor treatment CHESS User Meeting, Cornell University, Ithaca NY, USA, 9 – 10 Jun 2009
- A. Diethert, E. Metwalli, J. Perlich, W. Wang, S. V. Roth, A. Timmann, Y. Peykova, N. Willenbacher, P. Müller-Buschbaum Surface enrichment in statistical copolymer films HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- A. Diethert, S. V. Roth, Y. Peykova, N. Willenbacher, P. Müller-Buschbaum Surface enrichment in statistical copolymer films
 Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- A. Diethert, E. Metwalli, J. Perlich, W. Wang, S. V. Roth, P. Müller-Buschbaum Surface-near structures in pressure sensitive adhesive films GISAS 2009, Hamburg, 20 – 23 Sep 2009
- S. Ener Magnetic, magnetoelastic and dynamical properties of martensitic Heusler alloys: Phonon spectra SPP 1239-Klausur, Duisburg, 16 Feb 2009
- A. Golosova, G. Richter, A. Timmann, R. Jordan, C. M. Papadakis Sidewall functionalization of carbon nanotubes for preparation of nanocomposites HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- A. Golosova, G. Richter, A. Timmann, R. Jordan, C. M. Papadakis Sidewall functionalization of carbon nanotubes for preparation of nanocomposites DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- A. Golosova, A. Timmann, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* Nano-Workshop DTU, Copenhagen, Denmark, 6 May 2009

- A. Golosova, A. Timmann, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- A. Golosova, A. Timmann, S. S. Funari, R. Jordan, C. M. Papadakis *Chemical functionalization of carbon nanotubes for preparation of nanocomposites* JCNS 2009, Tutzing, 5 – 8 Oct 2009
- R. M. Hengstler, L. Beck, C. Bogenberger, H. Breitkreutz, W. Carli, G. Gradel, C. Jarousse, R. Jungwirth, W. Petry, W. W. Schmahl, W. Schmid, J. Schneider, N. Wieschalla *Physical properties of monolithic U8wt.-%Mo* RRFM 2009, Wien, Austria, 22 – 25 Mar 2009
- E.T. Hoppe, A. Münzer, C.M. Papadakis Viscosity and density at the polymer-solid interface
 DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- E.T. Hoppe, A. Münzer, C.M. Papadakis Viscosity and density at the polymer-solid interface Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- E.T. Hoppe, C.M. Papadakis Density and viscosity at the polymer-solid interface Schwerpunkttreffen SPP 1369, Frankfurt am Main, 26 Jun 2009
- E.T. Hoppe, C.M. Papadakis Density and viscosity at the polymer-solid interface JCNS 2009, Tutzing, 5 – 8 Oct 2009
- G. Kaune, M. Memesa, R. Meier, M. A. Ruderer, A. Diethert, J. S. Gutmann, P. Müller-Buschbaum
 Preparation of hierarchically structured titania thin films by polymer templating
 Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- V. Körstgens, R. Meier, J. Wiedersich, J. Perlich, S. V. Roth, P. Müller-Buschbaum Development of the new μGISAXS instrument including imaging ellipsometry for the MINAXS beamline at PETRA3 HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- D. Magerl, V. Körstgens, P. Müller-Buschbaum Movement of microliter and submicroliter droplets on inclined surfaces
 DFG SPP 1164 Nano- & Microfluidics Workshop, Bad Honnef, 29 – 31 Jul 2009
- R. Meier, M. A. Ruderer, G. Kaune, A. Diethert, S. V. Roth, P. Müller-Buschbaum *Surface and structure analysis of thin polymer blend films based on MEH-PPV and PVK* DPG Frühjahrstagung, Dresden, 22 27 Mar 2009
- R. Meier, M. A. Ruderer, G. Kaune, R. Georgii, P. Müller-Buschbaum Neutron reflectivity study addressing the solvent content in thin conducting polymer films EMRS 2009, Strasbourg, France, 8 – 12 Jun 2009
- R. Meier, M. A. Ruderer, G. Kaune, A. Diethert, S. V. Roth, P. Müller-Buschbaum Surface and structure analysis of thin polymer blend films based on MEH-PPV and PVK GISAS 2009, Hamburg, 20 – 23 Sep 2009

