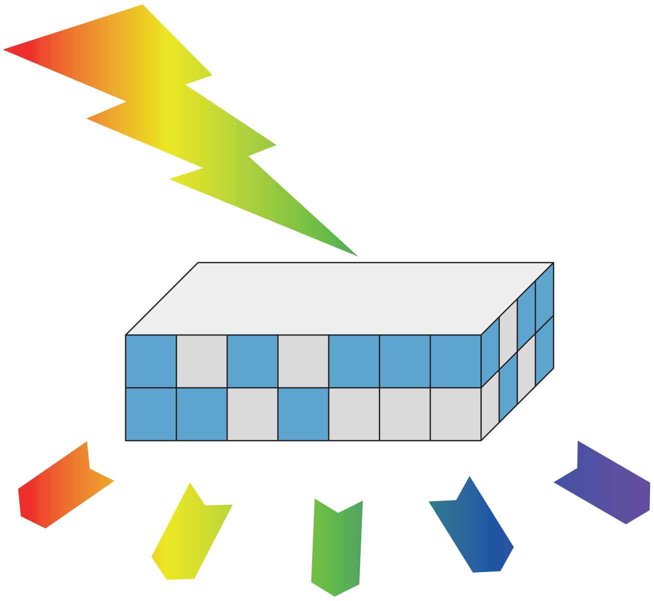
Berlin-Brandenburgischer Verband
für Polymerforschung e.V.

Polydays 2012: Polymers and Light



September 30 - October 2, 2012
Humboldt-Universität zu Berlin – Campus Adlershof

Polydays 2012: Polymers and Light

Content

Polydays 2012: Polymers and Light

Dear Participants,

It is our great pleasure to welcome you to the “Polydays 2012” – a symposium, which is organized biannually by the Berlin-Brandenburgischer Verband für Polymerforschung (BVP). The topic of this year’s symposium is “Polymers and Light”.

We would like to invite you to meet with your colleagues from all over the world to share and discuss your results as well as to initiate new cooperations and further existing ones. “Polydays 2012” aims to highlight the exciting science currently going on at the interface of polymers and light. Therefore, we hope that you will enjoy the many interesting lectures given by a number of leading scientists in the field as well as the poster sessions featuring young talented researchers.

We wish you an inspiring, exciting meeting and are looking forward to this symposium!

Yours sincerely,

Stefan Hecht

Scientific Chairs

Sunday, September 30, 2012

Guided Tour (Deutsches Technikmuseum Berlin) and Boat Trip

15:30	**Departure shuttle service from Hotel Dorint to the Deutsches Technikmuseum** *Hotel Dorint, Rudower Chaussee 15, 12489 Berlin*
16:30-17:30	**Guided tour** Through a selection of the current exhibition of the *Deutsches Technikmuseum Berlin,* *Trebbiner Straße 9, 10963 Berlin-Kreuzberg*
18:00-21:00	**Guided boat trip incl. dinner** Departure: *Pier ”Reederei Riedel“, Hallesches Tor, 10961 Berlin* Arrival: *Pier ”Reederei Riedel”, Ernst-Ruska-Ufer, 12489 Berlin* (10 minutes by foot to Hotel Dorint)

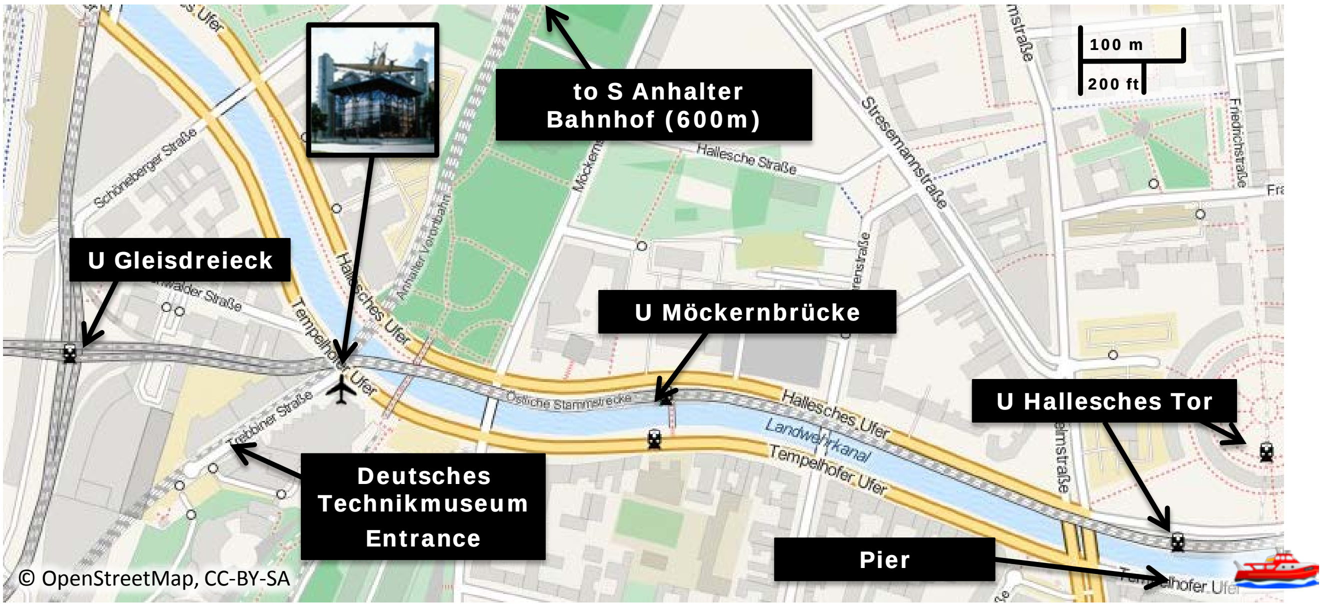
Social Programme

We are happy to invite you to the Deutsches Technik Museum Berlin (http://www.sdtb.de/Englisch.55.0.html) on Sunday, September 30 for a guided tour through a selection of the current exhibition. The tour starts at 4.30 pm and lasts one hour. We offer a shuttle service from Dorint Hotel to the Deutsches Technik Museum.

Subsequently a guided trip with the boat "Rixdorf" is planned at 6.00 pm starting nearby the museum. The Rixdorf will take us via the Spree, Landwehrkanal and Teltowkanal along Berlins most favorite sight-seeing points. We will have dinner on the boat and will finally arrive at 9.15 pm close to the Dorint Hotel in Berlin-Adlershof.

Please let us know during the registration procedure whether you want to participate in the social programme or not. If you have already registered without referring to this point, please inform us about your plans via e-mail.

Both, the museum and the pier can easily be reached via public transport system. Close stations are U Gleisdreieck (U1, U2), U Möckernbrücke (U1, U7) and Hallesches Tor (U1, U6). The S-Bahn station S Anhalter Bahnhof (S1, S2, S25) is also within walking distance.



Programme Monday, October 1, 2012

Erwin-Schrödinger-Zentrum, Rudower Chaussee 26, 12489 Berlin

08:00 **Registration**

09:00-09:15 **Opening**
Lecture Hall 0.115

09:15-10:00 **Plenary Talk**
Lecture Hall 0.115
“High resolution imaging technology for microelectronics”
C. Grant Willson (University of Texas at Austin, U.S.A.)

10:00-10:30 **Coffee Break**

10:30-11:15 **Plenary Talk**
Lecture Hall 0.115
“Lessons from nature about solar light harvesting: A little bit of coherence?”
Gregory D. Scholes (University of Toronto, Canada)

11:15-12:00 **Plenary Talk**
Lecture Hall 0.115
“THz Spectroscopy: A novel experimental tool to study water network dynamics”
Martina Havenith (Ruhr-Universität Bochum, Germany)

12:00-13:30	**Lunch**
13:30-15:00	**Parallel Session Solar I** *Lecture Hall 0.307*
13:30	*"Tailor-made absorber polymers for efficient organic solar cells"* Silvia Janietz (Universität Stuttgart, Germany)
14:00	*"Charge generation and extraction in polymer-based solar cells"* Dieter Neher (Universität Potsdam, Germany)
14:30	*"NMR investigations of crystallinity and supramolecular organization in polymers for photovoltaics applications"* Kay Saalwächter (Martin-Luther-Universität Halle Wittenberg, Germany)
13:30-15:00	**Parallel Session Characterization I** *Lecture Hall 0.310*
13:30	*"Infrared - transition moment orientational analysis"* Friedrich Kremer (Universität Leipzig, Germany)
14:00	*"Characterization of shape switching of polymers induced by light"* Michael Maskos (Institut für Mikrotechnik Mainz, Germany)
14:30	*"Oscillation of DNA recognition observable on fluorescence shift?"* Nikolaus Ernsting (Humboldt-Universität zu Berlin, Germany)
15:00-15:30	**Coffee Break**

15:30-17:00 **Parallel Session Solar II**

Lecture Hall 0.307

15:30 *“Blockcopolymer - nanocrystal hybrids for optoelectronic applications”*
Rudolf Zentel (Universität Mainz, Germany)

16:00 *“Modular polymer-based architectures for efficient multiple charge-separation: Redox-active polymers and decoration with luminescent ruthenium complexes”*
Michael Jäger (Friedrich-Schiller-Universität Jena, Germany)

16:30 *“Polymeric heptazine networks for photocatalytic water splitting”*
Kailasam Kamalakannan (Technische Universität Berlin, Germany)

15:30-17:00 **Parallel Session Characterization II**

Lecture Hall 0.310

15:30 *“Polymer characterization using hard X-rays for revealing solution and solid state structures”*
Andreas Thünemann (Bundesanstalt für Materialforschung, Berlin, Germany)

16:00 *“Characterization of nanoporous polymers by X-ray scattering”*
Jens Weber (Max-Planck-Institut für Kolloid- und Grenzflächenforschung Potsdam, Germany)

16:30 *“Smart microgel capsules and model colloids tailored by photocrosslinking in droplet-based microfluidics”*
Sebastian Seiffert (Helmholtz-Zentrum Berlin, Germany)

17:00-18:00 **Short oral presentation of selected posters**

Lecture Hall 0.115

18:00-19:00 **Poster Session**

Lecture Hall 0.115

19:00-21:00 **BBQ**

Cafeteria (TIM's Canadian Deli)

Programme Tuesday, October 2, 2012

Erwin-Schrödinger-Zentrum, Rudower Chaussee 26, 12489 Berlin

09:00-10:00	**Gerhard Kanig-Lecture** *Lecture Hall 0.115* *“Electroactive polymers in energy conversion”* Jean M. J. Frechet (King Abdullah University of Science and Technology, Saudi Arabia)
10:00-10:30	**BVP Awards** *Lecture Hall 0.115* **Kurt Ueberreiter-Award** Jing Cui (BASF Construction Chemicals GmbH Trostberg, Germany) **Georg Manecke-Award** Daniel Zehm (Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam, Germany) **Award Lecture** *“Amphiphilic Brush Block Copolymers - Putting Different Bristles onto Polymeric Chains”* Daniel Zehm (Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam, Germany)
10:30-11:00	**Coffee Break**
11:00-11:45	**Plenary Talk** *Lecture Hall 0.115* *“Azo polymers for bio-surface switching and the photo mechanical effect”* Christopher J. Barrett (McGill University Montreal, Canada)

11:45-12:30 **Plenary Talk**

Lecture Hall 0.115

“Advanced molecular design of functional materials”
Takuzo Aida (University of Tokyo, Japan)

12:30-13:45 **Lunch**

13:45-14:30 **Plenary Talk**

Lecture Hall 0.115

"Exploring structure and function of natural polymeric materials with synchrotron radiation"
Peter Fratzl (Max Planck Institute of Colloids and Interfaces, Germany)

14:30-16:00 **Parallel Session Solar III**

Lecture Hall 0.307

14:30 *“Use of alkene metathesis for the synthesis of pentacene-containing materials”*
Uwe Bunz (Universität Heidelberg, Germany)

15:00 *“Conjugated polymers via step growth and chain growth polymerizations”*
Michael Sommer (Universität Freiburg, Germany)

15:30 *“Defined nanostructured & supramolecular precision biopolymer architectures as photonic building blocks”*
Stefan Schiller (Universität Freiburg, Germany)

14:30-16:00 **Parallel Session Lithography**

Lecture Hall 0.310

14:30 *“Ultrafast photopolymers for lithographic printing applications”*
Bernd Strehmel (Hochschule Niederrhein, Krefeld, Germany)

15:00 *“Carbon nanomembranes engineered from molecular monolayers”*
Armin Gölzhäuser (Universität Bielefeld, Germany)

15:30 *“Trailored star block copolymer architecture for high performance chemically resists”*
Christian Neuber (Universität Bayreuth, Germany)

16:00-16:30 **Coffee Break**

16:30-18:00 **Parallel Session Optomechanics**

Lecture Hall 0.307

16:30 *"Correlation between local pressure and fluorescence in mechanoresponsive polyelectrolyte brushes"*
Andreas Fery (Universität Bayreuth, Germany)

17:00 *"Polymer films with optically controlled shape and actuation on a nanometer scale"*
Svetlana Santer (Universität Potsdam, Germany)

17:30 *"Photo-shrinkable rigid-rod polymers as building blocks for photodynamic materials"*
David Bléger (Humboldt-Universität zu Berlin, Germany)

16:30-18:00 **Parallel Session Display**

Lecture Hall 0.310

16:30 *"Lithographic patterning of semiconducting polymers"*
Peter Strohriegl (Universität Bayreuth, Germany)

17:00 *"Polymers as universal matrix for highly efficient phosphorescent OLEDs and display applications"*
Hartmut Krüger (Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam, Germany)

17:30 *"Active and passive polarization elements for LC Displays"*
Joachim Stumpe (Fraunhofer-Institut für Angewandte Polymerforschung, Potsdam, Germany)

Abstracts Talks

High Resolution Imaging Technology for Microelectronics

C. Grant Willson

University of Texas at Austin, USA

During the last half century scientists and engineers have devised methods and materials that enable the manufacturing of incredibly small and ever shrinking structures that are the basis of the microelectronics industry. The ability to manufacture such structures and the devices derived from them is a tribute to the ingenuity of man; an accomplishment that has changed society in remarkable ways. This has required fundamental advances in many areas including optics and imaging materials chemistry. Classical photolithography, the process that has enabled this process has now reached physical limits. Efforts to push that technology to provide still higher resolution by the historical paths of wave length reduction, increase in numerical aperture and reduction in the Raleigh constant have been abandoned. Is this the end? Can scaling continue?? Of course it can! It is not over yet!

