

Annual Report 2010



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Cover-page picture:

2D grazing incidence wide angle X-ray scattering (GIWAXS) pattern of a highly crystalline poly(3-hexylthiophene) (P3HT) film and the deduced molecular arrangement of the P3HT chains. P3HT is one of the most promising conducting polymers in terms of application in organic electronic like for organic solar cells and printable electronics. The 3 μ m thick P3HT film was solution casted on a silicon substrate and thermally annealed at 140 °C to allow further ordering of the polymer chains. The 2D scattering pattern revealed a highly crystalline P3HT film. The highlighted areas (blue, red and green sectors) in the scattering patterns are used to perform so called sector integrals to obtain quantitative structural information such as the lattice constants and crystalline orientation. The P3HT molecules in the solution casted film are mainly edge-on orientated, i.e. the conjugation plane is perpendicular to the substrate. The resulting structure including the lattice constants *a* and *b* is shown in the schematic representation which illustrates the formation of conjugation planes.

1 Preface

It is a great pleasure to present in the name of the staff of the Chair of Functional Materials the annual report for the year 2010, 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 fundamental physics of material properties using mainly 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 2010, the chair activities covered the specific areas of water based polymer systems, thin polymer films, polymer films for application in photovoltaics, polymer-hybrid systems, dynamics, and methodological and instrumental developments. The activities in the fields of water-based polymer systems and polymer-hybrid systems have increased significantly.

The in-house experiments available in the laboratories of the chair were supplemented by the lively activities at numerous large scale facilities, comprising synchrotron radiation and neutron scattering experiments. Moreover, the developments in methods and instrumentation extended to the large scale facilities: A major upgrade of the instrument TOF-TOF at the research reactor FRM II was started. Moreover, the development of micro-beam grazing incidence small angle x-ray scattering (μ GISAXS) was finalized at the newly constructed MiNaXS instrument at PETRA III in Hamburg. The development of μ GISAXS in combination with in-situ imaging ellipsometry was successfully realized. Monika Rawolle and Volker Körstgens, both from our chair, were the first friendly users at the MiNaXS beamline.

In 2010, the Chair of Functional Materials comprised 9 fellows, 30 PhD students, 7 diploma students, 7 master students, 4 bachelor students, 10 student assistants and 10 administrative and technical staff members. 4 PhD theses were accomplished, moreover, 4 diploma and 4 master theses as well as 4 bachelor theses were finished. Again, we had the pleasure to host several guests from abroad which stimulated a lively atmosphere.

In general, all members of the chair were very active at conferences and workshops, participating with both talks and posters. Moreover, important conferences were organized by members of the chair: two Edgar-Lüscher Seminars were again organized, this year on the subjects 'Astro- and particle physics' and 'Energy and Environment'. The 2nd TUM-HASYLAB Colloquium 'The metal-polymer interface' took place in Hamburg. Moreover, a Focus Session on 'Structure and Dynamics of Responsive Hydrogels' was organized in the framework of the spring meeting of the Condensed Matter Division of the German Physical Society in Regensburg. For the chair, a very important event this year was the summer school at the Rudolfshütte in Austria – at an altitude of 2315 m, all members of the chair gave talks on general subjects from the field of polymer physics. Everybody enjoyed the extensive discussions in combination with a fascinating landscape a lot!

Regarding teaching activities of the chair, we offered general physics lectures for students of mechanical engineering (Müller-Buschbaum) and in the new Bachelor of Engineering Science at the Munich School of Engineering (MSE) (Papadakis). Specialized lectures comprised 'Polymer physics' (Müller-Buschbaum/Papadakis), 'Nanostructured soft materials' (Müller-Buschbaum/Metwalli) and 'Neutron scattering and complementary methods' (Petry/Unruh).

Prof. Papadakis acted again as a women's representative of the Physics Department. Moreover Prof. Müller-Buschbaum is heading the activities in the area of 'Renewable Energies' in the MSE.

This annual report comprises a selection of the different research topics and projects carried out in the individual groups of the chair. It highlights the engaged and successful research activities and collaborations with other groups and large scale facilities. We wish all chair members a fruitful continuation and a successful year 2011.

Peter Müller-Buschbaum and Christine Papadakis

March 2011

Contents

1	Pref	ace	3		
2	Wate 2.1 2.2	er based polymer systems Thermoresponsive poly(2-oxazoline)s in aqueous solutions	7 8		
	2.3	Dynamics in concentrated solutions of thermoresponsive di- and triblock copoly-	10		
	2.4	Kinetics of structural changes in thermoresponsive triblock copolymer solutions after a temperature jump	12		
	2.5 2.6	Cononsolvency in thermoresponsive block copolymers	16 18		
	2.7	Gold-sputter-deposition on PNIPAM-based triblockcopolymer thin films	20		
3	Thin polymer films 23				
	3.1	Density of polybutadiene melts at the polymer-solid interface	24		
	3.2	Near-surface composition profiles of pressure sensitive adhesive films	26		
	3.3 3.4	Near-surface solvent content profiles evolving during solution casting Surface-induced breakout crystallization in cylinder-forming P(I- <i>b</i> -EO) diblock	28		
	3.5	copolymer thin films	30		
	. .	novel combination of optical ellipsometry and GIWAXS	32		
	3.6 3.7	Exploring different substrates for functional photoactive thin polymer films In-situ study of lamellar poly(styrene- <i>b</i> -butadiene) diblock copolymer thin films during heat treatment	34		
4	Dala		20		
4	roiy	Super-structuring of papoporous titania films for application in photovoltaics	39 40		
	4.1 4.2	Novel structuring routine of PEDOT PSS applied to organic photovoltaics	42		
	4.3 4.4	Temperature induced surface tuning of novel structured conducting polymer films Influence of annealing and blending of photoactive polymers on their crystalline	44		
		structure	46		
	4.5	Characterization of ternary systems for organic photovoltaics	48		
	4.6 4.7	STXM-studies on the solvent content of thin conducting polymer films Influence of different solvents on the morphology in P3HT:PCBM bulk hetero-	50		
	4.8	junction systems for organic photovoltaics	52 54		
5	Polymer-hybrid systems 57				
	5.1	Large area sponge-like titania nano-structures	58		
	5.2	Layer-by-layer fabrication of an anatase titania multilayer with gradual sponge- like morphology	60		
	5.3	Hierarchically structured titania thin films by iterative block copolymer based sol-gel templating	62		
	5.4 5.5 5.6	Effect of external magnetic field on the alignment of metal-polymer nanocomposites Improvement of carbon nanotube dispersability by chemical modification Lithium-containing diblock copolymer thin films for solid-state micro-batteries .	64 66 68		

	5.7	Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT	70		
	5.8	Determination of the local gold contact morphology on a photoactive polymer	70		
		film using nanobeam GISAXS	72		
	5.9	Growth and morphology of aluminum thin films on P3HT surfaces	74		
	5.10	Creating colloidal nanocomposites using the solution casting method	76		
	5.11	Flow induced surface attachment of gold nanoparticles - an in situ x-ray investi-			
		gation with micro-fluidic cell	78		
6	Dynamics				
	6.1	Nanoscopic dynamics of phospholipid molecules	82		
	6.2	Water migration into a casein micellar film: A neutron radiography study	84		
	6.3	The effect of the Rouse model on a polyethylene melt	86		
	6.4	ne effect of magnetic field and mechanical stress on the phonons of five layered	00		
	65	Effect of temperature and composition changes on phonon properties of	00		
	0.5	Ni-Mn-Ga	90		
	6.6	Inelastic neutron and Raman scattering of low-frequency excitations in glasses for	20		
		Raman gain applications	92		
7	Met	hodological and instrumental developments	95		
	7.1	Neutronic and thermal hydraulic calculations of a 49.9% enriched disperse UMo			
		core for FRM II	96		
	7.2	Irradiation induced creep and growth of zirconium-based alloys for PWR guide			
		tubes	100		
	7.3	Sample cell for Brillouin scattering	102		
	7.4	Combination of μ GISAXS and imaging ellipsometry at the synchrotron source	101		
		PETRA III	104		
8	Teac	hing and conferences	107		
	8.1	Lectures, seminars and lab courses	107		
	8.2	Conferences	108		
9	Pub	lications, talks and funding	117		
	9.1	Publications	117		
	9.2	Talks	120		
	9.3	Posters	127		
	9.4	Invited talks at LS Funktionelle Materialien	132		
	9.5	Funding	133		
10	The	chair	136		
	10.1	Graduations	136		
	10.2	Staff	137		
	10.3	Guests	140		

2 Water based polymer systems



ANNUAL REPORT 2010

2.1 Thermoresponsive poly(2-oxazoline)s in aqueous solutions

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Amphiphilic copolymers in aqueous solution exhibit a wide range of morphologies ranging from micellar and other colloidal structures to hydrogels at high concentrations. Poly(2oxazoline)s represent a very attractive class of materials, as their properties can be tuned from hydrophilic via thermoresponsive to hydrophobic by changing the side group R (see fig. 2.1). Thermoresponsive polymers react reversibly with a change of behavior from hydrophilic to hydrophobic upon raising the temperature above their lower critical solution temperature (LCST). Moreover, the fraction of thermoresponsive and hydrophobic blocks in the copolymers as well as the architecture of the polymer can be varied [1,2]. Thus, they can be tailored for medical applications [3]. Here we present an investigation of a poly(2-*i*-propyl-2-oxazoline)₅₀ (P*i*PrOx₅₀) homopolymer as well as gradient copolymers where several *i*PrOx monomers have been replaced by 2-*n*-nonyl-2-oxazoline (NOx) monomers (P[*i*PrOx₄₈NOx₂]_{grad} and P[*i*PrOx₄₆NOx₄]_{grad}) [4].



Figure 2.1:

Inset: Structure of a poly(2-oxazoline) monomer. Schematics of the aggregation behavior of a) $PiPrOx_{50}$, b) $P[iPrOx_{48}NOx_2]_{grad}$ and c) $P[iPrOx_{46}NOx_4]_{grad}$

Small angle neutron scattering (SANS) experiments were performed using 20 mg/ml solutions in D₂O at the KWS-1 beamline, JCNS, FRMII. Representative scattering curves are shown in fig. 2.2. The curves feature both, single chain scattering above 0.02 Å^{-1} and forward scattering due to large aggregates. The single chain scattering is described by a Debye function; i.e. Gaussian coils, whereas the aggregate scattering in the low *q*-region is described by a form factor for solid homogeneous spheres. For P[*i*PrOx₄₆NOx₄]_{grad}, in contrast, the single chains are more compact, i.e. homogeneous spheres. In all cases, the large aggregates are larger than $\approx 500 \text{ Å}$.



Figure 2.2: Representative SANS curves for $PiPrOx_{50}$ (a), $P[iPrOx_{48}NOx_2]_{grad}$ (c) and $P[iPrOx_{46}NOx_4]_{grad}$ (e). The intensities are shifted for better visibility by factors of 2, 4 and 16. (b, d, f) give resulting chain radii (see text). Temperatures are (from bottom to top): a) 24.8° C, 32.3° C, 37.4° C, 41.6° C; c) and d) 12.2° C, 20.6° C, 24.8° C, 29.0° C. The full lines are fits. The dashed lines are the cloud points from turbidimetry and the dash dotted lines the upper limits of the intermediate aggregation regime (see text).

The temperature-dependent aggregation behavior of the different polymers is detailed in fig. 2.1. For $PiPrOx_{50}$, large aggregates form immediately at the LCST (2.2b). The gradient copolymers behave differently. $P[iPrOx_{48}NOx_2]_{grad}$ forms small aggregates already at temperatures below the LCST. These aggregates consist of a few chains, and the intermolecular interaction is mediated by the hydrophobic NOx groups which form bridges between the chains. When crossing the LCST from below, these small aggregates remain stable and do not immediately form large aggregates. Only a few K above the LCST, large aggregates form (2.2d). Thus, above the LCST an intermediate regime is encountered. The behavior is very similar for $P[iPrOx_{46}NOx_4]_{grad}$, but here, intramolecular bridging is more probable. Thus, small aggregates are more stable which results in a more pronounced intermediate regime than in $P[iPrOx_{48}NOx_2]_{arad}$ (see fig. 2.2f).

The increase of the single chain radii of the homopolymer and the gradient copolymers is described by a power law, $R = R_0 \cdot (T_C/(T_C - T))^{\nu}$. T_C is in all cases similar to the cloud point from turbidimetry, thus the formation of large aggregates is related to the collapse of the single chains. Interestingly, the critical exponents are significantly lower than the field prediction $\nu = 0.5$.

We conclude that, in contrast to the homopolymer, the gradient copolymers display an intermediate aggregation regime in a temperature range of 3 to 4K above the LCST where small aggregates are stable. Only above, large aggregates dominate. Moreover, we have found hints to a critical nature of the collapse transition at the LCST.

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2.2 The collapse transition in a concentrated solution of a thermoresponsive diblock copolymer

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Poly(N-isopropyl acrylamide) (PNIPAM) is well known for its thermoresponsive behavior. When heated above the lower critical solution temperature (LCST) of $\sim 32^{\circ}$ C, PNIPAM chains undergo a coil-to-globule transition, where water is released from the polymer backbone. If PNIPAM is copolymerized with other polymer blocks, new thermoresponsive materials are obtained which are of great interest for applications such as controlled ultrafiltration. Copolymerizing PNIPAM with water-insoluble polystyrene (PS) offers the opportunity to form thermoresponsive star-like micelles by self-organization in aqueous solution [1].

In the present work, we elucidate the temperature-dependent structures of a concentrated solution of P(S-*b*-NIPAM) having block molar masses of 5000 and 18000 g/mol in D_2O (470 mg/ml). We carried out small-angle neutron scattering (SANS) experiments at the instrument KWS 2 at JCNS, FRM II [2]. The accumulation time per image was 5 min for each sample-detector distance (2m and 8 m) with a waiting time of 8 min after each temperature change. All data reduction and normalization was performed with the software QtiKWS provided by JCNS.

The SANS curves are shown in Figure 2.3A. Apart from form factor oscillations at high *q*-values, a micelle-micelle correlation peak is observed which moves to higher *q*-values between 26 and 30° C along with a strong increase of forward scattering intensity. These changes reflect the collapse of the micellar shells, and the formation of closely packed clusters, which grow in size and where the inner correlation increases. The curves were analyzed using the Daoud-Cotton model for spherical core-shell micelles [3] where the micellar core consists of a homogeneous PS melt and a solvent-swollen PNIPAM brush with a radially decreasing concentration [4]. In the swollen state below the LCST, the liquid-like correlation between the swollen micelles was modeled by a Percus-Yevick structure factor which includes the hard-sphere radius between the micelles, r_{HS} . Two scenarios were distinguished to describe the cluster formation of the micelles upon collapse: (i) At the collapse transition, small clusters are formed which are described by a structure factor with the cluster-cluster correlation dominating over the internal correlation between micelles. (ii) Further above the collapse transition, large clusters are formed which give rise to Porod-like forward scattering and in which the micelles have a liquid-like internal correlation.

Whereas the core radius is quite constant, the micellar radius increases with temperature below the collapse transition and then decreases (Figure 2.3B). Below the collapse transition, the latter follows critical behavior, $r_{mic}(T) \propto (T_c/(T_c - T))^{1/2}$, with a critical temperature $T_c = 31.3 \pm 1.2^{\circ}$ C. T_c is higher than the temperature where the collapse transition is observed (27-29°C); the divergence of r_{mic} at T_c is thus pre-empted by the collapse of the micellar shell and the resulting cluster formation. The strong incress of r_{HS} at 27°C is due to the formation of many small clusters from micelles. Above 30°C, r_{HS} decreases and stays constant, as expected for the aggregation of micelles with a collapsed shell in large clusters. We conclude that the collapse transition is complex (Figure 2.3C) and involves the collapse of the micellar shell and the formation of small clusters of collapsed micelles which eventually merge into large clusters. This work is funded by the DFG within the project SPP1259 "Intelligent Hydrogels".



Figure 2.3:

(A) Representative SANS curves (symbols) together with fits (solid lines). From bottom to top: 10°C, 18°C, 26°C, 27°C, 28°C, 29°C, 30°C, 33°C and 35°C. (B) Results from the fits. Filled squares: r_c , filled circles: r_{mic} , filled triangles: r_{HS} , filled stars: r_{cl} . The line is a fit to r_{mic} , see text. (C) Resulting scheme of the collapse transition: (a) The micelles are swollen below the LCST. (b) At the LCST, the micelles collapse and form small clusters. (c) The clusters grow, and their number increases. (d) Large clusters are formed from the small clusters.

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2.3 Dynamics in concentrated solutions of thermoresponsive di- and triblock copolymers

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Di- and triblock copolymers, consisting of one or two hydrophobic polystyrene (PS) endblocks and a longer hydrophilic poly(N-isopropyl acrylamide) (PNIPAM) middleblock form star-like or flower-like core-shell micelles in aqueous solution [1-3]. When they are heated up above the lower critical solution temperature (LCST), the PNIPAM block becomes hydrophobic and releases water from the micellar shell, which consequently collapses. In order to use thermoresponsive copolymers for drug delivery, as sensor or in ultrafiltration applications it is necessary to understand both, the kinetics of structural changes and the altered dynamics in the thermoresponsive shell, when going from the swollen to the collapsed state.

Therefore, we performed neutron spin-echo spectroscopy (NSE) experiments at J-NSE at FRM II in Garching. We used concentrations ranging from 200 to 300 mg/ml in D₂O for the di- (PS₄₈-b-PNIPAM₁₆₁) and triblock (PS₁₁-b-PNIPAM₂₉₀-b-PS₁₁) copolymer. The PS blocks in the diblock were fully hydrogenated whereas they were fully deuterated (PS- d_8) in the triblock copolymer. As D₂O has nearly the same scattering length density as PS- d_8 , only the dynamics of the PNI-PAM segments were monitored in the triblock copolymer. For the diblock copolymer, one expects to observe the dynamics of the PS-segments at high Fourier times, because the micellar core is glassy. Therefore, we are able to determine the fast dynamics in the thermoresponsive shell and characterize the influence of the polymeric architecture on the temperature behavior of the segmental dynamics.

Figure 2.4a shows the intermediate scattering functions for both copolymer architectures and temperatures below the LCST. For micellar systems three contributions to the intermediate scattering function are expected: (i) The segmental motion of PNIPAM leads to a fast decay (decay rate $\Gamma_{internal}$) in the intermediate scattering function. (ii) Micellar diffusion is slower than segmental motion. (iii) As PS is supposed to be glassy, its dynamics also contribute to the slow decay. Processes (ii) and (iii) overlap and are described by a single decay rate Γ_{slow} . The following equation was used to fit the intermediate scattering functions from NSE:

$$\frac{S(q,t)}{S(q,0)} = c \times [A_{\text{fast}} \exp(-\Gamma_{\text{internal}}t) + (1 - A_{\text{fast}})\exp(-\Gamma_{\text{slow}}t)]$$
(2.1)

S(q,t)/S(q,0) is the intermediate scattering function, t is the Fourier time and c is a factor accounting for S(q,t)/S(q,0) not reaching one at low t.

q-dependent measurements allow us to distinguish between the cooperative breathing mode and the single-chain Zimm dynamics of the PNIPAM shell. $\Gamma_{internal}(q)$ is found to be proportional to q^2 , thus the breathing mode is the dominating process for star- and flower-like micelles. The resulting diffusion coefficients, $D = \Gamma_{internal}/q^2$ are displayed in figure 2.4b as a function of temperature. Di- and triblock copolymer show the same behavior: Below the LCST, $D_{internal}$ is lower than above where, furthermore, it is independent of concentration. We attribute these findings to the following mechanism: Above the LCST, PNIPAM collapses and forms an immobile melt around the PS core. A few PNIPAM chains still stick out into the solvent. Only these, now very mobile, chains are monitored in the NSE experiment. From SANS it is known, that, above the LCST, the structure of the PNIPAM melt is independent of polymer concentration, thus the same dynamical behavior is expected there. Moreover, the diblock copolymer exhibits much faster dynamics than the triblock copolymer. This is explained by three major differences in the architecure of the micellar shell of both block copolymers. (i) In the flower-like micelles formed by the triblock copolymers, the PNIPAM blocks fold back into the core, i. e. both ends of the PNIPAM blocks are tethered to the core, in contrast to the star-like micelles formed by the diblock copolymer, where only one end of the PNIPAM block is tethered. (ii) Bridging of micelles occurs in the triblock copolymer system, which lowers the number of degrees of freedom for chain movement drastically. (iii) The PS block in the diblock copolymer is much longer than in the triblock copolymer investigated, which leads to a larger core radius and thus reduces the grafting density of PNIPAM on the PS core from 0.60 nm^{-2} to 0.20 nm^{-2} , which enables faster dynamics.

NSE is a powerful tool to follow the fast dynamics of the cooperative breathing mode in micelles from di- and triblock copolymers, consisting of PS and PNIPAM blocks, and thus leads, together with SANS, to a detailed understanding of thermoresponsive micellar networks.

This work is funded by the DFG within the project SPP1259 "Intelligent Hydrogels".



Figure 2.4:

(a) Intermediate scattering functions for di- (filled symbols) and triblock (open symbols) copolymer solutions at concentrations of 200 mg/ml (squares) and 300 mg/ml (circles); q = 0.15 nm^{-1} . T = 23.6 °C for di- and T = 24.0 °C for the triblock copolymer; the lines are fits of equation 2.1. (b) Diffusion coefficients for di- (filled symbols) and triblock (open symbols) copolymer solutions are calculated from the decay constant $\Gamma_{internal}$. The grey bar denotes the temperature range, where the collapse transition of the diblock copolymer occurs. The dotted line is the LCST of the triblock copolymer.

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ANNUAL REPORT 2010

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Kinetics of structural changes in thermoresponsive triblock copolymer solu-2.4 tions after a temperature jump

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Thermo-responsive polymers have received increasing attention because they respond with a strong volume change to a small variation 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 of 32 °C.

We investigate triblock copolymers consisting of 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. When heated above the LCST, the PNIPAM block becomes hydrophobic and releases water from the micellar shell, which consequently collapses. This volume change is reversible [2].

Time-resolved small-angle neutron scattering (SANS) experiments allow to investigate the kinetics of the collapse of the micellar shell and the cluster formation with an excellent time resolution (0.1 s) and give information on a wide range of length scales. For that purpose, a stoppedflow apparatus was used at beamline D22 at ILL. The triblock copolymer solutions (PS-d₈-b-PNIPAM-*b*-PS- d_8 in D₂O) were kept in a reservoir at a temperature below the LCST. To realize a fast temperature jump above the LCST, the solution was injected into the preheated sample cell and the time-resolved measurement was started. The curves were fitted using a model for spherical core-shell micelles together with different form and structure factors for their clusters (fractal [3], Porod [4]). The resolution functions were taken into account.

In figure 2.6, four different regimes are observed: (i) Before the LCST is reached, the micellar structure is nearly unchanged and the form factor of core-shell micelles together with a hardsphere structure factor [2] describe the data well. (ii) As soon as the micellar shell collapses and becomes hydrophobic, the micelles start to form fractal clusters. The fractal dimension, d_f , and the cluster size show, that, after an initial growth step, the fractal clusters rearrange and become more compact, thus d_f increases while the cluster size stays constant. (iii) After the fractal dimension $d_f = 3$ is reached the compact clusters continue to grow and reach a size of ~ 60 nm. In regime (iv), the cluster size appears to fluctuate. We attribute this to merging of the clusters. In the experimental scattering curve, one observes a decrease in the intensity of the forward scattering, indicating a reduction of the specific surface in the solution. Figure 2.5 summarizes the four regimes.

Thermoresponsive triblock copolymer solutions thus show a complex behavior of their collapse transition, when heated quickly above the LCST. We are able to gain insight into different steps of shell collapse and cluster formation using SANS with a high time-resolution.

This work is funded by the DFG within the project SPP1259 "Intelligent Hydrogels".



14



Figure 2.6:

(a) Temperature profile for a jump from 19.6 to 34.6 °C at a concentration of 50 mg/ml. (b) Core radius (filled circles), micellar radius (filled squares) and hard sphere radius (open squares). (c) Cluster size (filled squares) and fractal dimension d_f (open squares).

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2.5 Cononsolvency in thermoresponsive block copolymers

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Thermoresponsive polymers are smart materials which have attracted great attention because of their potential applicability in controlled ultrafiltration, drug delivery systems and sensors [1]. Among these, poly(N-isopropyl acryl amide) (PNIPAM) changes its conformation in water at a characteristic lower critical solution temperature (LCST) of *ca.* 32° C. The associated size variations thus result in a phase separation between water and the polymeric molecules. It has been shown that the addition of organic solvents shifts the transition temperature in mixed aqueous solutions by several Kelvin. Quite unexpectedly, this occurs in case of good organic solvents for PNIPAM. For instance, at room temperature (RT), both methanol (MeOH) and water (H₂O) are good solvents for the polymer; yet certain MeOH/H₂O proportions result in the precipitation of PNIPAM, indicating that the LCST has dropped below the ambient temperature. This rare phenomenon has been named *cononsolvency* and the organic solvent is regarded as the *cononsolvent* of the binary medium [2].

Large interest has been devoted to the homopolymer PNIPAM, however no thorough study in respect with cononsolvency has so far considered block copolymers that bear PNIPAM blocks. In order to overcome this gap, we have started the investigation of amphiphilic diblock copolymers consisting of a long PNIPAM block and a short polystyrene (PS) block in water/methanol mixtures. In diluted plain aqueous solutions, these species self-assemble into micelles with PNI-PAM blocks as the corona and PS blocks as the core of the aggregates. Upon increasing temperature and crossing the LCST, a phase separation occurs, attributed to the reduced solubility of the PNIPAM moieties which become hydrophobic and release water molecules from the outer part of the aggregates [3]. Turbidimetry and dynamic light scattering (DLS) techniques are used to monitor the LCST and the size of the aggregates formed in presence of methanol.



Figure 2.7:

Temperature-dependent results of a 0.6 mg/mL aqueous solution of the studied P(S-*b*-NIPAM): a) R_h from DLS; b) Light transmittance while heating and cooling the sample. The dashed lines depict the transition temperature

Our study focuses on a diblock copolymer (M = 27000 g/mol) consisting of 14 styrene and 238 NIPAM monomeric units. The DLS measurements point at the formation of micelles at room

temperature with a hydrodynamic radius (R_h) of about 30 nm. Upon increasing temperature, their size diminishes until, after crossing the LCST, objects of *ca*. 33 nm are detected, accounting for the generation of large clusters which precipitate in water (figure 2.7a). The phase separation is also shown by turbidimetry experiments, which confirm a reversible temperature-induced transition and an LCST of 30°C in pure water (figure 2.7b).

Maintaining constant the concentration of the polymer, solutions with a volume fraction of MeOH up to 35% were also investigated (figure 2.8 a, b). Even in presence of MeOH, the molecules self-organize into micelles with $R_h \approx 50$ nm when T<LCST. However, the addition of increasing amounts of MeOH promotes sharper and more pronounced phase transitions that lead to the formation of very large clusters when the LCST is crossed. More interestingly, the concentration of MeOH plays a remarkable role in tuning the values of the LCST, proving that MeOH acts as a cononsolvent also for amphiphilic block copolymers.

We tentatively attribute these findings to the replacement of the hydrating H_2O within the PNI-PAM blocks at the periphery of the micelles by larger MeOH molecules. Hence, the polymers form larger and less compact aggregates compared to the ones generated in pure water. At the same time, as the content of water to be released by the micelles has diminished, phasetransitions are expected to occur sharply and at lower temperatures.

In conclusion, the combination of turbidimetry and DLS techniques has successfully proved that the cononsolvency effect is operative in thermo-responsive block copolymers. Further studies are in progress to determine the morphology and the dynamics of the aggregates formed in mixed $H_2O/MeOH$ solutions.

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Figure 2.8:

Temperature-dependent results of a 0.6 mg/mL mixed aqueous solution of the studied P(S-b-NIPAM). The legend reports the concentration of MeOH as volume fraction percentage. a) R_h from DLS; b) Light transmittance while heating and cooling the sample.

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2.6 Switching kinetics of PMDEGA based thermo-responsive hydrogel films probed by in-situ neutron reflectivity

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Thermo-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]. A novel thermo-responsive poly(monomethoxy diethyleneglycol acrylate) (PMDEGA) exhibits a higher value of the lower critical solution temperature (LCST), as compared to the frequently investigated thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM). The LCST of PMDEGA is around 40 °C. Thus PMDEGA can be an interesting alternative to PNIPAM in tropical countries where the mean temperature is already above LCST of PNIPAM (32 °C).

In order to probe the swelling behavior and switching behavior of PMDEGA films under thermal stimuli, in-situ neutron reflectivity (NR) measurements are performed at the instrument D17 (ILL, Grenoble). The PMDEGA films were prepared by spin coating on Si substrates. In the NR experiment the film is mounted vertically in the customized aluminum chamber, the neutron beam is illuminating the sample through the aluminum foil window on one side, then the reflected beam forwards to the detector through the aluminum foil window on the other side. The sample-detector distance is 3.4 m and the incident angle is 0.5 degree. In the NR measurement, TOF (time of flight) mode with a wavelength band from 0.2 nm to 2 nm is used.



Figure 2.9:

a) Static measurement for the PMDEGA film (data shown with black dots and model fit with solid line). b) Seleected eleven NR data probed during the swelling process shown together with a best model fit. c) Normalized film thickness of the PMDEGA film and d) volume percentage of D_2O absorbed inside the film shown as a function of time.

Fig. 2.9a shows the static NR data for a dry PMDEGA film. The experimental data are shown by the black points and the best model fit with the solid line. From the fit to the NR data, the total PMDEGA film thickness is obtained. For the investigated samples it is 35.9 nm. To start the kinetic experiment, 10 mL D_2O is injected into the reservoir of the sample chamber. Thus the PMDEGA film is exposed to a water vapor atmosphere and starts to swell due to the incorporation of water molecules. Due to the optimized TOF mode, a high flux neutron beam is available for kinetic measurement. We were able to probe the swelling of the PMDEGA with NR with a time resolution of 15 s for every full NR curve. In order to obtain the information about structural change during the swelling process, the individual NR curves are all fitted simultaneously. Fig. 2.9b presents eleven selected NR curves from the kinetic experiment together with a best model fit. In the NR data the distance between the second and third minimum is decreasing with time, which means that D_2O is absorbed by the PMDEGA film and the film thickness is increasing. From the fits to the NR data an increase in film thickness from 35.9 nm to 41.6 nm is found. The corresponding ratio of swollen film thickness normalized by the dry film thickness is obtained as shown in Fig. 2.9c. The calculated volume percentage of D_2O absorbed inside the PMDGA film is presented in Fig. 2.9d as a function of time. From both curves it can be concluded that the film thickness is increasing by 15 % when it is saturated after 3 hours swelling, and at that at maximum 18 % D_2O are absorbed inside the PMDEGA film.



Figure 2.10:

a) Selected eleven NR data probed during the temperature jump above the LCST. b) Normalized film thickness of the PMDEGA film and c) volume percentage of D_2O absorbed inside the film shown as a function of time.

When the swelling of the PMDEGA is equilibrated, the film is exposed to a temperature jump from 23 °C to 45 °C to probe its responsive behavior (switching). This change in temperature corresponds to a jump above the LCST of the PMDEGA polymer. In Fig. 2.10a a selection of eleven NR curves, probed after the temperature jump, are presented. The Fig. 2.10b and Fig. 2.10c present the normalized film thickness and volume percent of D_2O absorbed inside the film as a function of time after the temperature jump above the LCST. First the film thickness shrinks due to the collapse of the PMDEAG chains when the temperature is above LCST. Next a relaxation process sets in, which causes the film to re-swell. The reason for this additional relaxation process may be caused by a too strong water repelling during the temperature jump. After a first collapse the structure of the polymer chains can rearrange itself and thereby absorb some D_2O again because the film is still surrounded by water vapor atmosphere.

At the moment when the normalized PMDEGA film thickness has dropped from 1.15 to 1.02, the remaining amount of incorporated D_2O is still 9 %, which means that the PMDEGA film has holes and vacancies in it.