- A. Meier-Koll, A. Golosova, J. Adelsberger, W. Wang, P. Busch, V. Pipich, C.M. Papadakis, and P. Müller-Buschbaum *Temperature-resolved structures and kinetics of deswelling in PNIPAM hydrogels and solutions* DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- E. Metwalli, J.-F. Moulin, J. Perlich, W. Wang, A. Diethert, S.V. Roth, Peter Müller-Buschbaum
 Progressive selective gold deposition from a flowing stream of solution onto a polymer template HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- E. Metwalli, K. Schlage, V. Körstgens, S. Couet, R. Meier, G. Kaune, S.V. Roth, R. Röhlsberger, P. Müller-Buschbaum Real time GISAXS study of magnetic nanoparticles self-assembly on a polymer template EMRS 2009, Strasbourg, France, 8 – 12 Jun 2009
- E. Metwalli, J.-F. Moulin, J. Perlich, W. Wang, A. Diethert, S.V. Roth, Peter Müller-Buschbaum *Gold nanoparticle decoration of polymer template using a flow-stream technique* SAS09, Oxford, UK, 13 – 18 Sep 2009
- J. Neuhaus, S. Ener, W. Petry, K. Hradil, P. Link, R. Mole Lattice dynamics in ferromagnetic shape memory alloys FRM II Users' Meeting, Garching, 25 May 2009
- C.M. Papadakis, P. Černoch, P. Štěpánek, D.-M. Smilgies, S.V. Roth Formation of lateral structures in thin diblock copolymer films by vapor treatment DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- C.M. Papadakis, C. Darko, K. Troll, Z. Di, S. Förster, D.-M. Smilgies, A. Timmann Breakout crystallization in cylinder-forming diblock copolymer thin films DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- C.M. Papadakis, C. Darko, E. Metwalli, I. Botiz, G. Reiter, D.W. Breiby, J.W. Andreasen, S.V. Roth, D.-M. Smilgies *Multiscale study of crystallization in diblock copolymer thin films at different supercooling* DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- C.M. Papadakis, Z. Di, D. Posselt, D.-M. Smilgies Structural instability in a block copolymer thin film during solvent vapor treatment NanoDay 2009, Joint Meeting between Nano DTU, Nano-Science Center, NanoTUM and TU/e, Copenhagen, Denmark, 6 May 2009
- C.M. Papadakis, Z. Di, D. Posselt, D.-M. Smilgies Structural changes in thin block copolymer films during vapor treatment Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- C.M. Papadakis, C. Darko, I. Botiz, G. Reiter, D.W. Breiby, J.W. Andreasen, S.V. Roth, D.-M. Smilgies *Multiscale study of crystallization in diblock copolymer thin films at different supercooling* Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- C.M. Papadakis, C. Darko, I. Botiz, G. Reiter, D.W. Breiby, J.W. Andreasen, S.V. Roth, D.-M. Smilgies

multiscale study of crystallization in diblock copolymer thin films at different supercooling Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009

- C.M. Papadakis, Z. Di, D. Posselt, D.-M. Smilgies Structural instability in a block copolymer thin film during solvent vapor treatment GISAS 2009, Hamburg, 20 – 23 Sep 2009
- W. Petry SANS-1, the new Small-Angle Neutron Scattering instrument at the Forschubngs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) ICNS 2009, Knoxville, Tenessee, USA, 3 - 7 May 2009
- M. A. Ruderer, S. M. Prams, A. Diethert, R. Meier, G. Kaune, S. V. Roth, P. Müller-Buschbaum *Temperature influence on photoactive polymer blend films* HASYLAB Users' Meeting, Hamburg, 30 Jan 2009
- M. A. Ruderer, R. Meier, J. Perlich, G. Kaune, R. Cubitt, M. Haese-Seiler, R. Kampmann, P. Müller-Buschbaum Structure control of conjugated block copolymers via adding a homopolymer
 DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- M. A. Ruderer, R. Meier, J. Perlich, G. Kaune, R. Cubitt, M. Haese-Seiler, R. Kampmann, P. Müller-Buschbaum Structural control of conjugated block copolymer films via addition of homopolymer FRM II Users' Meeting, Garching, 25 May 2009
- M. A. Ruderer, R. Meier, J. Perlich, G. Kaune, R. Cubitt, M. Haese-Seiler, R. Kampmann, P. Müller-Buschbaum Structure control of conjugated block copolymers via adding a homopolymer SAS09, Oxford, UK, 13 – 18 Sep 2009
- M. A. Ruderer, S. M. Prams, W. Wang, Q. Zhong, R. Meier, S. V. Roth, P. Müller-Buschbaum Enhanced light harvesting in semiconducting nanoparticle/polymer composites
 GISAS 2009, Hamburg, 20 – 23 Sep 2009
- S. Salzinger, S. Huber, R. Jordan, C.M. Papadakis Collapse behavior of thermosensitive poly(2-oxazoline) copolymers DPG Frühjahrstagung, Dresden, 22 – 27 Mar 2009
- S. Salzinger, S. Huber, R. Jordan, C.M. Papadakis *Collapse behavior of thermosensitive poly(2-oxazoline) copolymers* Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009
- A. Sepe, Z. Di, C. Darko, D. Posselt, D.-M. Smilgies, A. Timmann, M.A. Singh, C.M. Papadakis *Thermal annealing of thin films of lamellar poly(styrene-b-butadiene) diblock copolymers* GISAS 2009, Hamburg, 20 – 23 Sep 2009
- J. Wiedersich, A. Diethert, P. Müller-Buschbaum, W. Petry Brillouin scattering on thin polymer films
 Frontiers in Polymer Science, Mainz, 7 – 9 Jun 2009