Various incredibly clever tricks based on relatively simple chemical principles have been devised that extend photolithography, some of which are already in use in full scale manufacturing, but these tricks add complexity to the patterning process and carry an associated increase in cost. The high cost of these clever, but complex processes and the even higher cost of the alternatives threatens to change the economics of the semiconductor manufacturing industry. We will review some of these resolution extension tricks including advances in organic materials for directed self-assembly of block co-polymers and a technique that doubles the resolution of the projection printing process by controlling the kinetics of photochemical steps, but requires no extra processing steps.

Lessons from nature about solar light harvesting: A little bit of coherence?

Gregory Scholes

University of Toronto, Canada

Plants turn sunlight into energy using abundant ingredients like water and carbon dioxide. This living solar cell is the energy hub for life on Earth. Despite such global impact, these are not highly efficient solar cells—but photosynthetic systems exhibit such diversity and agility in adapting to ambient conditions that they serve as inspiration[1]. Identifying and examining some of these inspirations in the context of solar energy conversion using organic materials are the goals of this talk. One aspect I will focus on is evidence for coherent dynamics following femtosecond laser excitation of photosynthetic light-harvesting proteins and what key questions are motivated by this work.

Reference

1 Gregory D. Scholes, Graham R. Fleming, Alexandra Olaya-Castro and Rienk van Grondelle, "Lessons from nature about solar light harvesting" Nature Chem. 3, 763–774 (2011).

THz Spectroscopy: A novel experimental tool to study water network dynamics

Martina Havenith

Ruhr-Universität Bochum, Germany

In recent years a new frequency window has been opened: The THz range. We could demonstrate that precise THz absorption measurements is a new tool to directly study the solvation dynamics of biomolecules[1]. THz absorption spectroscopy probes sensitively the fast (sub-psec) collective network dynamics of bulk water. Accompanying *ab initio* MD simulation unravel the underlying molecular motions: In contrast to the mid infrared regime - where the absorption peaks can be assigned to intramolecular motions - in the frequency regime below 1000 cm^{-1} intermolecular motions with concerted particle motions dictate the spectrum[2]. Precise measurements of absorption coefficients of solvated solutes in the THz regime allow now a detailed view on the role of the water for biological function[3,4,5].

References

1 S. Ebbinghaus, S. J. Kim, M. Heyden, X. Yu, U. Heugen, M. Gruebele, D.M. Leitner, M. Havenith, "An extended dynamical solvation shell around proteins," Proc. Natl. Acad. Sci. USA, 104, 20749 (2007).

2 M. Heyden, J. Sun, S. Funkner, G. Mathias, H. Forbert, M. Havenith, D. Marx Dissecting the THz spectrum of liquid water from first principles via correlations in time and space. Proc. Natl. Acad. Sci. USA, 107, 12068 (2010).

3 D. A. Schmidt, Ö. Birer, S. Funkner, B. Born, R. Gnanasekaran, G. Schwaab, D. M. Leitner, M. Havenith, Rattling in the cage: Ions as probes of sub-ps water network dynamics, J. Am. Chem. Soc., 131(51), 18512 (2009).

4 S. J. Kim, B. Born, M. Havenith, M. Gruebele, Real-time detection of protein-water dynamics upon protein folding by terahertz absorption, Angewandte Chemie Intl. Edition 47 (34), 6486 (2008).

5 M. Grossmann, B. Niehues, M. Heyden, D. Tworowski, G. B. Fields, I. Sagi, M. Havenith (2010), Correlated structural kinetics and retarded solvent dynamics at the metalloprotease active site, Nature Structural & Molecular Biology, 18(10), 1102 (2010).

Tailor-made absorber polymers for efficient organic solar cells

Silvia Janietz, E. Katholing, L. Pabel, A. Lange

Fraunhofer-Institut für angewandte Polymerforschung IAP, Germany

Conjugated polymers have the possibility to be applied as absorber materials in low cost organic photovoltaic. These polymers offer the possibility to be used by solution-processing like printing, doctor blading or spray deposition. The bulk-heterojunction cell concept is used most widely. It consists of a light absorbing conjugated polymer and a fullerene derivative for the ultra fast charge transfer. Poly(3-hexylthiophene) (P3HT) is often studied as the light absorbing polymer in bulk heterojunction solar cells.

P3HT does not present the optimum HOMO and LUMO energy levels with respect to its acceptor counterpart [6,6]-phenylC61-butyric acid methyl ester (PCBM)and with respect to the solar spectrum. A defined lowering of the bandgap, as well as a lowering of the energy offset between the donor-LUMO and the acceptor-LUMO will be desirable. Therefore many research activities were done to design polymers with optimized HOMO and LUMO energy levels to match the solar emission better. Such polymers can be realized through the introduction of alternating electron donating and electron accepting moieties along the polymer backbone to reach bandgaps between 1.8 -1.3 eV. Fluorene based terpolymers with different content of dialkyl substituted diphenyl-benzopyrazine or diphenyl-thienopyrazine and triphenylamine units (MR) were synthesized by Suzuki polymerization. Special attention was spent to increase molecular weights and the solubility of these polymers. Polymers were realized with high molecular weights and with very good solubility in organic solvents. The additional introduction of triarylamine units helps to reach sufficient charge mobilities of such kind of terpolyfluorenes. The alignment of the LUMO energy positions is possible through the introduction of different donor acceptor units in this class of polymers. The introduction of dialkyl substituted diphenyl-benzopyrazine for example in the fluorene main chain leads to LUMO-energy level of 3.1eV and in solar cells to an open circuit voltage of 0.96 V. Different compositions of the terpolymers were studied in solar cells. Organic solar cells were prepared with inkjet printed or spin coating active layers consisting of the novel absorber polymer blended with PC61BM in a ratio of 1:2. Different solvent systems were used when inkjet printing including chloro-/trichlorobenzene or anisole/tetralin. It was found that devices prepared from the chlorine-free system showed only slightly lower efficiencies with respect to the chlorinated system, 2.5 as compared to 3.5%, respectively.

Charge generation and extraction in polymer-based solar cells

Dieter Neher

University of Potsdam, Germany

The performance of polymer-based organic solar cells has dramatically improved during the last years. Understanding the photocurrent loss in present material systems by quantifying the efficiencies of elementary steps governing generation und extraction of carriers is of major importance for future device optimization.

In this talk, generation and extraction of charge in polymer-based solar cells is quantified by performing time-delayed extraction experiments. The results are related to chain aggregation in blends of conjugated donor polymers with small molecules or polymeric acceptors. Optical spectroscopy is used to determine the degree of crystallinity and to extract information on the size and perfection of polymer aggregates in such blends.[1] For P3HT:PCBM, the efficiency for free carrier generation in both as-prepared and annealed blends is found to be independent of electric field, meaning that the photogenerated current is entirely determined by the field-driven sweep-out of carriers in competition with non-geminate recombination.[2] We find that layer crystallinity is not a key parameter determining the solar cell performance, while the probability to extract photogenerated holes from the blend layer is highly correlated to the degree of energetic order in the polymer crystallites . In contrast, blends of the low bandgap polymer PCPDTBT with PCBM exhibit a pronounced field-dependence of charge generation, suggesting efficient geminate recombination.[3] We show that the efficiency of geminate and non-geminate recombination in these blends is correlated to the blend morphology, and that both decay channels are strongly reduced in blends with extensive interchain order.[4]

References

1 S.T. Turner, P. Pingel, R. Steyrleuthner, E.J.W. Crossland, S. Ludwigs, D. Neher, Adv. Funct. Mater. 2011, 22, 4640.

2 J. Kniepert, M. Schubert, J.C. Blakesley, D. Neher, J. Phys. Chem. Lett. 2011, 2, 700.

3 S. Albrecht, W. Schindler, J. Kurpiers, J. Kniepert, J.C. Blakesley, I. Dumsch, S. Allard, K. Fostiropoulos, U. Scherf., D. Neher, J. Phys. Chem. Lett. 2012, 3, 640.

4 S. Albrecht et al, JACS, in press DOI: 10.1021/ja305039j.

NMR investigations of crystallinity and supramolecular organization in polymers for photovoltaics applications

Ovidiu Pascui[1], Anja Achilles[1], Marcio F. Cobo[2], Eduardo deAzevedo[2], Jens Balko[1], Thomas Thurn-Albrecht[1], Kay Saalwächter[1]

[1]*Univ. Halle-Wittenberg, Institut f. Physik, Halle (Saale), Germany*

[2]*Univ. de Sao Paulo, Sao Carlos, Sao Paulo, Brazil*

Molecular weight and stereoregularity affect the morphology and the crystallinity of conjugated polymers and are thus of pivotal relevance for the mobility of charge carriers in electro-optical device applications. We use 13C and 1H solid-state NMR techniques, in combination with DSC and X-ray scattering techniques, to determine the crystallinity, the supramolecular arrangement, and details on crystal-crystal phase transformations in regioregular head-to-tail P3HT of well-defined molecular weight as well as in P(NDI2OD-T2). For P3HT, we could show that the crystallinity was previously severely underestimated[1]: typical crystallinities range between 40 and 70% upon increasing the molecular weight. We were able to derive a corrected reference melting enthalpy of about 37 J/g for use in DSC experiments. Using one- and two-dimensional NMR, we observe that the crystal-crystal phase transition between a 3D- and a 2D-ordered crystalline phase at around 60 °C entails a structural disordering process of the alkyl side chains, while not affecting the backbones. The formation of the 3D-ordered phase is kinetically suppressed at higher molecular weights. This phenomenon is studied in detail for different preparation conditions, focussing in particular on thin films. Details of the supramolecular packing arrangement of P(NDI2OD-T2) under different preparation conditions are studied by 1H high-field high-resolution NMR.

Reference

1 O. F. Pascui et al., Macromolecules 43, 9401 (2010).

Infrared - Transition Moment Orientational Analysis

Friedrich Kremer, W. Kossack, P. Papadopoulos

Universität Leipzig, Germany

A novel spectroscopic approach is presented, that reveals a complete characterization of the quadratic averaged orientation of infrared transition dipole moments in any IR-translucent material. Based on Maxwell's equations and the quantum mechanic transition probabilities, a connection between optical and molecular properties is derived, that enables one to characterize the molecular order in all three-dimensions displayed here as order parameter matrix [1-3]. Since the method takes advantage of the specificity of the IR spectral range the initial orientation distribution as well as its response to external excitation can be traced in detail for each moiety. The analysis is focused on the specific absorption bands; therefore, no refined knowledge of the dielectric tensor is achieved or needed.

As examples smectic liquid crystalline elastomer films[1], semi-crystalline polyethylene films[2] and liquid crystals confined in nanoporous silica membranes[3] are studied proving the versatility of the approach.

References

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2 Kossack, W., P. Papadopoulos, M. Parkinson, F. Prades, F. KremerPolymer 52, 6061-6065 (2011)

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Characterization of shape switching of polymers induced by light

R. Thiermann, D. Bléger, T. Liebig, J.P. Rabe, S. Hecht, Michael Maskos

Institut für Mikrotechnik Mainz, Germany

The light induced change of the shape of polymeric molecules still is a challenging task both, for synthesis and characterization. The investigation of artificial systems that undergo structural changes upon external stimuli are enjoys still steadily growing interest. We report on the state-of-the-art characterization of a polymer system with embedded photoswitches which act as hinges, which upon light induced isomerization lead to reversible shrinking and stretching of the polymer backbone. Especially the light scattering of the complex architecture will be presented and discussed. In addition, other examples of different methods of characterization of polymers and nanoparticles including light scattering will be presented, emphasizing the necessity of a combined analysis in order to gain insight into polymeric properties.

Oscillation of DNA recognition observable on fluorescence shift?