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2.7 Gold-sputter-deposition on PNIPAM-based triblockcopolymer thin films

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In our studies we investigate a ABA-triblock copolymer where the B-block consists of poly(Nisopropylacrylamide) (PNIPAM) and the A-blocks consist of poly(3,5-dibromobenzyl acrylate) (PDBA). The polymer was polymerized using RAFT-polymerization [1]. The combination of a hydrophilic center part (PNIPAM) in the triblock copolymer and a hydrophobic end part (PDBA) causes formation of star-like micelles in aqueous solution. From such solutions thin films were produced with spin-coating (2000 rpm, 60 s) on silicon substrates pre-cleaned with an aqueous solution of ammonia (NH₃) and hydrogen peroxide (H₂O₂) which leads to a very smooth hydrophilic surface. The basic idea is to build a similar structure as in the solution on the substrate, where cylindrical domains should be formed due to the ratio between PNIPAM block and the PDBA blocks. On top of this structure in-situ with grazing incidence small-angle X-ray scattering (GISAXS) at the beamline BW4 at HASYLAB, Hamburg.



Figure 2.11:

Left: 2D-GISAXS images recorded with start-stop sputtering. The calculated thickness of the gold film is given in the pictures, the color bar on the right bottom. For images with strong scattering a rod-like beamstop was used to shield the center part of the detector. Right: Horizontal cuts at the critical angle of the polymer, the curves are shifted from bottom (0 nm) to top (14 nm) for clarity. The black points show the data, the red lines are fits as explained in the text.

For the in-situ GISAXS measurement of the gold sputtering we used a Pilatus 300k detector with a resolution of 619×487 pixels and a pixel size of $172 \times 172 \ \mu m^2$. The accumulation time for each image was 1 second. In order to get higher resolution and better statistics we repeated the measurement with a start-stop sputtering mode. In this mode sputtering is done for a given time, then the sputtering was stopped, and a GISAXS measurement with another detector (MarCCD

with 2048×2048 pixels resolution and $71.9 \times 71.9 \ \mu\text{m}^2$ pixel size) was conducted. Accumulation time for GISAXS was increased to 20-30 minutes (depending on the intensity of the scattered signal) for better statistics. A comparison between images of both detectors with the same amount of gold deposited on the polymer film shows qualitatively very similar pictures. Therefore the 2D-images shown in figure 2.11 were all obtained with the higher resolution and better statistics using the start-stop sputtering mode.

The first 2D-image (0 nm in fig. 2.11) was taken before the start of the gold sputtering and shows a structure in the triblock copolymer film with a lateral size of roughly 35 nm, which is clearly seen in the out-of-plane cut shown on the right side of fig. 2.11 (bottom curve). All of the outof-plane cuts of the 2D GISAXS data have been fitted with an effective surface model to retrieve information about the position of the structure peaks. Already after deposition of nominally 2 nm of gold, the strong scattering of the gold dominates the scattering-image and the small peak visible before the beginning of the sputtering has vanished. A new peak is seen for high q_v-values that corresponds to the average distance of gold clusters formed on the surface. For longer sputtering times it can be clearly seen that this peak moves towards lower q_v-values, indicated by the red arrow in the graph, which denotes an increase in lateral structure size. The peak positions of the pure polymer film and the gold sputtered on top are at different values, so the formation of the gold clusters is not preferably at one block of the triblock copolymer and the polymer structure has no direct influence on the formation of the gold clusters in terms of defining a matrix with different sticking coefficients for gold. In the 2D-images also a peak along the q_z -axis is visible that, for longer sputtering times, moves to lower q_z -values, which corresponds to an increase in thickness of the deposited gold. In the image with nominally 14 nm deposited gold the second order peak is visible along the q_z -axis.



Figure 2.12:

Different growth stages for gold sputtered on polymer. The nucleation of small gold clusters (1) is followed by a lateral growth of these clusters (2). The larger clusters start coarsening (3) and then the gold film starts to grow vertically (4). [2]

It has been previously reported that the gold deposition on polymer thin films follows four steps that are shown in figure 2.12 [2]. The first step is nucleation of small gold particles on the surface that grow laterally in the second step. In the third step coarsening of the gold clusters takes place. By this coarsening, the cluster size as well as the average distance of the clusters increases. This increase in distance is what the out-of-plane cuts in figure 2.11 show. So the first two steps are too short to see them on the obtained GISAXS images. The fourth step is the vertical growth, which can be seen in the peaks in q_z direction as mentioned before.

In summary we have shown that the deposition of gold on a P(DBA-b-NIPAM-b-DBA) triblock copolymer is very similar to the deposition on a homopolymer film. The GISAXS-measurements clearly show that the polymer film is structured but the structure does not influence the growth of the gold film, which was investigated in-situ.

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3 Thin polymer films



3.1 Density of polybutadiene melts at the polymer-solid interface

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Close to the interface between a polymer film and a solid, the polymer properties have been found to deviate from the bulk and to form an interphase. This change in physical behaviour is of importance for the adhesion of polymer coatings to solids, e.g. in medical implants and in nanocomposites [1]. The properties of a polymer melt close to a solid interface may be significantly altered compared to the bulk, e.g. the density by chain conformations or free volume. However, not only the structural changes near a solid interface are of importance, but also the dynamics, i.e. the local mechanical properties. This may 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.

The goal of the project is to achieve an improved understanding of the interphase properties of a polymer-solid contact by correlating the mass density, i.e. the polymer structure, with the local viscosity, i.e. the polymer dynamics, near the solid interface as function of polymer-solid interaction. All techniques measure interphase and bulk properties at the same time enabeling a direct comparison between bulk and interphase properties. At this we have chosen 1,4-polybutadiene (PB) as a model system with a broad range of molar masses from 0.7 kg/mol to 2,200 g/mol. Polybutadiene melts from toluene solutions on oxidized silicon are studied as a model system. To tune the interface interactions between substrate and polymer melt, the substrate surface is modified chemically and by silanization.



Figure 3.1:

(a) TOF NR of a 280 nm silicon oxide layer on silicon with fit and scattering length density profile (inset). (b) Magnified interphase between silicon and silicon oxide. (c) TOF NR of (a) with an additional layer of d-PB with a molar mass of 55 kg/mol spin coated from a deuterated toluene solution. (d) Magnified interphase of d-PB at the silicon oxide interface

The mass density profile of PB near the substrate will be determined with high-resolution time-of-flight neutron reflectometry (TOF-NR) at REFSANS, GKSS. Toluene-rinsed, dry thermally oxidized silicon substrates are investigated (Fig. 3.1a) along with a film of deuterated polybutadiene with a molar mass of 55 kg/mol spin coated from a deuterated toluene solution (Fig. 3.1b). The magnification of the interphases between silicon and silicon oxide as well as the one between silicon oxide and PB show a scattering length density lower than the bulk value (Fig. 3.1c,d).

Surface plasmon resonace optical waveguide spectroscopy (SPR/OWS) is used to investigate the optical properties of PB films, e.g. the refractive index [2]. Near a gold coated heavy flint glass prism, a lower refractive index for PB at the interface is found compared to the bulk value. This is evident from the plasmon displacement between the measured plasmon position and the position expected from the bulk properties obtained from the fit of the waveguide modes (Fig. 3.2). We also found a slight increase of the refractive index with molar mass, whereas films of PB with molar masses lower than 10 kg/mol are not stable. We attribute this increase in refractive index with molar mass to an increase in density caused by a decreased amount of polymer end groups and the related decrease of free volume [3].



Figure 3.2:

(a) Reflectivity of laser beam on a gold-coated heavy flint prism with a 1.5 μ m thick PB film on top showing waveguide modes between 20 and 60 ° as well as the surface plasmon. Shown are the measured reflectivity (solid line) and a fit of a homogenous film (dashed line). The deviation between fit and experiment at the plasmon is caused by a polymer interphase with a lower refractive index than in the bulk. (b) Bulk refractive index of PB with molar masses between 10 and 2,200 kg/mol after each preparation step, showing a slight increase with increasing molar mass

In summary, we have investigated static properties of polybutadiene films and have found a lower density close to silicon oxide and a lower refractive index near gold interfaces.

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3.2 Near-surface composition profiles of pressure sensitive adhesive films

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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, 2]. The adhesive properties of the PSA films are mainly determined by near-surface regions. However, detailed information about near-surface structures of such adhesive films is still missing.

In the presented work we investigate the time dependent near-surface composition profile of P(EHA-stat-MMA) which is a statistical copolymer comprising 80% of the sticky monomer ethylhexylacrylate (EHA) and 20% of the glassy monomer methylmethacrylate (MMA). Due to the low glass transition temperature of PEHA ($-65^{\circ}C$) and the resulting high mobility of the components in the system, it can already be assumed that freshly prepared films differ from such which are stored for many days. The underlying reorganization process is also referred to as aging of the adhesive.

The PSA films were prepared with toluene based solution casting on pre-cleaned glass substrates under ambient conditions. During drying, the films are protected by a cubic box of approximately 30 cm. In order to provide an environment that is close to practical applications, the films are again stored under ambient conditions for the aging experiment.



Figure 3.3:

a) Fresnel-normalized x-ray reflectivity data and fits of P(EHA-stat-MMA) as a function of time (see labels) and b) the corresponding refractive index profiles in color-coded representation (pure PEHA is shown in white color and PMMA in black color).

To investigate the surface structure, we probed the refractive index 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 3.3a shows reflectivity curves of P(EHA-stat-MMA) 1, 2, 8, 134 and 359 days after casting the solution onto the substrate. The so-called Fresnel-normalized representation is chosen because it is beneficial for visualization of thin enrichment layers. The solid lines are the fits to the data. Since the sample consists of two components, the corresponding refractive index profiles can be directly converted into vertical composition profiles which are depicted in figure 3.3b. To emphasize the main differences, a zoom into the upper 200 Å is selected. The profiles are color coded in a way that pure PEHA is represented by white color and PMMA by black color.

For the freshly prepared sample, there is a strong enrichment of PMMA at the polymer-air interface which is more soluble with respect to toluene. A second, weaker PMMA-enriched zone is present in a depth of z = 65 Å. Underneath, we find a PEHA-dominated region converging towards homogeneous bulk material for all investigated sample ages. Already one day later, the top layers collapse and more and more PEHA enriches at the sample surface with time. This behavior can be explained by the surface tensions of the involved materials which are $\gamma_{\text{PEHA}} = 30 \text{ mN/m}$ and $\gamma_{\text{PMMA}} = 38.5 \text{ mN/m}$. As a conclusion, the material with the lower surface tension enriches at the surface.



Figure 3.4:

a) Representative tack curves for different sample ages (see labels), b) corresponding tack energy and c) stress maximum as a function of time.

Figure 3.4 shows the results of an aging series of P(EHA-stat-MMA) in a probe tack test [3]. Representative stress-strain curves are displayed in figure 3.4a. Prominent parameters such as the tack energy or the stress maximum are plotted as a function of time in figures 3.4b and 3.4c. As a result, these values exhibit no time dependence within the achieved experimental accuracy. To understand this result, the corresponding punch roughness, which was 51 Å, needs to be taken into account. An integration of the composition profiles over this thickness shows almost constant PMMA concentration for the probed time window. Thus, for the punch which was used in the tack experiment, the adhesive performance does not change with time [4].

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3.3 Near-surface solvent content profiles evolving during solution casting

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Solution casting is an important processing method for many polymeric films such as paints, corrosion protections, adhesives or organic electronic devices. A wide thickness range from a few nanometers up to millimeters is accessible and there is almost no limitation concerning the desired shape of the films. Among other parameters, solvent evaporation can be a driving force for the surface roughness or the morphology of the polymer coating [1] and thus, the knowledge of the underlying kinetics is of utmost importance.



Figure 3.5:

Left: In-situ NR data for the drying process of P(nBA-stat-MA) with a molecular weight $M_w = 54 \cdot 10^3$ g/mol. For clarity, the curves are shifted along the y-axis and split up into two graphs. The sample age increases from top to bottom. Right: corresponding SLD profiles in which the sample age increases from left to right. The SLDs of the involved materials are marked by the vertical lines as shown by the label.

Solvent loss rates reported in literature do not distinguish between different regions of a drying film and depend on time *t* as t^k where *k* can vary between $\frac{1}{2}$ and 1. Motivated by the importance

of the near-surface part of polymeric materials [2], we focus on the solvent distribution as a function of time within a near-surface part of a drying solution with in-situ neutron reflectometry (NR).

The NR experiments were performed at the FIGARO instrument of the Institut Laue-Langevin (ILL) in Grenoble (France). This high-flux time-of-flight (TOF) [3] instrument enables a time resolution of 2.5 min in the stages of high solvent content for our sample system. The sample was positioned perpendicular to the gravity field making it possible to measure liquid surfaces. The angle at which the neutrons impinged on the sample surface was selected to 0.624° . Although disturbing vibrations due to motor movements were avoided owing to the TOF mode, the sample chamber was additionally mounted on an anti-vibration table. A further advantage of the TOF mode is that the whole q_z -range of the probed reflectivity curve is averaged over the same time interval.

We start from a freshly coated, toluene based poly(n-butylacrylate-stat-methylacrylate) (P(nBAstat-MA)) solution with a molecular weight of $M_w = 54 \cdot 10^3$ g/mol, which represents a model system for pressure sensitive adhesives and perform continuously NR experiments until the extractable solvent has evaporated. Due to the choice of a protonated polymer and deuterated toluene, neutrons provide a very high contrast between the solvent and the polymers, whereas the components of the copolymer are not distinguishable on purpose.

From top to bottom, the figures 3.5a and c show the evolution of the NR curves (symbols) with time in the first 5 h after casting the solution onto the substrate. According to the achieved counting rates and the evaporation speed the data of several measurements were summed up. The black solid line is the fit to the data. The first seven curves are still equal to NR data of pure liquid toluene. During drying the critical edge shifts in an accelerated way before it converges to a constant value for large times t.

Figures 3.5b and d show the corresponding scattering length density (SLD) profiles. The data are fitted under the assumption of homogeneously distributed toluene except for a time interval of 10 min (see curves which are not constant in SLD). In this time interval, there is a 60 nm thick region at the top of the sample in which the solvent concentration is larger than in the bulk underneath. At the maximum, the solvent concentration at the interface exceeds the bulk value by 7.7 %. Repeating the experiment with polymers of different chain lengths revealed that the corresponding time interval and the amplitude of the concentration difference between bulk and surface increase with increasing molecular weight [4].

A possible explanation can be found in the free-volume theory which is crucial for transport phenomena of macromolecular materials [5]. The chain end density close to the sample surface is increased [6] which provides more free volume being occupied by the evaporating solvent. This mechanism can be responsible for the observed stage of inhomogeneous solvent distribution. It has to be noted, however, that also altered viscoelastic properties due to the presence of the interface might contribute to this phenomenon. Thus more theoretical work concerning this near-surface region during solvent evaporation would be beneficial.

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3.4 Surface-induced breakout crystallization in cylinder-forming P(I-*b*-EO) diblock copolymer thin films

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Polymer crystallization is dominated by the necessity to reorganize coiled polymer conformations into thin, crystalline lamellae. Confining crystallizable polymers chains has a drastic effect on both the nucleation and the growth of crystals. Confinement can, among others, be achieved by attaching an amorphous block to form a diblock copolymer with a crystallizing and an amorphous block. Breakout crystallization into layered crystals has, among others, been observed to occur in the hexagonal morphology [1].

We present here the (very slow) crystallization of a thin film of low molar mass, cylinder-forming P(I-*b*-EO) diblock copolymers having block molar masses 2100 and 1100 g/mol [2]. The thin film geometry allowed us to visualize the growth of the PEO crystals by atomic force microscopy (AFM). X-ray reflectometry (XR) and grazing-incidence small-angle X-ray scattering (GISAXS) enabled us to characterize the buried mesoscopic morphology in the thin film, and grazing-incidence diffraction (GIXD) provided information on the crystalline structure within the PEO microdomains. The sample was annealed above the melting point of PEO (32°C) for a few min and was then quenched to room temperature. GISAXS and GIXD were carried out at beamlines BW4 and BW2 at HASYLAB, DESY.

The AFM phase image of the as-prepared film reveals a striped texture (Figure 3.6a), suggesting PEO cylinders lying parallel to the film surface embedded in the PI matrix. XR on the as-prepared film (Figure 3.7a) reveals that the PEO cylinders are arranged in layers, as evident from the scattering length density (SLD) profile in Figure 3.7b. The Bragg reflections in the GISAXS image of the as-prepared film confirm the initial hexagonal morphology (Figure 3.7c). The GIXD curve for the freshly prepared film does not show any Bragg reflections from PEO (Figure 3.7d), i.e. the cylindrical PEO domains have not crystallized yet.



Figure 3.6:

Surface analysis: AFM phase image of the as-prepared film (a) and height image of the film after 148 days (b).

For weeks, no crystallization occured. After 148 days, the surface morphology showed terraces of height 120 ± 10 Å in the whole film area (Figure 3.6b) which are layers of crystallized PEO and amorphous PI. Crystallization thus started at the film surface. Breakout crytallization from the PEO cylinders results in a change of layer thickness by 20 %. GIXD reveals the weak 120 Bragg reflection from the upper crystalline PEO layers (Figure 3.7d) [3]. The XR curve confirms that the lower-lying layers are unchanged whereas the upper ones have a repeat distance ~ 120 Å (Figure 3.7a,b). The latter consist of alternating PI and crystallized PEO layers. The hexagonal morphology consisting of PEO cylinders lying in the PI matrix is thus destroyed by the PEO breakout crystallization at the film surface. The crystalline surface layers consist of once-folded, fully interdigitated PEO blocks together with the attached amorphous PI blocks. Inside the film, in contrast, the hexagonal morphology with D = 94.6 Å along the film normal



Figure 3.7:

(a) XR curves of the as-prepared thin film (upper red curve, shifted) and after 148 days (lower blue curve). (b) Resulting SLD profiles. Full red line: as prepared, dash-dotted blue line: after 148 days. (c) 2D GISAXS image from the as-prepared thin film. Symbols indicate the positions expected for the first-order Bragg reflections of the hexagonal lattice. (d) GIXD intensity profiles of the as-prepared thin film (lower red curve) and after 148 days (upper blue curve).

of the as-prepared is unchanged. Here, the mismatch between the desired layer thickness of the crystalline PEO/amorphous PI layers and the repeat distance of the hexagonal lattice is too strong, thus crystallization can only take place very slowly at the film surface. The strong change of repeat distance from the amorphous hexagonal to the crystalline lamellar phase at the film surface can only be accommodated by significant mass transport, which results in terraces and may be a reason why crystallization in this (soft) system is so slow.

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3.5 Thermally modified molecular arrangement of P3HT films probed in-situ with a novel combination of optical ellipsometry and GIWAXS

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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.

One very promising material is poly(3-hexylthiophen-2,5-diyl) (P3HT), which has proven its suitability in combination with a fullerene, e.g. PCBM, for the fabrication of organic solar cells with overall power conversion efficiencies of up to 5% [1]. Also in combination with n-type F8TBT high efficient all-polymeric solar cells have been already successfully manufactured by McNeill et al.[2]. Interestingly the efficiency of P3HT:F8TBT solar cells could be increased by almost a magnitude due to posterior annealing of the device. This is contributed to the strong tendency of P3HT to crystallize, which is also favored by heat treatment above the glass transition temperature ($T_g \approx 130^{\circ}C$). Such thermally induced highly crystalline P3HT thin films have also shown electrical conductivities magnitudes higher than untreated thin films.



Figure 3.8:

(a) Experimental set-up for in-situ combination of ellipsometry and GIWAXS measurements including an heating stage; (b) characteristic GIWAXS spectrum including the possible molecular ordering of the polymer chains.

Grazing incidence wide angle X-ray scattering (GIWAXS) can be used to probe the molecular ordering of polymer chains in photoactive thin films [3]. In combination with optical ellipsometry, which additionally reveals the film thickness and offers information about the refractive index *n* and the absorption coefficient *k*, a full study of the thin film properties can be achieved. Figure 3.8a shows the in-situ set-up as it was installed at the BW4, HASYLAB (Hamburg). The ellipsometer and the X-ray beam are oriented to each other in such a way that the same sample area can be addressed by both methods. A characteristic scattering signal of a pure P3HT film spin-coated on a solid silicon support is shown in figure 3.8b. The scattering along the α_f -direction indicates the ordering parallel to the support, whereas the maxima along 2θ are given by the orientation of the polymer chains vertical to the support (illustrated also by the insets). For the heat treatment five different temperature steps are chosen: $25 \, ^{\circ}C$, $90 \, ^{\circ}C$, $120 \, ^{\circ}C$, $150 \, ^{\circ}C$, and $180 \, ^{\circ}C$. Also the transition back to $25 \, ^{\circ}C$ was monitored. The temperatures were chosen



Figure 3.9:

a) Out-of-plane cuts taken along exit angles α_f for sample and b) corresponding elliprometric data probed at different annealing temperatures.

to be well below and above the glass transition temperature of the polymer. For all different steps the temperatures were kept constant during the GIWAXS and the ellipsometric measurements. Figure 3.9a shows the integrated cuts along the α_f -direction for all temperatures. For all stages prominent maxima at the (100), (200), and (300) Bragg peaks are visible. In addition with higher temperature the positions are shifted to smaller q-values indicating increasing lattice constants. Interestingly, the (010)-peak visible at larger angles is in comparison to the (100)-peak and its corresponding higher orders only slightly shifted. Also a strong tendency of the polymer chains to orient in a perfect lattice can be seen from the increasing acuity of the observed peaks. Whereas the untreated sample shows broad peaks indicating a wide orientation distribution, the annealed samples reveal a much better molecular ordering. After cooling down the lattice constants relax to the as-prepared values, but the ordering perfection remains constant as for the heated samples. This saved embedded ordering of the polymer chains finally leads to an increased electrical conductivity along the carbon backbone.

The simultaneous obtained ellipsometric measurements shown in 3.9b exhibit a strong variation in the characteristic Δ - and Φ -values. The Φ -values correspond to the relative amplitude ratio, whereas the Δ -values give information about the relative phase shift. Both values can be fitted with an optical model which finally depends on the film thickness, the refractive index, and the extincton coefficient. In the data the minimum position of the Ψ -value is shifted to smaller angles of incidence with increasing annealing temperature and the shape of the Δ -curves is flipped around at the glass transition temperature of the polymer. These characteristics already indicate a similar morphological change as observed with GIWAXS leading to altered absorption coefficients. In order to extract the full information the data analysis of the ellipsometric measurements is still ongoing.

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3.6 Exploring different substrates for functional photoactive thin polymer films

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Recently, conducting polymer films have been studied because of their promising application in touch screens, LCDs, OLEDs and solar cells [1-2]. Compared with conventional inorganic photoactive thin films, polymer films have many unique features, such as light weight, easy processibility, low cost and flexibility. There have been many studies on organic solar cells. However, so far only little attention is focused on flexible organic solar cells. Flexible polymer solar cells and panels will allow in future for several types of application to be introduced into the market including solar backpacks, solar thin film clothing and athletic apparel.

In this work, we chose a flexible polyethylenterephthalate (PET) foil as model substrate to replace the rigid glass substrate. The PET foil has an ITO electrode. The blend system poly(3hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) is used as the active polymer layer. In first experiments, the different efficiency of model solar cells with PET substrates and glass substrates are investigated.



Figure 3.10:

Representative I-V curves of the P3HT:PCBM based solar cells on ITO/PET substrates (red symbols) and ITO/glass substrates (black symbols) probed in the dark (squares) and under solar illumination (AM 1.5, 100mWcm, $^{-2}$) (circles).

The organic solar cells with PET substrates and glass substrates are made with the same preparation process of the functional stack. The ITO covered substrates are cleaned with alconox, ethanol, acetone and 2-propanol in an ultrasonic bath. The cleaned substrates are treated with O_2 plasma for 10 minutes. On top of the substrates PEDOT:PSS is spin coated and subsequently annealed for 15 min at 150 °C. Further spin coating is carried out to deposit the active P3HT:PCBM blend film, and the samples are completed by deposition of the Al top electrode by thermal evaporation. Finally, the solar cells are annealed in a glove box for 10 min at 150 °C. Thus the resulting functional stacks are not fully optimized towards device preparation but feature all necessary layers to allow for moderate efficiencies. Thus we can detect the influence of the used substrate on the device performance.

We investigate the photoactive properties of solar cells with ITO/glass and ITO/PET as substrates, separately. Representative I-V curves probed on the two types of systems are shown in Fig. 3.10. The change in the substrate changes the solar cell efficiency. For the selected functional stack build-up the solar cells on ITO/PET substrates have a 9 % lower efficiency as compared with the ones on ITO/glass substrates. In detail, the I-V curves probed without illumination in the dark are the same for both substrates. The shape of the I-V curves under illumination (AM1.5 condition) is still similar, which means both systems have a similar fill factor (FF). However, we find a value of the FF of 46.75 % for the solar cell on ITO/glass substrates and 49.59 % for the solar cells on the ITO/PET substrates, respectively. In addition, the open circuit voltages V_{oc} are nearly the same, coming from the same system used. The V_{oc} values are -0.62 V in solar cell on ITO/glass substrates and -0.61 V in solar cell on ITO/PET substrates. The largest difference is observed in the short circuit current I_{sc} . The value of I_{sc} of solar cell on ITO/PET substrates is 14 % lower than the one probed for the ITO/glass substrates. Consequently, less charge carriers are extracted from the solar cell on ITO/PET substrates as compared with the ITO/glass substrates.

For further investigation of the origin of the difference in I_{sc} of the two solar cells, the optical transmission spectra of the ITO/glass and ITO/PET substrates are examined. The results are shown in Fig. 3.11. Both curves show almost no transmission in the UV range below 300 nm. It can be seen that the transmission of ITO/PET substrates is lower than that of the ITO/glass substrates, especially in the range of 300 nm to 450 nm, which means ITO/PET substrates absorb more light than ITO/glass substrates. Consequently, less light reaches the active layer in the solar cell on ITO/PET substrates as compared with the ITO/glass substrates. So there are less charge carriers in solar cell on ITO/PET substrates generated, and it shows lower efficiency compared with the solar cell on ITO/glass substrates.





In summary, we find differences in the efficiency of the solar cells on ITO/PET substrates and ITO/glass substrates. Most likely, the lower performance of the ITO/PET system arises from the lower transmission of ITO/PET compared with ITO/glass substrates. Thus alternative foil materials with improved transmission can be a solution to reach identical efficiencies for flexible solar cells as for rigid ones on glass. However, a serious device optimization might overcome the found differences in efficiency between both types of carrier materials as well. At present we focus on alternative foils.

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3.7 In-situ study of lamellar poly(styrene-b-butadiene) diblock copolymer thin films during heat treatment

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Nanostructured block copolymer thin films find a number of applications, especially as templates for inorganic 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 to remove defects and thus to improve the orientation and the long-range order [2]. Annealing temperature is a key parameter because it influences both, the interfacial tension between the two blocks and the polymer mobility. The latter is of importance in the case that one of the blocks is in the glassy state at room temperature, such as the frequently used polystyrene (PS). Only above its glass transition temperature, T_g , the block is expected to be mobile enough to enable long-range diffusion of the block copolymer.

The poly(styrene-*b*-butadiene) P(S-b-B) system studied by us is well-suited to address the structural changes during thermal annealing because the initial lamellar orientation can be controlled. We have studied thin films of lamellar (P(S-b-B)) diblock copolymers having a molar mass of 216 kg/mol to elucidate the mechanisms of structural changes induced by thermal treatment. Initially, the lamellae have the perpendicular orientation [3]. In-situ grazing-incidence small-angle X-ray scattering (GISAXS) at beamline BW4, HASYLAB at DESY and VIS interferometry, as well as ex-situ atomic force microscopy (AFM) and X-ray reflectometry (XRR) were used. The annealing temperature was varied in a wide range (60 - 130°C).





2D GISAXS image (a), AFM height image, size 3 μ m \times 3 μ m (b) and 2D Fourier transform (b, inset), all at room temperature.

At room temperature, the 2D GISAXS image displays straight diffuse Bragg rods (DBRs) which indicates the perpendicular lamellar orientation (Fig. 3.12a). From their lateral positions, a lamellar thickness of 854 ± 5 Å is determined using Bragg's law. The AFM height image shows randomly oriented, small lamellar domains with many defects (Fig. 3.12b). The lamellae themselves are not continuous but consist of small round grains. The 2D Fourier transform (Fig. 3.12b, inset) displays a distinct ring. At temperatures between 60° C and 100° C, the DBRs bend inwards (Fig. 3.13, left). We attribute this bending to tilting of the lamellae away from the purely perpendicular orientation. Upon subsequent cooling down to RT (Fig. 3.13, middle), the straight diffuse Bragg rods (DBRs) reappear, i.e. the perpendicular orientation is recovered. In contrast, upon thermal treatment at 105° C and 120° C, the DBRs not only bend inwards, but their scattering intensity becomes very weak. Cooling down to RT, the DBRs vanish nearly completely, showing that the process is no longer reversible. After annealing at 130° C, the DBRs do
not reappear upon cooling down to RT, i.e. the structural changes are irreversible. AFM images of the surface were taken ex-situ after cooling to room temperature (Fig. 3.13, right). After annealing at temperatures between 60 and 100°C, the local order at the surface improves slightly. In contrast, after annealing at 105-115°C, the surface order is lost. We thus found that the processes during thermal annealing strongly depend on the treatment temperature. In particular, the highest glass transition temperature of the two blocks plays an important role: after annealing below the glass transition temperature of the PS block, T_g (PS), the perpendicular orientation is unchanged after cooling down to RT, whereas a more random lamellar orientation is observed after treatment above T_g (PS) and subsequent cooling.

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Figure 3.13:

Left: 2D GISAXS images at annealing temperatures of 85°C (a), 100°C (b), 105°C (c), 120°C (d), 130°C (e) and subsequent cooling down to RT (middle). Right: AFM height images, size 3 μ m × 3 μ m, and 2D Fourier transform after cooling down to RT from these annealing temperatures.

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4 Polymer films for applications in photovoltaics



4.1 Super-structuring of nanoporous titania films for application in photovoltaics

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Dye sensitized solar cells (DSSCs) are among the most promising candidates for thin-film, lowcost photovoltaics. A typical DSSC consists of a transparent conducting oxide (TCO) on a thin glass or foil substrate serving as front electrode and supporting medium for the solar cell. A thin layer of nanoporous titania film covered with a dye (e.g. ruthenium complexes), which acts as the active layer in which electric charge is generated, is attached to the TCO. Finally, a solid state hole conducting material or liquid electrolyte is used to connect the titania film with the back electrode, typically made from platinum. The nanoporous titania film is a very important trait of a DSSC. A monomolecular layer of dye has a very low absorption coefficient. The nanoporous film leads to an increase in surface area by several orders of magnitude compared to a bulk film. This was first utilized by Grätzel et al. to significantly increase the efficiency of DSSCs [1]. The addition of a microstructure to nanostructured titania films, as for example a periodic grating super-structure, promises improved device performance. For example, Niggeman et al. have shown that a microstructured active layer can enhance a thin film solar cells efficiency.[2]

A sol-gel process with a structure giving diblock copolymer was used to control the nanostructure of the fabricated titania films. Previously, Cheng et al. have shown that a large variety of structures can be achieved when applying different weight percentages of the materials used during the sol-gel process. During this work, poly(styrene-block-ethylene oxide) (PS-b-PEO) with molecular weights of the blocks of 16000 g/mol for the PS block and 5000 g/mol for the PEO block, which is commercially available from Polymer Source Inc., was used. It has a polydispersity index of P = 1.04 and was dissolved in 1,4-dioxane. As selective solvent, 37% hydrochloric acid (HCl) was used. The weight ratios during the sol-gel process were chosen to provide a foam-like nanostructure according to Cheng et al [3].



Figure 4.1:

Optical microscopy image of an example of a) soft embossed and b) a wet imprinted titania films. Both images have a magnification of $50 \times$.