 Q. Zhong, W. Wang, A. M. Bivigou-Koumba1, A. Laschewsky, C.M. Papadakis, M. Haese-Seiller, R. Kampmann, P. Müller-Buschbaum Characterization of pMDEGA based hydrogel film FRM II Users' Meeting, Garching, 25 May 2009

9.4 Invited talks at E13

- Prof. Thomas Bein, Chemiedepartment, Ludwig-Maximilian-Universität, Munich *Tuning functionality and morphology of periodic nanoporous materials* 29.01.2009
- Prof. Georg Fytas, Foundation for Research and Technology, Hellas *Tailoring sound propagation by mesoscopic engineering of soft matter* 03.02.2009
- David Polster, TU Chemnitz, Chemnitz Macroscopically and microscopic characterization of surface 05.02.2009
- Prof. Tommy Nylander, Lund University, Sweden Neutron reflectometry to investigate the delivery of lipids and DNA to interfaces 09.02.2009
- Dr. Petr Štěpánek, Institute of Macromolecular Chemistry, Prague, Czech Republic Hierarchical structure of self-organized microemulsions investigated by SAXS, SANS and USANS 20.04.2009
- Claus Hoejgaard Nielsen, Nanotech, Technical University of Denmark, Copenhagen, Denmark *Patterning of ultrathin sensor coatings* 29.04.2009
- Alessandro Sepe, Physikdepartment E40, Garching Magnetic and electronic properties of the Mn:Ge (111) system 08.05.2009
- Prof. Dr. Mukundan Thelakkat, University of Bayreuth, Bayreuth Block copolymer solar cells - advantages and challenges 19.05.2009
- Dr. Prashant Sinha, Institut f
 ür Polymerforschung, Dresden *Temperature induced collapse of Na-polyacrylate-Ca(II) coils: A comparative study by SANS and AFM* 27.05.2009
- Prof. Karlheinz Bock, Fraunhofer IZM Assembly and Packing Technologies for Microsystems, Munich Integration for organic and large area electronics 14.07.2009
- Dr. Sabine Ludwigs, Universität Freiburg, Freiburg From nanostructured block copolymer templates towards organic solar cells 21.07.2009

- Dr. Taras Slobodskyy, ISS, Forschungszentrum Karlsruhe, Karlsruhe *Surfaces and interfaces for self organization* 07.2009
- Dr. Ronald Gebhardt, Chair for Food Process Eng. and Diary Technol., Weihenstephan *GISAXS/SAXS/WAXS with micro-beams: New applications in soft condensed matter* 07.2009
- Dr. Chris McNeill, University of Cambridge, UK Polymer blends for photovoltaics 30.07.2009
- Sebastian Jaksch, Technische Universität Darmstadt Streuexperimente zur Untersuchung der Tensid Polymer Wechselwirkung in Mikroemulsionen 05.08.2009
- Martin Niedermeier, Walter-Schottky-Institut, Garching *Characterization of plasma-modification of diamond surfaces* 08.09.2009
- Lothar Sims, Ludwig-Maximilians-Universität, Munich Devices of organic solar cells 09.09.2009
- Florian Krezschmer, Leibniz-Institut f
 ür Festkörper- und Werkstoffforschung, Dresden Magnetization study on quasi-1d spin systems 10.09.2009
- Sushobhan Joshi, Universität Kiel, Kiel *Efficiency measurements systems using an asymmetric parameter conversation* 11.09.2009
- Dr. Sokol Ndoni, Technical University of Denmark, Copenhagen, Denmark From self-assembled block copolymers to nanoporous materials 20.10.2009
- Prof. Dr. Hellweg, Physikalische Chemie I, Universität Bayreuth, Bayreuth Dynamics of bicontinuous microemulsions and lipid vesicles 26.10.2009
- Holger Fiedler, TU Berkakademie, Freiberg *The conducting polymer PEDOT* 26.10.2009
- Stephan Ratzsch, Friedrich-Schiller-Universität, Jena Investigation of the eBeam resist FEP 171 by modeling and experiments 28.10.2009
- Prof. Peter Schurtenberger, University of Fribourg, Switzerland Responsive colloids as model atoms with tunable interactions 16.11.2009