M. Sajadi, K. E. Furse, X.-X. Zhang, L. Dehmel, S. A. Kovalenko, S. A. Corcelli, Nikolaus P. Ernsting

Humboldt-Universität zu Berlin, Germany

Low-frequency structural vibrations of proteins and DNA are important for their physiological functions, and these motions are altered when biomolecules interact with each other and with small molecules. As a model we examine the DNA duplex d(CGCAAATTTGCG)2 together with the bis-benzimidazole dye Hoechst 33258 (H33258), which recognizes and binds to A:T-rich regions in the minor groove. Dynamical aspects of recognition are increasingly seen to be essential for inter- and intracellular signaling networks, enzyme catalysis, and allosteric regulation. Improved strategies for drug discovery also consider the flexibility of the biomolecular target. But despite its importance, vibrational motion of ligand dye binding was not yet observed because (i) infrared spectroscopy is not selective for the binding coordinate and (ii) stationary Raman spectroscopy at low frequencies (~THz or 30 cm^{-1}) is dominated by Rayleigh scattering. Here we show that binding oscillations can be seen with the help of ligand fluorescence. Frequency modulation of the time-dependent Stokes shift (TDSS) may reflect coherent in/out motion of the ligand, synchronous with breathing of the minor groove. The observation method is spatially selective and sensitive, compared to THz absorption measurements, and may become useful through advances in fluorescence gating.

Blockcopolymer - Nanocrystal Hybrids for Optoelectronic Applications

Lisa zur Borg, Jaehoon Lim, Donggu Lee, Chang-Hee Lee, Seonghoon Lee, Kookheon Char, Rudolf Zentel

University of Mainz, Germany

Semiconducting polymers combined with inorganic semiconductors offer exciting possibilities for optoelectronic devices like LEDs or organic solar cells. The properties of the polymers can be adjusted by systematically tuning their chemical structure. The inorganic part, on the other hand, contributes high charge carrier mobility. Nanostructured materials in particular, such as quantum dots or tetrapods, display fascinating properties because of the quantum size effect. By bringing these two materials together, hybrids with improved performance ca be formed.

To get these hybrids we synthesized new block copolymers, which consist of long, solubility-enhancing semiconducting blocks, and short anchor blocks. Two different kinds of polymers have been synthesized: Poly-(p-phenylene vinylene) (PPV) with a defined end group by Siegrist polycondensation and a modified triphenylamine based polymer by RAFT Polymerization. Especially the PPV block copolymer offers a great variety of new functional block copolymers, because nearly any functionality can be easily introduced.

We show that CdSe tetrapods which are functionalized with PPV block copolymer can be well dispersed in a polymer matrix. On the contrary, a blend consisting of tetrapods and polymer without anchoring groups shows aggregates and a poor film formation. The assembly of the hybrid system can be precisely tuned by adjusting the amount of polymer on the surface. This morphology is considered ideal for hybrid solar cells because the tetrapods form a large interconnected network, with their thin arms allowing the exciton to easily dissociate.

Modular polymer-based architectures for efficient multiple charge-separation: Redox-active polymers and decoration with luminescent ruthenium complexes

Robert Schroot, Christian Friebe, Ulrich S. Schubert, Michael Jäger

Friedrich-Schiller-University, Jena, Germany

Modern polymer chemistry offers a variable design of functional materials, e.g. by controlled and living polymerization techniques, functional monomers and initiators, powerful analytical analyses etc. In view of the long-standing goal to efficiently convert light energy into (electro)chemical energy, a photoactive unit must be combined with suitable electron donor and acceptor sites to accommodate the generated charges. In order to prevent unproductive recombination processes, the individual energy and electron transfer steps must be well tuned. A polymer-based approach is devised, taking into account the most important functional and synthetic features and requirements for the design. The modularity of the strategy enables the individual tuning of the photo-redox properties, in particular of the ruthenium sensitizer. First experimental results of the nitroxide-mediated polymerization (NMP) of a few redox-active monomers (substituted triarylamines, or naphthalene diimide) are presented. The defined incorporation of a long-lived photoactive ruthenium complex at the chain terminus ensures the future directional charge separation and accumulation within the polymer chain, which is complemented by photophysical and electrochemical analyses.

Polymeric Heptazine Networks for Photocatalytic Water Splitting

Kamalakannan Kailasam, Arne Thomas

Technical University Berlin, Germany

Polymeric graphitic carbon nitrides, composed of amine bridged heptazine moieties have attracted much interest in recent years. This is mainly due to their semiconducting properties which make them efficient heterogeneous photocatalyst for the production of hydrogen and oxygen from water under visible light[1]. Various approaches to improve their performance as photocatalyst have been reported, e.g. doping with heteroatoms, the introduction of porosity or the formation of semiconductor composites[2-5]. Polymeric carbon nitrides are so far exclusively produced by high temperature treatment of precursors such as melamine, which however limits the control on the chemical structure and microstructure of the networks. Herein, we report the successful synthesis of a heptazine based monomer which can be polymerized in solution in a highly controlled manner, yielding polymeric heptazine based networks. By choosing different co-monomers the chemical structure of these networks can be tailored and different functionalities can be introduced. Furthermore the formation of heptazine based polymers with intrinsic microporosity is possible[6,7]. These polymers are potential candidates in emerging energy related applications, in particular as photocatalyst for water splitting and in photovoltaics. First results on the application of this novel class of polymer networks will be presented.

Reference

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2 F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, (2006) Angew. Chem.-Int. Edit., 45, 4467-4471.

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4 Y. Wang, Y. Di, M. Antonietti, H. R. Li, X. F. Chen, X. C. Wang, (2010) Chem. Mater. , 22, 5119-5121.

5 K. Kailasam, A. Fischer, J. Zhang, X. C. Wang, M. Antonietti, A. Thomas, To be submitted.

6 A. Thomas, (2010) Angew. Chem.-Int. Edit., 49, 8328-8344.

7K. Kailasam, J. Schmidt, H. Bildirir, A. Thomas, To be submitted.

Polymer characterization using hard X-rays for revealing solution and solid state structures

Andreas Thünemann

BAM Federal Institute for Materials Research and Testing, Berlin, Germany

We report on the characterization of polymers, nanostructured polymers and polymeric nanoparticles using hard X-ray methods such as small-angle X-ray scattering (SAXS). Recent advances in the field are reviewed and described in selected examples. Advantages and disadvantages of conventional X-ray instruments are compared with the strength and limitations of synchrotron X-rays.

Examples of investigation are light emitting diodes of nanostructured polyelectrolyte surfactant complexes, the development of polymer stabilized nanoparticles for modern reference materials (Nano-RMs), solid lipid and nano lipid nanoparticles.

The coupling of separation techniques such as field-flow fractionation with X-ray analysis of polymers and polymer stabilized nanoparticles is demonstrated for its use in investigation of commercial water-soluble polymers like poly(styrene sulfonate)s, poly(acrylic acid)s, poly(vinyl pyrrolidone)s etc.

The benefit of combining SAXS with X-ray absorption fine structure spectroscopy (XAFS) for revealing the structure of metal nanoparticles in polymeric micelles and metal-containing polyelectrolytes is explained.

Characterization of Nanoporous Polymers by X-ray Scattering

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Nanoporous polymers received increasing attention during the last years. They have potential in a broad variety of applications, such as separation science and catalysis. Significant advances have been made on the synthesis of such polymers. The characterisation of their porosity is however often not trivial compared to their inorganic counterparts. The flexibility and elasticity of porous polymers are responsible for a lot of effects such as pore collapse or deformation, which make it difficult to use classic porosimetry methods. Wide-angle and small-angle X-ray scattering (WAXS; SAXS) can be used to gain information about the porosity of polymers based on the electron density contrast between the polymer chains and the empty (or solvent-filled) pores.Here, we demonstrate the use of WAXS and SAXS for the characterization of microporous (D < 2 nm) and mesoporous (2 < D < 50 nm) polymers. The use of WAXS as a method to obtain a measure of interchain distances, which themselves can be regarded as a measure of the intrinsic microporosity, is presented.[1] The potential and limitations will be shortly discussed.

The main focus of the paper is on the use of SAXS to analyze the mesopore collapse/deformation process.[2] We present the results of in-situ SAXS observations of the processes upon solvent removal. The acting forces are discussed in order to understand the complex picture which is observed.

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Smart Microgel Capsules and Model Colloids Tailored by Photocrosslinking in Droplet-Based Microfluidics

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Micrometer-sized, responsive polymer gel particles can be produced with exquisite control through the use of droplet-based microfluidics. The idea of this approach is to use emulsion droplets as templates for the particle synthesis and to control the size, shape, and monodispersity of the microgels by controlling the size, shape, and monodispersity of the pre-microgel droplets. To extend this control towards controlling the material properties of the microgels, droplet-based microfluidic templating can be combined with the use of functional, macromolecular precursors that are selectively crosslinked by a photochemical pathway[1].This approach separates the polymer synthesis from the particle gelation and allows each to be controlled independently. In particular, the use of spatially-resolved photoreactions to achieve the microgel gelation allows complex particle morphologies such as hollow[1], anisotropic[2], or multi-layered microgels[3] to be formed and complexed with additives such as magnetic materials or living cells. These particles can then be used for the encapsulation and controlled release of actives[3].

In addition to their utility for encapsulation, responsive microgels can serve as model systems to explore how the particle composition affects the microgel thermodynamics[4]. An important parameter that has been overlooked or even ignored in many previous investigations is the nanometer-scale spatial heterogeneity of gels. While it is known where this inhomogeneity stems from, much less is known about how it affects the gel behavior, specifically how it affects the reversible swelling and deswelling of sensitive gels. To close this existing gap, microfluidic devices and photocrosslinking chemistry can again do a great job: the use of photocrosslinkable, macromolecular precursor polymers allows microgels to be formed that exhibit considerably higher internal nanoscale homogeneity than gels formed by classical, free-radical chain-growth reactions. These gels can then serve as models to systematically study the impact of polymer network inhomogeneities on the properties of sensitive microgels[4].

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Electroactive polymers in energy conversion

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The design of functional polymers for applications in energy conversion is explored. For example organic polymers or blends of polymers and small molecules are attractive for the conversion of light into energy, or energy into light. Therefore, site isolation of light emitting chromophores within block copolymers[1] or discrete organic nanoparticles[2] may be used to create organic white light emitting diodes based on a single multichromophoric organic layer. Similarly, light absorbing conjugated macromolecules may be designed for application in photovoltaics. In this instance molecules capable of transporting electrons must be combined with hole transporting molecules in blends for which the required critical control of phase morphology is achieved through molecular design[3-5].

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Azo Polymers for Bio-Surface Switching and the Photo-Mechanical Effect

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Polymers based on azobenzene are mimics of the retinal photo-switch that enables vision, responding physically and mechanically to permit solar energy to be converted directly to mechanical work. Reversible changes in surface energy are also inducible as a result, for a variety of reversible surface energy switching applications via light. Irradiation with light in the solar spectrum at sun-like intensities has been shown to lead to a measurable reversible photo-expansion of these coatings, of up to a few %, allowing the materials to function as photo-mechanical switches or light energy harvesters and actuator devices. New azo polymers to optimize this effect were developed, and some simple macroscopic devices were fabricated with them to that take mechanical advantage of this effect for larger scale motion driven by sunlight, such as bending, 'walking', rolling and other applications as 'artificial muscles'. The mechanism for this effect will be discussed from studies using ellipsometry, light-bending of AFM cantilevers, surface plasmon resonance spectroscopy, and neutron reflectometry. Examples of switching at the biological interface will also be presented, using visible light to remotely control and direct cell growth and function.

Advanced molecular design of functional materials

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Owing to a tremendous progress in supramolecular chemistry, one can now construct and tailor a variety of desired nanostructures, where assembling events involved mostly operate thermodynamically. On the other hand, if one may consider developing materials for practical applications, we certainly need to design kinetically preferred hierarchical structures. However, there is no rational molecular design strategy for this issue.

Here we report some of our recent achievements related to this issue. The first topic focuses on how one can translate a tiny molecular motion into a macroscopic motion.[1] We found that, by hot pressing using unidirectionally drawn Teflon sheets, a polymer brush containing triply connected azobenzene units in its side chains form a hierarchically ordered bimorph film, where all the cylindrical brush objects align homeotropically with respect to the film plane, and the film shows a macroscopic photomechanical motion. The second topic features the development of 'aqua material', characterized by an ultralow content of organic components and an ultrahigh content of water.[2] This material can be prepared by mixing in water clay nanosheets and a dendritic molecular binder with sticky guanidinium ion functionalized dendron wedges on both sides of a poly(ethylene glycol) spacer, giving rise to the formation of a well-developed 3D network over a macroscopic length scale. The third topic features our quite recent achievement on the formation of a linear semiconducting heterojunction by stepwise supramolecular polymerization.[3,4] This sequential control in supramolecular polymerization gives a clue for how to escape from a thermodynamic equilibrium. We also succeeded in designing the first columnar ferroelectric liquid crystal.[5]

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Exploring structure and function of natural polymeric materials with synchrotron radiation

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Natural materials as different as bones, teeth, wood, grass, mussel byssus, spider cuticle or glass sponge are generally based on proteins, polysaccharides and various inorganic minerals. Through evolutionary adaptation they have acquired multifunctional properties deriving from a complex internal structure over several length scales. Synchrotron radiation provides powerful tools to help elucidating the relation between the materials' properties and their hierarchical structures. The talk will discuss examples for the use of position-resolved and in-situ x-ray scattering in the study of protein- and polysaccharide-based biomaterials with mechanical function.