A master fabricated via soft lithography was used to transfer the microstrucutre onto thin titania films and thereby super-structure the nanostructured titania films. As probed with atomic force microscopy (AFM) the selected masters grating has an average depth of 90 nm, a width of 2.35 μ m and a periodicity of 1.60 μ m.

Two methods of transferring the masters structure were persecuted: soft embossing and wet imprinting. At soft embossing a thin titania/polymer hybrid film prepared via spin coating is

heated up to a defined temperature and held at this temperature for half an hour to soften the material. During heating, master and sample are held together tightly using a bar clamp. An increase in film thickness is wanted for a better imprinting result, thus different concentrations of the sol-gel solution were investigated. Using white light interferometry (WLI) it has been verified that an increase in the polymers concentration leads to an increase in film thickness after spin coating. The resulting nanostructure of the film was investigated via field emission scanning electron microscopy (FESEM).

Various soft embossing experiments have been realized at a set of different temperatures. The temperature has to be chosen carefully as the polymer/titania matrix has to soften sufficiently without making it stick to the master. Figure 4.1a) shows an example of a soft embossed titania film.

Wet imprinting is the process of coating the substrate with the prepared sol-gel solution before carefully placing the master upside down onto the wet film. Light pressure is applied on the masters back until all solvent has evaporated. After 24 hours the master is carefully removed. It was found that it is absolutely necessary to spin coat a thin layer of poly(dimethylsiloxane), denoted PSMS, onto the master prior to the wet imprinting. Without this treatment, no clean lift off could be achieved at all. An example of a wet imprinted film shown with optical microscopy is given in figure 4.1b). As it can be seen, a microstructured titania film over a large area is fabricated using wet imprinting.



Figure 4.2:

FESEM pictures from a tilted angle onto the breaking edge of a sample on silicon substrate with soft embossed microstructure after calcination: a) area view and b) close up view on the step at a channel's border within the dashed rectangle.

The last preparation step in order to tranfrom the hybrid film into a pure nanoporous titania film is the calcination. For this purpose, the samples are being heated up to 400 °C to entirely remove the polymer matrix. The calcination step at this temperature also ensures that the resulting titania is in its anatase phase. When comparing the imprinted structure before and after calcination using AFM, a change in the grating is observed. It is likely that the very high temperatures during calcination make the polymer melt, resulting in a deformation of the channel structure. This change is also seen using FESEM as displayed in figure 4.2. Albeit the channel structure is still visible, it is not as clear cut as the initial structure of the master.

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4.2 Novel structuring routine of PEDOT:PSS applied to organic photovoltaics

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Organic photovoltaics are recently a hot topic of worldwide research. This is mainly due to the great potential of conjugated polymers to fabricate solar cells on a mass production scale at low-costs. Nevertheless a lot of challenges have to be overcome before final commercialization. Compared to the conventional competitive solar cells made of silicon, organic devices still provide low efficiencies. Recent investigations are therefore concentrating on the synthesis of novel photoactive polymers with a higher absorption rate and better electrical properties and on morphology studies to improve the charge carrier separation processes. In addition advances in the optical design of the device by the nano- and micro-structuring of the polymer layers also show a promising way to increase efficiency by optimization of light harvesting and charge carrier separation in solar cells.



Figure 4.3:

Atomic force microscopy images and corresponding profile cuts taken perpendicular to the channel structure of a) structured PEDOT:PSS and b) spin coated organic polymer blend of P3HT:PCBM on top

Here we present a novel micro-structuring method based on wet-imprinting principles, which can be applied on an electron blocking layer of poly(3,4-ethylenedioxythiophene) (PEDOT) poly(styrenesulfonate) (PSS) as it is commonly used in organic photovoltaics. The prestructuring is used to achieve a periodic pattern of the photoactive layer in order to increase the overall performance caused by "light-trapping" effects.

Because PEDOT:PSS lacks a glass transmission temperature common mechanical imprinting methods (e.g. NIL) are not suited for its patterning. However micro-contact imprinting of PE-DOT:PSS using a PDMS mold is reported by adding glycerol as a plasticizer result in channel structures with a spacing down to 200 nm and a height of 40 nm. [1] In our approach of wet-imprinting on structured polycarbonate molds the PEDOT:PSS can be processed unmodified and therefore a full conservation of its electrical properties is guaranteed. The process is highly reproducible and the total film-thickness can be controlled accurately.

For the imprinting process a polycarbonate mold consisting of a channel pattern with a bar width of 0.5 μ m, a channel width of 1 μ m and a height of 175 nm was used. Wet-imprinting

was performed in a casting chamber, placing a 20 x 20 mm² indium thin oxide (ITO) covered glass substrate on top of the mold covered with a solution of 1.3 wt% of PEDOT:PSS. After drying for at least 72 hours the substrate was released by bending. Figure 4.3a shows an atomic force microscopy image and the corresponding profile cut of a negatively imprinted PEDOT:PSS layer. Due to the drying process a shrinking in height of 25 nm and a formation of a double peak structure with a height of 16 nm can be found on top of the structured PEDOT:PSS in comparison to the flat mold.

Compared to flat spin coated PEDOT:PSS films UV/VIS spectroscopy studies of structured PE-DOT:PSS layers already show a promising increase in absorption in combination with an reduced reflectivity. For photovoltaic application a polymer blend of poly(3-hexylthiophen-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) dissolved in dichlorobenzene is spin-coated onto such structured substrates. As it can be seen in Figure 4.3b the symmetric double peak structure still remains with a height of 10 - 20 nm. Due to spin coating the width of the peaks appears broader as compared to the peaks of a structured but uncoated PEDOT:PSS film. Finally aluminum was thermally evaporated on top as a cathode.

Simulations of "light trapping" effects in organic solar cells as they were modeled by H. Hoppe for thin films [2] or by M. Niggemann for integrated diffraction gratings [3] lead to an enhanced light harvesting. According to the theory first experiments on our novel structured devices also show already promising results. Power conversion efficiencies of 1.6 % for the structured cell and 1.5 % for a planar cell were reached if measured in a solar simulator at AM 1.5 condition. In Figure 4.4a the angular dependence of a structured solar cell is shown. The material depending open circuit voltage stays constant, whereas the produced current decreases due to less effective illuminated area. Interestingly the performance under higher light incident angles undergoes a smaller decrease for the structured device in comparison to a planar cell structure (fig. 4.3b). This is already a strong indication that structured device architectures can indeed lead to higher efficiencies.



Figure 4.4:

a) Characteristic U-I-plots of structured solar cell measured at various incident angles. b) Comparison of relative decrease of efficiencies due to variation of angle of incidence α_i between structured solar cell (perpendicular and parallel to incidence) and plane solar cell.

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4.3 Temperature induced surface tuning of novel structured conducting polymer films

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

Organic solar cells (OSCs) have been put in focus of worldwide research over the last decades. The solution based processability and the possible large scale fabrication at low cost provide organic photovoltaics a potential for future electricity generation. However, the low efficiency of this cell type is up to now the greatest challenge. To improve the overall power efficiency, the idea of structuring the polymer-polymer active layer is proposed. Here we discuss a novel fabrication routine for micro-structured polymer films and accessible surface changes via thermal treatment.

Structuring a periodic grating is a promising approach to improve optical absorption by light trapping without increasing the active-layer thickness. This idea is depicted in Fig 4.5 and has already shown good result for polymer-fullerene organic photovoltaic cells [1]. For the unstructured organic photovoltaic cell, the optical pass length of the solar light in the active layer is only twice the active layer thickness. On the other hand, with the structured active layer, the optical pass length is longer due to the additional diffraction of the solar light resulting from the diffraction grating effect. The increase of the optical pass length contributes to the cell efficiency. In order to achieve the diffraction grating effect, this report shows a novel fabrication routine for periodic gratings based exemplary on the conducting polymer F8BT ([poly(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole)]).



Figure 4.5:

The optical absorption of organic solar cells can be increased by a periodic grating surface morphology due to additional light diffraction.

A pre-structured silicon master is used, which can easily be fabricated via standard photolithography and reactive ion etching methods. It has equidistant channel structures with a size of 2 μ m in width, a periodicity of 4 μ m, and a depth of 150 nm. The photoactive polymer was spin coated onto the pre-structured master and afterwards floated of the substrate in a deionized water bath. Afterwards the floating polymer film was picked up upside-down with a glass or silicon substrate. The resulting surface topology shows an inverted planarized structure shape of the master used.

The structure of the F8BT thin films after the fabrication is investigated with atomic force microscopy (AFM) and the surface and morphology depending grazing incidence X-ray scattering technique (GISAXS).

Since many polymers have a low glass transition temperature post-production heat treatment is as an easy accessible parameter to adjust the shape of the grating. To investigate the influence of

temperature, in-situ GISAXS measurements have been applied. With short measurement times it provides a very good time resolution and additionally good sample statistics are given by the large footprint on the sample. Figure 4.6a shows the two-dimensional GISAXS scattering images of a structured F8BT thin film at 25 °C, 100 °C, 110 °C, 120 °C, and 130 °C. In the intensity, the ring structure around the Yoneda peak is due to a cut with the Ewald's sphere and is best seen next to the specular peak, which is shielded behind the beam stop. The prominent truncation rods in all images result from the scattering on a perpendicular inclined surface in respect to the incoming X-rays. The centering of these truncation streaks indicates a constant collapsing and smearing of the channel structures. These differences are also seen by corresponding simulations based on the software *IsGISAXS* [2]. Fig 4.6b also shows the AFM topography images of the sample before and after heat treatment. The image of the annealed sample indicates crystallization of the F8BT induced by heat treatment above its glass transition temperature ($T_g = 130$ °C). Additionally after the heat treatment, the rectangular shaped channels smear as already seen in the GISAXS images and become more triangular.

Thus polymer thin films can be structured with periodic grating structures using the applied method. The GISAXS measurements prove that the shape of the grating structure is tunable via heat treatment. The structuring the polymer thin film with tunable gratings can be done by floating pre-structured film. Since the structuring of the active layer of organic solar cells can improve the efficiency and also might be a crucial step for the future of organic photovoltaics, these films are interesting for future application.



Figure 4.6:

a) In-situ GISAXS measurements of surface tuned channel structures via heat treatment. b) AFM measurements of pristine and annealed F8BT channels showing an additional crystallization.

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4.4 Influence of annealing and blending of photoactive polymers on their crystalline structure

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In the past decade, immense interest in conducting polymers evolved due to their high potential for applications in lightweight and cheap organic electronics such as OFETs, OLEDs, and organic photovoltaics. Furthermore, the almost inexhaustible possibilities to vary the polymeric structure and consequently tailor the absorption behavior as well as the electronic characteristics of conducting polymers make a broad usage feasible. Thus, a wide range of different types of conducting polymers, such as polythiophenes, poly(phenylenevinylene) copolymers, etc., are commercially available and are extensively studied. Most conducting polymers are so called conjugated polymers, i.e. the polymer backbone consists of alternating single and double carbon bonds, and therefore are among the so called semi-crystalline polymers. It was found that the crystallinity of such polymers is crucial for their conductivity. Higher conductivity is achieved with high crystalline order which can be enhanced with thermal annealing processes. While in OFETs one type of polymer is used, in OLEDs and organic photovoltaics the combination of two or more different organic compounds is state of the art. For organic photovoltaics it was shown that a so-called bulk heterojunction system, i.e., a blend of an n-type and a p-type material, increased the performance significantly as compared to a bilayer or a one-component system. Concerning the crystallinization process the type of materials as well as the influence of blending two materials becomes important. To reveal information on the crystalline structure including the crystallite orientation in thin films grazing incidence wide angle X-ray scattering (GIWAXS) is the method of choice.[1]



Figure 4.7:

Sector integrals derived from 2d GIWAXS data of P3OT (a) and CN-PPV (b). Black curves correspond to as-spun films, red curves to annealed films. The solid lines correspond to vertical and the dashed lines to horizontal cuts as indicated by the pictograms (insets). For clarity of presentation, the dashed curves are shifted in the y-direction with regard to the solid curves. Prominent scattering features are indicated.

We investigated the effect of thermal annealing and blending on the crystallinity of thin films containing the p-type polymer poly(3-octylthiophene-2,5-diyl) (P3OT) and the n-type polymer

poly(2,5-di(hexyloxy)cyanoterephthalylidene) (CN-PPV). Both polymers fit very well concerning their electronic structure. Thin films are prepared via spin coating from THF solutions. For the blended films a ratio of 1:2 (P3OT:CN-PPV) fitting their critical blending ratio was used.[2] Fig. 4.7 shows sector integrals in vertical and horizontal direction from 2d GIWAXS data of asspun and annealed homopolymer films. For P3OT (see Fig. 4.7a) the first three orders of the scattering signal in (100) direction are visible in the vertical sector integrals. The (010) peak in the horizontal sector integrals is also already observable for as-spun films. Due to thermal annealing, the scattering signal changes. The shift of the peak positions to higher q values represents a decrease of the lattice constants. In addition, the intensities of the peaks are changing with thermal annealing. This is attributed to a change of orientation from an edge-on to a face-on arrangement. In the case of CN-PPV only a weak crystallinity is detected for as-spun homopolymer films (see Fig. 4.7b). After thermal annealing also the first three orders of the scattering signal in (100) direction evolve. However, no scattering signal in (010) direction was detected which is related to the cyano-group in the polymer backbone. The cyano-groups do not lay in the conjugation plane of the polymer and therefore disturb the arrangement in (010)

direction. Generally speaking, the crystallinity in both homopolymer films is increasing with



Figure 4.8:

Sector integrals derived from 2d GIWAXS data of blend films of P3OT and CN-PPV. Black curves correspond to as-spun film, red curves to annealed film. The solid lines correspond to vertical and the dashed lines to horizontal cuts as indicated by the pictograms (insets). For clarity of presentation, the dashed curves are shifted in the y-direction with regard to the solid curves. Prominent scattering features are indicated.

When now these two polymers are blended we found a decreased crystallinity of P3OT and no crystalline structure of CN-PPV for as-spun films (see Fig. 4.8). In addition, thermal annealing influences the crystallinity only very little. Consequently, blending these two polymers hinders the crystallinization process significantly which is crucial for their conductivity. This is also an explanation for the low photovoltaic performance of solar cells made from this material combination.[3]

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4.5 Characterization of ternary systems for organic photovoltaics

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In the last decades the interest of research groups as well as industry in organic photovoltaics increased dramatically. The potential in light weight and cheap application supports the progress currently taking place. At present polymer-based systems reached efficiencies of 7.4 %.[1] Nevertheless, efficiency as well as lifetime of organic solar cells are still too low for a broad application. One of the main disadvantages is the large energy gap of organic semiconductors used in polymer-based solar cells. Consequently, the absorption range covers only a small region of the solar spectrum compared to inorganic solar cells. Besides the synthesis of new conducting poylmers with smaller energy gaps and therefore a better absorption range so-called ternary blends promise an increase in absorption and therefore in device performance. In this approach a third component is added to a bulk heterojunction system used in photovoltaics to increase the absorption. Thus the third component has to absorb in a wavelength range in which the primary components do not absorb.



Figure 4.9:

a) Comparison of thickness corrected absorbance spectra of P3HT (blue), PCBM (red), OPc (green), a ternary blend with a dye concentration of 0.24 g/l (black) and a calculated curve for this blend (brown). b) X-ray reflectivity data of a OPc film (top) and a ternary blend film (bottom). The curves are shifted along the y-axis for clarity.

In this work we investigate a bulk heterojunction system containing the conjugated polymer P3HT (poly(3-hexylthiophene-2,5-diyl)) and the methano fullerene PCBM ([6,6]-phenyl-C61 butyric acid methyl ester) which is probably the best investigated polymer-based system for photovoltaic applications. While PCBM absorbs mainly in the UV-regime up to 400 nm P3HT absorbs in the maximum of the solar spectrum between 400 nm and 600 nm (see Fig. 4.9a). Both components complement one another. Nevertheless, light with wavelengths above 600 nm is not absorbed in this system. Therefore we introduce the organic dye OPc to the P3HT:PCBM system. OPc absorbs mainly above 600 nm with a maximum at 850 nm. In Figure 4.9a the thickness corrected absorbance which is proportional to the absorption coefficient of P3HT, PCBM and OPC is shown. In addition, the absorbance of the as-spun ternary blend of P3HT:PCBM:OPc (12 g/l:12 g/l:0.24 g/l)is plotted. The features related to all three components are clearly visible. For comparison the absorbance spectra of the single components are summed up to the absorbance spectrum of the ternary blend by linear superposition. A closer look reveals shifts in peak position of the absorption spectrum. In general, the absorption peak position gives information on the band gap of the material. With increasing ordering of the material (i.e. for semiconducting polymers the conjugation length) the absorption peak shifts to lower wavelengths as more electronic states overlap. As the absorption peaks shift to lower wavelengths for all three components a decreased ordering is expected due to blending. In addition, vibrational excitations seen as shoulder like features in the absorption spectrum which occur for high ordered P3HT are less pronounced. This again supports the low order in the ternary blend. X-ray reflectivity measurements of pristine OPc and a ternary blend film (see Figure 4.9b) reveal further evidence of less ordered dye in the ternary blend films. While for the OPc film a Bragg peak at $q_z = 0.4$ Å⁻¹ representing high order is clearly visible no feature in the ternary blend film is detected. Consequently, pure OPc is highly ordered while adding OPc to the P3HT:PCBM system ordering is completely suppressed.



Figure 4.10:

Comparison of thickness corrected absorbance spectra of as-spun (black solid line) and annealed (red dashed line) 12 g/l:0.24 g/l P3HT:PCBM:OPc ternary blend films.

To increase crystallinity in organic solar cells and therefore increase conductivity and device performance typically post production treatments such as thermal annealing are performed. In Figure 4.10 thickness-corrected absorbance spectra of as-spun and annealed ternary blends are shown. While thermal annealing does not change the features attributed to PCBM and OPc at 330 nm and 780 nm, respectively, the P3HT peak shifts and changes in shape. The shift of the absorption peak of P3HT to higher wavelength is due to an increased conjugation length as mentioned above. In addition, shoulder-like features occur in the region from 580 nm to 600 nm which are related to vibrational excitations in P3HT crystallites and therefore to higher ordering of P3HT.

In summary, blending P3HT, PCBM and the dye OPc results in decreased ordering of all three components as seen in absorption investigations and X-ray reflectivity measurements. Thermal annealing increases crystallinity of P3HT. However, the arrangement of OPC and PCBM is not influenced by thermal annealing.

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4.6 STXM-studies on the solvent content of thin conducting polymer films

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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.

The solvent content of thin polymer films has been investigated by Perlich et al. [1] using neutron reflectivity (NR), utilizing the contrast between protonated and deuterated solvents. They reported a significant enrichment of solvent at the substrate/polymer interface in thin polystyrene films, still present after different annealing and storage conditions. In our work we used Scanning Transmission X-ray Microscopy (STXM) to be chemically sensitive to the solvent used for sample preparation. While the used conductive polymers (PVK, F8BT) had no oxygen in their chemical structures, the solvents (THF, cyclohexanone) contained oxygen. This way we were able to look for solvent residuals by the use of x-rays of energies around the oxygen K-absorption edge of about 540 eV. These measurements were performed at the PolLux beamline at the Paul Scherrer Institute (PSI) in Switzerland [2]. This beamline not only offers the necessary energy range, but also a highly focused beam of 20 nm, which allowed us to study solvent uptake in different homopolymer domains of a phase separated polymer blend film. This set-up made it possible to get a spatially and quantitatively resolved distribution of remaining solvent in the thin polymer blend films.

Our samples were prepared via spin-coating from a polymer solution on two different kinds of substrates. The first kind of substrates were TEM-grids. To get the samples onto the grid, we first prepared the film on a silicon wafer and then transferred it onto the TEM-grid by using the floating-technique with de-ionized water. To rule out any oxygen-uptake during the contact with water we also prepared films directly spin-coated on SiN-membranes. These membranes have a thickness of 100 nm and are transparent to x-rays.



Figure 4.11:

STXM-images of the same region of a PVK-sample with a thickness gradient were taken at two different energies, one energy before the absorption edge, the other at the energy of a prominent feature in the solvent's spectrum at the edge. From these images we extracted the transmitted intensity (dashed line) and the Optical Density (solid line) along the gradient. Only very little variations of the OD indicate a thickness-independent solvent uptake.

To investigate the thickness-dependence of the solvent content, we prepared a sample with a thickness gradient from a solution of PVK in cyclohexanone via solution casting on a SiN-membrane. We recorded two transmission images at the same position on the sample, but at two different energies. The first energy was chosen to be lower than the energy of the absorption edge of about 540 eV, in this case $E_1 = 520$ eV. For the second energy we chose $E_2 = 531.5$ eV because at this very energy we found a well pronounced peak in the solvent's spectrum. Thereby the second energy was used as a marker for solvent, while the first image was used to normalize for film-thickness and photon-flux at each particular energy. Using these two images we were able to calculate the Optical Density and a transmission profile along the gradient. The dashed line in fig. 4.11 shows the normalized transmitted intensity along the gradient, the solid spectrum represents the optical density (OD) of the film along the gradient. It can be seen that at higher *x*-values the OD stays quite constant, indicating a thickness-independent solvent uptake in the film. As the film gets thicker (lower *x*-values) the transmitted intensity decreases until side effects (e.g. dark currents, stray light, etc.) dominate the OD.

The polymer blend film we investigated was composed of PVK and F8BT and prepared from THF. After spin-coating the solution on a silicon wafer the film was floated onto a TEM-grid. Fig. 4.12(a) and (b) show the transmission images at the energies 520 eV and 531.5 eV respectively. In fig. 4.12 the OD, calculated from (a) and (b), can be seen. To test the high resolution offered by PolLux we also recorded images of a size of $5x5 \ \mu m^2$ and calculated the OD-image (fig. 4.12(d)). The graph in fig. 4.12(d) represents a line-cut through the OD-image across different domains. Although the OD is corrected for thickness differences one can easily see different relative amounts of oxygen uptake.



Figure 4.12:

STXM images of a PVK-F8BT blend: (a) Image recorded at E = 520 eV. (b) Image recorded at E = 531.5 eV. (c) Optical Density, calculated from (a) and (b), showing regions of different oxygen uptake which correspond to the phase separation. (d) Optical Density of an area of $5x5\mu m^2$ and the extracted line-cut across different domains, representing the normalized oxygen content.

The results from the thickness-gradient correspond to the findings of Perlich et al. [1], as a solvent-enriched layer at the polymer-substrate-interface could explain the constant OD in fig. 4.11. The results from the investigation of the polymer blend film shows the influence of the polymer chemistry on the solvent uptake. Here we saw different amounts of oxygen uptake even after thickness- and flux-normalization. Other impacts on solvent residuals have not been tested yet. Such are for example the solubility parameters of the components in the sample, chain length and chemical structure of the polymers.

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4.7 Influence of different solvents on the morphology in P3HT:PCBM bulk heterojunction systems for organic photovoltaics

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Polymer-based solar cells (PSC) have attracted tremendous interests due to low production cost, mechanical flexibility, light-weight property, and similar theoretical power conversion efficiency (PCE) as silicon-based solar cells (around 16%) [1]. There are several factors influencing the morphology of the polymer thin film layer (active layer), for instance, the used polymer and solvent, the chosen concentration of the polymer solution, as well as some post treatments like thermal annealing, all of which together determine the final efficiency of the PSC. In our research, the influence of different solvents on the morphology of the active layers and the PCE are investigated. The active layers are spin-coated from a mixture of poly(3-hexythiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) dissolved in four different solvents, namely trichloromethane, toluene, chlorobenzene and xylene. By applying grazing incidence small angle x-ray scattering (GISAXS), the inner morphology of the active layers is revealed, combined with the surface structure information obtained from atomic force microscope (AFM), the whole morphology of the active layer is accessible.



Figure 4.13:

(a) Absorption curves of P3HT:PCBM films made from different solvents: trichloromethane (black), toluene (red), chlorobenzene (green) and xylene (blue). Four two-dimensional GISAXS images of annealed samples made from (b) trichloromethane, (c) toluene, (d) chlorobenzene and (e) xylene

To allow for comparison, samples with similar film thickness are examined by UV/Vis spectroscopy, and the absorption curves are shown in figure 4.13 a. These curves are obtained from different active layers of the samples spin-coated from polymer solution of 7 mg/mL in trichloromethane, 18 mg/mL in toluene, 24 mg/mL in chlorobenzene, and 24 mg/mL in xylene. As seen from this figure, the absorption spectra of the blends follows a linear superposition of the spectrum of the individual materials, indicating that significant ground-state charge transfer does not occur in these blends [2].

The images in Figure 4.13b to 4.13e show two-dimensional GISAXS images of the four annealed samples prepared from different solvents. GISAXS provides molecular resolution of the buried interfaces of the thin films or multilayer systems. Different morphology information are revealed by different shapes of 2d GISAXS intensity distribution. As seen in these 2d data, a broad specular peak for the annealed sample made from trichloromethane results from an ill defined structure inside this film. Therefore, the efficiency of a corresponding solar cell is merely 0.34 %. However, for the samples made from toluene, chlorobenzene and xylene, well defined structure are revealed by the 2d GISAXS data, which is in good agreement with the high efficiency of the

solar cells, that is, 1.77 %, 1.74 %, and 1.89 %, respectively (for non optimized solar cells). In addition, a broad Yoneda peak appears both in the annealed samples made from toluene and xylene, which may be correlated with the fact of higher efficiency. But to get more specific structural information, the out-of-plane cuts are fitted using so-called effective surface approximation as shown in Figure 4.14a.



Figure 4.14:

(a) Out-of-plane cuts from the GISAXS 2d data and (b) PSD curves of the AFM data of the annealed samples. The used solvents trichloromethane, toluene, chlorobenzene and xylene (from bottom to top). All curves are shifted along the y-axis for more clarity

From the AFM measurements, not only the topography and the corresponding roughness information of the samples is obtained, but also the power spectrum density function (PSD) of the films, showing the characteristic length scale of the surface structure of the polymer films, is extracted. PSDs are shown in figure 4.14b. It can be seen that the surface structures for the four samples are mainly around several hundreds nm, whereas the inner structure sizes are between 35 and 85 nm as obtained from GISAXS (see figure 4.14a). Thus, the surface structures of the blend films are bigger as compared to the inner film structures for all the annealed samples [3]. In sum, strong influence of different solvents on the morphology of the active layers is observed by different experimental techniques. In addition, a good phase separation of the polymer active layer is formed due to thermal annealing, breeding higher efficiency. The annealed xylene-based solar cell has the optimized phase separation due to the influence of the solvent properties and the applied annealing process in correspondence with the highest probed efficiency.

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4.8 Modification of the electrical conductivity in thin conjugated polymer films

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Conjugated polymers in thin films are of great interest for various applications such as organic photovoltaics and organic field effect transistors. Therefore, the selective modification and control of their electrical conductivity has special importance. Poly(3-hexylthiophene) (P3HT) in particular attracted a lot of attention due to its high intrinsic conductivity [1]. According to the Peierl's transition the ground state complies with a valence and conduction band separated by an energy gap. If an electron is lifted into the conduction band and leaves a positive hole in the valence band, both will polarize their surroundings, resulting in structural changes in the chain. The combination of their charge and the polarization leads to additional states in the band gap, which in turn increase the conductivity. These states are referred to as quasi-particles and are already present after the polymerization and at room temperature. More of these charge carriers can be introduced by doping. In this context, doping refers to either oxidation or reduction of the backbone of the polymer. An iodine atom takes an electron from the highest occupied molecular orbital (HOMO) of the polymer and stays at the backbone to maintain electrical neutrality. Hence, the iodine induces holes to the valence band and a structural defect, and therefore - in the case of polythiophene - introduces a positive charged quasi particle. However, this doped state is unstable due to de-doping and the conductivity decreases over time.

In recent years there has been a fast progress in synthesizing conjugated polymers. In this work, we investigate thin films of poly(3-hexylthiophene) in respect to heat treatment and doping with iodine in order to gain knowledge about the de-doping process on a molecular level.





P3HT films were prepared from toluene solution. Glass substrates were cleaned for 15 minutes at 80 °C in an acidic solution within two hours previous to their use. Then, in a box impermeable to light the films were processed over night through solution casting under ambient conditions. The conductivity of solution-cast thin P3HT films is measured with a 4-point measurement setup. Figure 4.15a shows the conductivity of films annealed for 2 h at different temperatures. The values are in the order of 10^{-7} S/cm and 10^{-5} S/cm, which is in the expected range [2]. Each point is the average of four measurements at different positions on the film surface and the error is the standard deviation. Because the conductivity is very low for the undoped P3HT films, the current applied in the measurement is below 10^{-7} A. The highest conductivity is found for P3HT films annealed at 140 °C with $(1.3 \pm 0.3) \cdot 10^{-5}$ S/cm. The lowest conductivity

of $(6.0 \pm 1.2) \cdot 10^{-7}$ S/cm belongs to not-annealed films. From Figure 4.15a, it can be concluded that the annealing temperature to obtain maximal conductivity is at 140 °C.

The conductivity of the P3HT films is increased by the oxidant iodine. To achiev this, the films were placed in iodine vapor for 24 h. The results are shown in Figure 4.15b. A specific trend due to different annealing temperatures can not be noticed, the conductivity of all P3HT films is at (95 ± 20) S/cm. Compared to the undoped films an increase of conductivity by over 10⁶ S/cm has been achieved. For the not-annealed P3HT films, the conductivity improved even more with eight orders of magnitude. The increase of the conductivity from a poor metal to a metal-like state can be considered as a Mott insulator-to-metal transition [3]. Significant to the metal-like state is that the conductivity is mainly independent of the otherwise very important semi-crystalline structure of P3HT. In the semi-crystalline polymer small crystallites are embedded in an amorphous matrix. The crystallites are investigated by grazing incident wide-angle scattering (GIWAXS). Figure 4.16 shows a two-dimensional (2d) GIWAXS image of a P3HT film annealed at 140 °C. The points of high intensity are assigned to Bragg reflections from the crystal structure. In vertical direction three orders of the (100) Bragg reflections and in horizontal direction the (020) peak are revealed. In addition, further features with lower intensities are detected which are assigned to several crystalline orientations. A quantitative analysis (not shown here) allows the determination of the unit cell of the P3HT crystallites and their dependence on heat treatment and doping.



Figure 4.16:

2d GIWAXS image of a P3HT film annealed at $140 \,^{\circ}\text{C}$ for 2 h. Peaks of high intensity correspond to Bragg reflections from the crystalline structure in the film.

Further experiments have to show the development of the conductivity over time. Long time stability of the conductivity can open the way to new application and also improve existing organic electrical devices.

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5 Polymer-hybrid systems



5.1 Large area sponge-like titania nano-structures

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The structuring of thin titania films on a nanoscale is of high interest for a variety of applications, as for example in biotechnology, gas sensing, photocatalysis or photovoltaics. In the case of photovoltaics two concepts exist: the dye-sensitized solar cell, also called Graetzel cell [1], where the charge separation takes place at the interface of titania and the dye, and an inorganicorganic hybrid solar cell, where the charge separation takes place at the interface between titania and the hole-conducting organic material. For these applications a large surface area of the thin tiania film in combination with percolation paths for the separated charges are necessary. A sponge structure with a pore size of a few tens of nanometers, as shown in the scanning electron microscopy (SEM) image in figure 5.1, is a promising morphology for titania to meet these demands.



Figure 5.1:

SEM picture of the sponge structure of titania: the film was nano-structured by means of diblock copolymer templating combined with sol-gel chemistry as described in the text. After nano-structuring the film was calcined at 400 °C in nitrogen atmosphere for four hours to combust part of the organic template while converting the PDMS block of the template to a SiOC-type ceramic and the previously amorphous titania to the semiconducting anatase polymorph.