9.5 Funding

- Deutsche Forschungsgemeinschaft:
- Within DFG priority program SPP 1164 Non-equilibrium flow at gradient surfaces: Fluid kinetics of droplets and particle motion Grant Number: MU 1487/2-3 Project Leader: Prof. Peter Müller-Buschbaum
- Within DFG priority program SPP 1181 Nanostrukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien Grant Number: MU 1487/5-1 Project Leader: Prof. Peter Müller-Buschbaum
- Within DFG priority program SPP 1181 Hierarchisch strukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien Grant Number: MU 1487/5-2 Project Leader: Prof. Peter Müller-Buschbaum
- *Einfluss von Grenzflächeneffekten auf die Adhäsion weicher Polymere* Grant Number: MU 1487/6-1 Project Leader: Prof. Peter Müller-Buschbaum
- Within DFG priority program SPP 1259 Struktur und Kinetik stimuli-rexponsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren Grant Number: MU 1487/8-2 Project Leader: Prof. Peter Müller-Buschbaum
- Within DFG priority program SPP 1239 Änderung von Mikrostruktur und Form fester Werkstoffe durch
 äußere Magnetfelder Grant Number: NE 1405/1-2 Project Leader: Dr. J
 ürgen Neuhaus
- Steigerung der Berechnungsgenauigkeit der Eigenspannungsverteilung im Aluminiumformguss mittels Neutronendiffraktometrie Grant Number: PE 580/6-2 Project Leader: Dr. Michael Hofmann
- Rolle der Mikrospannungen bei der Eigenspannungsanalyse mittels Neutronenbeugung in mehrphasigen Hochleistungslegierungen Grant Number: PE 580/7-1 Project Leader: Prof. Winfried Petry
- Inelastische Neutronenstreuung bei hohen Temperaturen und Drücken zur Aufklärung der Lösungs- und Transportmechanismen von Wasser in wasserhaltigen Silikatschmelzen Grant Number: PE 580/8-3 Project Leader: Prof. Winfried Petry
- Thin Films of Crystalline Diblock Copolymers: Crystalline and Mesoscopic Structures and their Macroscopic Alignment

Grant Number: PA 771/3-1, Folgeprojekt PA 771/3-2 Project Leader: Prof. Christine M. Papadakis

- Within DFG priority program SPP 1259 Struktur und Kinetik stimuli-responsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren Grant Number: PA 771/4-1, Folgeprojekt PA 771/4-2 Project Leader: Prof. Christine M. Papadakis
- *Multicompartment systems based on poly (2-oxazoline)s* Grant Number: PA 771/6-2 Project Leader: Prof. Christine M. Papadakis
- Lokale Viskosität und Dichte in der Grenzphase von Polymeren an einer festen Grenzfläche -Fluoreszenz-Korrelationsspektroskopie und Neutronenreflektrometrie Grant Number: PA 771/7-1 Project Leader: Prof. Christine M. Papadakis
- Bundesministerium für Bildung und Forschung:
- Entwicklung und Aufbau von muSISAXS am muSAXS/WAXS Instrument am Synchroton PETRA III
 Grant Number: 05KS7WO1
 Project Leader: Prof. Peter Müller-Buschbaum
- Others:
- Research Cooperation Johannes Gutenberg-Universität Mainz Feldtheoretische Beschreibung von Eigenschaften weicher kondensierter Materie Project Leader: Prof. Winfried Petry
- International Graduate School: Material Science of Complex Interfaces *Thin films of photoactive semi-conducting polymers with incorporated metal nanoparticles* Project Leader: Prof. Peter Müller-Buschbaum
- International Graduate School: Material Science of Complex Interfaces Strukturelle Änderungen in nanostrukturierten Blockcopolymerfilmen - Zeitaufgelöste in-situ-Untersuchungen mit Röntgenkleinwinkelstreuung unter streifendem Einfall Project Leader: Prof. Christine M. Papadakis
- Copenhagen Munich Center of Soft Nanostuctured Material (CMC-SNN) Incentive Fund for Research Collaborations between Technische Universität München and the Danish Technical University Project Leader: Prof. Christine M. Papadakis, PD Dr. Rainer Jordan (Department Chemie, Technische Universität München), Prof. Martin E. Vigild (Department of Chemical Engineering, Danish Technical University)
- Incentive Fund for Research Collaborations between Technische Universität München and the Technical University of Denmark