Use of Alkene Metathesis for the Synthesis of Pentacene-Containing Materials

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We have developed a synthetic approach towards novel pentacene containing polymers using ring-opening metathesis polyerization (ROMP). We present herein the synthesis of the advanced monomers, the synthesis of the polymers and their optical and structural properties. We also discuss their use in thin film transistors. While these polymers contain pentacene units they are not formally conjugated but carry the acene units as part of a polynorbornene structure. The material can be obtained easily in large quantities and with excellent purity.

Conjugated polymers via step growth and chain growth polymerizations

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Conjugated polymers (CP) are intriguing materials for the use as active materials in organic electronic devices. Understanding structure formation in semi-crystalline CPs is key prior to the use of such complex materials in applications. Here we present chain growth and step growth polymerizations to synthesize semicrystalline donor and acceptor conjugated polymers, and present detailed structural investigations. The Kumada Catalyst Transfer polymerization (KCTP) is used to prepare end-functionalized poly(3-hexylthiophene) (P3HT), defect-free P3HT with a regioregularity of 100 %, and naphthalene-diimide thiophene (NDI-T2) copolymers. Step growth polycondensations such as Suzuki and Stille coupling are used where chain growth polymerizations reach their limit, specifically for the preparation of electron acceptor polymers NDI-Tx copolymers with assymmetric repeat units. End group analysis, molecular weight, polydispersity and structure formation are discussed in detail, from which general conclusions are drawn.

Defined Nanostructured & Supramolecular Precision Biopolymer Architectures as Photonic Building Blocks

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The advantageous properties of biological polymers include the ability to custom design & tune their chemical composition and structure allowing for defined & highly reproducible hierarchically organized biohybrid nanoarchitectures.[1]

Building blocks which allow for the defined synthesis of large nanoscopic structures in 2 and 3D are of special interest for nanoscopically structured catalysts and light harvesting bio- platforms.[2] This approach is complemented with additional tools to improve the ability to control protein functionality. These techniques comprise the site-selective incorporation of unnatural amino acids with bioorthogonal reactivity in vivo. Striving for new functional architectures for light converting biohybrid materials we utilize the power of synthetic biology combined with organic and macromolecular chemistry to create new protein conjugates e.g. for yoktowell sized protein architectures.

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Ultrafast Photopolymers for Lithographic Printing Applications

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Digital exposure of lithographic materials for printing applications based on photopolymers can be carried out either in the NIR (810 or 830 nm) nm or in the violet part (405 nm) resulting in a photospeed of 30-100 mJ/cm² and 30-100 µJ/cm², respectively. Such high speed systems require the design of light sensitive materials and thermal stable initiator systems with acceptable resolution. They usually work on the basis of an electron transfer system based on a singlet mechanism in which three components irreversibly generate initiating radicals with high efficiency. These are the sensitizer absorbing either in the violet or NIR and two coinitiator components. Such systems prevent the electron back transfer although the photochemical reaction scheme bases on a singlet mechanism. Furthermore, the monomer and the binder possess also a key function in such systems.

The study of such systems requires to establish methods reliably characterizing photospeed, resolution, stability of microstructure elements on press, and the transfer of functional materials to the substrate in the press machine. Applications can be widely found in the printing industry (newspapers, commercial printing, printed electronics), where such materials have been accepted as consumables, and imaging. A few examples will show the development of digital lithographic materials operating in computer to plate (CtP) systems. Our examples demonstrate the ultimate interplay of all components (initiator system, monomers, binder, contrast dye, additives) to obtain finally a lithographic system fulfilling the requirements of modern printing.

Carbon Nanomembranes Engineered from Molecular Monolayers

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A scheme for the fabrication of extremely thin (~1nm) carbon nanomembranes is presented. The first step is the formation of a self-assembled monolayer (SAM) of amphiphilic molecules. Then the SAM is exposed to electron or UV-irradiation that leads to a dehydrogenation, followed by a cross-linking between neighboring molecules. The cross-linked SAM can be released from the surface, forming a self-supporting carbon nanomembrane (CNM) with properties that are determined by the constituting molecular monolayer. CNMs can be further processed, for example perforated or surfaces functionalized. Pyrolysis transforms CNMs into graphene. It will be shown that CNMs can be engineered with a controlled thickness, conductivity, permeability and elasticity. Advanced microscopic (helium ion microscopy) and spectroscopic methods as well as functional tests are applied to investigate the CNMs.

Tailored Star Block Copolymer Architecture for High Performance Chemically Amplified Resists

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We present for the first time star block copolymers for their application as high performance resist materials. This polymer architecture offers besides their controlled spherical shape also defined monomer incorporation and positioning due to the shell-like structure. The tailored star block copolymers were synthesized utilizing the core-first ATRP route by full conversion of a first monomer and in-situ polymerization of additionally added monomer resulting in narrow polydispersity indices (PDIs < 1.2). The new star block copolymers demonstrated their excellent solubility contrast in the exposed state and their up to eight times increased sensitivity in comparison to the reference linear polymer. The most sensitive star block copolymer was investigated in a ternary combinatorial library - exposure dose and feature size, PEB temperature, and development time - for its lithographic performance. In the optimized sector, well-defined 1:1 line/space patterns down to 66 nm with LER values of about 6 nm were achieved utilizing a 20 kV electron-beam tool. As future high resolution resists for even smaller feature widths will be limited by molecular size, further investigations concerning star block copolymers with reduced molecular weight and reduced monomer block composition will provide opportunities for further improvement of patterning performance. In summary we have successfully demonstrated that tailoring the molecular architecture towards a star block copolymer provides a significant improvement in realizing a new generation of high-sensitivity and high performance resist materials.

Correlation Between Local Pressure and Fluorescence in Mechanoresponsive Polyelectrolyte Brushes

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Mechanoresponsive materials convert mechanical stimuli into optical, electrical or chemical signals. In this contribution we introduce cationic, fluorescently labeled polyelectrolyte brush, in which brush compression results in fluorecence quenching as a novel approach towards mechano-optical coupling. Sensitivity and lateral resolution of these systems are gauged using the so-calledsoft colloidal probe technique[1]: A soft elastomeric bead is attached to an AFM cantilever, such that it can be integrated into a combined AFM-Confocal Laser Scanning Microscopy (CLSM)system. The in situ combination with CLSM permits to correlate local pressure in the beads contact area with local fluorecence. Thus a fluorecence-response function for a range of pressures can be determined. We find a high pressure sensitivity in the order of (1 kPa) and a lateral resolution better than 1 μm^2, making these systems very attractive for studaing pressure distributions in complex contact or adhesion scenarios. We discuss perspectives in the field of bioinspired adhesion.

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Polymer films with optically controlled shape and actuation on a nanometer scale

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We have recently suggested that it should be possible to move or reposition strongly adsorbed nano-objects with relative ease, in large number and simultaneously. The essential idea is not to put more effort in fighting against the prevailing surface forces but rather to utilize them - in clear contrast to current techniques of nanomanipulation with atomic force microscopy (AFM)[1]. For this, the topography of hosting film should be capable of reversibly switching between different states by changing the external conditions, and producing morphology changes at the scale of the size of objects to be moved.

In this work, we choose light as stimulus for changing the polymer topography. Here we present photosensitive azopolymer thin films[2,3] with integrated optically active metal elements supposed to support and steer the response of polymer films to external UV-illumination by acting as nanoscale antennas. During UV irradiation at a certain wavelength surface plasmon waves are generated on a metallic mask. The interaction of the surface plasmon waves with azopolymers results in printing of near field intensity distributions in to film topography with the pattern size below the diffraction limit. We found that the topography can be driven to change patterns reversibly by changing polarization or wavelength of the incident light. We also examine how the structuring process depends on the size of the metal patterns. The results are confirmed by FDTD simulations.

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Photo-shrinkable rigid-rod polymers as building blocks for photodynamic materials

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Photochromic molecules, capable of efficient and reversible photochemically induced interconversion between (at least) two (meta)stable isomers associated with markedly different properties, are being implemented in a variety of systems for applications ranging from optical devices to stimuli-responsive materials.[1] We have recently been engaged in using macromolecular scaffolds to exploit photoswitches for the translation of a light stimulus into macroscopic motion.[2] For this purpose, photoswitchable anisotropic oligomers and polymers have been designed[3] that dramatically change their geometry upon light irradiation. In their main chain the rigid rod polymers incorporate azobenzene photochromes, which upon light-induced isomerization reversibly shrink and stretch the backbone, resembling light-orchestrated macromolecular accordions.[4] It is anticipated that the large photodeformation that azobenzene-containing rigid rods experience at the single-molecule level could - after alignment - be collected and further amplified, giving rise to materials exhibiting photoactuations of large amplitude.

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Litographic patterning of semiconducting polymers

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Semiconducting polymer have gained large interest during the last decade due to potential applications in OLED-displays, organic electronics or organic solar cells. In particular OLEDs are already used in flat panel displays. In view of the applications mentioned above patterning techniques are of particular interest for the production OLED devices, organic solar cells and organic field effect transistors. A number of patterning techniques are known, which can be divided into top-down and bottom-up approaches. A typical bottom-up approach uses the self-assembly of materials (e.g. block copolymers). With this strategy very small feature sizes are accessible, but there are severe limitations in the shape of possible structures, which is predetermined by the interplay of forces between different materials in the self-assembly process. The formation of patterns with arbitrary shape is a big advantage of top-down methods like printing and lithography. Usually small feature sizes in the range of 100 nm are the domain of photolithography.

We present a lithographic approach for the formation of polymer multilayers and micrometer sized microstructures from photocrosslinkable polyfluorenes and polyfluorene copolymers.

For this purpose we synthesised fluorene based polymers with photopolymerisable acrylate groups. Subsequent photopolymerisation leads to densely crosslinked and insoluble polymer films. By using a µm-sized photoresist test mask patterns of semiconducting polymers with a minimum size of 500 nm are formed.

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Polymers as universal matrix for highly efficient phosphorescent OLEDs and display applications

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The application of polymer based phosphorescent light emitting devices is very attractive for the preparation of large area and fine-pixel displays. In this case the light emitting layer can be prepared by wet processes like ink-jet printing. So, phosphorescent small molecules together with charge transport materials were blended with a polymer matrix like polyvinylcarbazole (PVK) to be used as the emitting layer in PLEDs[1]. Migration and aggregation processes and phase separation could be appearing during device lifetime when the different molecules are not attached covalently to the polymer matrix. These processes could be responsible for the extraordinary fast degradation in such phosphorescent blend layers.

An alternative strategy is to link covalently the charge transport molecules and the phosphorescent dopands to a non-conjugated polymer. In such matrix systems the polymer backbone does not take place in charge transport or emission. It realizes an unlimited mixing of active side groups, making it responsible for a stable morphology. In this context we used polystyrene for a phosphorescent triplet emitter system because of its chemically inert and optical stable backbone. First, simple well-known hole-transporting, electron-transporting and phosphorescent molecules were attached covalently as side chains to the polystyrene backbone[2,3]. The composition of the copolymers is verified concerning the three comonomers to optimize the device parameters.

Later on, more accelerated Ir–complexes, electron-transporting and hole-transporting molecules were synthesized as components for these polymer phosphorescent systems[4]. They were used like a tool box for the further optimisation of the PLED performance and lifetime. The maximum performance reached in our device setup was 61 cd/A @ 1000 cd/m^2 with a lifetime LT$_{50}$ of 66.000 h @ 1000 cd/m^2 for green which is an outstanding performance for polymers.

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Active and Passive Polarization Elements for LC Displays

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Thinner, lighter, faster, cheaper LCDs are distinguished by lower power consumption, improved view angle and brightness. The next step will be 3D displays which require a significant improvement of the light management. For the optical functions in LCDs a number of different polymer based optical films, such as photo-aligning layer, thin film polarizer, retarder, waveguide, antireflection layer, diffuser and polarization gratings are required. Photo-alignment of LCs, reactive LCs and LC polymers opens new ways for a wide range of passive and active polarization elements. Different methods of bulk photo-alignment of polymers and LC composites will be discussed. A new way to achieve aligned films is the light induced orientation of photosensitive polymers. Advantages of such processes are the defined control of the orientation direction, tilt angle, order parameter and their pixelwise modification at room temperature. Using LC polymers the photo-induced order at room temperature can be significantly amplified by the thermotropic self-organization annealing above Tg. It results in extraordinary high values of optical anisotropy. Electrically switchable polarization sensitive diffraction gratings were generated by interference exposure of LC composite materials. Holographic photo-polymerization generates phase separation forming a stripe-like periodic structure consisting of polymer walls alternated with channels of planar aligned LCs. The droplet-free morphology of switchable polarization holograms provides diffraction efficiency of about 99% with excellent optical properties.