We focus on the preparation of titania thin films with such a sponge-like morphology spread out over surfaces with an area of several square-centimeters. The large area is essential for applications in organic photovoltaics. Block copolymers can be used as templates in a 'goodpoor solvent pair' induced phase separation process coupled with sol-gel chemistry to create nano-structured titania films in a reproducible way. Thus we use the amphiphilic diblock copolymer poly(dimethylsiloxane)-block-methyl methacrylate poly(ethylene oxide) [PDMS-b-MA(PEO)] as templating agent.[2,3] The polymer is first dissolved in tetrahydrofuran and 2propanol, which are good solvents for both the hydrophobic and the hydrophilic part of the diblock copolymer. After complete dissolution hydrochloric acid (HCl) as selective solvent and titanium tetraisopropoxide (TTIP) as titania precursor are added in a well-defined way. On the one hand, HCl and TTIP are the source for the sol-gel process and, on the other hand, they act as poor solvents for the hydrophobic part and therefore induce the phase separation which leads to the nano-structures in the film. The films are prepared via spin-coating of the diblock copolymer containing sol-gel 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) type, 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 are investigated. The morphology investigations with neutrons are of special interest, because a large surface area is illuminated with the neutron beam and the corresponding scattering experiment gives a good statistical average of the large area structure with nanometer resolution. Moreover, it is possible to tune the scattering contrast by the addition of deuterium dioxide (D_2O). Grazing incidence small angle neutron scattering (GISANS) was performed at the beamline KWS1 of the Jülich research center at FRM2, Garching. Figure 5.2 shows results of the GISANS measurements. The measurements are done with spin-coated titania films calcined at different temperatures. The figure shows one sample with a size of 4.5 by 8 square-centimeters which was investigated in air as well as in D_2O vapor.

By the addition of D_2O , we observe no change in the size of the small pores in the sponge structure, as it can be seen from the unchanged structure peak in figure 5.2b (at the position marked with an arrow). This structure peak refers to a titania structure of about 37nm. Structure information on larger pores is hidden in the resolution of the set-up with a sample-to-detector distance of about 666cm and a wavelength of the neutrons of about 4.8Å.



Figure 5.2:

GISANS measurements of the same calcined titania film as shown in figure 5.1, measured at the beamline KWS 1: a) 2-dimensional scattering image of the sample measured in air. A beamstop in the center of the detector image shields the direct beam. The upper part, above the sample horizon which is visible as darkest horizontal line above the direct beam, shows the GISANS signal. The lower part around the shielded direct beam shows the transmitted signal. b) Out-of plane cuts at the position of the titania Yoneda peak, from bottom to top in air, during heating up in D_2O vapor, after 4.5 hours in D_2O vapor and after 10 hours in D_2O vapor. The cuts in b) are shifted along the y-axis for illustrative purposes.

For the measurement in air the contrast between air, with a scattering length density (SLD) of approximately zero, and the porous titania, with a SLD of the bulk material of $2.61 \cdot 10^{-6} \text{\AA}^{-2}$, is not very big. When the pores of the titania sponge-like structure are filled with D₂O, with a SLD of $6.366 \cdot 10^{-6} \text{\AA}^{-2}$, the contrast is increased. Correspondingly, the intensity in the structure peaks increases by a factor of about 2.3 when measured in D₂O instead of air, while the intensity of the specular peak even diminishes slightly. As a consequence, the overall measurement time can be significantly decreased. For the titania nano-structure in air an overall counting time of 10 hours per sample was necessary to obtain the statistics shown in figure 5.2a. Such good statistics are probed in less than 4.5 hours if the titania nano-structure is filled with D₂O. Moreover, higher order gets better visible in the enhanced contrast conditions.

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5.2 Layer-by-layer fabrication of an anatase titania multilayer with gradual spongelike morphology

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The formation of nanostructured titania thin films has attracted considerable interest in the past years due to their physical properties suited for a variety of applications including photovoltaics and photocatalysis. The performance significantly depends on the morphology of the nanostructured titania. 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.



Figure 5.3:

Schematic representation of the multilayer approach for the preparation of hierarchical titania nanostructures and FE-SEM images of the prepared sponge-like titania morphology after the process steps I, II and III in top view. The insets show the respective FFT pattern of the image. The scale bar corresponds to a length of 1 μ m.

The approach presented within this investigation focuses on the preparation of a gradual multilayer with altering porosity in an iterative layer-by-layer spin-coating approach as schematically presented in Fig. 5.3 [1]. The first layer of titania nanostructures with a sponge-like morphology 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-pairinduced phase separation coupled with sol-gel chemistry. By adjusting the preparation conditions to a small extent, a second layer yielding a similar morphology, but different pore sizes is deposited on top of the preceding layer, hence resulting in a bilayer of gradually changing porosity. Finally, sponge-like nanostructures with an again different pore size are deposited yielding a triple layer, e.g. multilayer. Hence, the ensemble of sponge-like titania layers with slightly different porosity forms a gradual multilayer system.

The structural investigation was performed with scanning electron microscopy (SEM) and complemented by grazing incidence small angle X-ray scattering (GISAXS). The GISAXS measurements were performed at the synchrotron beamline BW4 at HASYLAB using a moderate microfocused X-ray beam. Fig. 5.3 presents the FESEM images in top view of the prepared titania morphology after the intermediate process steps I and II and the final step III. After each process step, the nanostructured titania exhibits a typical morphology consisting of a foam- or spongelike mesoscale network. After process step I, the surface clearly shows cracks (\leq 100 nm) in the sponge-like network structure. From the magnified detail of the nanostructures typical lateral length scales of 50 nm $\leq \Lambda \leq$ 300 nm are assigned. The deposition of a further titania thin film by process step II results in a more homogeneous and dense sponge-like morphology. The FE-SEM images show a periodic arrangement of dark spots, which are identified as an additional hole structure. The direct comparison of the magnified details of process steps I and II reveals a denser, but also more filigree structure after step II. The process step III yields a seemingly enlargement of the filigree structure, hence resulting in an apparent increase of the titania surface roughness.



Figure 5.4:

(a) Composite image comprising the 2D scattering patterns after process step I, II and III. (b) Horizontal line cuts from the 2D GISAXS intensity at the critical angle of titania. The solid lines are fits to the data. The characteristic structural length scale is marked with A. The arrows indicate the position of the characteristic length scale as a function of the preparation step.

Fig. 5.4a shows the corresponding GISAXS patterns after the process steps I, II and III. The absence of a distinct intensity maximum in the scattering intensity along the horizontal scattering angle results from minor lateral ordering of the sponge-like structure, which is in agreement with the shown FFT patterns obtained from the FESEM images. The deposition of a similar sponge-like structure by process step II results in no significant change of the 2D scattering pattern due to the marginal modification of the characteristic length scales. The minor broadening of the intensity distribution is explained by an increase in surface roughness as well as the increase in film thickness and hence scattering volume. As clearly identified from the FE-SEM images, the filigree or fineness of the structure increases, whereby the smaller structural lengths contribute scattering intensity at larger Ψ . The final process step III results in a further broadening of the scattering intensity distribution.

Because of the reduction of the effective density by the porous sponge-like structure of the titania multilayer system, the effective critical angle is smaller than for the originally assumed compact titania volume material. Within the scattered intensity distribution this effect is expressed by a shift of the material-specific (titania) Yoneda maximum in direction of smaller q_z or exit angle α_f , respectively. From the new position of the Yoneda maximum, the following porosities for the titania multilayer system after the process steps I, II and III are extracted: $\Phi_I = 68 \%$, $\Phi_{II} = 69 \%$ and $\Phi_{III} = 64 \%$ [1]. This quantities proof nicely the preserved porosity of the multilayer system, because a filling of the respective pores end hence a sealing upon calcination would result in a drastic change of the critical angle and thus the obtained porosity.

For a more quantitative explanation of the scattering data with respect to most prominent lateral length scales horizontal cuts from 2D GISAXS data have been extracted at the respective effective critical angle of titania and are shown in Fig. 5.4b. In the framework the effective interface approximation, the titania structure is described with a most prominent characteristic length scale Λ_A . After the process steps I, II and III the resulting values are $\Lambda_{A,I} = (255 \pm 10)$ nm, $\Lambda_{A,II} = (273 \pm 10)$ nm and $\Lambda_{A,III} = (225 \pm 10)$ nm.

In summary, the applied layer-by-layer spin-coating approach of sol-gel templated titania nanostructures allows for a very simple fabrication of a gradually hierarchical multilayer system formed by porous titania thin films with altering porosity. In each process step the porosity of the preceding step is preserved. From the obtained porosity, the thickness of the individual layers as well as the analysis of the GISAXS scattering data it can be concluded, that a high effective porosity is provided after the third process step and the once prepared sponge-like morphology is preserved throughout the complete three step process. Therefore the spin-coating of the polymer-nanocomposite film, using the described conditions, induces neither filling of the already prepared pores nor the subsequent calcination induces morphological transition of the preceding structures.

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5.3 Hierarchically structured titania thin films by iterative block copolymer based sol-gel templating

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Using the nano-phase separation of block copolymers to transfer nanostructures into inorganic materials has become largely popular over the last years. However, in many applications hier-archically structured materials with a superstructure on a larger size scale and a combination of different types of morphologies are favorable. We use the concept of combining sol-gel templating with an iterative layer-by-layer spin-coating approach [1] to combine different morphologies. A foam-like structure (sample I) is put together with granulas (sample II) multiple times (sample III) with proving the preservation of the respective individual morphologies throughout the preparation steps. As a consequence, we obtain a hierarchically structured material consisting of different types of morphologies.

For our studies the diblock copolymer poly(styrene-block-ethyleneoxide), denoted P(S-b-EO), was chosen as a structure directing agent for the use in the sol-gel process based on 1,4 dioxan, 37% HCl and titanium tetraisopropoxide (TTIP). By adjusting the weight fractions of the sol-gel components the two different morphologies were selected [2]. After the iterative spin-coatings the polymer matrix was combusted and the titania film was transferred to its anatase phase by a calcination step in ambient air.



Figure 5.5:

SEM images of the titania films after calcinations: Top views of the surfaces of sample a) I, b) II and c) III respectively and d) cross-section of sample III.

Scanning electron microscopy (SEM) was employed as real space imaging technique to obtain first information about the morphologies which are present at the sample surfaces. Figure 5.5ac show top views of the three different samples. The foam-like morphology of sample I with an average pore size of roughly 40-50 nm is seen in figure 5.5a. Figure 5.5b shows the nanogranulas which are obtained from a change in sol-gelcomposition. Most prominently, the large granula in the left half of figure 5.5b has a size of roughly 600 nm. Indicated by its darker inner part, this large granula resembles more a biconcave disc shape instead of a simpler flat disc or sphere like shape. Furthermore, smaller granulas, having a round shape with a diameter around 20 nm, are seen in figure 5.5b. Their size and shape also match the lacerated outer edge of the biconcave discs, indicating that a lot of these mid-sized granulas aggregate together to form the big biconcave discs. Finally, an even smaller particle type is faintly seen in between the granulas with a size of about 10 nm. In sample III these both morphologies are combined together. Figure 5.5c shows a top view of sample III. The foam-like morphology as well as large granulas with the characteristic frayed edges from sample I and II are present, respectively. However, the size of the granulas is different to sample II. Firstly, the larger granulas are now only about 200-250 nm large and secondly, the mid-sized granulas seem to have agglomerated to bigger objects, similar to the larger ones with an average size of approximately 80-110 nm. The very small granulas are not observable anymore. This change in morphology results from the fact, that for sample II the sol-gel was spin-coated on the silicon substrate, whereas for sample III the sol-gel for the granulas was directly spin-coated on the polymer/titania composite, hence, on a different surface.

Figure 5.5d shows a cross-section of sample III. In the very bottom the silicon substrate is slightly visible. Next, the foam-like morphology is found, followed by the first layer of granulas which was spin-coated directly on top of the foam-like structure, a second layer with the foam-like structure and the very upper layer of granulas. Remarkably, the granula which is sandwiched between the two foam-like structures still is very similar to the ones on top, shape and size wise.



Figure 5.6:

Cuts of 2d GISAXS data in horizontal direction taken at the Yoneda peak of TiO_2 for all samples (I, II and III), as indicated inside at the respective curves. The dashed vertical line shows the resolution limit of the experiment. The arrows 'a', 'b' and 'c' show characteristic lengths that could be found in sample I and II respectively and which were preserved for sample III throughout all the preparation steps.

To gain a more complete understanding of the installed morphologies, grazing incidence small angle X-ray scattering (GISAXS) was performed. For quantitative analysis horizontal line cuts were taken from the measured 2D patterns which are shown in figure 5.6 together with the respective fitting curves. For the foam-like structure of sample I a characteristic size was found to be 45 nm. In good agreement with the SEM data, we attribute this to the size of the holes in the foam-like structure. A second lateral length is seen at 270 nm which we attribute to longdistance domains within the foam-like structure. The horizontal line cut of sample II shows three distinctive structure sizes. The smallest one is found at 15 nm which probably is related to the very small granulas which were observable in the SEM data. This is followed by a structure of 105 nm, coinciding with the mid-sized granulas. Finally, a structure size of 560 nm is found which we assign to the diameter of the large biconcave discs. The horizontal line cut of sample III also shows three structure sizes. The smallest one is 45 nm which was also observed at sample I and hence can be attributed to the hole size of the foam-like structure, indicate by the arrow, labeled 'a'. The next lateral length at 105 nm which was also found in sample II as indicated by the arrow labeled 'b'. As a third characteristic length 250 nm was found. Since the characteristic hole size of the foam-like structure was observed it is not surprising to also find the long-distance domains which were already observed for the foam-like structure of sample I. This is also indicated in figure 5.6 by the arrow labeled 'c'. As a consequence, the GISAXS investigation verifies that the morphologies of sample I and II, respectively, remain preserved in the hierarchical nanostructured titania film on a large sample area, as it was already suggested locally from the SEM analysis.

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5.4 Effect of external magnetic field on the alignment of metal-polymer nanocomposites

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Block copolymers embedded with magnetic nanoparticles have attracted strong interest as a method to fabricate hybrid nanocomposites for wide potential applications in functional devices [1]. Furthermore, the control over the alignment of the nanoparticles within the polymer matrix is essential for producing well-aligned highly-oriented metal-polymer nanopatterns. Controlled alignment of block copolymers or metal-polymer composites was already achieved via various methods [2,3]. In this work, we investigate the alignment of magnetic nanoparticles, which are maghemite nanoparticles, in poly(styrene-*b*-methylmethacrylate) diblock copolymer films. Films are prepared by solution casting. An external magnetic field is applied to the samples during the casting step. We study the emerging morphologies under the influence of both nanoparticle concentration in the polymer film and the external magnetic field strength at different direction relative to the sample surface. The structures of the metal-polymer composite films are characterized using optical microscopy, atomic force microscopy (AFM), and grazing incidence small angle neutron scattering (GISANS).

The polymer-nanoparticle solutions are prepared in toluene and the concentration of polymer is 10mg/ml, while the concentration for the nanoparticles in the resulting film is 2 wt%, 1 wt%, 0.5 wt%, 0.1 wt%, 0.05 wt%, 0.02 wt%. The silicon substrate is pre-cleaned in an acid solution. In order to learn about the magnetic field affect on the morphology of polymer films, samples are prepared under different magnetic fields, either parallel or vertical with respect to sample surface.



Figure 5.7:

Optical microscope images show the width of metal nanoparticle aggregates at different concentrations of nanoparticles (0.02wt% to 2wt%) and magnetic fields, which are a) 132 G, b) 320 G. c) Relationship between nanoparticles concentration and the width of observed metal stripes.

The width of the metal stripes is monotonically increasing with increasing the concentration of the nanoparticles as probed at two different magnetic field strengths of 132 G and 320 G (see Fig. . 5.7).



Figure 5.8:

AFM images showing the position of nanoparticles in the thin film under the condition of a) no magnetic field and b) parallel magnetic field B = 400 G.

As shown in Fig. 5.8a, in absence of external magnetic field, the nanoparticles are selectively deposited into the PS domains of the micro-phase separated diblock copolymer film. The white part in the Fig. 5.8a show the position of nanoparticles. However, in a magnetic field of about 400 G, the nanoparticles are aligned and form long stripes of aggregated nanoparticles (see Fig. 5.8b).

The formation of submicron stripe-like metal nanoparticles aggregates is involving a limited modification of the polymer morphology. A limited enhancement of the orientation of the PS nanodomains parallel to the metal stripes (marked with an ellipse in the AFM image of Fig. 5.8b. The latter improved orientation of the polymer near the metal stripes may attributed to either i) a confinement effect by a hard wall(metal stripes), or ii) magnetic induced alignment on the polymer nanodomains containing the metal nanoparticles. The dispersion of the metal nanoparticles in the polymer matrix is investigated using GISANS to understand the correlation between the metal nanopatterns and the morphology of the polymer film. The analysis of these data is in progress.

In summary, highly oriented wire-shaped metal patterns of magnetic nanoparticles can be achieved by using external magnetic fields, and the different metal stripe width of nanoparticle aggregates aligned parallel to the magnetic fields are due to the different nanoparticle concentrations and magnetic field strengths.

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5.5 Improvement of carbon nanotube dispersability by chemical modification

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Carbon nanotubes (CNTs) are attractive for nanocomposite applications due to their outstanding physical properties. However, in solvents or polymer matrix CNTs, because of effective van der Waals attraction and hydrophobicity, tend to form large agglomerates losing their unique characteristics [1]. Thus, the quality of the CNTs' dispersion has a direct impact on the properties of a final nanocomposite. Chemical modification of CNTs is an elegant way to improve the dispersibility of CNTs along with their compatibility with the matrix [2]. To form stable polystyrene (PS) grafts on CNT framework, we use self-initiated photografting and photopolymerization [3], which was found to be effective for functionalization of both single- (SW) and multi-walled (MW) CNTs [4].

The effect of modification on the structure and aggregation behavior of the CNTs in solution was studied using SANS/USANS at D11, ILL. Dispersions of native SW and MW CNTs and the ones modified with PS grafts of different grafting density and length of polymer (which is dependent on time of polymerization — 1 or 3 days for the samples 1SW(MW)PS or 3SW(MW)PS, respectively [4]) were prepared by ultrasonication in toluene. Using deuterated toluene (C_7D_8 , D-toluene) or the mixture $C_7D_8/C_7H_8 = 11/89$ vol.% (HD-toluene) as a solvent, the polymer shell or the bare CNTs were highlighted.

To fit the experimental data, we consider a dispersion of CNTs as a system of cylinders or hollow tubes forming agglomerates, approximated by including a fractal structure factor. Thus, on a base of the package "SANS & USANS Analysis with IGOR Pro" (NIST) we generated models for fractal aggregates from homogeneous cylinders (for SW CNTs) or from core-shell cylinders (for MW CNTs). As an example, we present here the analysis of the SANS data for MW CNTs with different levels of functionalization. The model fits the experimental curves well (Fig. 5.9a) with reasonable parameters (Table 1), compatible with the results of atomic force microscopy (AFM) (dimensions of CNTs) and thermo gravimetric analysis (TGA) (level of functionalization, which mainly alters the scattering length density (SLD) of the shell) [4].

01					
	Core	Shell	Length, Å	SLD shell,	SLD core,
	radius, Å	thickness, Å	_	10^{-6} Å^{-2}	10^{-6} Å^{-2}
MW CNTs in HD-toluene	18	36	690	2.74	1.40
MW CNTs in D-toluene	22	43	970	5.39	5.66
1MWPS in D-toluene	12	43	8460	5.29	5.66
3MWPS in HD-toluene	16	34	7100	2.72	1.40
3MWPS in D-toluene	8	58	9700	5.24	5.66

Table 1: Fitting parameters from the fractal/core-shell cylinder model

The fitting parameters indicate an increase of the length of the cylinders with increasing level of functionalization, thus, a better dispersion of the CNTs modified with PS grafts. Nevertheless, the fractal dimension was found to be close to 3 in all the cases, meaning that even with increasing mesh size, the agglomerates of the CNTs stay quite compact. Moreover, the cut-off length of the agglomerates is high, varying within $10^4 - 10^5$ Å. The radii of the CNTs modified with PS grafts are larger compared to the native ones in case of the dispersion in D-toluene, as expected. In HD-toluene, where only the bare CNTs are highlighted, the radii stay approximately the same. From these values, we conclude that the thickness of the PS shell



Figure 5.9: (a) Example of the fitting the experimental SANS curves by a fractal/core-shell cylinder model; (b) core-shell cylinder model of the modified MW CNTs.

is ~ 20 Å. The dependence of the SLD of the cylinder shell on the solvent used and the level of functionalization of the CNTs is consistent with the suggested model, where the complex shell of MW CNTs consists of 3–15 graphene layers (according to specifications of the MW CNTs), filled with the solvent in between, and an outer layer of the grafted PS and a solvent (Fig. 5.9b). Deviations of the fitting curve from the experimental data are presumably due to the complexity and high polydispersity of the real system.

To conclude, SANS experiments at D11 gave detailed insight into the behavior of the CNTs in the solution and the influence of the modification procedure on both the morphology and dispersability of the CNTs. We found out that the modification of the CNTs with PS grafts indeed leads to a better dispersion of the CNTs in the toluene solution with a significant increase of the mesh size.

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5.6 Lithium-containing diblock copolymer thin films for solid-state micro-batteries

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Lithium-containing polyethylene oxide has been extensively studied as solid ion-conductive electrolytes for solid-state Li batteries [1, 2]. The ion-conducting solid polymer electrolyte should have the ability to accommodate a high fraction of free ions, as they contribute to the net charge transport, while maintaining outstanding mechanical/thermal stability. Mostly, solvent-free composites have been made via a dry mixture of the semi-crystalline polyethylene oxide (PEO) polymer, lithium salt, and other filling components, such as ceramic fillers, inorganic plasticizers, nanoparticles, or ionic crystals. However, a major drawback of the solvent-free composites is that the polymer electrolyte solid matrix does not attain a homogeneous mixing level with the lithium salt, thus, only limited improvement in the conductivity performance is gained.



Figure 5.10:

Topography (left) and phase (right) AFM images of lithium-containing P(S-b-EO) diblock copolymer thin film with different Li/PEO ratios. At a critical cLi/PEO ratio, a nanostructured films with cylindrical PS domains in PEO matrix is formed (c,d). At ratios larger than cLi/PEO, no more Li salt can be injected into the polymer thin film. The Li salt significantly aggregates at the surface of the polymer film, creating large-size particles (e,f).

The complex forming capability of PEO with lithium ions appears to be best achieved by mixing a solution of both PEO and lithium salt. Thus, wet chemical routes can offer an interesting alternative to the common solvent-free preparation. Here, we report on the morphology of block copolymer electrolyte thin hybrid films based on the diblock copolymer (DBC) polystyrene-block-polyethylene oxide, denoted P(S-b-EO), and the alkali salt of lithium (bis) trifluoromethanesulfonimide; Li[N(CF_3SO_2)₂]. To achieve very thin films, the solid-state electrolyte films have been prepared via spin coating from a solution containing both components (DBC and Li salt).



Figure 5.11:

a) Horizontal cuts in q_y -direction and b) vertical cuts in q_z -direction of the 2d GISAXS data of lithium-containing P(S-b-EO) diblock copolymer thin films with different Li/PEO ratios. The Li/PEO ratio increases from bottom to top. The second q_y profile from the bottom represents a nanostructured film with a critical cLi/PEO ratio.

The thin hybrid films are investigated using optical microscopy (OM), atomic force microscopy (AFM) and grazing incidence small angle scattering (GISAXS). The DBC is used to obtain a micro-phase separation structure. The block ratio between PEO and PS is chosen to have a major PEO component as a potentially high ion conducting phase, while the PS block is a minor component that forms glassy nanodomains. The hard, glassy PS domains, within the soft PEO matrix, can allow for better mechanical stability of the resulting solid-state electrolyte thin films. The results (Fig. 5.10) have shown that the PEO is subject to crystallization, due to a strong tendency for PEO chain folding. The addition of lithium salt up to a very small critical concentration cLi/PEO prohibits PEO chain aggregation and, hence, hinders crystallization. Instead, a micro-phase separation process is dominant, and nano-sized cylinders of PS domains in a PEO matrix are formed (Fig. 5.10c,d). Upon further increase of the lithium salt concentration, the PEO chains lack the ability to solvate more lithium ions. Lithium salt aggregates on the surface are observed (Fig. 5.10e,f). The solvation ability of the PEO to lithium ions is mainly limited by the excessive strain effect to wrap around the lithium ions in case interfaces are present in thin film geometry. Large-size salt particles on the sample surface of high lithium-content films ruin the initially established morphology of the DBC film (Fig. 5.10e, f). The q_y profile of the film with a cLi/PEO ratio (second from bottom in Fig. 5.11a) shows a significantly strong structural peak at $q_u = 0.11$ nm⁻¹. For the cylindrical composition DBC thin film, the perpendicular orientation of the cylinders (PS domains within the PEO matrix) can only be formed as long as the crystallization of the PEO is suppressed. The observed peaks in the GISAXS data (Fig. 5.11a) appears due to cylindrical domains with a radius, R, of 18 nm and height, H, of 51 nm (perfectly matching the 50 nm thickness film) and are separated by an average interparticle distance, D, of 57 nm in a liquid-like ordered structure.

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5.7 Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT

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Hybrid solar cells consisting of both the organic and the inorganic semiconductor parts are a potential source for low cost green electricity. Titanium dioxide is used as the inorganic material which tailor-made nano-structured morphology enhances device performance by increasing the active surface area for interfacial interactions [1].



Figure 5.12: a) SEM image of pure titania sample where nanopores are clearly visible and b) AFM image of pure titania sample obtained after calcination.

A sol gel approach based on an amphiphilic diblock copolymer, poly(dimethyl siloxane)-blockmethyl methacrylate poly(ethylene oxide), denoted P(DMS-b-MA(PEO)), acting as a structure directing agent is used to obtain a sponge-like titania nanoporous structure via spin coating on pre-cleaned glass substrates. A plasma etching step is performed under optimized parameters after spin coating to remove a correct amount of the soft PDMS polymer block in order to uncover the titania surface. The final step is calcination which converts the remaining PDMS block into a ceramic of silica oxy-carbide (SiOC) layer which finally acts as the blocking layer thereby preventing the electron-hole recombination. The porous structure of the titania film consisting of nanopores has been visible in the SEM and AFM images prominently after the calcination step as shown in figure 5.12a and b respectively.



Figure 5.13:

Selected 2D scattering images for a) the pure titania film and b) the backfilled titania film by applying a subsequent spin coating technique. The images are taken at mean neutron wavelengths of 2.7 Å, 3.5 Å, 4.6 Å, 7.4 Å, 10.7 Å and 14.2 Å.

For applications in photovoltaics, the titania nanopores are infiltrated with the hole-conducting polymer poly(3-hexylthiophene), denoted as P3HT, combined with a ruthenium based dye commercially known as N-719 via applying a subsequent spin coating technique.

Information regarding the porosity and the degree of backfilling of the nanoporous titania film is obtained from grazing incidence small angle neutron scattering (GISANS) measurements performed at the TOF-REFSANS beamline of FRM II, Munich.

Figure 5.13a and b show the 2D GISANS scattering images within a neutron wavelength range of 2.7 Å to 14.2 Å for the pure and the backfilled titania samples, respectively. The lateral structure peak visible in the 2D GISANS images is due to the nanopores in the titania film.



Figure 5.14:

Vertical cuts at $q_y = 0$ for a) the pure titania film and b) the backfilled titania film. $\alpha_i + \alpha_f$ denotes the scattering angle, the dashed lines mark the shifting of the Yoneda components for the glass substrate and the composite film. As indicated, the neutron wavelength increases from bottom to top.

The vertical cuts at $q_y = 0$ from the 2D GISANS data for both, the pure and backfilled titania samples, are shown in figure 5.14a and b, respectively. In the cuts of the pure titania sample, the splitting in the Yoneda peak is due to the different scattering length densities (SLD) of the glass substrate and the pure titania (see figure 5.14a). For the backfilled sample, splitting of the Yoneda peak is again observed. The Yoneda peak at lower $\alpha_i + \alpha_f$ values is associated with a composite layer of titania and P3HT and the peak at a higher $\alpha_i + \alpha_f$ values is associated with the glass substrate (see figure 5.14b). From the calculated SLD values of the pure and backfilled titania samples, the porosity of the pure titania film is found to be 59% and the degree of backfilling is 45% which is higher as compared to the literature value of 25% for single spin coating step for polymer infiltration [2]. This demonstrates the possibility of increasing the infiltration of the polymer inside the titania film using the subsequent spin coating method which helps in a gradual filling up of the titania nanopores by increasing the mobility and diffusion of the polymer chains inside the pores.

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5.8 Determination of the local gold contact morphology on a photoactive polymer film using nanobeam GISAXS

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In organic electronics mostly inorganic materials are used as the electrode material, e.g. to extract current from an organic solar cell. One possibility to install an electrode is the usage of a transparent, conducting substrate, such as doped tin oxides, on which the conducting polymer is coated. In addition, metals (e.g. Al, Au, ...) are used as electrode material. The metal is deposited on top of the polymer film by thermal evaporation or sputtering. It is well known for standard polymers that metals tend to diffuse into polymer films. In the case of conducting polymers this is of major interest as a complex metal-polymer interface influences the electronic band structure and therefore e.g. the charge carrier extraction in organic solar cells.



Figure 5.15:

(a) Selection of 15 two dimensional nGISAXS patterns to illustrate changes in the scattering pattern along the gradient range y = 57-127, displaying every 5th image). (b) AFM image of the uncovered polymer surface. (c) Line scan through the edge region of the gold contact showing the height profile as seen with imaging ellipsometry. (d) AFM image of the gold contact

We investigated the edge morphology of a gold electrode on a photoactive polymer film using nanobeam grazing incidence small angle X-ray scattering (nGISAXS). As the photoactive polymer film the diblock copolymer poly(styrene-b-paraphenylene) (P(S-b-PP)) is used. This copolymer forms micelles with a PPP core covered with a PS shell in toluene solution. Choosing the right thickness (in the range of 80 nm) the micelles are transferred on a substrate via spin coating. On a silicon substrate the micelles form a densely packed film.[1] On this nanostructured polymer film a gold contact is evaporated using a shadow mask.

Fig. 5.15c shows the gold edge profile measured with imaging ellipsometry which revealed a 82 nm thick polymer film covered with a 50 nm thick gold contact. AFM images of the pure
polymer film (see Fig. 5.15b) and the gold contact (see Fig. 5.15d) show typical surface topographies of these materials. The profile of the gold gradient is scanned using nGISAXS with a resolution of 1 μ m (see Fig. 5.15a).

The analysis of the vertical cuts of the scattering data allows to determine the chemical composition of the gold edge profile. In Fig. 5.16a the intensity ratio of the Yoneda peaks of gold and polymer is plotted. This presentation reveals the shape of the gold edge. The edge shape is fitted with a tanh-function which exhibits a well defined edge width of 5 μm . Nevertheless, a foot like extension of the gold contact of 20 μm is found which is not seen by optical measurements. This increased electrode area is explained with gold diffusion on the polymer surface. Consequently, the electrode size is typically larger as measured with standard optical techniques.





(a) Intensity at the Yoneda peak position of gold I_{gold} normalized by the intensity at mean the Yoneda peak position of the two polymers PS and PPP $I_{polymer}$ shown as a function of the scan position y. The solid line is a tanh-function. (b) Intensity at the q_y position resembling the presence of a lateral structure in the diblock copolymer film (filled symbols) and in the gold film (open symbols). The vertical dashed line marks the edge of the gold contact as determined from the vertical scans.

The horizontal scans contain lateral structure information. The change of intensity at the q_y position resembling the lateral structures represents a change in scattering contrast. A constant intensity along the profile means no change. In Fig. 5.16b the intensities for the lateral structure of the copolymer and the gold are shown. The intensity curve of gold shows a clear edge which is identical with the edge revealed from the analysis of the vertical cuts. This confirms the determination of the gold edge position. The intensity representing the lateral structure in the polymer film increases already before reaching the edge which just happens when the contrast in the diblock copolymer film is changing. Consequently, gold diffused selectively into the diblock copolymer film.