Crystalline, mesoscopic and long-range order in thin films of crystalline block copolymers Project Leader: Prof. Christine M. Papadakis, Dr. Jens Wenzel Andreasen (Risø National Laboratory, Technical University of Denmark)

 International Graduate School of Science and Engineering (IGSSE) Preparation and characterization of functional nanocomposites by directed assembly of modified carbon nanotubes in block copolymer matrices Project Leader: Prof. Christine M. Papadakis, PD Dr. Rainer Jordan (Department Chemie, Technische Universität München)

10 The chair

10.1 Graduations

• Accomplished PhD thesis

Jan Perlich

Nanostrukturierte Filme aus anorganisch-organischen Hybridmaterialien für die Photovoltaik

Fan Yang

Dynamics of water bearing silicate melts as seen by quasielastic neutron scattering at high temperature and pressure

• Accomplished diploma thesis

Stefan Prams

In situ Untersuchung der Morphologie leifähiger Polymerfilme für die Anwendung in Solarzellen

Oleksandr Khegai *Optimierung von spektral-räumlichen Bildgebungssequenzen für hyperpolarisierte 13C Magnetresonanzbildgebung*

• Accomplished master thesis

Xin Xia Nanostructured diblock copolymer films embedded with magnetic nanoparticles

Matthias Hirzinger

Physikalische Grundlagen der Leistungsparameter und Zuverlässigkeit von thermoelektrischen Wandlern

• Accomplished bachelor thesis

Ahmed Omran Magnetische Eigenschaften magnetischer Nanoteilchen in einer Diblock-Kopolymer-Matrix Fabian Markl Structuring of an electronblocking PEDOT:PSS layer in organic electronics Marta Krawczyk Characterization of diblock copolymer films for application in photovoltaics Matthias Demharter

Optical properties of polymer films in photovoltaics

10.2 Staff

Chair: Prof. Dr. Winfried Petry **Head:** Prof. Dr. Peter Müller-Buschbaum

Professors

Prof. Dr. Christine M. Papadakis Prof. Dr. Walter Schirmacher

Fellows

Dr. Ralf Gilles Dr. Michael Hofmann Dr. Ezzeldin Metwalli Ali Dr. Volker Körstgens Dr. Jürgen Neuhaus Dr. Tobias Unruh Dr. Johannes Wiedersich

PhD students

Josef Adelsberger Harald Breitkreutz Sebastian Busch Zhenyu Di Alexander Diethert Semih Ener Anastasia Golosova Rosemarie Hengstler Christian Hesse Tilo Hoppe Rainer Jungwirth Gunar Kaune Robert Meier Andreas Meier-Koll Martin Niedermeier Ian Perlich Katharina Rolfes Monika Rawolle Julia Repper Matthias Ruderer Wolfgang Schmid Martin Schmiele Alessandro Sepe Roxana Valicu Weinan Wang Fan Yang Qi Zhong

Diploma students

Stefan Dirndorfer Christoph Geissinger Stefan Guldin Tim Hülsheger Michael Jungwirth Andreas Nathan Stefan Prams Markus Schindler

Master students

Hsin-Yin Chiang Matthias Hirzinger David Magerl Besira Mekonnen Mihiretie Mahmout Rabie Xin Xia

Bachelor students

Matthias Demharter Marta Krawczyk Fabian Markl Ahmed Omran

Students assistants

Christopher Birkenstock Nicolas Hörmann Martin Müller Alexandra Münzer Maria Pilar Garces Günther Reithmaier Annkatrin Sommer Constantin Tomaras

Technical/administrative staff

Philipp Bork Petra Douglas Susanna Fink Reinhold Funer Lukas Hein Tobias Heller Werner Hornauer Raffael Jahrstorfer Josef Kaplonski Dieter Müller Jandal Ringe Günther Seidl

10.3 Guests

- Nora Kristen, Technische Universität Berlin 04.-06.02.2008
- Claus Hoejgaard Nielsen, Technical University of Denmark 27.04.-01.05.2009
- Prof. André Laschewsky, Anna Miasnikova, Universität Potsdam 13.05.2009
- Achille Mayelle Bivigou Koumba, Universität Potsdam 14.-18.09.2009
- Prof. André Laschewsky, Universität Potsdam 09.11.2009