Abstracts Posters

Polymer characterization across the entire optical spectrum

Polymethacrylates Containing Conjugated Oligo(phenylene ethynylene)s as Side Chains for Resonance Energy Transfer and Energy Funneling

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Nowadays, molecular comb-polymers are underrepresented in the area of optical active materials. In order to overcome the bad solubility behavior of conjugated polymers, the optical active moieties were directly attached to the polymer backbone as side-chains in this contribution. The design and synthesis of new comb polymers with π-conjugated oligomers as side-chains is described in order to combine the well-defined optoelectronic properties of a series of oligomers (i.e. various monodisperse oligo(phenyleneethynylene)s attached to a methacryl end group) with typical processing properties of common polymers. The monomers were polymerized using the reversible addition fragmentation chain transfer (RAFT) method. The precisely defined length, conformation, and constitution of the monomers allow a reliable prediction of structure- property relationships, which is not the case for π-conjugated polymers. The close spatial arrangement of the conjugated oligomers in the polymer chain leads to increased intermolecular interactions (e.g., via π-stacking) compared to the isolated and independent oligomers. As a consequence, the polymers presented are capable to act as light harvesters possibly for artificial photosynthetic systems. Due to short inter-chromophore distances and adequate spatial arrangement, the polymers at hand allow for resonance energy transfer (RET) and energy funneling from a donor to an acceptor.

A competitive displacement of labeled analytes - read out through fluorescence quenching for multiple recognition as a diagnostic tool

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Fast and reliable detection of viruses like influenza or MRSA is still one of the major problems in medicine. In particular fast test systems giving a reliable read out of the specific virus type are often required for preventing the spread out of a disease or for fast medical treatment. The Lab in a Hanky project focuses especially on a simple to use fast read out in vitro sensor test for viruses or bacteria. The approach we are following in our part of the project is based on the read out of a binding or non binding event of a virus through a fluorescence-fluorescence quenching read out. Using sample recognition-analyte systems like Avidin-Biotin or Cyclodextrin-Adamantan we are labeling the complementary pair with a fluorophor and a quencher. When binding to the complementary which is covalently bound to a polymer backbone the quencher and the fluorophor should be in a distance to each other where efficient quenching can occur. Through displacement of one of the labeled components by a better binding partner fluorescence enhancement should take place und thus signalize the binding event. Having multiple fluorescence-fluorescence quenching events by using different fluorophor-quencher systems more specific detection can be generated.

New insight into colloid-solvent interactions analyzed by Thermal field-flow fractionation

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Chemical and physical properties of colloids in aqueous dispersions are dominated by their surface properties caused by the large surface to mass ratio. Investigation of interactions at the particle-solvent interface provides information about the particle surface. In addition, slight variations of the particle-solvent interface generate substantial alteration of thermophoresis, which itself is still a not completely understood phenomenon [1]. This phenomenon is studied in thermal field-flow fractionation (ThFFF), a quasi-chromatographic technique to fractionate colloids with respect to their thermophoretic mobility [2]. We present the influence of zeta potential and type of electrolyte on retention behavior in ThFFF [3]. A relation to theoretical models of thermophoresis is revealed by observation of thermoelectric effects. The capability of ThFFF to separate particles with equal hydrodynamic size, as determined by dynamic light scattering (DLS) and asymmetrical flow field-flow fractionation (AF-FFF), is demonstrated. In addition, we discuss the potential to determine particle surface properties by thermophoretical investigations.

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Photon Density Wave spectroscopy for the optical characterization of highly concentrated polymer dispersions

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The optical characterization of highly concentrated polymer dispersions is often hindered by the combined occurrence of absorption and multiple scattering of light. For such systems, Photon Density Wave (PDW) spectroscopy permits the independent and dilution-free measurement of the absorption and reduced scattering coefficient. These properties describe the material in its physical and chemical condition. PDW spectroscopy is based on transport theory for photon propagation in multiply scattering material. In conjunction with Mie theory and theories for dependent light scattering, sizes of the polymer particles are deduced. Dilution-free characterization can be performed for both nano- and micrometer sized particles. Thus, with a time resolution > 1 min^{-1}, it is the only suitable process analytical technology for both size ranges at the moment. For example, PDW spectroscopy was applied successfully for the characterization of the formation of polymer particles. Suspensions and emulsion polymerization of statistical copolymers in industrial scale will be discussed. Additionally, as an example for the optical characterization of functional polymers, the temperature induced switching of Poly-N-isopropylacrylamide (PNIPAM) was investigated. In a dispersion of core-shell-particles, with PNIPAM as a layer on a polystyrene core, it was found that the scattering and absorption properties change independently of each other. The individual temperature dependencies of the optical coefficients can be understood on basis of the molecular switching process. Thus, PDW spectroscopy provides a fascinating insight into physical and chemical processes within such dispersions. Improved process understanding and modeling should therefore give a new key to innovative ideas for functionalized polymers.

Boronic acid containing polymers as sugar sensors

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Well-defined glucose responsive polymers are favourable for the development of glucose responsive drug carriers but also as soluble glucose sensing systems. Hydrogels that consist of boronic acid monomers combined with thermoresponsive monomers to amplify the solubility response were recently established to undergo sugar induced swelling. In this work we introduce the development of a simple synthetic procedure for preparing boronic acid containing polymers. Moreover, the copolymerization of solvatochromic dyes was intended to lead to glucose sensors. This aim was followed by translation of the polymer phase transition, which is accompanied by a change in the polarity around the polymer chain, translating it into an optical or fluorescent response of the solvatochromic dyes. Such sensing mechanisms are not yet known for glucose-responsive or molecule- responsive polymers.

Phosphorescent sensitive paints based on platinum dyes

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Dual imaging is of importance in life science, medicine, as well as in aerodynamics. Special sensitive paints are required for dual imaging of barometric pressure and temperature. For this, sensitive coatings are prepared, which are comprised of three different microparticles that are dispersed in a film of a polyurethane hydrogel. In our current approach we introduce the fabrication of sensitive microparticles that carry dyes also on a phosphorescent basis. Therefore, the reference dye 9,10-diphenylanthracene (DPA) is incorporated in poly(acrylonitrile) (PAN) microparticels. The temperature indicator [platinum(II)(2-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline)(2,2,6,6-tetramethylheptane-3,5-dione)] [Pt(II)(Br-thq)(acac)] is dispersed in poly(vinylidene chloride-co-acrylonitrile) (PVDCAN). For oxygen sensing, microparticles made of a polystyrene (PS) core and a poly(vinyl pyrrolidone) (PVP) shell were doped with platinum(II)-5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin (PtTFPP). The characterization of all of these microparticles is is shown as well.

Probing the Phase Transition of a Thermoresponsive Polymer in Aqueous Solutions by Utilizing a Conjugated Polyelectrolyte

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Smart polymers undergo massive changes of their macroscopic properties in response to small changes in their external environment. Introducing external stimuli or molecular recognition events alter the conformation of polymer chains in water, which translates into macroscopic responses such as coil-to-globule transition of single chains followed by the aggregation of dehydrated globules[1]. This particular process makes this class of polymers particularly attractive for the molecular design of autonomous sensors. Here, we present a novel concept to optically visualize the temperature-regulated interpolymeric interactions of a nonionic dye-labeled thermoresponsive polymer with a cationic conjugated polyelectrolyte using Förster resonance energy transfer (FRET). The aqueous mixtures of the two polymers at room temperature exhibit reduced fluorescence intensity from the responsive polymer, accompanied by an enhanced emission from the polyelectrolyte, indicative of FRET mechanism. Heating this mixture above its cloud point reduces the efficiency of energy transfer, resulting in a distinct change of the emission color. A detailed study of the effect of solution ionic strength on temperature- activated FRET showed that the system performs best at isotonic conditions. With the aid of the dynamic light scattering studies, we propose that the two macromolecules form mixed aggregates at room temperature, and that these aggregates exhibit a remarkable structural change upon phase transition. We propose that this visualization scheme shall also be applicable to biochemical sensors.

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Dye Labelled Polymers for Sensing Applications

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The synthesis and spectroscopic propertys of coumarin and naphthalimide labeled p(NIPAm) and p(OEGMA) polymer systems are presented. The dye labeled systems shows different spectroscopic properties depending on the given polymers. No change in optical properties is found for the coumarin and the naphthalimide labeled p(OEGMA) systems by heating the polymer solutions above the cloudpoints. The naphthalimide p(NIPAm) possesses a temperature depending fluorescence on/off switch. No fluorescence is visible below the cloudpoint. By heating the polymer solution above the cloudpoint, the solution becomes fluorescent. In contrast, the coumarin p(NIPAm) system displays no change in the optical properties upon heating and cooling. p(OEGMA) copolymers of both dyes show FRET independent on temperature whereas for the dye labeled p(NIPAM) polymers FRET is regulated by temperature. No FRET is observed in the swollen state, but FRET is induced in the collapsed state. Both effects are visible by the naked eye. This behaviour makes such systems promising for biosensing

Internal Stresses in Drying Latex FilmsProbed by Birefringence Imaging

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Films formed from waterborne latex dispersions are of outstanding practical relevance. Critical to a successful film formation is stress relaxation in the drying coating, where the stresses per se cannot be avoided because of the volume shrinkage. Importantly, stress occurs in the form of a drying front, propagating from the edge to the center of the film. We report on stress-birefringence imaging as a technique to visualize the pattern and quantify the results.

The results can be summarized as following:

- The principle axes of stress are along and perpendicular to the direction of drying. The drying front experiences tangential tensile stress.
- The magnitude of stress depended on the amount and the type of rheology modifiers added to the dispersion.
- Large stresses are found with additives inducing shear thinning
- These results suggest that a slip motion at the interparticle boundaries makes a significant contribution to stress relaxation.

Multifunctional Fluorescent Poly(organosiloxane) Nanoparticles: Synthesis and Characterization in Biological Environment by Dynamic Light Scattering

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We present the synthesis and characterization of multifunctional, fluorophore-labeled, charge- or sterically stabilized poly(organosiloxane) core-shell NPs with tunable surface properties.
Fluorescent core-shell NPs were synthesized by co-condensation of different alkoxysilanes with fluorophore- labeled monomers in aqueous dispersion. To adjust surface properties and to provide electrostatic stabilization of the NPs, reactive sides, e. g. carboxy and amino groups, were introduced on the particle surface. Grafting of heterobifunctional poly(ethylene oxide) (PEO) leads to sterically stabilized biocompatible NPs.
The spectroscopic properties of dye-labeled NPs were investigated by fluorescence and absorption spectroscopy. To determine the influence of dye-labeling and subsequent surface functionalization with PEO on fluorescence quantum yield, we compared the absolute fluorescence quantum yield of free monomer and the absolute quantum yields of NPs before and after functionalization.
The size of NPs in solution was determined by angle dependent Dynamic Light Scattering (DLS) and Asymmetrical Flow Field-Flow Fractionation (AF-FFF) and NPs were visualized by electron microscopy (TEM). Furthermore, the properties of amino- and carboxy-functionalized, polymer coated poly(organosiloxane) NPs and charge stabilized silica NPs were compared in biological environment. Thus significant differences between poly(organosiloxane) NPs and silica particles were observed.
Due to the modular structure and ease of functionalization of poly(organosiloxane) NPs a wide field of biomedical applications can be envisioned. Furthermore, cell studies are in process and carried out applying the NPs to lung-tissue models.

Intra- and inter-molecular dynamics probing the molecular signature of the dynamic glass transition in polymers

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The intra- and intermolecular interactions of glass forming polymeric model systems (polystyrene, PS; polyvinyl acetate, PVAc and polymethyl-metacrylate, PMMA) are studied by Fourier-Transform Infrared (FTIR) and Broadband Dielectric Spectroscopy (BDS). By analysing the temperature dependencies of the spectral position and the oscillator strength of specific IR absorption bands, it is demonstrated that each molecular moiety in the polymer has its own characteristics in the course of the dynamic glass transition. Particularly, for PS and PVAc discontinuities in the temperature dependencies are observed well below the calorimetric glass transition temperature TG for vibrations of the aromatic rings and the carbonyl group, respectively; whereas for the main-chain vibrations a pronounced kink is found only at TG. In contrast, the carbonyl and C-O stretching bands of PMMA exhibit distinct changes at TG, with no additional features for lower temperatures. These findings enable one to unravel the detailed molecular interactions in the evolution of the liquid to glass transition beyond coarse-grained models.

Revisiting photo-stimulated discharge spectroscopy for the investigation of charge trapping in polymer electrets

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The method of photo-stimulated discharge spectroscopy is revisited with an emphasis on the interpretation of experimental data on insulating polymers. Comparative measurements of photo-stimulated discharge, thermally stimulated discharge and charge-density distributions (by means of thermal-pulse experiments) were carried out on corona-charged polyethylene-terephthalate samples. Photo-stimulated discharge spectroscopy was also performed on a series of selected commercially available polymers that are suitable for space-charge electrets. We describe the striking differences in the activation energies for thermal and optical de-trapping of charges, as well as models for charge trapping and transport in polymers – models that are based on energy bands in semiconductors and on molecular excitons. Last, but not least, we discuss the problems of defining and explaining charge "traps" in polymers.