In summary, nGISAXS is a powerful tool to determine the local profile of an electrode edge. This investigation revealed an increased electrode area compared to optical investigations. The underestimated electrode size influences e.g. the calculation of the photovoltaic performance of organic solar cells significantly when typical small electrodes are used. Furthermore, selective gold diffusion into the polymer template was found.[2]

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5.9 Growth and morphology of aluminum thin films on P3HT surfaces

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In electronic devices based on polymers as active components thin metal coatings are widely used as electrodes to pick up or inject electric currents. By deposition of the metal film directly on top of the polymer an intimate contact between the active layer and the electrode has to be achieved, which is crucial for the interchange of charge carriers and the performance of the device [1]. How the interface between the metal and the polymer is structured mainly depends on the growth process of the metal film on the polymer surface, therefore understanding of this process and its relation to chemical and structural interactions at the interface are of high importance to optimize the properties of the devices.

In an in-situ study a thin film of poly(3-hexylthiophene) (P3HT) was coated with aluminum (Al) and the growth of the metal film observed with grazing incidence small-angle X-ray scattering (GISAXS). The structural parameters of the growing film were extracted by simulation of the scattering images and related to the interactions at the interface. The experiment was performed at the beamline BW4 at HASYLAB and the Al film deposited by DC magnetron sputtering. A deposition rate of 0.92 nm/min was used and the sputtering chamber operated in high vacuum conditions with an argon working pressure of 5*10⁻³ mbar. Deposition was carried out continuously for 30 min and scattering images collected with a framing rate of 12 images per minute. A GISAXS setup with an incidence angle of 0.384° and a beam wavelength of 0.138 nm was used. The scattering images were modeled with the IsGISAXS software by describing the Al layer with an arrangement of ordered cylinders. Figure 5.17 shows a comparison of selected scattering images together with the corresponding simulations.





Measured (upper row) and simulated (lower row) scattering images of the P3HT-aluminium layer system at different stages of deposition. The thickness of the Al film increases from 0 to 27.7 nm.

The scattering images are characterized by a pronounced order in vertical direction and the absence of a lateral structure. The maxima in vertical direction evolve with the growth of the Al film and are connected to the film thickness. The film thickness increases constantly with time, in accordance with a homogeneous layer growth. The absence of lateral structures in the scattering images shows the absence of lateral structures in the growing film, i.e. no clusters or ordered structures form during the growth process. Instead, the film grows in a two-dimensional mode by successive addition of atomic layers.

This behavior is in strong contrast to the growth of gold on poly(N-vinylcarbazole), where the formation of spherical clusters and their growth to continuous layer was observed [2]. The difference results from dissimilar chemical interactions at the interface. While the gold:PVK system is inert, a strong chemical reaction is found for P3HT and Al [3]. Al atoms adsorbed on the P3HT surface are covalently bond to the polymer and thus fixed in their position on the surface (figure 5.18). This lowers the mobility of the adatoms and suppresses their agglomeration to three-dimensional cluster-like structures. Instead, a high density of adatoms is achieved and the surface rapidly covered with an Al monolayer. On this first monolayer further Al atoms can adsorb and form a second monolayer. This process continues as long as deposition continues and a homogeneous Al film without voids or interspaces is formed [4]. With respect to the device, this growth mode brings advantages in terms of contact resistance and adhesion, since a large contact area between metal and polymer is achieved.

In summary, the growth of an Al contact on a thin film of P3HT was investigated and related to the interactions at the interface. Chemical bonding between Al and P3HT favors the growth of a dense and homogeneous layer, as it is favorable for application in organic electronic devices.



Figure 5.18:

Schematic drawing of the growth process. The process is dominated by chemical bonding of the aluminium to the P3HT, which suppresses clustering and initiates a layer-by-layer growth.

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5.10 Creating colloidal nanocomposites using the solution casting method

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Polymer-metal nanocomposites are very important materials for many technological applications, e.g. surface enhanced Raman scattering (SERS), colorimetric detection of biopolymers or sensors [1,2]. Among the coating methods, solution casting is a very efficient coating process to install designed colloidal and biopolymeric thin films, including tailored morphologies and gradients for combinatorial investigations. Thus the understanding of the wetting and flow behavior of colloidal solutions on top of nanostructured substrates is of crucial importance.



Figure 5.19:

a) microbeam grazing incidence small-angle scattering x-ray $(\mu GISAXS)$ data taken before droplet deposition (t=0s) and after drying (t=696s). Shown is a simulation of the data using IsGISAXS and the different contributions from the Au layer and PS layer. The arrows indicate the Bragg peaks from the hexagonal PS layer (red) and from the domains in the rearranged layer (green) as well as from the Au agglomerations (blue). b) Atomic force microscopy images of the domains in the rearranged layer (left), the Au agglomerations (middle), and the pristine hexagonal PS layer (right).

We investigated in-situ the kinetic during casting of an aqueous solution of gold (Au) nanoparticles on top of a nanostructured colloidal polystyrene layer with hexagonal ordering. In fig. 5.19b) we present the atomic force microscopy images of the pristine PS layer and the nanocomposite. The PS layer was prepared using PS colloids of 100 nm diameter, spin-coating and toluene treatment. To observe the solution casting of the Au nanoparticles (20 nm diameter) aqueous solution, we combined two methods, namely microbeam grazing incidence small-angle x-ray scattering (μ GISAXS) and imaging ellipsometry. To do so, we installed an imaging ellipsometer (surface probe ellipsometric microscope (SPEM) of Nanofilm Technologie GmbH) at the micro- and nanofocus x-ray scattering beamline (MiNaXS) P03 at the high-brilliance synchrotron radiation source PETRA III of DESY, Hamburg, Germany. We used a micro-focused beam with a size of 35 x 22 μm^2 (HxV) at the sample position at an x-ray beam energy of E=12.78 keV. In fig. 5.19a) we show the out-of-plane (oop) cuts of the μ GISAXS data before solution casting (t=0s) and after drying of the droplet solution (t=696s) including a simulation of the nanocomposite structures. Clearly the pristine PS layer, prior to casting, shows very good hexagonal





Droplet drying kinetics. Top: Temporal evolution of the Yoneda Peak of PS and Au. Bottom: Temporal evolution of Δ and Ψ . The dashed vertical lines indicate, that the curves follow the same temporal behavior. The three distinct different regions are: D - diffusional rearrangement, P - Au precipitation, C - Compaction.

ordering (fig. 5.19b), right image). After solution casting, an Au layer has been installed, visible as agglomerations of Au nanoparticles around $q_y \approx 0.4 \text{ nm}^{-1}$, see also fig. 5.19b), middle image. Moreover, the perfect ordering of the PS layer has been lost. Instead, a roughness increase if observed, the PS colloids cluster into larger domains, as seen in the left image of fig. 5.19b). In the oop cuts, the rearrangement of the PS layer is clearly seen as a loss of long-range hexagonal order around $q_y \approx 0.06 \text{ nm}^{-1}$. Fig. 5.20a) shows the temporal evolution of the Yoneda peak intensity of PS and Au as well as the temporal evolution of the ellipsometric parameters Δ and Ψ in fig. 5.20a). Clearly, the curves' temporal behavior coincides and different regimes of diffusional rearrangement, precipitation and compaction can be observed.

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5.11 Flow induced surface attachment of gold nanoparticles - an in situ x-ray investigation with micro-fluidic cell

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The deposition of metallic nano-particles onto solid surfaces is of interest in a wide range of topics from nanoelectronics and nanosensors to nanocatalysts. One way of to achieve patterns of ordered nanoparticles is to apply a continuous flow over the substrate via a microfluidic channel [1, 2]. X-rays are a useful probe for the investigation of flow and processes in micro-fluidic systems. In transmission geometry SAXS (small angle x-ray scattering) growth processes or the orientation of nanoparticles can be followed. With the application of a reflection geometry in GISAXS (grazing incidence small angle x-ray scattering) and a special designed fluidic cell also surface sensitive investigations are possible [1]. With this method the selective immobilization of gold nanoparticles on one block of a micro-phase separated block-copolymer surface was investigated in-situ leading to the growth of gold nanowires [2].



Figure 5.21:

Set-up of micro-fluidic cell **a**: installation at MiNaXS beamline; arrow indicates the incoming x-ray beam **b**: top part cell design with Luer connectors for one inlet and two outlets

In figure 5.21a the set-up of the micro-fluidic cell at the micro- and nanofocus x-ray scattering beamline (MiNaXS/P03) at the third generation synchrotron source PETRA III at DESY in Hamburg is shown. The x-ray beam was focused to a size of 35 μ m x 22 μ m by beryllium compound refractive lenses. The arrow in figure 5.21a depicts the x-ray beam from the position of guard slits to the position hitting the micro-fluidic cell. The fluidic cell for GISAXS investigations comprises a top part made of a copolymer based on cyclic olefines shown in figure 5.21b. The material is transparent to visible light and has a relative low absorption in the x-ray range used in the experiments. The top part is connected to the surface to be investigated (e.g. a thin polymer film on a glass slide with a metallic clamp as shown in figure 5.21a). The channel geometry (1 mm wide and 1.3 mm deep) enables the study of the solid-liquid interface during the continuous flow stream of a solution with a broad range of flow rates. There are two inlets allowing for mixing experiments and chemical reactions.

In this study the attachment of high aspect ratio gold nanorods to surfaces of calcium-alginate is investigated. Spin-coating of thin films of sodium-alginate and subsequent cross-linking with divalent calcium ions leads to water insoluble films. The high aspect ratio gold nanorods with a size of 25 nm x 256 nm are stabilized with cetyltrimethylammoniumbromide (CTAB). The polyanion alginate serves as a counterpart to the nanoparticles with net-positive charge. Only

one of the inlets of the micro-fluidic cell is used to pump the aqueous nanoparticle dispersion with 0.05 ml/min. A scan of the micro-fluidic channel (along y-direction in figure 5.21b) is carried out, collecting scattering data for 0.5 s at 70 positions in 250 μ m distance from each other. The duration of one scan is 180 s. The flow experiment is run for 1 h with 20 subsequent scans along the channel. This procedure offers a time resolved as well as a position resolved investigation of the attachment of nanoparticles at the same time.





2d detector patterns for flow experiment with gold nanorods on alginate surface; arrows indicate Bragg reflection spots

In figure 5.22 the 2d GISAXS detector patterns are shown for one of the positions on the channel. The 2d patterns are marked with the number of the scan. The first scan shows the GISAXS pattern of the dry alginate film. The characteristic features arising with flow of the nanoparticle dispersion are Bragg reflections indicated with arrows in the 4th scan of figure 5.22. The Bragg reflections are accompanied by a ring shaped intensity centered by the direct beam. With following scans (6th and 20th run are shown in figure 5.22) the Bragg reflections as well as the ring shaped intensity are more pronounced and observed at smaller q-values. The scattering patterns with Bragg reflections indicate domains of 2d cylindrical hexagonal structures oriented parallel to the surface.



Figure 5.23: Contour plots of vertical cut of 2d detector pattern for 70 positions on the micro-fluidic channel

In figure 5.23 the GISAXS data dependent on the position of the micro-fluidic channel are illustrated with a contour plot of a vertical (detector) cut for the 70 positions on the channel investigated. The contour plots for the 4th and the 20th run are shown. Whereas in the 4th run one Bragg reflection is clearly observable, in the 20th run this reflection is shifted to smaller q_z to the area which is not accessible by the detector because of the frame bordering two modules of the Pilatus detector (see also 20th run in figure 5.22). Further data evaluation and the additional use of real space imaging techniques for the nanoparticle covered alginate surface after the flow experiment will allow for the description of the attachment of gold nanorods dependent on time and position on the fluidic channel during the flow experiment.

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6 Dynamics



6.1 Nanoscopic dynamics of phospholipid molecules

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Phospholipid molecules are the main single component of cell membranes. They are amphiphilic, i. e. they have a hydrophilic and a lipophilic part. When in water, the molecules arrange in bilayers in order to minimize the contact of the lipophilic part with water. This is the basic structure of a cell membrane which contains also other substances embedded in this matrix. In addition to proteins, which give the membrane its active functionality, a major component is cholesterol. Cholesterol influences the fluidity of the membrane, its concentration varies strongly between cells. There are also industrial applications for phospholipids. Two examples are the pharmaceutical and the food industry where the amphiphilic character of the molecules is used to disperse lipophilic molecules in water.

A challenge for this dispersion are droplets of lipophilic substances which undergo a phase transition, e.g. from liquid to solid, during the production process. In their liquid form, surface tension keeps them spherical with a diameter of about 100 nanometers. When solidifying, the substance forms a single crystal. As these have mostly a very oblate shape, the surface of the lipophilic material increases suddenly. It is known that it is only with the addition of a co-stabilizer such as sodium glycocholate possible to avoid aggregation of the particles during the crystallization process. One of the questions we asked ourselves was if the stabilizing mechanism of the co-stabilizer sodium glycocholate was linked to a possible influence on the mobility of the phospholipid membranes.

To study the motions of the phospholipid molecules, we employed quasielastic neutron scattering (QENS) at the neutron time-of-flight spectrometer TOFTOF at the FRM II (Garching bei München, Germany). The observation time was adjusted to approximatively 50 picoseconds and 900 picoseconds by changing the energy resolution of the spectrometer. During this observation time, the correlation function of the positions of the scatterers in the sample is probed. As hydrogen has a much larger scattering cross section than all the other atoms in the sample and also than its heavy isotope deuterium, one can assume that only the correlation function of the hydrogen atoms is probed.

A first experiment was performed on the pure protonated phospholipid dimyristoylphosphatidylcholine (DMPC) hydrated with deuterated water in order to probe the motions of the phospholipid molecules [1]. These motions had been studied already in the 1990s with QENS. Assuming simple diffusion of the molecules, those experiments gave a very high diffusion coefficient, much higher than the macroscopically observed value. This was explained by the picture that a phospholipid molecule rattles with high speed in a cage of neighbours which would be the motion observed by QENS. When thermal fluctuations opened up a void next to molecule, it could break out of this cage of neighbours. This step is much slower than the rattling in the cage and is the one that determines the macroscopic diffusion. However, this event of breaking out of a cage of neighbours was never observed, neither in experiments nor molecular dynamics (MD) simulations.

With our experiment [1], we were able to support the picture which recently emerged from MD simulations [2]: the phospholipid molecules do not perform a simple diffusion at very short times, escaping the cage of neighbours now and again but they rather perform flow-like motions in a cluster *together* with their neighbours. The experimentally determined values for the flow velocity of these dynamically assembled clusters are in very good agreement with the ones obtained from the simulation.

The flow events in the membrane resemble the *dynamic heterogeneities* known from glass physics very closely [3]. We think therefore that the description of the membrane dynamics would benefit from a new loan from glass physics – as for example from the concept of cooperatively rearranging regions developed by Adam and Gibbs. This will be subject of our research in the future.

As the slow long range motion of the phospholipids has a very small effect on the line shape of the neutron scattering spectra, we have also studied the influence of two possible sources of errors, namely multiple scattering and fitting artifacts [4]. One of the basic assumptions in our evaluation of neutron scattering spectra [1] was that every detected neutron was scattered only once in the sample. Studying pure protonated water, a very strong scatterer, with different thicknesses, we were able to demonstrate that the evaluation of the long range motion is not influenced by multiple scattering.



Figure 6.1:

Half width at half maximum of the narrow component of a two-Lorentzian fit to the measured scattering function of H₂O. Different symbols indicate different thicknesses of the sample (indicated in the figure). The amount of multiple scattering increases with the sample thickness. It can be seen that the quadratic dependence of the line width on the absolute value of the scattering vector, Q, is not influenced by multiple scattering. As the diffusion coefficient is linked to this width via $\Gamma = \hbar DQ^2$, it can be reliably determined even from very strongly scattering samples.

The convolution of the theoretical scattering function with the instrumental resolution, which was shown to be error prone before [5], influences the extracted line width of very narrow lines. However, also this effect does not influence the conclusion of flow-like motions in phospholipid membranes [1].

Building on our knowledge of the microscopic diffusion mechanism of the phospholipid molecules, we studied the influence of additives such as cholesterol and sodium glycocholate on the dynamics of the phospholipid molecules [3]. The well-known effect of cholesterol to decrease the mobility in the membrane was clearly visible. With this proof that changes in mobility are observable by QENS, we checked the influence of sodium glycocholate which we suspected to increase the dynamics in the membrane. Contrary to this assumption, no effect was visible.

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6.2 Water migration into a casein micellar film: A neutron radiography study

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Milk and milk components are used to make related food products. One component of milk is casein protein, which forms hydrated casein micelles about 100-300 nm in diameter. Because casein proteins do not denature in dry form, preparation of thin, dry casein film is possible [1]. In a very recent experiment [2] we investigated the time-evolution of water uptake of casein micelle films 1.42 μ m thick in a water-vapor atmosphere using time-resolved grazing incidence small angle neutron scattering (GISANS). The initial dry casein film, spin-coated onto silica, was exposed to water vapor at 30 °C. This thin film reached an equilibrated hydrated state after 11 min with total content of 0.36 g water/g protein. The latter study provided insights into the structural reorganization of casein micelles with respect to their size and size-distributions upon water-vapor swelling. The present work is aiming on information about macroscopic water diffusion into thicker casein films. The penetration of water into casein-based materials is an important physical phenomenon that might give insights into durability and mechanical stability and, hence, the performance of casein-based adhesive films. Here, we report on the time-evolution of a water diffusion profile in thick sub-millimeter films of casein micelles. The diffusion and self-diffusion of water molecules into the casein micelle film can be detected by use of the neutron transmission method and by employing the phase contrast in D₂O-H₂O systems.



Figure 6.2:

Set of neutron transmission images showing the initial water injection in an aluminum cell where a 0.3 thick dry casein micelle film is located in the center of the cell. The time zero is set to a time at which the film is completely surrounded by water instead of air.

A gel resembling casein micelles in D_2O (50 wt%) was prepared and cast on an open-cell aluminum plate. After a few minutes, the sample was squashed using the second aluminum plate of the cell to create a disk-like film with thickness of 0.3 mm (Fig.6.2). Two small openings in opposite sides of the cell were used as an inlet and an outlet for water injection. The casein film in the cell was heat-treated at 50 °C for 30 min to create a *dry* film and remained at room temperature for 1 h before neutron transmission measurements. The *dry* casein film is submerged in H₂O, and water migration in the film is monitored in real-time mode via imaging of transmission of fast neutrons. The neutron transmission experiment was performed at the neutron imaging facility ANTARES at the research reactor FRM II in Munich. The water content, θ (volume fraction), of the casein micelle film was estimated from image pixel brightness B corrected for both black current and the detector pixels' sensitivities. Experimental water distribution profiles were determined for different time periods (30-8000 s) following the water injection step. The data (Fig.6.3b) were fitted using the solution to a one-dimensional diffusion equation[3]. Profiles of water concentration were successfully probed. The study has demonstrated the use of neutron radiography as a viable method for determination of the diffusion profile of water in casein films. The diffusion constant for water in the dry casein micelles film was estimated to be about $1.31 \times 10^{-3} \text{ mm}^2/\text{s}$. A constant diffusion regime and boundary water equilibrium were reached after the same time of about 630 s, consistent with our previous observation [2] of the hydration kinetics of casein micelle thin films in saturated water vapor (an equilibrated hydration state at 660 s), as revealed by GISANS method.



Figure 6.3:

(a) Normalized intensity profiles (radially averaged) of the neutron radiographs from the casein micelle film in contact with water. (b) Spatial distribution of the water content at different time viz. 600, 1200, 1800, 3600, and 5400 s; fitted with the solution of a diffusion equation (solid lines).

By imaging the water concentration in a casein micelle film, we concluded that two diffusion processes are involved: (a) fast diffusion with a decaying diffusion constant, resulting from water exchange with the hydration water bound to the casein proteins, and (b) slow and constant diffusion due to Fickian water transport into the voids and holes between the casein micelles and their aggregates in the porous film. After the casein micelle film was in contact with water for a sufficient time, large casein micelle aggregates become visible in the neutron transmission images. These casein micelle aggregates are observable because of an improved contrast via neutron attenuation by H_2O sorption in the rest of the film. The aggregates are part of the initially prepared film in which D_2O was used. The aggregation of casein micelles, leading to a formation of large particles, is a well-known phenomenon that depends on the pH and temperature of the casein micelle solution [1].

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6.3 Test of the Rouse model on a polyethylene melt

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The description of transport mechanisms in molecular liquids is a challenging task. Especially the mechanism of molecular self-diffusion in liquids of organic medium-chain molecules is not completely understood yet. The dynamics of polymer melts covers wide range of time and length scales. With time-of-flight quasielastic neutron scattering (TOF-QENS), it is possible to get experimental access to the motions on a molecular length scale in the pico- to nanosecond time regime. In this regime one has to assume a superposition of several (intra)molecular motions ranging from methyl group rotation to long-range diffusion. It has been demonstrated by molecular dynamics (MD) simulations for the *n*-alkane $C_{32}H_{66}$ that in the 1 ps time range tumbling motions of the hydrogen atoms dominate while small chain deformations dominate after 20 ps [1].

The Rouse model may be considered as the standard model for polymer chain dynamics. The bead-spring model was developed to describe large scale chain motions. It considers a chain consisting of N freely joint Gaussian segments in a heat bath where springs stand for the entropic forces between the hypothetic beads. Excluded volume effects are disregarded. The solution of the Langevin equation results in a spectrum of normal modes which account for the internal motion of the chain [2]. Since the expected tumbling motions of hydrogen atoms in polyethylene melts at short observation times are not taken into account by the Rouse model, the model should predict a rather slow decay of the correlation function in this time regime.

As the Rouse model should not be able to characterise the short time dynamics of the polymer chain, one might additionally describe the atoms as Brownian particles in harmonic potentials. In order to test the models, TOF-QENS experiments were performed on a polyethylene melt (n- $C_{100}H_{202}$). The chains are long enough to show gaussian chain statistics in their confirmations but are still in the unentangled regime so that it was possible to check the validity of the Rouse model on this time and length scale.

Fig. 6.4 shows the measured intermediate scattering function and the Rouse prediction for several values of the momentum transfer $\hbar Q$. It can clearly be seen that the Rouse predictions lie throughout below the measured data. Thus the Rouse model predicts a faster decay than actually measured. Any additional models, accounting for further motions, cannot enhance the description of the data.



Figure 6.4:

Normalized intermediate scattering function for n-C₁₀₀H₂₀₂ (symbols) and the Rouse prediction (solid lines) for three values of momentum transfer Q. One crucial parameter of the Rouse model is the segmental friction coefficient ζ . One can assume that this friction coefficient might not be constant but rather increases with increasing mode number p. This assumption can be interpreted in terms of internal viscosity effects. This leads to a mode-dependent friction coefficient ζ_p which we adopted to be linearly dependent on the mode number p: $\zeta_p = \zeta + s \cdot p$. Higher modes (shorter wavelengths) are now damped stronger than the lower modes.



Figure 6.5:

Normalized intermediate scattering function for n-C₁₀₀H₂₀₂ (symbols) and the Rouse prediction with mode dependent friction coefficient ζ_p (solid lines) for three values of momentum transfer Q.

The result of the fit with the mode dependent friction coefficient is shown in fig. 6.5. The fit agrees nearly perfectly with the measured data although no fast motion as tumbling motions of hydrogen atoms were taken into account. But since those motions are expected in the 1 ps time regime, this improved Rouse model is obviously unphysical for the description of our data. A new approach to understand the short time dynamics of polymer chains will not consist of the entire Rouse model any more. A modified Rouse model, contributing only to the motion of lower modes (slower, large scale motion), might allow the integration of additional terms. As can be seen in fig. 6.6, many Rouse modes contribute to the Rouse model in the investigated Q-range. The decay of the first mode relates to the strongest decay of the Rouse prediction. It is then further necessary to perform MD simulations in order to identify the additional motions, e.g. tumbling motions.



Figure 6.6: Contribution factors of the different modes to the Rouse model for n-C₁₀₀H₂₀₂.

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6.4 The effect of magnetic field and mechanical stress on the phonons of five layered modulated Ni₄₉Mn₃₂Ga₁₉

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Ferromagnetic shape memory alloys (FSMAs) have gained attention of many researchers due to the exhibition of large reversible strain upon application of magnetic field. Magnetic field can induce two effects on FSMA: magnetic field induced transition (MIT) and/or magnetic field induced variant reorientation (MIR). The highest reversible strains in FSMAs through MIR are exhibited by Ni-Mn-Ga alloys ($\sim 10\%$) and hence they have been used in actuators and sensor applications [1].

Our previous studies of Ni₄₉Mn₃₂Ga₁₉ alloy showed that, a softening anomaly occurs in the transverse acoustic phonon branch TA₂[$\xi\xi$ 0] on approaching the structural phase transition at a particular region in the Brillouin zone. Additionally, in the martensite phonon dispersion low energy excitations of the modulated martensitic structure are observed as shown in figure: 6.7 [2]. These low energy excitations show modulations at commensurate wave vectors ξ =0.4 and 0.8 r.l.u which match with the elastic superstructure Bragg peaks of the modulated martensite structure. Therefore, the origin of these low energy excitations can be attributed to the presence of five-layered modulated superstructure in the martensite phase.



Figure 6.7:

The low energy excitations of five-layer modulated phase of Ni₄₉Mn₃₂Ga₁₉ along transverse [$\xi \xi 0$] direction with modulations at commensurate positions of ξ =0.4, 0.8 r.l.u [2].

In the present work, we have tried to verify the origin of these low energy excitations by studying the effect of magnetic field and uni-axial mechanical stress on the low energy excitations of Ni₄₉Mn₃₂Ga₁₉. The vibrational properties of five layered modulated Ni₄₉Mn₃₂Ga₁₉ sample have been measured using inelastic neutron scattering method with three axis spectrometer PUMA at FRM II.

The low frequency region of the [$\xi \xi 0$] phonon dispersion of the five-layered modulated phase of Ni₄₉Mn₃₂Ga₁₉ alloy is measured while applying a vertical magnetic field parallel to the *c-axis* of the sample which is also the easy axis for the magnetization. Figure: 6.8.(a) shows that the applied magnetic field does not effect the TA₂[$\xi \xi 0$] phonon frequencies.

This could be due to the single variant state of the sample arising from the training which is used to achieve maximum possible reversible strain where no further variant reorientation occurs. Therefore, another experiment was carried out to study the effect of flipping the magnetic field direction on the rotation of magnetic moments which could effect the phonon frequencies. The results shown in figure: 6.8.(b) reveal that the frequencies of low energy excitations and $TA_2[\xi \xi 0]$ branch do not change implying that the flipping of the direction of external magnetic field has no effect on the vibrational properties of the low energy excitations.

The application of the magnetic field parallel to the *c-axis* had no effect to the vibrational properties, but it is known that if we apply the magnetic field perpendicular to the *c-axis* we will observe the MIR effect. Unfortunately, it was not possible to apply the magnetic field perpendicular to



Figure 6.8:

(a) The TA₂[$\xi \xi 0$] phonon branch in the presence of magnetic field of 4T and 5T, (b) The effect of magnetic field on the frequencies of low energy excitations and TA₂[$\xi \xi 0$] phonon branch at wave vectors, $\xi = 0.35$, 0.375 and 0.45 r.l.u.



Figure 6.9:

(a) The elastic scattering of Ni₄₉Mn₃₂Ga₁₉ along [220] in the transverse direction under the effect of uni-axial merchanical stress of 0 MPa and 3 MPa, (b) The inelastic scattering of Ni₄₉Mn₃₂Ga₁₉ at ξ =0.35 r.l.u under the effect of uni-axial mechanical stress of 0 MPa and 3 MPa.

the *c-axis* so we decided to mimic the effect of magnetic field by applying a mechanical stress. The elastic scattering along [220], as shown in the figure: 6.9.(a) exhibits an increase in the intensity of the superstructure peaks. This effect is also observed in the inelastic scattering, shown for ξ =0.3 r.l.u in figure: 6.9.(b), carried out in the low energy part of transverse [$\xi\xi$ 0] direction. The reason behind the increased intensity is not yet well understood and further investigation is required to understand the phenomena. Also, the inelastic measurements could not be analyzed to extract information regrading frequency shifts due to the poor background to signal ratio. The inelastic measurements of non-modulated Ni_{49.2}Mn_{30.4}Ga_{20.4} (examined as another part of this work) have revealed that the alloy does not have low energy excitations confirming that the low energy excitations are related to the presence of modulated structures in the martensitic phase. But, this could not verified successfully by the above explained experiments.

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6.5 Effect of temperature and composition changes on phonon properties of Ni-Mn-Ga

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Materials which are able to recover their original shapes after a plastic deforation are called shape memory materials. Ni-Mn-Ga alloys are mostly used materials for magnetic shape memory applications due to their particular properties like magnetic field induced structural transition (MIT) and magnetic field induced variant reorientation (MIR). Stress recoveries of 6% and 10% for off-stoichiometric compositions of the Ni₂Mn_{1+x}Ga_{1-x} alloys have been observed for 5- and 7-layered structures [1,2] in the martensite phase, respectively.

The aim of this work is to investigate the vibrational properties of Ni-Mn-Ga alloys by using inelastic neutron scattering to understand the nature of the shape memory effect. Previous studies showed that in the high temperature phase, the TA₂[$\xi \xi 0$] phonon branch softens on lowering the temperature at specific q-vectors related to the low temperature martensite phase. To understand the reason of this phonon anomaly and to compare the experimental phonon dispersion to first principle calculations we performed inelastic neutron scattering experiments on the thermal three axis spectrometer PUMA at the FRM II in Garching.



Figure 6.10:

The phonon dispersions of the (a) stoichiometric Ni₂MnGa and (b) off-stoichiometric Ni₄₉Mn₃₂Ga₁₉ alloy for the high symmetry directions of [$\xi \ 0 \ 0$], [$\xi \ \xi \ 0$], [$\xi \ \xi \ \xi$] and low symmetry direction of [$2\xi \ \xi \ 0$]. The solid lines are the theoretical phonon calculations for the stoichiometric composition.

Figure 6.10 shows the full phonon dispersions of a stoichiometric Ni₂MnGa and offstoichiometric Ni₄₉Mn₃₂Ga₁₉ alloy in the high temperature L2₁ phase. The solid lines show first principle calculations of Ni₂MnGa at 0 K. They agree quite well with the experimental results in the case of the stoichiometric alloy. For the off-stoichiometric composition Ni₄₉Mn₃₂Ga₁₉ the the optical branches get flattened, which is the most remarkable difference in the overall dispersion. The first principle calculations show imaginary phonon frequencies in the TA₂[$\xi\xi$ 0] phonon branch which indicates the instability of the high temperature structure at 0 K. Both samples show phonon softening in a particular region of the TA₂[$\xi\xi$ 0] phonon branch. Whereas the Ni₂MnGa alloy shows a more pronounced dip at $\xi = 1/3$ indicating the instability towards the 3M intermediate phase, the off-stoichiometric alloy transforms either to a 5M or 7M structure depending on tiny concentration changes. To investigate the relation of the lattice weakness as seen by the phonons to the structural and magnetic transitions we have taken detailed measurements on the dynamics, the structure and magnetization as a function of temperature as depicted in Figure 6.11.



Figure 6.11:

Temperature dependence measurements of Ni₄₉Mn₃₂Ga₁₉. (a) Phonon frequency square of selected ξ points around the softening minimum, (b) magnetization as a function of temperature under low magnetic field, inset figure shows the DSC measurement, (c) temperature dependence of magnetic and nuclear Bragg peaks.

The figure 6.11(a) shows the temperature dependence of the phonon frequency squares for selected reciprocal space points around the softening minimum at TA₂[$\xi\xi 0$] phonon branch. The phonons are getting soft while approaching the structural phase transition temperature from both sides. At 580 K the slopes of the phonon frequencies change which had been attributed to the magnetic ordering in literature [3] for a stoichiometric alloy. The temperature dependent measurements of the magnetization and the DSC measurements, however, show that the austenite-martensite structural transition as well as the magnetic ordering (fig.6.11(b)) occurs around 365 K. For the stoichiometric composition the slope change in the high temperature phase coincides with the magnetic ordering temperature (not shown here).