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Evolution of Interparticle Cohesion and Particle Deformation in Drying Latex Films Determined with Förster Resonance Energy Transfer and Turbidimetry

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Polymers, in contrast to low molecular weight substances, can easily form tough films upon drying on a substrate. A prominent application is the field of coatings. Importantly, film formation fails if the material cracks. Cracking is caused by the volume contraction during drying. For polymer latexes, most of the shrinkage occurs during the particle deformation stage. If sufficient cohesion between particles develops earlier than the tensile stress, cracking is prevented. We report on a novel setup, which detects cohesion and particle deformation simultaneously at the same point. Particle deformation is determined via turbidimetry, while cohesion is quantified with Förster Resonance Energy Transfer (FRET). FRET is a proximity probe, which monitors the interdiffusion of polymer chains across interparticle boundaries. Interdiffusion induces cohesion. The results are the following: - Interdiffusion starts before the deformation of the particles is finished. - Soft polymers show more interdiffusion than hard ones, but there is no significant effect of softness on the relative timing between interdiffusion and particle deformation. - There is a weak dependence of the relative timing and the degree of interdiffusion on the amount and type of the surfactant employed. The dependency is weak because the surfactant only partially covers the particle surface.

Dye-doped polymers and organic-inorganic nanocomposites for holographic fabrication of DFB lasers

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We present distributed feedback (DFB) lasers based on holographic volume transmission gratings formed in dye-doped organic-inorganic nanocomposites and polymethylmethacrylate (PMMA). The nanocomposite gratings have been fabricated via one-step UV (364 nm) holographic exposure of acrylate monomers containing inorganic ($LaPO_4$) nanoparticles with high refractive index, photoinitiator and a laser dye. The gratings in PMMA were formed by means of photografting of phenanthrenquinine (PQ) to the polymer molecules during holographic exposure (514 nm) followed by thermal activated diffusion of rest of PQ at 55 °C. Pyrromethene 567 was used as a laser dye in both cases. The second and the third order DFB lasing emission have been demonstrated upon pumping with the 532 nm ns laser pulses. The threshold pump energy of ~0.3 µJ/pulse and of ~1.1 µJ/pulse was achieved for the nanocomposite- and PQ-PMMA-lasers, correspondingly. The output emission is s-polarized with a polarization contrast as large as 0.95 when a pump light is s-polarized. The lasing line-width of ~0.4 nm was observed for both types of lasers. The emission from the nanocomposite DFB laser was tuned across a range of ~60 nm by using the gratings with different period and of ~10 nm by varying the nanoparticles content in the material. The doped nanocomposite and PQ-PMMA matrices provide the stability of the laser emission of about 10^4 shots at 10 Hz repetition rate at a pump energy 10 times higher than the lasing threshold.

Talbot Imaging Phenomena on Polymer Particle Arrays

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Self-assembly of monodisperse microspheres into 2D or 3D ordered array structures has attracted a lot of attention due to simplicity, flexibility, and low costs. As lattice constants can be adjusted by the particle diameter (d) the photonic and diffractive properties of such arrays can be easily customized. These structural templates are of particular interest as model systems for 2D and 3D optical phase gratings, whose diffractive properties can be used in the development of new optical sensor concepts. In this contribution we focus on spectroscopic and diffractive properties of hexagonally close packed µm scale polystyrene particle arrays (mono- and bi-layers, hierarchical systems) in the optical near-field (Talbot interferences) and middle-field as this is of special interest for sensor applications based on direct coupling between the grating and a CCD matrix (Talbot illumination). By means of optical microscopy, using parallel white light illumination and a motorized micro-stage, the Talbot imaging planes behind the arrays were observed and classified. Monochromatic self-imaging planes were observed at distances $Z_T=3d^2/2\lambda$ and polychromatic fractional Talbot planes at distances $Z=Z_T\,p/q$ (with p,q - coprime integers). Fractional Talbot sub-images maintain the hexagonal order and match in the original particle arrangement by means of the scaling parameter q. The fully-spectral resolution of the Talbot imaging planes was investigated by means of a microscope spectrometer.

Syntheses and characterizations of oligoethylene glycol materials functionalized with desaminotyrosine and desaminotyrosyltyrosine

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The aromatic compounds desaminotyrosine (DAT) and desaminotyrosyltyrosine (DATT) have been successfully used to functionalize gelatin in order to form physically crosslinked networks via π-π interaction and hydrogen bonds of the introduced phenols. In this study, it was investigated whether this concept can be applied to a synthetic polymer not engaging in additional interactions such as triple helix formation in gelatin, allowing a network formation by physical interactions. As synthetic polymer for the backbone structure we chose oligoethylene glycols (OEG), which have been used extensively for biomedical applications due to their biocompatibility. Linear OEG with amino functionalities as endgroups as well as 4-arm amino OEG have been functionalized with DAT and DATT. The compounds have been characterized by NMR and IR spectroscopy. Rheological behavior of aqueous solutions of the materials was studied varying concentration, frequency, and temperature. All materials were water soluble and the rheological measurements showed a decrease of storage modulus G′ and loss modulus G′′ compared to the unfunctionalized OEG. The critical micelle concentration (CMC) was determined by a fluorescence spectroscopic analysis using the hydrophobic fluorescent dye pyrene. For the linear OEG-DATT a CMC could be determined ($c = 0.1\ \mathrm{mg \cdot mL^{-1}}$). In this study, the syntheses of OEG functionalized with the aromatic compounds DAT and DATT was described. The polymers showed the properties of a surfactant, which can be explained by the structure of the macromolecule with a large hydrophilic core and two hydrophobic end groups. In principle these macromolecules can be used as surfactant to solubilize hydrophobic compounds such as drugs in water.

Structural dynamics of lipid membranes by time resolved X-ray reflectivity

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Collective excitations in synthetic as well as biological polymers are of major importance for the understanding of numerous processes in artificial as well as living systems. Biological membranes, as natures most important interface, are among the most prominent representatives of biological polymers. Out-of-equilibrium membrane dynamics as driven by external forces, i.e. due photoactive membrane proteins or external electrical fields strongly influence the elastic properties and interaction forces of the lipid bilayer as well as functional aspects such as diffusion and active transport. However, a direct observation of out-of-equilibrium dynamics in the time domain in combination with high spatial resolution poses significant experimental challenges. We present time resolved reflectivity experiments in the pump-probe scheme [2] at in-house femtosecond Cu-K_α, synchrotron (ESEF, PETRAIII) and free electron laser (FLASH) sources, using optical, high Voltage and surface acoustic wave (SAW) excitation mechanisms. Importantly, we were able to record time resolved specular and diffuse scattering at a signal level compatible with full lineshape analysis and to reconstruct the time resolved electron density profile of the lipid bilayer at molecular resolution.

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Polymers for display applications

Novel Quantum Dot Light Emitting Diodes based on Indium Phoshide

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Quantum dots (QDs) show unique optical properties: By adjusting the particle size in a scale range below a few nanometers it is possible to tune the emission wavelength through the whole visible spectrum. The full width at half maximum of the emission, can be configured incomparably narrow (< 50 nm). In consequence, colloidal QDs are a highly attractive luminescent material for the use in thin film LED. The best investigated material is cadmium selenide. As consequence, quantum dot light emitting devices (QLED) mark the latest development in the display research area and have been demonstrated with good performance using cadmium based QDs. However, due to the inherent toxicity of cadmium compounds the use in electronic consumer commodities is strongly restricted. Especially in Europe compliance is regulated by the RoHS (Restriction of Hazardous Substances) directive.

Indium phosphide (InP) is therefore considered to be the most promising alternative. Hence, we report a novel fast and one-pot synthesis method for InP/ZnSe/ZnS multishell QDs.

The resulting optical characteristics like narrow and bright emission as well as the high stability enabled the substitution of cadmium-based QDs by indium-based ones.

Using this QD material, we manufactured QLEDs with excellent performance like a maximum luminance of more than 5000 cd m^{-2}, a current efficiency of 12 cd A^{-1}, and an outstanding color purity.

This is the first time that a cadmium-free QLED with application-relevant performance is reported. The excellent color gamut which can only be achieved by QLED will ameliorate the brilliance and color saturation of displays in an extraordinary way.

Illumination applications by using phosphorescent copolymers

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Even though large effort has been undertaken, the development of high molecular weight phosphorescent copolymers that have been prepared for low-cost solution-processing applied in efficient light-emitting devices is to date still behind the expectations. This development holds true in both, color purity and device efficiency. In this work, we describe the synthesis and characterization of conjugated main-chain iridium(III) emitters, that are copolymerized to yield fluorene-typed derivatives. The different heteroleptic Ir(III) complexesare intended to emit orange to red light and to support hole trapping. Using both, either a straight-forward Yamamoto C-C coupling reaction or a Suzuki coupling protocol, allows to further modify the Ir(III) emitters with respective fluorene- and fluorenone-based comonomers. Thus, the respective polymeric Ir(III) emitters serve to transport holes and electrons due to their p- and n-type nature and are therefore useful as bipolar on- chain charge acceptors. The application of such phosphorescent metallo-copolymers in efficient light-emitting devices will moreover be examined.

Pre-Alignment of Liquid Crystal Molecules in Electrically Poled Ferroelectric Polymer-Dispersed Liquid Crystals

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Polymer-dispersed liquid crystals (PDLCs) are composite materials made of liquid crystal (LC) filled droplets embedded in a transparent polymer matrix. Due to external electric fields the refractive index of the LC can be varied resulting in a matching or a mismatching state with the refractive index of the polymer. This switching process is visible as a change of transparency of the film. In the matching state the film appears nearly transparent whereas in the mismatching state the film scatters incoming light efficiently. Such films can be used for display applications without the need of further elements like polarizers. In the present work the nematic liquid crystal 4-cyano-4′-hexylbiphenyl (6CB) was dispersed in ferroelectric poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)). P(VDF-TrFE) contains polar crystallites which were oriented by applying high electric fields (80 to 100 V/µm) to the film. After that poling procedure the oriented crystallites provides a static internal field acting as a bias voltage. Due to that field the LC molecules were pre-aligned in field direction and the film transparency was increased permanently. Furthermore the films show a polarity-dependence of the transmittance on external voltage which was not observable before poling. These effects could be possibly used for PDLC displays with lower driving voltage or for sensor applications.

Orientation of Polymers Due to the Interaction With Polarized Light

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The preparation of anisotropic films is of great interest for the production of a wide range of polarization elements. Linearly polarized light offers an easy and efficient way to introduce anisotropic properties in polymer films. The contribution compares the classical way of photo-orientation of azobenzenes in polymer films due to the irradiation with linearly polarized light as developed within the last 20 years with a couple of new orientation methods based on alternative photosensitive moieties.

Our presentation shows that photo-induced anisotropy can be achieved in multifunctional polymers, containing photochromic, mesogenic and further functional side groups. We show that anisotropy can be also introduced using alternative photochromic groups. Permanent, reversible or temporary anisotropy is induced by photoorientation in the steady state of isomerisation reactions, by photo-cycloaddition or photo- degradation processes. A new material was developed characterized by the same reversible orientation capability as known from azobenzenes but with the advantage being transparent in the visible range. Different concepts for the induction of anisotropy in polymer films and bulk-alignment of multifunctional LC polymers will be discussed. The photo-induced anisotropy can be significantly increased by thermotropic self- organisation upon annealing in the mesophase. In these ways extraordinary high values of birefringence (0.3), dichroism (up to 0.9) and emission anisotropy (8) have been achieved.

Specific mesoscopic structures by self-assembly of ABC ternary block copolymers in the super-strong segregation regime

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Photonic crystals are periodic dielectric media suited to manipulate light. Polymers enable the facile preparation of the needed regular mesoscopic structures. So far beside latex particles, diblock copolymers with classical superstructures (lamella, cylinders etc.) have been studied in this context. Now, we are exploring pathways to linear ABC ternary block copolymers with mutually incompatible blocks as novel materials for an even more versatile self-assembly into 1D, 2D and 3D periodic structures. Thus, we synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization new ABC ternary block copolymers that fall into the super-strong segregation regime, bearing a hydrophilic A block and two mutually incompatible hydrophobic blocks B and C. Previous work based on hydrocarbons and fluorocarbons as the latter two blocks has exemplified the wealth of novel superstructures which may be accessible in this way [1-3]. The new polymers are made of poly(oligoethyleneglycolacrylate) as hydrophilic block, and benzylacrylate and tris(trimethylsiloxysilyl)propyl acrylate as apolar blocks, replacing the formerly used perfluorinated acrylates to tailor the relative domain structures and sizes. These copolymers are amphiphilic and thus self-organize not only in bulk, but also self-assemble in aqueous solution into micellar aggregates with a microphase-separated core. The direct imaging by cryogenic transmission electron microscopy (Cryo-TEM) revealed indeed complex multicompartment micellar ultra-structures.

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Electrically switchable diffractive and photonic elements based on photo-curable monomer - LC composites

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Switchable/tuneable diffraction gratings based on liquid crystals are key components for electro-optical thin film devices in spectroscopy, light-management or optical communication networks. In order to overcome the disadvantages of H-PDLCs (*h*olographic *p*olymer *d*ispersed *l*iquid *c*rystals), those applications are restricted by light-scattering due to µm sized LC-droplets; a new type of switchable holographic gratings characterized by a droplet-free morphology was developed. New photo-curable composites, consisting of monomers undergoing different photopolymerization reactions, nematic LCs and photo-initiators as well as a suitable holographic structuring method were created. One-step interference exposure results in photopolymerization induced phase separation of the material components and in the planar LC alignment forming stripe-like periodic structures consisting of polymer walls alternating with channels of neat LCs. The uniform droplets-free morphology provides diffraction efficiency of about 99% in the spectral range from the UV up to the NIR along with an excellent optical transparency in both electrical Off- and On-states. The application of an electric field of few V/µm is enough to "reorient" the LC director thereby switching On/Off the grating in a sub-ms timescale. Electrically switchable diffractive elements of different functionalities, such as beam-switchers/-splitters/-steering elements, light-in/out-couplers, polarization valves, displays elements and thin film tunable laser have been demonstrated.

Polymers for optomechanics

Metal ion exchange in self-assembled coordination polymer films

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Recent studies[1,2] have shown that the sequential assembly of divalent metal ions such as Ni(II), Cu(II) or Zn(II) and polymers with terpyridine (tpy) or benzimidazolylpyridine (bip) substituent groups such as P1 and P2 results in the formation of electroactive coordination polymer network structures. The metal ions are fixed in the film via coordinative interactions with the ligand groups. The present study is concerned with the exchange of the metal ions in the film for other metal ions. Using spectroscopic methods (UV, XPS) it is demonstrated that the immersion of the films in solutions of other metal ions results in ion exchange to a large extent. For example Zn(II) ions can be replaced by Fe(II) ions and vice versa. The exchange mechanism is discussed on the basis of the equilibrium constants of complex formation for the different ions. The exchange proceeds under strong colour changes. By dipping into an aqueous solution of NaCl the metal ions ca n also be removed from the films almost quantitavely. These films can be used repeatedly to detect small amounts of ions with sensitivity in the ppm range. Possibilities to use the ionochromism for application in metal ion sensing devices are discussed.

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Electric tunable polymer laser

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Here we report on a compact monolithic organic laser device that allows for direct voltage controlled wavelength shift. The device consists of an elastomeric distributed feedback (DFB) laser coupled to a Dielectric Elastomer Actuator (DEA), also known as "artificial muscles", essentially a sandwich of insulating rubber between two soft electrodes capable of reversible deformation under applied voltage. Second order DFB laser is composed of a polymeric diffraction grating covered with a thin layer of a laser dye doped polymer. To create the voltage tunable elastomer laser (VTEL) the photonic element is placed in the center of the DEA. The actuator is designed to induce a homogeneous compression at this position using pre-stretched elastomer and patterned soft electrodes. Under applied voltage the deformation is directly coupled into the DFB laser and results in a decrease of grating period and thus in a change of emission wavelength. The increase of actuation voltage to 3.25 kV decreased the emission wavelength from 604 nm to 557 nm, a change of 47 nm and the largest continuous laser wavelength shifts in the visible range ever reported for soft matter DFB lasers. The measured shift in wavelength can be analytically described based on the chosen geometry of the VTEL and the independently measured.

Reversible photo-induced shrinking of rigid-rod polymers

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Synthetic molecular systems that undergo structure and property changes as a response to external stimuli offer a series of relevant functions. Their direct use in solution, immobilized at surfaces, or integrated into adequate matrices, allow for the elaboration of nano-carriers, molecular electronic memory circuits, adaptive systems, artificial muscles, or healable materials, among others. Reversible systems are commonly generated by utilizing molecular switches as responsive bi-stable molecules. Of particular interest are switches controlled by non-invasive triggers, especially light, which can display high spatial and temporal resolution. Herein we report on the synthesis of rigid-rod polymers consisting of azobenzene photo-chromes in the main chain and the dramatic change of their shape induced upon irradiation. The embedded photo-switches act as hinges, which upon light-induced isomerization lead to reversible shrinking and stretching of the polymer backbone in solution.

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Synthesis and Characterization of Cinnamylidene Acetic Acid Functionalized Oligoethers

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Stimuli-responsive polymers, which can be triggered by light, have attracted tremendous interest in biological applications as they enable non contact actuation at ambient temperature. Various photosensitive molecules such as azobenzenes, benzopyranes[1] and cinnamates[2] have been explored as active components.

Here photoreversible oligomer systems from oligo(ethylene glycol) (OEG) and oligo(propylene glycol) (OPG) were synthesized by the reaction of the oligoether endgroups with cinnamyliden acetic acid. While cinnamylidene acetic acid is capable of a [2+2] cycloaddition when irradiated with light of wavelength > 260 nm and reversible photocleavage when irradiated with light of wavelength < 260 nm, the oligoether were selected due to their water solubility and biocompatibility. The functionalization reactions were performed in the melt at 65 °C resulting in a degree of functionalization of up to 97%. The chemical structure, thermal properties and molecular weight of the obtained oligoethers was determined by NMR, DSC and MALDI-TOF. Such photoresponsive biocompatible oligoethers are promising candidates for biomedical applications.

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New water-soluble polyacrylates bearing azobenzene side chains: Combining photo- with thermo-sensitive behavior

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The thermo-sensitive behavior of many polymers in aqueous solution is well-known. In particular, most non- ionic water-soluble polymers show a volume phase transition of the Lower Critical Solution Temperature (LCST) type. This phenomenon is much discussed currently for producing "smart materials". In fact, temperature is a convenient, reversible and non-invasive trigger suited for materially closed systems. Yet in a number of cases, the advantageous typical LCST transition profile is desired, though the aspired use requires an isothermal switching process. This apparent contradiction can be remedied by modulating the hydrophilic-hydrophobic balance HLB of a polymer with LCST transition by a second superimposed stimulus, e.g., by light [1]. In this context, we have designed new copolymers based on methoxydiethylenglycolacrylate (MDEGA) and an azobenzene analog. The homopolymer of the former is the polyacrylate bearing the shortest possible oligoethylenox ide side groups for still achieving water-solubility, and distinguishes advantageously from the macromonomer character of the typical oligoethylenoxide (meth)acrylates [2-4]. The HLB of such statistical copolymers can indeed be modified by the cis-trans photo-isomerization of incorporated azobenzene groups, thus modulating their LCST in aqueous solution. However against "common wisdom", the effects observed are not straightforward and often even counter-intuitive, as will be discussed.

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Thermo-mechanical Characterization of Nanocomposites based on Oligo(ω-pentadecalactone) and Magnetite Nanoparticles

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Magnetosensitive shape-memory polymers (SMP) obtained by incorporating magnetic nanoparticles in a SMP are an emerging class of multifunctional materials. The incorporation of the nanoparticles enhanced the mechanical properties and in addition enabled remote actuation by exposure to alternating magnetic fields. However, the nanoparticles tend to agglomerate due to their high surface energy and in most cases are very difficult to disperse uniformly into the SMP matrix. [1-3]

Here, we report on the shape-memory properties of nanocomposites based on oligo(*ω*-pentadecalactone) (OPDL) switching segments and silica encapsulated magnetite nanoparticles (mgNP). The silica encapsulation of the mgNP enhanced the compatibility and distribution of the nanoparticle in the polymer matrix. A series of nanocomposites were prepared by crosslinking of oligo(*ω*-pentadecalactone)dimethacrylate (M_n = 2800 g·mol^{-1} and 5100 g·mol^{-1}) in the presence of silica encapsulated mgNP. Thermal and mechanical properties of the nanocomposites were explored as a function of OPDL chain length and nanoparticle weight content. All nanocomposites exhibited excellent shape-memory properties with shape fixity rates between 86% and 93% and shape recovery rates above 97%. [4] In order to further improve the distribution and strengthen the interaction of the mgNP with the polymer matrix, OPDL coated mgNP were used as filler to develop the hybrid nanocomposites. Here, a highly efficient dispersion of the mgNP in the polymer matrix was observed. [5] Potential applications for such shape-memory nanocomposites include smart implants, medical instruments, which could be controlled on demand by indirect magnetic heating.

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Pyrrole-Thiophene Oligomers with Alternating Sequence Structure and Tunable Absorption Properties

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A new group of π-conjugated oligomeric materials with a low band gap consisting of alternating pyrrole (P) and thiophene (T) units with a PTPTP sequence were created and characterized by H-NMR, IR, UV and PL spectroscopy, as well as by elemental analysis. The synthesis of these compounds was performed by Stille coupling reaction [1] of a TPT core unit with new synthesized pyrrole derivatives. The presented PTPTP cooligomers possess a high solubility in common solvents and feature additional telechelic carboxyl groups, which enable further postfunctionalization with e.g a degradable matrix [2]. The obtained cooligomers displayed an absorption at λ_{max} between 341 and 379 nm in solution and in the solid state between 346 and 410 nm, which could be tuned by introduction of different electron donor substituents such as alkyl or alkoxy chains. Furthermore a strong red shift of the absorption up to 850 and 1000 nm could be observed by generation of additional charges within the conjugated system such as by the oxidation with Fe^{2+} or by protonation with trifluoroacetic acid on the nitrogen moiety. These novel cooligomers might be potentially used as IR sensitive dyes in photoacustic imaging [3, 4] or sensors for oxidative monitoring.

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Reversible light-induced microgel swelling using photosensitive surfactant

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Stimuli responsive gels have been intensively investigated for applications in biology and medicine as well as in development of micro-fluidic devices and micro-sensors. These applications are possible thanks to the unique swelling behavior of hydrogels which can change in response to surrounding conditions (temperature, pH, ionic strength, solvent). In order to realize remote control of a hydrogel by external stimuli such as light, electric or magnetic field, a variety of nanoparticles (e.g., silicate, metal, magnetic, or carbon nano-tubes) were incorporated into polymer networks.

Recently, we have demonstrated a new strategy for the light-induced reversible switching of the swelling of microgel particles, in which photo-isomerization and the resulting binding/ unbinding of a photosensitive azobenzene-containing surfactant to a microgel is employed. Addition of the surfactant above a critical concentration leads to contraction of the microgel. UV-light irradiation results in trans-cis isomerization of the azobenzene unit incorporated into the surfactant tail and causes an unbinding of the more hydrophilic cis isomer from the microgel and its reversible swelling. The reversible contraction can be realized by blue light irradiation that transfers the surfactant back to the more hydrophobic trans conformation, in which it binds to the microgel. Detailed investigation of the complex at different microgel concentration allows construction of the phase diagram (aggregation, contraction, and precipitation ranges). This gives understanding of the transitions mechanisms and allows selection of appropriate conditions for realization of the light-induced reversible control of the microgel swelling.

Growth of silver nanowires within nanotubular J-aggregates

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It was demonstrated earlier that ultrathin but long Ag nanowires with diameters less than 7 nanometer and length exceeding micrometers can be fabricated by reduction of silver salt using uniform nanotubular Jaggregates of amphiphilic cyanine dyes as templates [1]. Here we report on the growth mechanism of these Ag wires as revealed by electron microscopy. The growth of the wires wires is photo-initiated by short illumination with blue light and is terminated at different time steps by removing Ag^+ ions upon adding NaCl to the solution. In this case the Ag^+ ions react with the Cl^- ions to form AgCl nanocrystals. At times shorter than 2 hours, small and well separated fragments of silver wires are found along the aggregates with a broad length distribution in the range of ten to hundred nanometers. At times later than 2 hours, homogeneous wires are found with lengths of microns filling almost the entire aggregates. By high resolution TEM one finds microcrystalline domains with sizes up to 100 nm. These findings show that the growth of the wires starts independently at distinct nucleation centers and proceeds to fill the entire aggregate. This growth and annealing process must be supported by transport of Ag^+ ions through the tubular wall membrane.

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Synthesis of Semiconductor Nanowires Based on Tubular J-Aggregates Template

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Organic/inorganic hybrid nanomaterials, that combine strengths of individual material while compensating for deficits, have recently attracted more and more attention. Quasi one-dimensional (1-D) nanomaterials, such as wires and tubes, have been intensively investigated owing to the beneficial influence of dimensionality on electronic and optical properties [1]. Based on former results on silver [2], this work focuses on the fabrication of quasi 1-D organic-inorganic hybrid nanostructures consisting of nanotubular J-aggregates self-assembled from amphiphilic cyanine dyes filled with semiconductor nanowires such as ZnO. Owing to electrostatic interactions, zinc ions might adsorb at the outer and inner wall of the negatively charge surface of the tubular J-aggregates. Following the procedures of ammonia precipitation and subsequent heating to moderate temperatures, the transformation from zinc ions into ZnO within the hollow space of the tube with diameters less than 10 nanometers is supposed to be realized. The as-synthesized inorganic structures are identified by transmission electron microscopy and UV-Vis spectroscopy.