To get more detailed information about the structural and magnetic ordering we took temperature dependent elastic measurements using the single crystal diffractometer RESI at the FRM II. The results of the elastic measurements are shown in figure 6.11(c). All of the measured Bragg peaks give information about the structural changes but (200) and (220) peaks also give information about the the magnetic structure. Around 440 K the intensities of these two magnetic Bragg peaks increase indicating the onset of the magnetic ordering. The elastic measurements on the single crystalline sample could not be extended below 370 K due the structural transition at 365 K. For the high temperature region some of the nuclear Bragg peaks show changes around 580 K, however at this temperature neither a signal in the heat capacity nor in the magnetization is observed. This disagreement in the temperature behaviour remains unexplained so far.

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6.6 Inelastic neutron and Raman scattering of low-frequency excitations in glasses for Raman gain applications

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We have investigated the low-frequency enhancement of vibrational excitations ("boson peak") in niobium-phosphate glasses through the combination of inelastic neutron and polarization resolved Raman scattering. The spectra of these glasses reveal an enhancement of the vibrational density of states and of the cross section for spontaneous Raman scattering in the frequency range be low 150 cm⁻¹. A recent theoretical model that is based on fluctuating elastic and elasto-optic (Pockels) constants provides a unified description of the measured neutron and Raman spectra including the depolarization ratio $\rho(\nu) = I_{VH}(\nu)/I_{VV}(\nu)$.

Glasses with broad and intense Raman-active modes have attracted attention for applications in all-optical amplification systems as the Raman-gain coefficient depends significantly on the cross section for spontaneous Raman scattering. Therefore it is advantageous to have a material with a smooth and not too small Raman spectrum down to the low-frequency regime.

Concerning the interpretation of the low-frequency Raman scattering in glasses and/or the enhancement of the vibrational density of states (DOS) over the Debye ν^2 law, a large number of conflicting views exist in the literature. Originally one thought that the Raman intensity would be proportionally to the DOS (as measured by neutron scattering or extracted from specific-heat data), but later on one invented a frequency dependent prefactor (light-vibration coupling factor $C(\nu)$) to allow for a discrepancy between spectra extracted from Raman and neutron intensities. Recently two of the present authors developed a theoretical model, in which the light-vibration coupling is modelled by spatially fluctuating Pockels constants, thereby allowing for the violation of the local momentum and angular-momentum selection rules [1]. The vibrational spectrum of the disordered solid was modelled by generalizing elasticity theory to allow for spatial fluctuating Pockels constants allowed to treat inelastic X-ray, neutron and Raman scattering on the same footing. The theory accounts for the differences in the "boson peak" as seen by Raman scattering compared to neutron scattering.

In this contribution we present the results of a combined experimental and theoretical investigation of low-frequency vibrational excitations in 20 Nb₂O₅ - 80 NaPO₃ and 40 Nb₂O₅ - 60 NaPO₃ glasses. These materials show a broad and intense Raman spectrum, and they are therefore good candidates for all-optical Raman-gain applications [4]. We have combined inelastic neutron scattering with polarization-resolved low-frequency Raman scattering in order to explore the role of fluctuations in both the elastic medium and the coupling to light.

In the left part of Fig. 6.12 we compare the Raman data for 20 Nb₂O₅ - 80 NaPO₃ with the reduced DOS $g(\nu)/\nu^2$. It is clearly seen, that the latter quantity has a maximum near 40 cm⁻¹, whereas the maximum of the Raman data occurs near 55 cm⁻¹. Results of theoretical calculations according to our theory are represented by the full lines. To provide a stringent test for the theory it is essential to have light-scattering data for VH as well as for VV geometries. It is remarkable that the theory reproduces not only the absolute value, but also the spectral shape of the depolarization ratio $\langle \rho \rangle$. The depolarization ratio varies between 0.44 and 0.39 over the frequency range from 10 to 150 cm⁻¹. As the value of $\langle \rho \rangle$ is controlled by the ratio of the mean-square Pockels constant fluctuations $\langle \Delta a_1^2 \rangle/\langle \Delta a_2^2 \rangle$, which turned out to be ~ 2.1, we conclude that the "longitudinal" fluctuations Δa_1 are rather strong in the niobium-phosphate glass. This



Figure 6.12:

Left: a) Depolarization ratio $\rho = I_{VH}(\nu)/I_{VV}(\nu)$. b) Reduced Raman intensities (upper: VV, lower: VH), compared with theory. c) Reduced DOS $g(\nu)/\nu^2$, compared with theory, using the same parameters for the elastic model. Right: a) Depolarization ratio $\rho = I_{VH}(\nu)/I_{VV}(\nu)$. b) Reduced Raman intensities (upper: VV, lower: VH), compared with theory. c) Reduced DOS $g(\nu)/\nu^2$, compared with theory, using the same parameters for the elastic model.

reflects the structural and geometrical characteristics of the scatterers. In the right part of Fig. 6.12 we compare the Raman data for 40 Nb₂O₅ - 60 NaPO₃ with the reduced DOS $g(\nu)/\nu^2$. Again the theory is in good agreement with the Raman spectrum for both polarizations and the neutron data. The disorder parameter γ is fixed by the density of states from neutron scattering, and the Raman data provide a value for the fluctuations in the elasto-optical constants. With the increase in Nb concentration the depolarization ratio is slightly lower indicating an even more pronounced contribution of the longitudinal Pockels constant fluctuation. Structurally, in the niobium-phosphate glasses progressive introduction of Nb_2O_5 may lead to the formation of corner shared NbO₆ octahedra chains and a 2d phospho-niobate network. This in turn would decrease the correlation length in the fluctuations of the elasto-optical constants for the same Debye wavenumber k_D . In conclusion we have shown that the measured inelastic neutron and low-frequency Raman spectra of niobium-phosphate glasses can be quantitavely described by a unified model that includes spatial fluctuations in both the elastic constants of the disordered medium and the elasto-optical (Pockels) constants. The value of the depolarization ratio for Raman scattering is determined by the mean-square Pockels constant fluctuations, while its frequency dependence is modulated by the vibrational disorder of the elastic medium.

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7 Methodological and instrumental developments



7.1 Neutronic and thermal hydraulic calculations of a 49.9% enriched disperse UMo core for FRM II

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Introduction

In the framework of the HEU-MEU conversion process of FRM II, new fuels are being developed and new reactorphysical calculations have to be performed, accordingly. Since 2007, a new coupled calculation scheme, X², has been developed in this framework. This program system basically consists of three different codes, MCNPX for the neutronics, MonteBurns / Origen2 for the depletion and CFX for the thermal hydraulics. Using these codes, highly detailed 3D calculations are carried out, using only few approximations.

The Codes

MCNPX is a Monte Carlo neutronic code, "solving" the Boltzmann Transport equation for neutrons and gamma radiation by using random numbers. The working principle is to "sit" on a particle and model its destiny by applying the random numbers in a physical manner. If this is repeated often enough, the central limit theorem ensures that a result close to the "real" solution is obtained, with some statistical uncertainty. CFX is a widely used thermal hydraulics codes, solving the Navier-Stokes Equation via finite volumes. The codes were coupled using a set of Perl scripts and FORTRAN programs to handle the data transfer between the different applications.

Verification of the Program System

The code system was verified by a comparison to the former design calculation system DOT / NBK for FRM II and also to measured values as far as they were available. The results were generally in good agreement for integral as well as local parameters. Due to the conservative approach that was used in NBK, the traditional calculation scheme yields higher maximum surface heat flux densities and temperatures (Fig. 7.1) at the fuel plate edges.

A rather detailed comparison was performed regarding burn-up and fission products. Minor remaining discrepancies with respect to absorber products will be further resolved. The first coupled burn-up calculations which did not use an averaged but a detailed representation of the user installations in the heavy water tank confirmed all relevant former results, especially the slightly asymmetric power distribution. This asymmetry is most pronounced at the beginning of the cycle (5% in core mid plane). It is reduced to only 2% at the end of the cycle. Therefore, the slight asymmetry of the burn-up has only negligible influence on the reactivity loss.

A further verification which includes the direct comparison to a finite elements code, COMSOL, is performed in cooperation with the Oak Ridge National Laboratory. This comparison will help to tell apart possible implementation issues in CFX and will also be a tool to rate the uncertainty of the thermal hydraulic results better.

Results for MEU and Core Compaction

A lower enriched fuel element will in general yield a lower neutron flux due to the increasing parasitic absorption of the higher amount of U-238 in the fuel. Parameter studies were performed for FRM II to minimize the flux loss as far as possible. Unfortunately, the higher absorption in the fuel also leads to less convenient power distribution in the core, especially the borders of the fuel plate suffer from a higher heat load. In return, the increased precision of the





Surface temperatures of the cladding of a disperse UMo plate. The plate has the same shape as the current fuel plates. In the fuel element, the control rod would be located on the left top side of the plate, the D_2O on the lower right side. Cooling water is entering from top-right. The maximum surface temperature is 90 C at the hotspot in the lower inner corner (very left border of the picture).

thermal hydraulic calculations and the higher density of the disperse UMo fuel could allow for a further compaction of the fuel element, which results in an increasing peak neutron flux in the D_2O tank.

In the first calculations for a conversion to disperse UMo fuel with an enrichment of 49.9% with same core geometry and same density ratios (see Fig. 7.2), a thermal neutron flux loss of 7.7% was expected. Preliminary neutronic optimisation calculations, which continue the work performed so far, showed that the flux loss can be reduced to 5.2%, if the length of the fuel element is reduced from 70 cm to 64 cm and the cooling channels are widened from 2.2 mm to 2.4 mm. The current cycle length of 60 days is kept. In this partly optimised case, the U-235 inventory is increased from 7.5 kg (current HEU fuel) to 9.7 kg, which is 1 kg less than the amount required in the constant geometry conversion scenario (10.7 kg). The thermal hydraulic investigation of this scenario is still on the way, however, concepts were developed to reduce the heat load in the critical areas, especially in the hot stream filament. An example for these concepts is the usage of a slightly skew density step rather than a strictly vertical step.

The further compaction also poses high qualification burdens for the new fuel, requiring stability up to a maximum fission density of $2.49 \cdot 10^{21} \text{ cm}^{-3}$, compared to $2.30 \cdot 10^{21} \text{ cm}^{-3}$ for the first conversion calculations and $1.98 \cdot 10^{21} \text{ cm}^{-3}$ for the current fuel element. It is yet unknown



Figure 7.2:

Expected loss of thermal neutron flux for the initial conversion calculations to disperse UMo compared to the current situation. The loss in the thermal flux maximum is about 7.7%, located at r = 21 cm, z = -10 cm. The black part are the fuel plates, left of them is the control rod, right of them the D₂O tank. The multicoloured part in the top left is in the hafnium absorber of the control rod and is statistical noise.

if the new fuel will be able to withstand such a high fission density. Burn-up calculations using X^2 showed that the radioactive waste will increase significantly, including the sevenfold amount of Pu, again conforming former results.

Other possible scenarios besides the further compaction include an increased reactor power or a longer cycle length. However, especially the first option poses very high burdens and is unlikely to be feasible. A longer cycle length will not increase the actual neutron flux but the cycle integrated fluence. This leaves much more room for a thermal hydraulic optimisation but increases the demands regarding burn-up even further. In the scenarios calculated so far, a "safety margin" of about 3-5 days of operation is left to allow for further installations in the D_2O tank.

Summary

The HEU-MEU group is continuing its efforts to develop a solution for a new, lower enriched core for FRM II, keeping the impact on the users of the reactor as small as possible. Besides the development and qualification of two different fuel candidates, the required calculations and optimisations towards a flux loss as small as possible are performed. The design can benefit especially from the improved thermal hydraulic calculations using up-to-date CFD codes, providing more accurate safety margins.

[1] H. Breitkreutz et al., PHYSOR 2010

- [2] H. Breitkreutz, PhD Thesis, 2010
- [3] A. Röhrmoser et al., RERTR 2005
- [4] H. Breitkreutz et al., RRFM 2010
- [5] J. Sarvas, Diploma thesis, 2011
- [6] A. Röhrmoser, RERTR 2010

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

R. M. Hengstler-Eger¹

¹ AREVA NP GmbH, Erlangen, Germany

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. Since in-pile experiments in PWR environments require time frames of several years, 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 activated by ion irradiation, and the ion doses corresponding to fuel assembly end-of-life neutron doses are short which provides a very cost effective method for the study of irradiation-induced 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.

In 2010, recrystallized Zr1Nb, a PWR guide tube alloy, was irradiated with 2.5 MeV Zr-90 at the material's in-pile operating temperature of 300°C at tandem accelerators of the Max-Planck-Institute for plasma physics and Forschungszentrum Dresden-Rossendorf. The induced defects were studied by positron Doppler spectroscopy ("DBS") and positron lifetime measurements at FRM II' NEPOMUC facility. DBS showed that the vacancy-like defect structures are of a significantly lower density in material irradiated at 300°C than at room temperature. Also, positron energy scans imaged the depth-dependence of the defect structure that is caused by the inhomogeneous ion damage profile. As the hydrogen content of the alloy is a possible parameter influencing the irradiation defect structure, samples with and without hydrogen were measured at DBS. The results show a significantly lower vacancy-like defect density in the samples loaded with 209 ppm H₂ that in the as-fabricated samples. With a new heating stage at the CDBS facility, in-situ-DBS was conducted during the heating of irradiated samples from 300°C to 600°C. The vacancy-type defect density reached the level of an unirradiated standard sample at a temperature of 450°C, showing a complete annealing of the defects within the measurement accuracy.

An irradiated sample loaded with hydrogen has been studied with positron lifetime spectroscopy; while the final data evaluation is still in process, positron lifetimes corresponding to dislocations of two different sizes have been measured.

To observe the development of the irradiation induced defects with the dose, experiments were conducted at the Argonne National Laboratory's IVEM-Tandem facility. The facility uses a transmission electron microscope coupled to a tandem accelerator to observe the irradiation structure in-situ; images and electron diffraction patterns can be taken at intermediate doses of interest. Also, movies observing a certain sample region during the ongoing ion irradiation can be shot. Both methods have been used to observe the formation of a- and c-component dislocation loops during irradiation in Zr1Nb samples held at 300°C. The loops' size and density distributions are in the same order of magnitude as known from in-pile neutron-irradiated Zr1Nb material. It can be concluded that ion irradiation under the used experimental conditions is a good experimental method for the simulation of in-pile neutron damage. Samples with and without hydrogen have been studied; the sample loaded with 209ppm H₂ showed a significantly lower density of c-type dislocations than the as-fabricated material, confirming the results obtained by the DBS measurements.

Further beamtimes at the IVEM tandem facility and at NEPOMUC are planned in 2011 for more detailed studies of the observed correlation between the irradiation induced defect structures and the material's hydrogen content.



Figure 7.3: c-component dislocation loops after 13 dpa Zr-90 dose

[1] G. S. Was, Fundamentals of Radiation Materials Science (2007)

7.3 Sample cell for Brillouin scattering

J. Wiedersich

In the past, the use of the Sandercock tandem Fabry-Perot interferometer at LS Funktionelle Materialien has been focused on broad band depolarized light scattering on liquids and glasses. With the imminent extension to Brillouin scattering on polymers, hydro gels and ultra-thin polymer films, the existing cryostats have turned out to be inadequate, because they only allow for small samples – thus far only cuvettes with circular cross-section have been used – and the sample compartments are too small to be used with the flat precision cuvettes required for accurate Brillouin scattering experiments.

A sample cell suited for experiments of Brillouin scattering in the so-called platelet geometry is developed.



Figure 7.4:

Platelet geometry for Brillouin scattering. The scattered light is deflected by the angle α with respect to the incoming beam. In this special geometry the frequency of the Brillouin lines *does not* depend on the refractive refractive index of sample or cuvette. The scattering vector \vec{q} is along the direction of the cuvette. If the thickness of the sample is large enough, the light scattered from sample and cuvette, respectively, can be separated by a spacial filter (not shown).

scattered light

A conventional back scattering geometry is often conveniently used for Brillouin scattering because of its simple alignment and advantages for the recording of weak signals. The back scattering geometry benefits from the fact that essentially only one beam has to be aligned, because the scattered light takes almost the reverse path of the incident laser beam, and thus only small or even no adjustments are necessary as the sample is (re)-placed. In this geometry, however, the frequency of the Brillouin line depends both on the sound velocity v_s and the refractive index nof the sample. Especially in the presence of phase transitions this hampers proper interpretation of the measured data and its analysis. In order to unambiguously determine the sound velocity, which is directly related to the elastic modulus, the so-called platelet geometry is usually chosen. In this special 'transmission' geometry (depicted in figure 7.4) the frequency of the Brillouin line ν_B does not depend on n, but is directly given by $\nu_B = \frac{2\pi}{\lambda}v_s$.

This advantage, though, requires better optical properties of the sample and more efforts with alignment. In the platelet geometry the foci of both incident and collecting lens have to be carefully aligned to superimpose at the sample position.

Unfortunately, such measurements have not been possible at other temperatures than room temperature with the existing cryostats and sample cells.

With the help of both LS Funktionelle Materialien's as well as the physics departments' workshops a sample cell was designed and built that should ideally fit the requirements for our Brillouin scattering experiments (figure 7.5). The entrance and exit windows have a clear diameter of close to 50 mm and extend about 62 mm from the centre of the sample cell. Therefore the







Sample cell for Brillouin scattering. The left figure shows a horizontal cut through the sample cell. The space between the inner cell (green) and the outer cell (blue) holds the insulation vacuum. A sample is shown in 90° platelet geometry. The right picture shows the assembled sample cell on the optical table.

cell perfectly matches the f = 80 mm lenses for focusing the laser and collecting the scattered light. At the same time the aperture matches that of the best lenses available and allows for large ranges of different scattering angles.

The main challenge for the mechanical construction was in the tight spatial requirements for the windows and the small available distance between inner and outer cells. The sample compartment is designed for sample sizes up to 50 mm in diameter and 80 mm in height (this compares to a diameter of about 10 mm and height of some 30 mm used with the existing sample environments).

The accessible temperature range of -20 °C < θ < 80 °C is achieved with a refrigerated heating circulator via copper tubes. The cell is carefully designed to maintain a very low temperature gradient over the large size of the sample compartment. This is achieved by the delicate placement of the heating/cooling tubes and by placing the inner cell within an insulating vacuum. It will be possible to extend the temperature range up to some 200 °C by acquiring a thermostat with an extended temperature range.

Apart from the insulation vacuum, a second vacuum and gas handling system is attached to the inner sample chamber. This allows to place the sample in vacuum or to establish a desired pressure level of protective gas, depending on the requirements of the investigated samples. Finally, a new type of sample cuvettes has been developed which is optimized for the new sample environment. Samples of supreme optical quality are obtained by vacuum sealing liquid or even highly viscous samples between a pair of plane parallel high quality optical windows.

7.4 Combination of μ GISAXS and imaging ellipsometry at the synchrotron source PETRA III

V. Körstgens, M. Rawolle, A. Buffet¹, R. Döhrmann¹, K. Stassig¹, S.V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

The possibilities of the surface sensitive scattering method grazing incidence small angle x-ray scattering (GISAXS) were expanded by the integration of imaging ellipsometry recently [1]. In autumn 2010 we were able to install the combined instrument at the micro- and nanofocus x-ray scattering beamline (MiNaXS/P03) at the third generation synchrotron source PETRA III at DESY in Hamburg.



Figure 7.6:

Ellipsometer installation at beamline MiNaXS **a**: imaging ellipsometer mounted on positioning system **b**: sample environment with 1: entrance window of flight tube towards detector, 2: beamstops for direct beam, 3: laser arm of ellipsometer, 4: sample stage of ellipsometer, 5: AFM, 6: guard slits; the arrows show the direction of the x-ray beam from the source

The imaging ellipsometer SPEM, a single wavelength (532 nm) instrument, of Nanofilm Technologie GmbH, is installed at the beamline MiNaXS as shown in figure 7.6. 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 set-up. The whole stack of positioning stages including 2-circle segment is mounted on a base which can be moved in the experimental hutch by air pads is depicted in figure 7.6a.

A singular calibration of the instrument is necessary to ensure that the laser beam and the xray beam cross each other at one known point on the sample surface. In figure 7.7 an in-situ measurement of a thin films of polymer material especially sensitive to x-ray radiation damage, as used for calibration, is shown. The field of view of the imaging ellipsometer depends on the angle of incidence of the laser beam and the objective chosen. For an angle of 55° and an objective with 20x magnification a field of view of 201 μ m x 263 μ m develops. With three different assigned regions of interest (ROIs)(figure 7.7a) the course of Δ and Ψ averaged over every pixel of the according ROI can be followed as the x-ray beam illuminates the surface. Due to the sensitive sample an instantaneous change in Δ and Ψ for the central ROI with switching on the x-ray beam is shown in figure 7.7c with open circles. If x-ray illumination is stopped Δ and Ψ immediately show constant values. The width of the foot print visible live in the field of view during x-ray illumination, shown in figure 7.7b, corresponds to the beamsize of 35 μ m x 22 μ m used in this experiment. An alternative to the acquisition of Δ and Ψ in chosen ROIs is the recording of 2d images in the full field of view (Δ and Ψ -maps) [1].



Figure 7.7:

Measurement of calibration sample **a** field of view of imaging ellipsometer with three chosen regions of interests (ROIs, green line) **b** visible foot print of x-ray beam due to x-ray illumination **c** course of ellipsometric values Δ and Ψ in different ROIs during illumination with x-ray beam; open symbols: central ROI

The combination of μ GISAXS and imaging ellipsometry is particularly suited for the investigation of kinetic processes. As an example given in figure 7.8 the drying of a droplet of gold nanorods in aqueous dispersion along a gradient of polydimethylsiloxane (PDMS) on silicon substrate is followed. Δ and Ψ are recorded in three different ROIs (figure 7.8a) analogue to the measurement of the calibration sample described above. The corresponding 2d GISAXS scattering patterns counted for 2 s are shown in figure 7.8b (time since start of data acquisition is indicated). After 6 s the scattering pattern corresponds to the sample surface before droplet deposition. With droplet deposition there is an immediate change in Δ and Ψ (7.8a). The corresponding scattering intensity (figure 7.8b: 100 s) is very low in comparison to the substrate before droplet deposition. Only weak intensity is displayed on the detector because the large droplet volume absorbs strongly the transmitting x-ray beam.



Figure 7.8:

In situ experiment of a drying droplet of gold nanorod dispersion **a** course of ellipsometric values Δ and Ψ in different ROIs **b** detail of 2D GISAXS pattern with time; 1: specular beamstop; 2: frame bordering modules of Pilatus detector

The arrangement of nanorods on the surface is evident not before 810 s, when the scattering pattern with much higher intensity evolves (figure 7.8b: 810 s). Notably, for the duration of the drying experiment the Δ and Ψ values shown in figure 7.8a at any given time are similar for all three chosen ROIs. In case of severe damage of the sample due to the high brillance x-ray beam Δ and Ψ values would differ over time for the ROIs in- and outside the footprint of the x-ray beam as shown in figure 7.7c.

This work has been financially supported by the BMBF (grant number 05KS7WO1).

 V. Körstgens, J. Wiedersich, R. Meier, J. Perlich, S.V. Roth, R. Gehrke, P. Müller-Buschbaum, Anal. Bioanal. Chem. 396, 139-149 (2010)

8 Teaching and conferences

8.1 Lectures, seminars and lab courses

Spring semester 2010

Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik 2 für Maschinenwesen

Prof. Dr. Christine M. Papadakis, Angewandte Physik: Polymerphysik 2

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

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

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar: Polymere

Prof. Dr. Winfried Petry, Prof. Dr. Peter Böni, Prof. Dr. Klaus Schreckenbach, Seminar über Neutronen in Forschung und Industrie

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar über Struktur und Dynamik kondensierter Materie

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar über spezielle Probleme der weichen Materie

Fall semester 2010/2011

Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik 1 für Maschinenwesen

Prof. Dr. Christine M. Papadakis, Experimentalphysik 1 für Ingenieurwissenschaften

Prof. Dr. Christine M. Papadakis, Angewandte Physik: Polymerphysik 1

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

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar: Polymere

Prof. Dr. Winfried Petry, Prof. Dr. Peter Böni, Prof. Dr. Klaus Schreckenbach, Dr. Wolfgang Häußler, *Seminar über Neutronen in Forschung und Industrie*

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar über Struktur und Dynamik kondensierter Materie

Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine M. Papadakis, Seminar über spezielle Probleme der weichen Materie

Lab courses 2010

Theoretische und praktische Einführung in AFM (Fortgeschrittenenpraktikum) *Thermische Analyse* (Fortgeschrittenenpraktikum) *Neutronenstreuung am FRM II* (Fortgeschrittenenpraktikum) *JCNS Laboratory Course - Neutron Scattering* (Forschungspraktikum)

8.2 Conferences



RLFB-Tagungsprogramm

34. Edgar-Lüscher-Seminar am Gymnasium Zwiesel

Thema: Astro- und Teilchenphysik

&

Gründung des TUM Schulclusters Bayerischer Wald

Freitag, 19. März bis Sonntag, 21. März 2010

Veranstalter: Der Ministerialbeauftragte für die Gymnasien in Niederbayern, Ltd. OStD Klaus Drauschke

Wissenschaftliche Leitung: Prof. Dr. Walter Schirmacher, TU München, Prof. Dr. Stephan Paul, TU München, Prof. Dr. W. Petry, TU München, Prof. Dr Peter Müller-Buschbaum, TU München mit Unterstützung des TUM-Excellence Clusters "Origin and Structure of the Universe"

Org. am Gymnasium Zwiesel: OStD Hans-Werner Janda, OStR Claus Starke, OStR Wolfgang Achatz

TUM-Schulcluster: Prof. Dr. Wilfried Huber, TU München

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

Freitag, 19. März 2010 10.00 - 11.30 Schüler forschen an der TU München: Dr. Andreas Kratzer, TU München Naturwissenschaften zum Anfassen 11.30 - 13.00 Andrea Kick, Carolin Kölbl, Dr. Christian Studienberatung für Kollegstufe, Teilnahme der Schüler der 5 Clus-Kredler, Prof. W. Petry, TU München tergymnasien 14.30 - 15.30 Begrüßung und Festakt zur Gründung MB Drauschke, Prof. Wilfried Huber, OStD des TUM-Schulclusters Bayerischer Janda, Bürgermeister Zwiesel, Landrat Wölfl, Wald Rektoren der Clusterschulen (Zwiesel, Grafenau, Freyung, Viechtach, Kötzing) 15.30 - 16.30 Perspektiven der Lehrerbildung und Prof. Dr. Manfred Prenzel, -Fortbildung (Arbeitstitel) Gründungsdekan TUM School of Education 16:30 - 16:45 Diskussion 16.45 - 17.15 Kaffeepause 17.15 – 18.30 Die Entwicklung des Universums Prof. Dr. Stephan Paul, TU München 18.30 - 19.30 Prof. Dr. Stephan Paul, TU München Diskussion des Dozenten mit den Schülern über Entwicklung des Universums 20.00 - 22.00 Empfang der Stadt Zwiesel Bürgermeister Zwiesel
RLFB-Tagungsprogramm

Samstag, 20. Mä	Samstag, 20. März 2010		
9.00 - 10.15	Dem Rätsel der Geisterteilchen auf der	Prof. Dr. Tobias Lachenmaier, TU München	
	Spur – Experimente mit Neutrinos		
10.15 – 11.00	Diskussion und Kaffeepause		
11.00 – 12.15	Die dunkle Seite des Universums	Prof. Dr. Stefan Hofmann, LMU München	
12.15 – 12.30	Diskussion		
14.30 – 15.45	LHC: Erster Bericht über das größte	Prof. Otmar Biebel, LMU München	
	Physikexperiment der Menschheit		
15.45 – 16.30	Diskussion und Kaffeepause		
16.30 – 17.45	Schwarze Löcher am LHC?	Dr . Frank Simon, MPI für Physik München	
17.45 – 18.00	Diskussion		
18.00 – 19.15	Sternentstehung	Prof. Dr. Andreas Burkert,	
	-	MPI für extraterrestrische Physik	
		und LMU München	
19.15 – 19:30	Diskussion		

Sonntag, 21. März 2010

9.00 - 10.15	Strings und die frühe Phase des Uni-	PrivDoz. Dr. Johanna Erdmenger
	versum	Max Planck Institut für Physik München
10.15 – 11.00	Diskussion und Kaffeepause	
11.00 – 12.15	Warum die Antimaterie im Weltall	Prof. Dr. Konrad Kleinknecht
	verschwunden ist.	Universität Mainz & LMU München
12.15 - 13.00	Diskussion: Neues Thema	

Focus Session on "Structure and Dynamics of Responsive Hydrogels" In the framework of the spring meeting of the division Condensed Matter of the Deutsche Physikalische Gesellschaft (DPG) Regensburg, 22 March 2010

Interactive hydrogels:

Walter Richtering - Physical Chemistry, RWTH Aachen University, Aachen, Germany

Structure of thermoresponsive polymer hydrogels:

Christine M. Papadakis¹, Joseph Adelsberger¹, Amit Kulkarni¹, Abhinav Jain¹, Andreas Meier-Koll¹, Weinan Wang¹, Achille M. Bivigou-Koumba, André Laschewsky², Peter Müller-Buschbaum¹ – ¹TU München, Physikdepartment, E13, Garching; ²Universität Potsdam, Institut für Chemie

Salty Microgels - Smart Microgels in Presence of the Hofmeister Series:

Michael Zeiser^{1,2}, Yvonne Hertle^{1,2}, Peter Busch³, and Thomas Hellweg^{1,2} –¹ University of Bayreuth, 95440 Bayreuth, Germany; ² Bayreuth Center for Colloids and Interfaces, 95440 Bayreuth, Germany; ³ Jülich Center for Neutron Science, Forschungs-Neutronenquelle Heinz Maier-Leibnitz, 85747 Garching, Germany

On the finite-extensibility effect of a single polymer chain:

Bing Miao¹, Thomas A. Vilgis¹, Stefanie Poggendorf², Gabriele Sadowski² — ¹Max-Planck-Institute for Polymer Research, Mainz, Germany; ²Laboratory of Thermodynamics, Department of Biochemical and Chemical Engineering, Technische Universität Dortmund, Dortmund, Germany

New pNIPAM microgels for immobilization of proteins:

Kornelia Gawlitza, Marcel Richter, Regine von Klitzing – TU Berlin, Stranski-Laboratorium, Strasse des 17. Juni 124, 10623 Berlin, Deutschland

Temperature sensitivity of colloidal gels measured by multispeckle DLS:

Martin Medebach, Michael Gradzielski, Regine v. Klitzing – Stranski Laboratory, Technische Universität Berlin, Strasse des 17.Juni 124, 10623 Berlin

Smart Biocompatible Hydrogels constructed with oligo(ethylene glycol) (macro)monomers:

Jean-Francois Lutz - 1Fraunhofer Institute for Applied Polymer Research, Potsdam, André Laschewsky - University of Potsdam

Dynamics of thermosensitive microgel particles:

Matthias Ballauff - Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin

Current mechanistic and experimental views on the heat-induced phase transition of aqueous poly(Nisopropylacrylamide) solutions:

Francoise Winnik — Faculty of Pharmacy and Department of Chemistry, University of Montreal, Montreal, QC Canada

Molecular simulation study of the volume transition of hydrogels:

Jonathan Walter¹, Viktor Ermatchkov¹, Jadran Vrabec², Hans Hasse¹ — ¹Laboratory of Engineering Thermodynamics, University of Kaiserslautern, 67663 Kaiserslautern, Germany; ²Thermodynamics and Energy Technology, University of Paderborn, 33098 Paderborn, Germany

Thermodynamics of aqueous solutions containing N-isopropyl acrylamide hydrogels:

Viktor Ermatchkov, Luciana Ninni Schäfer, and Gerd Maurer – Laboratory of Engineering Thermodynamics (LTD), Department of Mechanical and Process Engineering, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

Free volume and swelling in thin films of poly(N-isopropylacrylamide) end-capped with nbutyltrithiocarbonate:

Stephan Harms¹, Klaus Rätzke¹, Franz Faupel¹, Werner Egger², Luca Ravelli², André Laschewsky³, Weinan Wang⁴, and Peter Müller-Buschbaum⁴ – ¹CAU Kiel, Institut für Materialwissenschaft –

Materialverbunde; ²Universität der Bundeswehr München; ³Potsdam Universität, Inst. Chemie; ⁴TU München, Physik-Department LS E13

Crosslinking and Patterning of Sensitive Polymers with Electron Beam Lithography: Sensoric Application:

Claudia Kaiser¹, Ingolf Moench², and Karl-Friedrich Arndt¹ – ¹ Physical Chemistry of Polymers, Department of Chemistry, TU Dresden, 01062 Dresden, Germany; ² Leibniz-Institute for Solid State and Materials Research Dresden, Germany

Structure and response of pNIPAM microgels loaded with gold particles under thermal and optical stimuli:

Adrian Carl, Regine von Klitzing – Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin

Swelling, structure and hybrid microgel particles:

Antonio Fernandez-Barbero — Department of Applied Physics, University of Almería, 04120-Almería, Spain



E13 Summer School 2010

16. – 19. June 2010 - Rudolfshütte, Austria

Wednesday, 16.06.2010

- 9.00 12.00 Uhr Arrival from Garching
- 12:00 14:00 Uhr Lunch
- 14:00 17:00 Uhr Light scattering Dr. Johannes Wiedersich
 - Introduction to polymers Semih Ener
 - Polymer blends Robert Meier
 - Block copolymers Alessandro Sepe
- 17:00 20:00 Uhr Dinner
- 20:00 21:00 Uhr FCS- and DLS-measurements of poly(2-oxaoline)s Carola Alonso de Celada Casero
 - Block copolymer electrolytes for solid-state battery Man Nie
 - Surface energy determination of pressure sensitive adhesive films Katherina Ecker
 - Lattice dynamics of ferromagnetic shape memory alloy: $Nio_{49}Mn_{32}Ga_{19}$ Shravani Chillal

Thursday, 17.06.2010

9.00 – 12:00 Uhr - Imaging Ellipsometry + AFM – Dr. Volker Körstgens - Homopolymer thin films – Tilo Hoppe

- Polymer brushes Joseph Adelsberger
 Crystalline polymers David Magerl
- 12.00 14.00 Uhr Lunch
- 14.00 17.00 Uhr Excursion
- 17.00 20.00 Uhr Dinner
- 20.00 21.00 Uhr Die Forschungsneutronenquelle Heinz Maier-Leibnitz -Prof. Dr. Winfried Petry

Friday, 18.06.2010

- 9.00 12.00 Uhr Optical spectroscopy Dr. Gabriele De Paoli
 - Conducting polymers Monika Rawolle
 - Polymer based photovoltaics Matthias Ruderer
 - Dye-sensitized solar cells Martin Niedermeier
- 12.00 14.00 Uhr Lunch
- 14.00 17.00 Uhr STXM-studies on residual solvent in conjugated polymer blend films – Markus Schindler Discussion
- 17.00 20.00 Uhr Dinner
- 20.00 21.00 Uhr Tuning conductivity of thin conjugated polymer films and beyond Andreas Nathan
 - Structural characterization of polymers for application in organic photovoltaics – Shuai Guo
 - Structuring of the Top-Electrode of Organic Photovoltaics for Enhanced Device Performance - Hsin-Yin Chiang
 - Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT polymer – Kuhu Sarkar

Saturday, 19.06.2010

- 9.00 12.00 Uhr Surface scattering Dr. Ezzeldin Metwalli Ali
 - Micelles from Amphiphilic Block Copolymers Sebastian Jaksch
 - Temperature responsive polymers Qi Zhong
 - Polymer mechanics Alexander Diethert
- 12.00 14.00 Uhr Lunch
- 14.00 Uhr Departure to Garching

TU München /Lehrerfortbildungsakademie Dillingen

Edgar-Lüscher-Fortbildungskurs für Physiklehrer

Thema: Energie und Umwelt

11. bis 15. Oktober 2010

Wissenschaftliche Leitung: Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Walter Schirmacher, TU München

Organisatorische Leitung: Werner Ettinger, Akademie Dillingen

Montag, 11. Oktober		
15.00 - 15.45	Lehrgangseröffnung	Prof. Peter Müller-Buschbaum, TU München,
		Werner Ettinger, Akademie Dillingen
15.45 – 17.00	Konventionelle Photovoltaik	Prof. Martin Stutzmann, TU München
17.00 - 17.15	Diskussion	
18.30 – 19.45	Konventionelle Photovoltaik	Prof. Martin Stutzmann, TU München
19.45 - 20.00	Diskussion	

Dienstag, 12. Oktober

U ,		
08.30 - 09.45	Organische Photovoltaik	Dr. Andreas Opitz, Univ. Augsburg
09.45 - 10.00	Diskussion	
10.15 – 11.30	Organische Leuchtdioden für zukünftige energieeffiziente Beleuchtung	Prof. Wolfgang Brütting, Univ. Augsburg
11.30 – 11.45	Diskussion	
15.30 – 16:45	Regionale Klimasimulationen	Dr. Klaus Keuler, BTU Cottbus
16:45 - 17.00	Diskussion	
18.30 – 19.45	Risiken durch Katastrophen	DiplGeogr. Ernst Rauch, Münchner Rück
19.45 – 20.00	Diskussion	

Mittwoch, 13. Oktober

,		
08.30 - 09.45	Elektromobilität – Schlüsseltechnologien	Stefan Grubwinkler, TU München
	und Herausforderungen	
09.45 - 10.00	Diskussion	
10.15 – 11.30	MUTE – ein Elektrofahrzeugkonzept	Stefan Grubwinkler, TU München
11.30 – 11.45	Diskussion	
15.30 – 16:45	Das Shell-Eco-Marathon-Fahrzeug der Hochschule München	Prof. Jochen Melzer, Hochschule München
16:45 – 17.00	Diskussion	
18.30 - 19.45	Energiesparhäuser	W. Schölkopf, ZAE Bayern, Garching
19.45 - 20.00	Diskussion	
Donnerstag, 14. O	ktober	
08.30 - 09.45	Klimawandel und Klimasimulationen	Dr. Ingo Kirchner, FU Berlin
09.45 - 10.00	Diskussion	
10.15 – 11.30	Klimawandel und Klimasimulationen	Dr. Ingo Kirchner, FU Berlin
11.30 – 11.45	Diskussion	
15.30 – 16:45	Gruppenarbeit: Energie und Umwelt im Unterricht	Werner Ettinger, Akademie Dillingen
16:45 - 17.00	Diskussion	
18.30 - 19.45	Energiekonzepte der Zukunft	Prof. Dr. Hardo Bruhns, ArbKr. Energie der DPG
19.45 - 20.00	Diskussion	

Freitag, 15. Oktober		
08.30 - 09.45	Brennstoffzellentechnologien	Prof. Katharina Krischer, TU München
09.45 - 10.00	Diskussion	
10.15 – 11.30	Energieversorgung in Zeiten des Klima- wandels	Prof. Dr. Konrad Kleinknecht, Universität Mainz und Excellence Cluster Universe, LMU München
11.30 – 11:45	Diskussion	

2nd TUM-HASYLAB Colloquium "The metal-polymer interface"

Tuesday 02 November 2010 at **10:00** to Wednesday 03 November 2010 at **17:00** (Europe/Berlin) at DESY, Notkestraße 85, 22607 Hamburg, bldg. 48e, seminar room L202 (Bldg. 48e, seminar room L202)

Description:

The 2nd TUM-HASYLAB Colloquium "The metal-polymer interface" follows the very successful meeting at the TUM in 2007 and will give an overview over the research in the field of metal-polymer nanocomposites and their applications. Today, metal-polymer nanocomposites are used in a wide variety of applications, ranging from optical, photovoltaic to magnetic devices. In this colloquium the different applications and strategies for tailoring, such as sputter deposition and microfluidics will be discussed profoundly.

This colloquium will feature invited keynote and invited talks as well as poster contributions. We are happy to announce our keynote speakers:

F. Faupel (CAU Kiel, Germany)M. Trebbin (U Bayreuth, Germany)M. Schlüter (TU Hamburg-Harburg, Germany)W. Wurth (U Hamburg, Germany)

With kind regards The organisation committee R. Gehrke, R. Röhlsberger, S.V. Roth (DESY, Hamburg) P. Müller-Buschbaum (TU München, Germany)

Tuesday 02 November 2010

10:00 - 11:00	Registration
11:00 - 11:15	Welcome 15'
	Speakers: Hermann Franz (DESY)
11:15 - 12:00	Keynote: Metal-polymer nanocomposites for functional
	applications 45'
	Speakers: Franz Faupel (University of Kiel)
12:00 - 12:15	On the microscopic origins of friction 15'
	Speakers: Ralf Röhlsberger (DESY)
12:15 - 12:30	Modelling GISAXS data using IsGISAXS 15'
	Speakers: Peter Müller-Buschbaum (Technical University of
	Munich)
12:30 - 12:45	Polymer hybrid structures 15'
	Speakers: Martin Niedermeier (Technical University of Munich)
12:45 - 13:00	Large scale magnetic nanopatterning with polymer templates 15' Speakers: Kai Schlage (DESY)
13:00 - 14:15	Lunch and Poster Session

14:15 - 15:00	Keynote: Opportunities to study ultrafast dynamics with LASH 45' Speakers: Wilfried Wurth (University of Hamburg)
15:00 - 15:15	Morphologies of bulk heterojunctions for polymer based photovoltaics 15'
	Speakers: Matthias Ruderer (Technical University of Munich)
15:15 - 15:30	Polymer Thin Films Investigated with GISAXS 15'
	Speakers: Robert Meier (Technical University of Munich)
15:30 - 15:45	Spray coated PS spheres as templates 15'
	Speakers: Adeline Buffet (DESY)
15:45 - 17:00	Coffee Break and Poster Session
17:00 - 17:15	Sputter deposition and colloidal surfaces: recent developments 15'
	Speakers: Stephan V. Both (DESY)
17:15 - 17:30	Sputter deposition on polymeric colloidal crystals 15'
	Speakers: Matthias Schwartzkopf (DESY)
17:30 - 17:45	Real time GISAXS investigation of metal nanoparticle aggregation on polymer template 15'
	Speakers: Ezzeldin Metwalli (Technical University of Munich)
17:45 - 18:00	Metal-Blockcopolymer nanocomposites 15' Speakers: Mottakin Abul-Kashem (DESY)
19:00 - 21:00	Dinner (DESY Bistro (Bldg. 9a))

Wednesday 03 November 2010

09:00 - 09:45	Keynote: Microscale flow and concentration measurements - limitations and perspectives 45'
	Speakers: Michael Schlüter (Technical University of Hamburg- Harburg)
09:45 - 10:00	Biological nanocomposites 15'
	Speakers: Jan Perlich (DESY)
10:00 - 10:15	Polymer hydrogel films 15'
	Speakers: David Magerl (Technical University of Munich)
10:15 - 10:30	Microfluidics and μ GISAXS 15'
	Speakers: Volker Körstgens (Technical University of Munich)
10:30 - 10:45	3D-colloidal structures - pole figures 15'
	Speakers: Rainer Gehrke (DESY)
10:45 - 11:30	Coffee Break
11:30 - 12:15	Keynote: A microfluidic sample environment >at a microfocus beamline - basics and perspectives 45'
	Speakers: Martin Trebbin (University of Bavreuth)
12:15 - 12:30	Combination of micro-fluidics and sol-gel chemistry 15'
	Speakers: Monika Rawolle (Technical University of Munich)
12:30 - 12:45	Metal/polymer colloidal nanocomposites using microfluidics 15' Speakers: Gerd Herzog (DESY)
12:45 - 14:30	Lunch
14:30 - 16:30	Site Visit 2h00'(PETRA III Experimental Hall (Bldg. 47c))
10:00 - 10:15 10:15 - 10:30 10:30 - 10:45 10:45 - 11:30 11:30 - 12:15 12:15 - 12:30 12:30 - 12:45 12:45 - 14:30 14:30 - 16:30	Speakers: David Magerl (Technical University of Munich) Microfluidics and µGISAXS 15' Speakers: Volker Körstgens (Technical University of Munich) 3D-colloidal structures - pole figures 15' Speakers: Rainer Gehrke (DESY) Coffee Break Keynote: A microfluidic sample environment >at a microfocus beamline - basics and perspectives 45' Speakers: Martin Trebbin (University of Bayreuth) Combination of micro-fluidics and sol-gel chemistry 15' Speakers: Monika Rawolle (Technical University of Munich) Metal/polymer colloidal nanocomposites using microfluidics 15' Speakers: Gerd Herzog (DESY) Lunch Site Visit 2h00'(PETRA III Experimental Hall (Bldg. 47c))

9 Publications, talks and funding

9.1 Publications

• J. Adelsberger, A. Kulkarni, A. Jain, W. Wang, A.M. Bivigou Koumba, P. Busch, V. Pipich, O. Holderer, T. Hellweg, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis Thermoresponsive PS-b-PNIPAM-PS micelles: Aggregation behavior, segmental dynamics, and thermal response

Macromolecules 43, 2490-2501 (2010)

- A.M. Bivigou-Koumba, E. Görnitz, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis Thermoresponsive amphiphilic symmetrical triblock copolymers with a hydrophilic middle block made of poly(N-isopropylacrylamide): synthesis, self-organization, and hydrogel formation Colloid. Polym. Sci. 288, 499-517 (2010)
- H.-G. Brokmeier, C. Randau, W. Tekouo, M. Hofmann, W. Gan, M. Müller, A. Schreyer, W. Petry The robot concept at STRESS-SPEC for the characterisation of semi-finished products Mater. Sci Forum 652, 197-201, (2010)
- S. Busch, C. Smuda, L.C. Pardo, T. Unruh Molecular Mechanism of long-rnge diffusion in phospholipid membranes studied by quasielastic neutron scattering J. Am. Chem. Soc., 132, 3232-3233, (2010)
- Z. Di, D. Posselt, D.-M. Smilgies, C.M. Papadakis Structural rearrangements in a lamellar diblock copolymer thin film during treatment with saturated solvent vapor Macromolecules 43, 418 (2010)
- A. Diethert, Y. Peykova, N. Willenbacher, P. Müller-Buschbaum Near-surface composition profiles and the adhesive properties of statistical copolymer films being model systems of pressure sensitive adhesive films ACS Appl. Mater. Interfaces 2, 2060-2068 (2010)
- W. Doster, S. Busch, A.M. Gaspar, M.-S. Appavou, J. Wuttke, H. Scheer Dynamical transition of protein-hydration water Phys. Rev. Lett., 104, 098101, (2010)
- W. Doster, T. Gutberlet *The protein-water energy seascape preface* Biochimica et Biophysica Acta-Proteins and Proteomics, 1804, 1-2, (2010)
- W. Doster The protein-solvent glass transition Biochimica et Biophysica Acta, 1804, 3-14, (2010)
- C. Ganter, W. Schirmacher Rayleigh scattering, long-time tails and the harmonic spectrum of topologically disordered systems Phys. Rev. B, 82, 094205 (2010)
- A.M. Gaspar, S. Busch, M.-S. Appavou, W. Haeussler, R. Georgii, Y. Su, W. Doster Using polarization analysis to separate the coherent and incoherent scattering from protein samples

Biochimica et Biophysica Acta, 1804, 76-82, (2010)

- R. Gebhardt, S.V. Roth, M. Burghammer, C. Riekel, A. Tolkach, U. Kulozik, P. Müller-Buschbaum Structural changes of casein micelles in a rennien gradient film with simultaneous consideration of the film morphology Int. Dairy J. 20, 203-210 (2010)
- R. Gebhardt, M. Burghammer, C. Riekel, U. Kulozik, P. Müller-Buschbaum Investigation of surface modification of casein films by rennin enzyme action using micro-beam grazing incidence small angle x-ray scattering Dairy Sci. Technol. **90**, 75-86 (2010)
- S. Guldin, S. Hüttner, M. Kolle, M.E. Welland, P. Müller-Buschbaum, R.H. Friend, U. Steiner, N. Tetreault Dye-sensitised solar cells based on a three-dimensional photonic crystal Nano Lett. 10, 2303-2309 (2010)
- S. Harms, K. Rätzke, F. Faupel, W. Egger, L. Ravello, A. Laschewsky, W. Wang, P. Müller-Buschbaum
 Free volume and swelling in thin films of poly(N-isopropylacrylamide) end-capped with n-butyltrithiocarbonate
 Macromol. Rapid Commun. 31, 1364-1367 (2010)
- R.M. Hengstler, L. Beck, H. Breitkreutz, C. Jarousse, R. Jungwirth, W. Petry, W. Schmid, J. Schneider, N. Wieschalla
 Physical properties of monolithic U8 wt.%-Mo J. Nucl. Mat., 402, 74-80 (2010)
- A. Jain, A. Kulkarni, A.M. Bivigou Koumba, W. Wang, P. Busch, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis Micellar solutions from symmetrical amphiphilic triblock copolymers having a temperatureresponsive shell
 Macromol. Symp. 291-292, 221-229 (2010)
- G. Kaune, P. Müller-Buschbaum *Gradient-doping of a conductive polymer film with a layer-by-layer approach* phys. stat. sol. (RRL) **4**, 52-54 (2010)
- G. Kaune, M. Haese-Seiler, R. Kampmann, J.-F. Moulin, Q. Zhong, P. Müller-Buschbaum TOF-GISANS investigation of polymer infiltration in mesoporous TiO₂ films for photovoltaic applications
 J. Poly. Sci. Part B. 48, 1628-1635 (2010)
- V. Körstgens, J. Wiedersich, R. Meier, J. Perlich, S.V. Roth, R. Gehrke, P. Müller-Buschbaum *Combining imaging ellipsometry and grazing incidence small angle x-ray scattering for an in-situ characterization of polymer nanostructures* Anal. Bioanal. Chem. **396**, 139-149 (2010)
- M.A. Mangold, M.A. Niedermeier, M. Rawolle, B. Dirks, J. Perlich, S.V. Roth, A.W. Holleitner and P. Müller-Buschbaum *Correlation between structure and optoelectronic properties in a two-dimensional nanoparticle as*-

sembly phys. stat. sol. (RRL), 1-3 (2010)

- E. Metwalli, J. Perlich, W. Wang, A. Diethert, S.V. Roth, C.M. Papadakis, P. Müller-Buschbaum *Morphology of semicrystalline diblock copolymer thin films upon directional solvent vapor flow* Macromol. Chem. Phys. **211**, 2102-2108 (2010)
- J. Perlich, J. Rubeck, S. Botta, R. Gehrke, S.V. Roth, M.A. Ruderer, S.M. Prams, M. Rawolle, Q. Zhong, V. Körstgens, P. Müller-Buschbaum *Grazing incidence wide angle X-ray scattering at the wiggler beamline BW4 of HASYLAB* Rev. Sci. Instr. 81, 105105 (2010)
- Y. Peykova, S. Guriyanova, O. Lebedeva, A. Diethert, P. Müller-Buschbaum, N. Willenbacher *The effect of surface roughness on adhesive properties of acrylate copolymers* Int. J. Adhes. Adhes. 30, 245-254 (2010)
- J. Repper, Th. Keller, M. Hofmann, Chr. Krempaszky, W. Petry, E. Werner *Neutron Larmor diffraction measurements for materials science* Acta Mater. **58**, 3459-3467 (2010)
- J. Repper, P.Link, M. Hofmann, Chr. Krempaszky, E.Werner, W. Petry Interphase microstress measurements in IN718 by cold neutron diffraction Appl. Phys. A, **99**, 565-569 (2010)
- S.V. Roth, A. Rothkirch, T. Authenrieth, R. Gehrke, T. Wroblewski, M.C. Burghammer, C. Riekel, L. Schulz, R. Hengstler, P. Müller-Buschbaum Spatially resolved investigation of solution cast nanoparticle films by x-ray scatterig and multidimensional data set classification Langmuir (Letter) 26, 1496-1500 (2010)
- M. Rovira-Esteva, A. Murugan, L.C. Pardo, S. Busch, M.D. Ruiz-Martin, M.-S. Appavou, J.L. Tamarit, C. Smuda, T. Unruh, F.J. Bermejo, G.J. Cuello, S.J. Rzoska *Microscopic structures and dynamics of high- and low-density liquid trans-1,2-dichloroethylene* Phys. Rev. B, 81, 092202 (2010)
- M.A. Ruderer, V. Körstgens, E. Metwalli, M. Al-Hussein, U. Vainio, S.V. Roth, R. Döhrmann, R. Gehrke, R. Gebhardt, M. Burghammer, P. Müller-Buschbaum *Determination of the local gold contact morphology on a photoactive polymer film using nanobeam GISAXS* Nucl. Instr. and Meth. B 268, 403-410 (2010)
- M.A. Ruderer, S.M. Prams, M. Rawolle, Q. Zhong, J. Perlich, S.V. Roth, P. Müller-Buschbaum Influence of annealing and blending of photoactive polymers on their crystalline structure J. Phys. Chem. B 114, 15451-15458 (2010)
- W. Schirmacher, C. Tomaras, B. Schmid, G. Baldi, G. Viliani, G. Ruocco, T. Scopigno *Sound attenuation and anharmonic damping in solids with correlated disorder* Condens. Matter Phys. **13**, 23605 (2010)

- L. Schulz, W. Schirmacher, A. Omran, V.R. Shah, P. Böni, W. Petry, P. Müller-Buschbaum *Elastic torsion effects in magnetic nanoparticle diblock-copolymer structures* J. Phys. Condens. Matter **22**, 346008 (2010)
- C. Tomaras, B. Schmid and W. Schirmacher *Anharmonic elasticity theory for sound attenuation in disordered solids with fluctuating elastic constants* Phys. Rev. B 81,104206 (2010)
- W. Wang, G. Kaune, J. Perlich, C.M. Papadakis, A.M. Bivigou Koumba, A. Laschewsky, K. Schlage, R. Röhlsberger, S.V. Roth, R. Cubitt, P. Müller-Buschbaum *Swelling and switching kinetics of gold coated end-capped poly(N-isopropylacrylamide) thin films* Macromolecules **43**, 2444-2452 (2010)
- W. Wiedemann, L. Sims, A. Alaa, A. Exner, R. Meier, K.P. Musselman, J.L. MacManus-Driscoll, P. Müller-Buschbaum, G. Scarpa, P. Lugli, L. Schmidt-Mende Polymer solar cells with a well-defined nanostructured interface Appl. Phys. Lett. 96, 263109 (2010)
- H. Breitkreutz, M. Jungwirth, R. Schenk, Franz M. Wagner, W. Petry Measurements and simulations of fission neutron spectra at the MEDAPP beam at FRM II and subsequent developments Conference proceedings, IRPA, Helsinki (2010)
- H. Breitkreutz, F. M. Wagner, W. Petry Die Messung schneller Neutronenspektren und darauf aufbauende Entwicklungen in der Neutronentherapie StrahlenschutzPRAXIS, (2 / 2010): 48-53 Mai (2010)
- R. Jungwirth, W. Petry, H. Breitkreutz, W. Schmid, H. Palancher, C. Sabathier Study of heavy ion irradiated UMo/Al miniplates: Si and Bi addition to Al and UMo ground powders Transactions of RRFM 2010, Marakech/Morocco, Mar 21 – 25, (2010)
- R. Jungwirth, W. Petry, A. Röhrmoser, J. Allenou, X. Iltis *IRIS-TUM: Microstructure of the unirradiated plates* RERTR 2010 Lissabon, Conference Proceedings (2010)
- A. Leenaers, S. van den Berghe, F. Charollais, P. Lemoine, C. Jarousse, A. Röhrmoser, W. Petry *EPMA of ground UMo fuel with and without Si added to the matrix, irradiated to high burn up* Transactions of RRFM 2010, Marakech/Morocco, Mar 21 – 25, (2010)
- F. Wagner, B. Loeper-Kabasakal, W. Petry Radiation therapy by use of fast reactor neutrons
 M.G. Avrorin und V.A. Simonenko, Editor, Xth Zababakhin Scientific Talks, page 245. Editor: RFNC - VNIITF, Snezhinsk, Russia, (2010)

9.2 Talks

• J. Adelsberger Structure and kinetics of structural changes in thermoresponsive triblock copolymer solutions after *a temperature jump* SPP 1259 Workshop "Analytik von Hydrogelen", Aachen, 07 – 08 Oct 2010

- S. Busch, T. Unruh Influence of additives on the short-time dynamics of the phospholipid DMPC DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- S. Chillal, S. Ener, J. Neuhaus, K. Hradil, R. Mole, W. Petry Lattice Dynamics on Ferromagnetic Shape Memory Alloys MaMaSELF status meeting, Rigi Kulm, Switzerland, 3 May 2010
- S. Chillal, S. Ener, J. Neuhaus, K. Hradil, R. Mole, W. Petry *Ferromagnetic Shape Memory Alloy: Ni-Mn-Ga* Joint Workshop of the Students in the Field of Materials Science, LMU, TUM and Erasmus Mundus, Germany 1 May 2010
- A. Diethert, V. Körstgens, D. Magerl, Y. Peykova, O. Lebedeva, N. Willenbacher, P. Müller-Buschbaum Surface-near structuring of pressure sensitive adhesive films DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- A. Diethert, S. V. Roth, P. Müller-Buschbaum Surface enrichment layers in pressure sensitive adhesive films DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- A. Diethert, Y. Peykova, N. Willenbacher, P. Müller-Buschbaum Near-surface composition profiles of pressure sensitive adhesive films and their influence on the mechanical properties
 World Congress of Adhesion and Related Phenomena, Arcachon, 28 Sep 2010
- S. Ener, J. Neuhaus, W. Petry, S. Aksoy, I. Titov, M. Acet, E.F. Wassermann, A. Dannenberg, M. Siewert, P. Entel Magnetic, magnetoelastic and dynamical properties of martensitic Heusler alloys SPP1239 Evaluation Meeting, Dresden, 4 Mar 2010
- S. Ener, J. Neuhaus, K. Hradil, R. Mole, P. Link, W. Petry Dynamical properties of Ni-Mn-Ga alloys
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- S. Ener, J. Neuhaus, R. Mole, K. Hradil, B. Pedersen, W. Petry *Phonon properties of Ni-Mn-Ga shape memory alloys* FRM II User Meeting, Garching, 15 Oct 2010
- A. Golosova, C. M. Papadakis, R. Jordan *Polymer modified carbon nanotubes for preparation of nanocomposites* TU München, Department Chemie, Lehrstuhl für Makromolekulare Chemie, Garching, 11 Feb 2010
- A. Golosova, R. Jordan, C. M. Papadakis *Polymer modified carbon nanotubes for nanocomposite applications* TU Denmark, Nanotech Department, Copenhagen, Denmark, 5 May 2010

- Shuai Guo Structural characterization of polymers for application in organic photovoltaics MaMaSELF status meeting, Rigi Kulm, Switzerland, 3 May 2010
- Shuai Guo Structural characterization of polymers for application in organic photovoltaics
 Joint Workshop of the Students in the Field of Materials Science, LMU, TUM and Erasmus Mundus, Germany 1 May 2010
- E.T. Hoppe, D. Magerl, M. Port, A. Sepe, M. Haese-Seiller, B. Menges, C.M. Papadakis Advanced sample preparation and interface sensitive measurements - density and viscosity at the polymer-solid interface
 DFG SPP1369 "Polymer-Solid Contacts: Interfaces and Interphases" Spring School, Fulda, 9 Mar 2010
- S. Jaksch Kleinwinkelneutronenstreuung an Poly-(2-oxazolinen) TU Dresden, Department Chemie, 30 June 2010
- R. Jungwirth, H. Breitkreutz, W. Petry, W. Schmid, H. Palancher, P. Martin, C. Sabathier, M.C. Anselmet, F. Charollais, P. Lemoine, C. Jarousse *Study of heavy ion irradiated UMO/AL miniplates: SI and BI additions into AL and UMO ground powders* RRFM 2010, Marrakesch, 21 – 25 March 2010
- V. Körstgens, S. V. Roth, P. Müller-Buschbaum Development of the new μGISAXS instrument including imaging ellipsometry for the MINAXS beamline HASYLAB User Meeting, Hamburg, 28 - 29 Jan 2010
- V. Körstgens, R. Meier, J. Wiedersich, J. Perlich, S.V. Roth, P. Müller-Buschbaum Influence of humidity on casein films - an in situ investigation with a combination of μGISAXS and imaging ellipsometry DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- V. Körstgens, R. Meier, J.Wiedersich, J. Perlich, S. V. Roth, P. Müller-Buschbaum Combining imaging ellipsometry and grazing angle incidence small angle x-ray scattering for characterization of polymer nanostructures Accurion In-house conference, Göttingen, 09 – 10 Jun 2010
- V. Körstgens *Microfluidics and microGISAXS* 2nd TUM-HASYLAB colloquium, Hamburg 2 – 3 Nov 2010
- D. Magerl, V. Körstgens, P. Müller-Buschbaum *Flow of droplets on inclined surfaces* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- D. Magerl, M. Rawolle, M. A. Niedermeier, V. Körstgens, E. Metwalli, J. Perlich, A. Buffet, M. Schwartzkopf, G. Herzog, S. V. Roth, A. M. Bivigou-Koumba, A. Laschewsky, P. Müller-Buschbaum *Polymer hydrogel films* 2nd TUM-HASYLAB Colloquium, Hamburg 2 – 3 Nov 2010

- D. Magerl, M. Rawolle, M. Niedermeier, E. Metwalli, V. Körstgens, P. Müller-Buschbaum Investigation of hydrogel thin films by grazing incidence small-angle X-ray scattering (GISAXS) SPP 1259 Workshop "Analytik von Hydrogelen", Aachen, 07 – 08 Oct 2010
- R. Meier, M.A. Ruderer, G. Kaune, A. Diethert, F. Markl, V. Körstgens, J. Wiedersich, S.V. Roth, P. Müller-Buschbaum Structural analysis of photoactive polymer blend films on textured polymeric and inorganic substrates
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- R. Meier, M. A. Ruderer, G. Kaune, A. Diethert, F. Markl, V. Körstgens, J. Wiedersich, S.V. Roth, P. Müller-Buschbaum
 Polymer blend thin films investigated with GISAXS 2nd TUM-HASYLAB Colloquium, Hamburg 2 3 Nov 2010
- 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* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- E. Metwalli, K. Schlage, V. Körstgens, S. Couet, R. Meier, G. Kaune, S.V. Roth, R. Röhlsberger, P. Müller-Buschbaum Self organized growth of magnetic cobalt nanoparticles on polymer template: Real time GISAXS study
 MACRO2010, 43rd IUPAC World Polymer Congress, Glasgow, Scotland 11 – 16 Jul 2010
- E. Metwalli, K. Schlage, V. Körstgens, S. Couet, R. Meier, G. Kaune, S.V. Roth, R. Röhlsberger, P. Müller-Buschbaum *Real time GISAXS investigation of metal nanoparticle aggregation on polymer template* 2nd TUM-HASYLAB colloquium, Hamburg 2 – 3 Nov 2010
- P. Müller-Buschbaum, X. Xia, H. Choe, M.M. Abul Kashem, E. Metwalli, E. Majkova, I. Capek
 Nanostructured diblock copolymer films with embedded magnetic nanoparticles
 2.TUM Nanomagnetik-Workshop, Garching, 13 Jan 2010
- P. Müller-Buschbaum Synchrotron radaition users at HASYLAB (DESY)
 1st EUSO Workshop, Lissabon, Portugal, 17 – 18 Jan 2010
- P. Müller-Buschbaum Report of the HASYLAB User Committe (HUC) - report 2009 HASYLAB User Meeting, Hamburg, 28 – 29 Jan 2010
- P. Müller-Buschbaum, M.A. Ruderer, V.Körstgens, E. Metwalli, M. Al-Hussein, U. Vainio, S.V. Roth, R. Döhrmann, R. Gehrke, R. Gebhardt, M. Burghammer Determination of local morphologies in photoactive polymer films using nanobeam GISAXS Nanobeam Workshop, Grenoble, France, 9 – 11 Feb 2010
- P. Müller-Buschbaum, D. Magerl, V. Körstgens, J. Perlich, A. Diethert, S.V. Roth, F. Varnik, P. Uhlmann, M. Stamm *Flow and structure of droplets on solid surfaces*

Abschlusstagung des DFG Schwerpunktprogramms "Mikro- und Nanofluidik", Norderney, 21 – 25 Feb 2010

- P. Müller-Buschbaum Struktur und Kinetik stimuli-responsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren DFG Schwerpunkbegutachtung "Intelligente Hydrogele", Dortmund, 1 Mar 2010
- P. Müller-Buschbaum
 Functional materials based on polymer- and hybrid-nanostructures
 DPG Frühjahrstagung, Regensburg, 21 26 Mar 2010
- P. Müller-Buschbaum Nano-structuring polymer surfaces and interfaces for organic photovoltaic applications Kolloquium des IGRTG 1524 "Self-Assembled Soft-Matter Nanostructures at Interfaces", Berlin, 20 – 21 Apr 2010
- P. Müller-Buschbaum
 Functional materials based on polymer- and hybrid-nanostructures
 Physikalisches Kolloquium der Universität Augsburg, Augsburg, 26 Apr 2010
- P. Müller-Buschbaum *Functional materials based on polymer- and hybrid-nanostructures* Kolloquium des CSEM (Centre Suisse d'Electronique et de Microtechnique), Basel, Schweiz, 7 – 9 May 2010.
- P. Müller-Buschbaum *Functional materials based on polymer- and hybrid-nanostructures* Kolloquium des Lehrstuhls für Nanoelektronik, München, 10 Jun 2010
- P. Müller-Buschbaum
 Polymer blend morphology
 PETRAIII Extension Workshop, Hamburg, 23 25 Jun 2010
- P. Müller-Buschbaum
 Functional materials based on polymer- and hybrid-nanostructures
 Joint Nanoworkshop cNM Research Day 2010, Eindhoven, Niederlande, 29 30 Jun 2010
- P. Müller-Buschbaum, A. Diethert, V. Körstgens, D. Magerl, Y. Peykova, O. Lebedeva, N. Willenbacher
 Surface enrichment layers in pressure sensitive adhesive films
 MACRO2010 43rd IUPAC World Polymer Congress, Glasgow, Scotland, 11 16 Jul 2010
- P. Müller-Buschbaum, G. Kaune, M. Rawolle, M. Memesa, J.S. Gutmann, R. Kampmann, J.-F. Moulin, M. Haese-Seiller *Tailoring hybrid solar cell nanostructures with insights from advanced neutron scattering* Neutrons for Global Energy Solutions NGSE Workshop, Bonn, 26 – 29 Sep 2010
- P. Müller-Buschbaum, J. Perlich, G. Kaune, M. Rawolle, M. Niedermeier, M. Memesa, P. Lellig, J.S. Gutmann Sol-Gel templated titaniumdioxide films for solar cell application SPP 1181 Nanomat Workshop, Darmstadt, 5 – 6 Oct 2010

- P. Müller-Buschbaum *Energie und Umwelt* Eröffnungsvortrag des "Edgar-Lüscher-Fortbildungskurs für Physiklehrer", Dillingen, 11 -15 Oct 2010
- P. Müller-Buschbaum *Tailoring hybrid solar cell nanostructures with insights from advanced neutron scattering* FRM II User Meeting, Garching, 15 Oct 2010
- P. Müller-Buschbaum *Polymer- and hybrid-nanostructures for applications in organic photovoltaics* Joint Colloquium of CeNS and the Department of Physics LMU, München, 22 Oct 2010
- P. Müller-Buschbaum *Modeling GISAXS data using IsGISAXS* 2nd TUM-HASYLAB Colloquium, Hamburg 2 – 3 Nov 2010
- P. Müller-Buschbaum Synchrotron radiation Users at HASYLAB (DESY)
 2nd EUSO Workshop, Warschau, Polen, 18 – 19 Nov 2010
- P. Müller-Buschbaum *Effects of wall structure and small scale corrugation on the structure and dynamics of polymeric interphases* Begutachtung des "SPP1369 Interphasen", Mainz, 1 – 2 Dec 2010
- M.A. Niedermeier, M.A. Mangold, M. Rawolle, J. Perlich, S.V. Roth, A.W. Holleitner, P. Müller-Buschbaum
 Polymer hybrid structures 2nd TUM-HASYLAB Colloquium, Hamburg 2 3 Nov 2010
- C.M. Papadakis Self-assembled, thermo-responsive polymer hydrogels from PS-b-PNIPAM-b-PS Copenhagen University, Denmark, 20 Jan 2010
- C.M. Papadakis Local viscosity and density in the interphase of polymers and solids
 DFG SPP1369 "Polymer-Solid Contacts: Interfaces and Interphases" Workshop, Frankfurt, 09 Jul 2010
- C.M. Papadakis Structural changes of block copolymer thin films in solvent vapor TU Denmark, Lyngby, 21 Jan 2010
- C.M. Papadakis, J. Adelsberger, A. Kulkarni, A. Jain, A. Meier-Koll, W. Wang, A.M. Bivigou-Koumba, A. Laschewsky, P. Müller-Buschbaum Structure of thermoresponsive polymer hydrogels
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- C.M. Papadakis Structural reorganizations in block copolymer thin films during solvent vapor treatment Universität Leipzig, 20 May 2010

- C.M. Papadakis Solvent vapor treatment of block copolymer thin films - a routine method with little surprises CHESS Users' Meeting, Cornell University, Ithaca NY, USA, 8 – 9 Jun 2010
- C.M. Papadakis Structural changes of block copolymer thin films in solvent vapor Leibniz-Institut für Polymerforschung Dresden e.V., 30 Jun 2010
- C.M. Papadakis Solvent vapor treatment of block copolymer thin films - a routine method with little surprises Lehrstuhl für Nanoelektronik, TU München, 28 Oct 2010
- W. Petry Scenario for sustainable molybdenum-99 production in Europe - the contribution of FRM II EU meeting, Supply of radioisotopes, Luxembourg, 4 May 2010
- W. Petry

Neutrons are beautiful Kick-off Meeting, TUM Gradudate School, Herrsching 10 Sep 2010

• W. Petry

A sustainable molybdenum-99 production in Europe - the contribution of Germany 2010 IAEA General Conference Side Event - Mo-99 Supply, Vienna, Austria, 22 Sep 2010

- W. Petry Ohne Kerne geht es nicht!
 Gigawatt - Highlights der Physik, veranstaltet von DPG, Augsburg, 14 Oct 2010
- W. Petry

From atoms to industrial products - materials science with neutrons Ringvorlesung am Physik-Department der TU München, 15 Nov 2010

- W. Petry
 Von der Schönheit der Neutronen
 Ortsektion Kerntechnische Gesellschaft, München, 7 Dec 2010
- M. Rawolle, M.A. Ruderer, S.M. Prams, Q. Zhong, D. Magerl, J. Perlich, S.V. Roth, P. Lellig, J.S. Gutmann, P. Müller-Buschbaum Combination of micro-fluidics and sol-gel chemistry 2nd TUM-HASYLAB Colloquium, Hamburg 2 – 3 Nov 2010
- M. Rawolle, K. Sarkar, M.A. Ruderer, S.M. Prams, Q. Zhong, D. Magerl, P. Lellig, J.S. Gutmann, J. Perlich, S.V. Roth, P. Müller-Buschbaum Nanostrukturierung dünner Titandioxidfilme für Anwendungen in der Photovoltaik Deutsche Physikerinnentagung, München, 5 Nov 2010
- M.A. Ruderer *Controlled embedding of semiconducting nanoparticles in a conducting polymer template* Complete Winter School, Antholz, Italy 8 – 22 Mar 2010
- M.A. Ruderer, S.M. Prams, W. Wang, Q. Zhong, R. Meier, S.V. Roth, J. Szeifert, T. Bein, P. Müller-Buschbaum Controlled embedding of semiconducting nanoparticles in a conducting polymer template DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010

- M.A. Ruderer, S. Guo, R. Meier, H.-Y. Chiang, V. Körstgens, J. Wiedersich, J. Perlich, S.V. Roth, P. Müller-Buschbaum Investigations of structural changes by modification of polymer systems for photovoltaic applications
 Polymeric Materials P2010, Halle, 15 – 17 Sep 2010
- M.A. Ruderer, P. Müller-Buschbaum *Polymers for applications in organic photovoltaics* SEEIT - Photovoltaic Workshop, Freiburg, 30 Sep 2010
- M.A. Ruderer, S.M. Prams, J. Perlich, S.V. Roth, P. Müller-Buschbaum Morphologies of bulk heterojunctions for polymer based photovoltaics 2nd TUM-HASYLAB colloquium, Hamburg 2 – 3 Nov 2010
- K. Sarkar, P. Müller-Buschbaum Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT polymer MaMaSELF status meeting, Rigi Kulm, Switzerland, 3 May 2010
- K. Sarkar, P. Müller-Buschbaum Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT polymer LMU workshop, Munich, 1 May 2010
- A. Sepe *Kinetics of structural changes in thin block copolymer films during thermal and solvent vapour treatment* Complete Winter School, Antholz, Italy, 8 – 22 Mar 2010
- A. Sepe, P. Černoch, P. Štěpánek, D.-M. Smilgies, S.V. Roth, A. Timmann, C.M. Papadakis Formation of lateral structures in thin diblock copolymer films by vapor treatment DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- W. Schmid, S. Dirndorfer, R. Grossmann, H. Juranowitsch, W. Petry, C. Jarousse *Sputtering as a coating technique for monolithic U-Mo fuel foils* RERTR 2010, Lissabon, Portugal, 10 – 14 Oct 2010
- Q. Zhong, W. Wang, G. Kaune, M. Rawolle, E. Metwalli, A. M. Bivigou-Koumba, A. Laschewsky, C.M. Papadakis, R. Cubitt, P. Müller-Buschbaum *In-situ neutron reflectivity as a tool to probe swelling of hydrogel films* SPP 1259 Workshop "Analytik von Hydrogelen", Aachen, 07 – 08 Oct 2010

9.3 Posters

- J. Adelsberger, A. Meier-Koll, W. Wang, A.M. Bivigou-Koumba, A. Laschewsky, T. Hellweg, O. Holderer, V. Pipich, P. Busch, P. Müller-Buschbaum, C.M. Papadakis Structure and dynamics of thermoresponsive block copolymer gels
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- J. Adelsberger, A. Meier-Koll, W. Wang, A.M. Bivigou-Koumba, A. Laschewsky, T. Hellweg, O. Holderer, V. Pipich, P. Busch, P. Müller-Buschbaum, C.M. Papadakis

Structure and dynamics of thermoresponsive poly(styrene-block-N-isopropyl acrylamide-blockstyrene) hydrogels

24th Conference of the European Colloid and Interface Society, Prague, 5 – 10 Sep 2010

- J. Adelsberger, A. Meier-Koll, W. Wang, A.M. Bivigou-Koumba, A. Laschewsky, T. Hellweg, O. Holderer, V. Pipich, P. Busch, P. Müller-Buschbaum, C.M. Papadakis Structure and dynamics of thermoresponsive poly(styrene-block-N-isopropyl acrylamide-blockstyrene) hydrogels
 FRM II User Meeting, Garching, 15 Oct 2010
- S. Busch, C. Smuda, L.C. Pardo, T. Unruh *Panta Rhei – flow behaviour in phospholipid membranes* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- S. Busch, J. Wuttke, M.-S. Appavou, A.M. Gaspar, H. Scheer, W. Doster *Fragile–strong–crossover in surface water?* SNI2010, Berlin, 24 – 26 Feb 2010
- S. Busch, M. Schmiele, C. Smuda, T. Unruh *Phospholipid dynamics and the influence of additives* SNI2010, Berlin, 24 – 26 Feb 2010
- S. Chillal, S. Ener, J. Neuhaus, K. Hradil, R. Mole, W. Petry *Effect of magnetic field on phonons in martensitic* Ni₄₉Mn₃₂Ga₁₉ FRM II User Meeting, Garching, 15 Oct 2010
- Z. Di, D. Posselt, D.M. Smilgies, C.M. Papadakis Structural rearrangements in a lamellar diblock copolymer thin film during treatment with saturated solvent vapor
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- S. Dirndorfer, W. Schmid, R. Jungwirth, H. Breitkreutz, W. Petry, C. Jarousse, M. Hirsch *Tensile tests on monolithic samples* RRFM 2010, Marrakesch, 21 – 25 Mar 2010
- S. Dirndorfer, W. Schmid, W. Petry, R. Jungwirth, H. Breitkreutz Characterization of bond strength of monolithic two metal layer systems RRFM 2010, Marrakesch, 21 – 25 Mar 2010
- S. Ener, T. Mehaddene, J. Neuhaus, K. Hradil, R. Mole, P. Link and W. Petry *Phonon properties of Ni₂mnGa in austenite and martensite phases* SNI2010, Berlin, 24 – 26 Feb 2010
- S. Ener, J. Neuhaus, K. Hradil, R. Mole, P. Link and W. Petry *Phonon properties of Ni*₂*MnGa in austenite and martensite phases* SPP1239 Evaluation Meeting, Dresden, 04 Mar 2010
- A. Golosova, R. Jordan, J. Adelsberger, A. Sepe, M. Niedermeier, S. S. Funari, P. Lindner, C. M. Papadakis *Chemical functionalization of carbon nanotubes (CNTs) for preparation of nanocomposites* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010

- A. Golosova, R. Jordan, S. S. Funari, P. Lindner, C. M. Papadakis *Chemical functionalization of carbon nanotubes with polymer grafts* ChemOnTubes, Arcachon, France, 11 – 15 Apr 2010
- A. Golosova, R. Jordan, S. S. Funari, P. Lindner, C. M. Papadakis *Chemical functionalization of carbon nanotubes for nanocomposite applications* All-Russian conference "Macromolecular nanoobjects and polymer nanocomposites", Moscow, 24 – 29 Oct 2010
- E.T. Hoppe, D. Magerl, M. Port, B. Menges, C.M. Papadakis Density and viscosity at the polymer-solid interface
 CONFIT 2010 – Dynamics in confinement, Grenoble, 03 – 05 Mar 2010
- E.T. Hoppe, D. Magerl, M. Port, B. Menges, C.M. Papadakis Density and viscosity at the polymer-solid interface
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- E.T. Hoppe, D. Magerl, A.Sepe, M. Port, B. Menges, C.M. Papadakis Density and viscosity at the polymer-solid interface
 DFG SPP1369 "Polymer-Solid Contacts: Interfaces and Interphases" Workshop, Frankfurt, 09 Jul 2010
- E.T. Hoppe, B. Wang, A.Sepe, M. Port, M. Haese-Seiller, J.-F. Moulin, B. Menges, C.M. Papadakis Density and viscosity at the polymer-solid interface FRM II User Meeting, Garching, 15 Oct 2010
- S. Jaksch, J. Adelsberger, S. Salzinger, S. Huber, R. Jordan, Z. Di, P. Busch, C.M. Papadakis Switching behavior of thermoresponsive poly(2-oxazoline) copolymers FRM II User meeting, Garching, 15 Oct 2010
- R. Jungwirth H. Palancher et al. Study of heavy ion irradiated UMo/Al miniplates: Si and Bi additions into AL and UMo ground powders RRFM 2010, Marrakesch, 21 – 25 March 2010
- R. Jungwirth et al *IRIS-TUM: Microstructure of the non-irradiated plates* RERTR, Lisbon, 10 – 14 Oct 2010
- V. Körstgens, R. Meier, J. Wiedersich, S.V. Roth, P. Müller-Buschbaum Development of the new μGISAXS instrument including imaging ellipsometry for the MINAXS beamline at PETRA3 HASYLAB User Meeting, Hamburg, 27 – 29 Jan 2010
- V. Körstgens, R. Meier, J.Wiedersich, J. Perlich, S. V. Roth, P. Müller-Buschbaum Combining imaging ellipsometry and grazing angle incidence small angle x-ray scattering for characterization of polymer nanostructures ESRF User Meeting, Grenoble, 09 – 12 Feb 2010
- R. Meier, M.A. Ruderer, G. Kaune, A. Diethert, F. Markl, V. Körstgens, J. Wiedersich, S.V. Roth, P. Müller-Buschbaum

Thin photoactive polymer films on textured substrates: A GISAXS study HASYLAB User Meeting, Hamburg, 27 – 29 Jan 2010

- R. Meier, M. A. Ruderer, G. Kaune, A. Diethert, S. V. Roth, P. Müller-Buschbaum *Morphology analysis of pretextured polymer blend films for photovoltaic application* cNM Research Day, Eindhoven, 29 Jun 2010
- E. Metwalli, J.-F. Moulin, J. Perlich, W. Wang, A. Diethert, S.V. Roth, P. Müller-Buschbaum Interaction of flowing colloidal nanoparticles with solid interfaces of different selectivity
 DFG Priority Program SPP 1164 Nano & Microfluidics, Norderney, 21 – 26 Feb 2010
- E. Metwalli, H. Choe, P. Busch, P. Müller-Buschbaum *Alignment of magnetic nanoparticles in diblock copolymer films under external magnetic field* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- E. Metwalli, H.E. Hermes, E. Calzada, R. Cubitt, U. Kulozik, S.U. Egelhaaf, P. Müller-Buschbaum
 Water diffusion profile measurements in casein films using neutron radiography
 FRM II User Meeting, Garching, 15 Oct 2010
- H. Morhenn, S. Busch, D. Richter, T. Unruh Short time dynamics of medium length molecules FRM II User Meeting, Garching, 15 Oct 2010
- P. Müller-Buschbaum, W. Wang, J. Perlich, G. Kaune, C.M. Papadakis, A. Bivigou Koumba, A. Laschewsky, R. Cubitt Switchability of nanoscale sensors based on thin hydrogel films SNI2010, Berlin, 24 – 26 Feb 2010
- M.A. Niedermeier, J. Perlich, G. Kaune, M. Memesa, J.S. Gutmann, P. Müller-Buschbaum *Hierarchically structured titania films for application in photovoltaics* Polymeric Materials P2010, Halle, 15 – 17 Sep 2010
- M.A. Niedermeier, G. Kaune, M. Rawolle, V. Körstgens, M.A. Ruderer, J.S. Gutmann, P. Müller-Buschbaum
 Fabrication of hierarchically ordered crystalline titania thin films DPG Frühjahrstagung, Regensburg, 21 26 Mar 2010
- C.M. Papadakis, J. Adelsberger, A. Meier-Koll, K. Troll, A. Kulkarni, A. Jain, W. Wang, Q. Zhong, P. Müller-Buschbaum, A.M. Bivigou Koumba, A. Miasnikova, A. Laschewsky *Thermoresponsive polymeric hydrogels formed by self-assembly* Freiburger Makromolekulares Kolloquium, Freiburg, 25 – 27 Feb 2010
- C.M. Papadakis, C. Darko, Z. Di, K. Troll, E. Metwalli, A. Timmann, G. Reiter, S. Förster Very slow breakout crystallization in cylinder-forming diblock copolymer thin films DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- C.M. Papadakis, S. Salzinger, S. Huber, J. Adelsberger, A. Golosova, A. Meier-Koll, P. Busch, S. Balog, R. Jordan *Collapse behavior of thermo-responsive poly(2-oxazoline) copolymers* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010

- C.M. Papadakis, Z.Di, D.Posselt, D.-M. Smilgies
 Structural changes in thin block copolymer films during vapor treatment
 24th Conference of the European Colloid and Interface Society, Prague, 5 10 Sep 2010
- S. Prams, M.A. Ruderer, M. Rawolle, Q. Zhong, R. Meier, J. Perlich, S.V. Roth, P. Müller-Buschbaum GISAXS and GIWAXS characterization of thin photoactive polymer films HASYLAB User Meeting, Hamburg, 27 – 29 Jan 2010
- M. Rawolle, M.A. Ruderer, S.M. Prams, Q. Zhong, M. Memesa, J.S. Gutmann, P. Müller-Buschbaum *Controlling the morphology of thin titania films for applications in hybrid solar cells* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- M. Rawolle, K. Sarkar, S.M. Prams, Q. Zhong, P. Lellig, M. Memesa, J.S. Gutmann, J. Perlich, S.V. Roth, P. Müller-Buschbaum Controlled titania sponge structures templated with block copolymers for applications in inorganicorganic photovoltaics
 Polymeric Materials P2010, Halle, 15 – 17 Sep 2010
- M. Rawolle, K. Sarkar, M.A. Niedermeier, P. Lellig, J.S. Gutmann, P. Busch, J.-F. Moulin, M. Haese-Seiller, P. Müller-Buschbaum Determination of porosity and degree of backfilling of nanoporous titania films for applications in photovoltaics NGES 2010, Bonn, 26 – 29 Sep 2010
- M. Rawolle, K. Sarkar, M.A. Niedermeier, P. Lellig, J.S. Gutmann, P. Busch, J.-F. Moulin, M. Haese-Seiller, P. Müller-Buschbaum Infiltration and backfilling of the network structure of nanoporous titania films for applications in photovoltaics FRM II User Meeting, Garching, 15 Oct 2010
- M.A. Ruderer, S. Guo, R. Meier, H.-Y. Chiang, J. Wiedersich, V. Körstgens, J. Perlich, S.V. Roth, P. Müller-Buschbaum Investigations of structural changes by modification of polymer systems for photovoltaic applications
 SPP1355 Workshop, Dresden, 22 Oct 2010
- A. Sepe, Z. Di, E.T. Hoppe, D. Magerl, J. Perlich, D. Posselt, D.-M. Smilgies, C.M. Papadakis Kinetics studies of lamellar poly(styrene-b-butadiene) diblock copolymer thin films during heat treatment

DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010

- A. Sepe, Z. Di, E.T. Hoppe, D. Magerl, J. Perlich, D. Posselt, D.-M. Smilgies, C. M. Papadakis Kinetics studies of lamellar poly(styrene-b-butadiene) diblock copolymer thin films during heat treatment
 CHESS Users Meeting, Cornell University, Ithaca, NY, USA, 8 – 9 Jun 2010
- J. Wiedersich, A. Diethert, P. Müller-Buschbaum, W. Petry Elastic properties of thin transparent polymer films
 DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010

- Q. Zhong, G. Kaune, M. Rawolle, E.M etwalli, A.M. Bivigou-Koumba, A. Laschewsky, C.M. Papadakis, R. Cubitt, P. Müller-Buschbaum *Characterization of PMDEGA based hydrogel films* DPG Frühjahrstagung, Regensburg, 21 – 26 Mar 2010
- Q. Zhong, J. Adelsberger, M. Niedermeier, A. Golosova, A. M. Bivigou-Koumba, A. Laschewsky, C.M. Papadakis, P. Busch, S. Botta, S.S. Funari, P. Müller-Buschbaum *The influence of different solvents on the LCST behavior of P(S-b-MDEGA-b-S) hydrogel films* FRM II User meeting, Garching, 15 Oct 2010

9.4 Invited talks at LS Funktionelle Materialien

- Prof. Dr. Françoise Winnik, Faculty of Pharmacy and Department of Chemistry, Université de Montréal, Canada Directed self assembly of amphiphilic telechelic polymers: from flower micelles to nanogels 18 Mar 2010
- Dr. Gabriele De Paoli, Gent, Belgien Design and investigation of novel soft materials
 7 Apr 1020
- Dr. Silvia Milani, University of Florence, Italy Self-assemblies of a new class of lipids for nanobiotechnology applications 12 Mar 10
- Gildardo Morga Ramirez, TU München, Germany Device preparation and optimization for photo diodes 12 May 10
- Deepak Kumar Tiwari, Universität Siegen, Germany In-situ characterization of P3Ht films with an applied electric field 12 May 10
- Dr. Martine Philippe, Prof. Jan-Kristian Krüger, Université du Luxembourg, Luxembourg On the interplay between structure formation and non-equilibrium transitions in a physical gel 19 – 20 May 2010
- Prof. Marc Foster, Department of Polymer Science, The University of Akron, USA Effect of tethering on surface fluctuations of polymer melt films
 4 Jun 2010
- Dr. Harald Walter, CSEM, Basel, Switzerland *Thin film optics* 15 Jun 2010
- Dr. Jean-François Moulin, GKSS at FRM II, Germany TOF-GISANS and TOF-REF at REFSANS 22 Jun 2010
- Dr. Periklis Papadopoulos, Universität Leipzig, Germany Novel applications of infrared spectroscopy in soft matter: Biopolymers, elastomers and ionic liquids 6 Jul 2010

- Christian Weigel, Universität Heidelberg, Germany Solution processed tandem cells
 30 Sep 2010
- Prof. R. Jayavel, Centre of Nanoscience and Technology, Anna University Chennai, India *Fabrication of organic/inorganic nano hybrid systems for photovoltaic applications* 8 Sep 2010
- Prof. Dr. Dorthe Posselt, IMFUFA, Department of Science, Systems and Models, Roskilde University, Denmark *Mesoscale structure and structural adaptability of chloroplast thylakoid membranes* 13 Sep 2010
- Dr. Wim Pyckhout-Hintzen, IFF, FZ Jülich, Germany Recent microscopic advances in the understanding of model nanocomposite systems 7 Dec 2010

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. Dr. 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. Dr. Peter Müller-Buschbaum
- Within DFG priority program SPP 1181: Nanoskalige anorganische Materialien durch molekulares Design: Neue Werkstoffe für zukunftsweisende Technologien, Anorganisch-organische Hybridfilme mit integrierter Funktion Grant Number: MU 1487/5-3 Project Leader: Prof. Dr. 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. Dr. Peter Müller-Buschbaum
- Within DFG priority programm SPP 1239 Änderung von Mikrostruktur und Form fester Werkstoffe durch äußere Magnetfelder Grant Number: NE 1405/1-2 Project Leader: Dr. Jürgen Neuhaus
- Within DFG priority program SPP 1259: Struktur und Kinetik stimuli-responsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren

Grant Number: PA 771/4-1, Follow-up project PA 771/4-2 Project Leader: Prof. Dr. Christine M. Papadakis

- *Multicompartment systems based on poly (2-oxazoline)s* Grant Number: PA 771/6-2 Project Leader: Prof. Dr. Christine M. Papadakis
- Within DFG priority program SPP 1369: Lokale Viskosität und Dichte in der Grenzphase von Polymeren an einer festen Grenzfläche - Fluoreszenz-Korrelationsspektroskopie und Neutronenreflektometrie Grant Number: PA 771/7-1 Project Leader: Prof. Dr. Christine M. Papadakis
- Rolle der Mikrospannungen bei der Eigenspannungsanalyse mittels Neutronenbeugung in mehrphasigen Hochleistungslegierungen Grant Number: PE 580/7-1 Project Leader: Prof. Dr. Winfried Petry
- Antrag der Christian-Albrechts-Universität zu Kiel auf Einrichtung und Finanzierung eines Sonderforschungsbereichs "Magnetoelektrische Verbundwerkstoffe - biomagnetische Schnittstellen der Zukunft"
 Grant Number: PE 580/11-1
 Project Leader: Prof. Dr. Winfried Petry
- Bundesministerium für Bildung und Forschung:
- Entwicklung und Aufbau von muGISAXS am muSAXS/WAXS Instrument am Synchroton PETRA III
 Grant Number: 05KS7WO1
 Project Leader: Prof. Dr. Peter Müller-Buschbaum
- MiNaXS-Microfluidik: Entwicklung und Aufbau des Mikrofluidik Messplatzes am Instrument NiNaXS am Synchrotron PETRA III Grant Number: 05K10WOA Project Leader: Prof. Dr. Peter Müller-Buschbaum
- Others:
- Im Rahmen des Internationalen Graduiertenkollegs: Material Science of Complex Interfaces
 Magnetic particles in supported polymer pape-structures

Magnetic particles in supported polymer nano-structures Project Leader: Prof. Dr. Peter Müller-Buschbaum

Im Rahmen des Internationalen Graduiertenkollegs: Material Science of Complex Interfaces

Strukturelle Änderungen in nanostrukturierten Blockcopolymerfilmen - Zeitaufgelöste in-situ-Untersuchungen mit Röntgenkleinwinkelstreuung unter streifendem Einfall Project Leader: Prof. Dr. 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. Dr. Christine M. Papadakis, PD Dr. Rainer Jordan (Department Chemie, Technische Universität München), Prof. Dr. Martin E. Vigild (Department of Chemical Engineering, Danish Technical University)
- Incentive Fund for Research Collaborations between Technische Universität München and the Danish Technical University *Crystalline, mesoscopic and long-range order in thin films of crystalline block copolymers* Project Leader: Prof. Dr. Christine M. Papadakis, Dr. Jens Wenzel Andreasen (Risø National Laboratory, Danish Technical University)
- Im Rahmen der 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. Dr. Christine M. Papadakis, PD Dr. Rainer Jordan (Department Chemie, Technische Universität München)
- Forschungskooperation Johannes Gutenberg-Universität Mainz Feldtheoretische Beschreibung von Eigenschaften weicher kondensierter Materie Project Leader: Prof. Dr. Winfried Petry
- BaCaTEC Hochschule International Bayerisch-Kalifornisches Hochschulzentrum *Combined neutron and raman spectroscopy of disordered and nanostructured materials* Project Leader: Prof. Dr. Walter Schirmacher

10 The chair



10.1 Graduations

• Accomplished PhD theses

Zhenyu Di

Structural changes in lamellar diblock copolymer thin films during solvent vapor treatment

Gunar Kaune

Strukturierung von anorganisch-organischen Hybridsystemen für Anwendungen in der Photovoltaik

Julia Repper

Einfluss von mikroskopischen Eigenspannungen auf die makroskopische Eigenspannungsanalyse mittels Neutronenbeugung

Weinan Wang Structure and kinetic of stimuli-responsive thin hydrogel films

• Accomplished diploma theses

Stefan Dirndorfer

Tensile tests on monolithic two metal layer systems for research reactor fuels

Tim Hülsheger

Angular behaviour of triple-junction solar cells for high temperature space missions

David Magerl Submikrolitertropfen auf Oberflächen

Andreas Nathan *Tuning conductivity of thin conjugated polymer films and its application* Markus Schindler

Bestimmung des Lösemittelgehalts in dünnen leitfähigen Polymerfilmen für die Photovoltaik

• Accomplished master theses

Hsin-Yin Chiang Enhanced optical absorption of structured conducting polymer thin films

Shravani Chillal Lattice dynamics of ferromagnetic shape memory alloys: Ni-Mn-Ga

Shuai Guo Structural characterization of polymers for application in organic photovoltaics

Kuhu Sarkar Inorganic-organic hybrid materials for applications in photovoltaics: titania, dye and P3HT

Carola Alonso de Celada Casero FCS- and DLS-measurements of poly(2-oxazoline)

• Accomplished bachelor thesis

Michael Hinterstocker Characterization of ternary systems for organic photovoltaics

Isabell Krisch Ordered nanoporous template from block copolymer thin films

Florian Schaff Structuring of nanoporous titania films for application in photovoltaics

Xuhu Shen Amphiphilic thermoresponsive triblock copolymers

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

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- Dr. Ezzeldin Metwalli Ali Dr. Joana Rebelo Kornmeier Dr. Volker Körstgens Dr. Peter Link Dr. Jürgen Neuhaus Dr. Tobias Unruh Dr. Johannes Wiedersich
- Dr. Giovanna Gulia Simeoni

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Technical/administrative staff

Philipp Bork Petra Douglas Erik Faber Susanna Fink Reinhold Funer Lukas Hein Raffael Jahrstorfer Josef Kaplonski Dieter Müller Jandal Ringe

10.3 Guests

- Prof. Dr. Françoise Winnik, Faculty of Pharmacy and Department of Chemistry, Université de Montréal, Canada 17 – 19 Mar 2010
- Prof. Dr. Alfons Schulte, Department of Physics, University of Central Florida, USA 7 Jun 3 Jul 2010
- Prof. Dr. Dorthe Posselt, IMFUFA, Department of Science, Systems and Models, Roskilde University, Denmark 10 – 17 Oct 2010