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Photoswitching of Porphyrin-Spiropyran Dyads at Interfaces between Solutions and Graphene within an STM

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Molecules can be switched between different molecular states with high repeatability, which provides a specific functionality. Photoinduced switching of a porphyrin-spiropyran dyad is investigated on a graphene surface with porphyrin as anchor and spiropyran as switch. Using light of a suitable wavelength spiropyran and the related dipole moment is switched, which may influence the tunneling current within the STM. The usage of graphene, which is a conductive as well as optically transparent substrate, allows measurement with STM simultaneously with an optimized irradiation by use of an optical microscope. The self-assembling dyads at the liquid-solid interface exhibit an adsorption of anchor porphyrin with the spiropyran switch pointing away from the surface into the solution. First measurements of adsorbed and irradiated dyads show strong STM contrast differences of the porphyrin. Further STM and fluorescence measurements are needed to support that the contrast difference results from switching.

Polymers for photolithography

Photopolymerization Studies of a HABI-Donor System

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Hexaarylbisimidazole (HABI) derivates have been used as radical initiator in photopolymer systems for a long time. Exposure of HABI results in formation of lophyl radicals, which produce initiating thiyl radicals in the presence of heterocyclic mercapto compounds. It has been believed for a long time that the lophyl radical abstracts hydrogen from the mercapto compound resulting in formation of highly reactive thiyl radicals. Photo-DSC experiments were carried out to explore the photopolymerization of a crosslinkable monomer in the presence of HABI and several mercapto donors. Most of them were derived from heterocyclic mercapto compounds. Only some of them were found to be very active in the system comprising HABI and hexanediol-1,6-diacrylate. Thus, the classical model describing hydrogen abstraction of the lophyl radical from the mercapto compound would not completely explain the results of our studies. This is supported by experiments using aliphatic mercapto compounds resulting in low photopolymerization rate. NMR experiments indicate that heterocyclic mercapto compounds contain the mesomeric thione as the major tautomeric form. Thus, electron transfer from the thione to the lophyl radical oxidizes the latter resulting in formation of thiyl radicals as well. Exposure of HABI in the absence of any mercapto compound shows only a low polymerization rate. This shows the need of appropriate donors reacting with the lophyl radical to form highly reactive initiating radicals.

Design of NIR-Photoinitiator Systems

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Application of photoinitiator systems operating in the near infrared (780-900 nm) have received increased interest in the graphical industry within the last 10-15 years. Nevertheless, photopolymers using NIR exposure have not attracted a wide range of applications outside of the graphical industry yet. One reason can be seen in the fact that NIR has been often related with heat necessary to start thermal events in chemistry. Substantial lack exists in the fact that NIR may also initiate photonic processes. This results in chemical crosslinking in photopolymers.

We started our investigations similarly as in CtP-photopolymers with triple systems comprising a sensitizer (Sens) selected from polymethine dyes, an iodonium salt (A) derived from cumene, mesitylene and t- butylbenzene and an electron donor (D) selected from tetraphenylborate or benzilate. These initiator system can be taylor made by introduction of appropriate substitution patterns.This helps to increase the compatibility in the multifunctional monomers and prepolymers chosen for photoinduced crosslinking. Although these systems operate on a singlet mechanism, the formation of radicals occurs with high efficiency based on an electron transfer mechanism. Such NIR-photopolymer systems can be applied for structuring techniques, sealing of devices with large coating thickness and the possibility to embed filter

Light-Induced Structure Formation in Drying Films

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Coatings are often designed to have an internal structure. Structures may develop spontaneously or may produced deliberately, for instance in a printing process or by the various modes of lithography. We have studied the formation of dimples upon locally heating the drying film with a laser. The formation of the dimples was followed in-situ by monitoring the pattern of transmitted laser beam. The results can summarized as follows: -Light-Induced elevated regions form in latex coatings as described previously[1]. The minimum achievable diameter is about 2 mm. -The process is much more efficient in films formed from aqueous solutions of dextran. The minimum achievable diameter is about 200 um. The peak height can exceed the average film height by a factor of two or three. -The formation of dimples is a rapid process occurring when the film solidifies. -The most plausible explanation is a light-induced coffee-stain effect. Buckling and the Marangoni effect possibly have some influence, as well.

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Polymers for solar energy conversion

Förster resonance energy transfer (FRET) experiments on tubular J-aggregates wrapped with dye labeled polyelectrolytes

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In this contribution we demonstrate the coating of tubular J-aggregates with dye-labeled polyelectrolytes. The tubular J-aggregates are formed by an amphiphilic cyanine dye in aqueous solutions [1]. These aggregates can be considered as cylindrical objects with 13 nm diameter, length exceeding microns and a negative surface potential. It is shown by cryogenic electron microscopy (cryo-TEM) that polycations can be adsorbed at the aggregate surface forming a homogeneous coating layer. Poly(diallyldimethyl ammonium chloride) (PDAC) and poly(allylamine hydrochloride) (PAH) labelled with different fluorescent dyes are used, acting as donors or acceptors within a Förster energy transfer (FRET) process. The donor and acceptor dyes are distributed homogeneously within the coating. The FRET is investigated by static optical absorption and fluorescence spectroscopy. The experiments demonstrate the possibility for symmetric energy transfer from donors to the aggregate and from the aggregate to acceptors. No indication for enhanced energy transfer due to exciton diffusion was found.

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Fluorinated PCPDTBT with Enhanced Open Circuit Voltage and Reduced Recombination for Highly Efficient Polymer Solar Cells

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A novel fluorinated copolymer (F-PCPDTBT) is introduced and shown to exhibit significantly higher power conversion efficiency in bulk heterojunction solar cells with PC70BM compared to the well-known low band-gap polymer PCPDTBT. Fluorination lowers the polymer HOMO level, resulting in high open circuit voltages well exceeding 0.7 V. Optical spectroscopy and morphological studies with energy-resolved transmission electron microscopy reveal that the fluorinated polymer aggregates stronger in pristine and blended layers, with a smaller amount of additives needed to achieve optimum device performance. Time delayed collection field (TDCF) and charge extraction by linearly increasing voltage (CELIV) are used to gain inside into the effect of fluorination on the field-dependence of free charge carrier generation and recombination. F- PCPDTBT is shown to exhibit a significant weaker field-dependence of free charge carrier generation combined with an overall larger amount of free charge, meaning that geminate recombination is greatly reduced. Additionally, a threefold reduction in non-geminate recombination is measured compared to optimized PCPDTBT blends. As a consequence, F-PCPDTBT blended with PC70BM exhibits a short circuit current of 14 mA/cm ^{2}, an open circuit voltage of 0.74 and a fill factor of 58%, giving an energy conversion efficiency of up to 6.2 %. The superior device performance and the low band-gap renders this new polymer highly promising for the construction of efficient polymer-based tandem solar cells.

Conjugated Microporous Polymer Networks with Incorporated Electron Donors/Acceptors

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Microporous materials such as zeolites, activated carbons or metal organic frameworks (MOFs) are important materials in the chemical industry due to their applications as ion exchangers, catalysts or catalysts supports or for gas sorption. Recently polymers of intrinsic microporosity (PIMs) and conjugated microporous polymers (CMPs) have been presented as organic counterparts to these materials.[1] These polymer networks are formed by covalent bonds, yielding high thermal and chemical stability, while the exclusively organic composition enables highest surface areas and excellent control over their chemical and physical functionalities. Herein we present novel conjugated microporous polymers with incorporated electron donor or acceptor molecules bonded in the network structures. This allows for reversibly charging of the networks either chemically or electrochemically. Molecular acceptors or donors can be furthermore introduced into the porous system to interact with the network functionalities. Thus interesting optoelectronic applications of such networks can be expected and first results will be presented.

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Precisely tailored compatibilizers for solubilizing and dispersing photoactive compounds

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Insolubility, high tendency to aggregate and poor dispersibility are general problems of many photoactive compounds. Frequently, improvement of solubility and therefore dispersibility involves cost-intensive structure optimization cycles and often leads to unfavored changes in photo properties of high potential candidates. Peptide-polymer conjugates can serve as valuable platform to overcome these drawbacks, making structure adaption potentially obsolete.

Herein we present a generic approach to develop peptide sequences with high affinity for non-covalent binding of a highly insoluble photosensitizer. The resulting bioconjugates successfully rendered the compound e. g. water soluble. These carrier complexes were investigated in terms of solubilization efficiency, cargo activity and release.

Precisely adapted formulation additives might provide solubility and compatibility of photoactive compounds.

Thus tailored compatibilizers improve both processability and dispersibility of active compounds in general.

Influence of interface dipoles on the open circuit voltage of polymer/PCBM and all-polymer photovoltaic cells

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During the last few years, promising results have been achieved for OPVCs using small molecules, polymers, or blends of both as active organic layer. On the one hand efficiencies up to 9.1% were achieved by understanding and optimizing the processing of these active layers, on the other hand fundamental questions are still open concerning the energy level alignment at the heterojunction and associated origin of the open circuit voltage (VOC). We investigated the energy level alignment at the respective heterojunctions with ultraviolet photoelectron spectroscopy (UPS), i.e. P3HT/PCBM or P3HT/P(NDI2OD-T2). Samples were prepared by spin coating the acceptor from dilute chloroform solution onto insolubilized polymer films to avoid intermixing of the two materials. In contrast to the assumed vacuum level alignment, significant vacuum level shifts of 0.15 eV are found for some material combinations that influence also the photovoltaic gap at the donor/acceptor junction. The results are discussed with respect to the potential existence of a non-equilibrium situation due to the illumination with synchrotron UV and external white light radiation. We show that illumination induced vacuum level shifts at the heterojunction can be measured in situ with UPS by using small metal clusters as electron collectors. However, effects due to external illumination have to be separated from energy shifts, whose origin lie in material properties of the two components.

Star-shaped columnar structures combined with P3HT and PCBM

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Thiophene-based copolymers but also small molecules on this basis received much attention in organic solar cells due to their high efficiencies. Contrary to their linear homologues, star-shaped molecules offer often different electronic properties and other characteristics like supramolecular organization resulting in a different morphology. To raise up the power conversion efficiencies of organic photovoltaic devices, it is necessary to develop new materials with higher absorption coefficients and broader absorption spectra. Consequently, donor-acceptor or rather push-pull molecules where an electron-rich moiety e.g. thiophene is followed by an electron-deficient one e.g. benzothiadiazole, are one strategy to achieve these requirements. We introduce star-shaped structures, which combine the concept of designed donor-acceptor-donor (D-A-D) segments with a central core. The application of such structures in thin films resulting in unusual morphologies will be discussed, as well as the application of blends of P3HT, PCBM and a star-shaped structure in a photovoltaic system will be introduced.

Using Chlorine-Free Solvent Systems to Inkjet Print Solar Cell Active Layers

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Organic solar cells are appealing with respect to inorganic devices because their functional layers can be processed from solution. For large scale production, technologies such as printing or coating are necessary because spin coating, which utilizes substrate rotation, is impractical. Among the various printing techniques, inkjet printing is especially useful because user-defined shapes can be generated. In this study, a novel polymer was synthesized, blended with fullerene and deposited with inkjet printing for solar cell applications. The new polymer offers advantages over traditional materials because of its enhanced solubility in chlorine- free, aromatic solvents in addition to its amorphous nature which eliminates the need for high temperature annealing. Blend films were analyzed with ultra-violet visible spectroscopy, atomic force microscopy in addition to energy filtered transmission electron microscopy. The surface topography and phase separation in the films were correlated to device performance. Efficiency values of 2.7% were found for devices with inkjet printed active layers when using a chlorine-free solvent system. Inkjet printing can be used to successfully process the active layers of organic solar cells consisting of novel polymers without sacrificing device performance.

Closing the gap: From linear to branched polythiophenes

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In recent years large effort has been made to optimize the efficiency in bulk heterojunction solar cells. The investigation of pi-conjugated polymers like poly(3-hexylthiophene) (P3HT) and the improvement of their optoelectronic and morphological properties have become a major topic in polymer research. In the following contribution we focus on the molecular architecture of donor polymers based on thiophene units. While the linear α-conjugated P3HT is well studied in literature, we investigate novel polythiophenes with an expanded pi-system in β-conjugation: two novel polythiophenes with either linear or branched alkyl-chains attached to a β-conjugated thiophene unit have been prepared and characterized. Coming from these 2D-polythiophenes we expanded the conjugated pi-system to a branched 3D-polythiophene system by polymerizing a terthiophene monomer. The influence of β-conjugation on electrochemical and optoelectronic properties of these 2D and 3D polythiophenes was studied in comparison to P3HT. The variation of the molecular design and the post-functionalization of polymer endgroups allow us further to synthesize polythiophenes with tailor-made propertieslike isotropic charge transport or solubility in water and ionic-liquids.

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Deeply Colored Polymers Containing 1,3,4,6-Tetraarylpyrrolo[3,2-b]pyrrole-2,5-dione (IsoDPP) Units in the Main Chain

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Recent publications have shown that conjugated polymers containing diketopyrrolo[3,4-c]-pyrrole (DPP) units are useful for applications as active compounds in light emitting[1] and photovoltaic devices.[2] While numerous studies were concerned with polymers containing the DPP unit, only very little has been reported on polymers containing the regioisomeric diketopyrrolo[3,2-b]pyrrole (isoDPP) unit. Because of their strong absorption in the visible they also might be interesting for electronic applications. Here we report a first study on synthesis and characteristic properties of conjugated polymers containing isoDPP units. Dibrominated tetraaryl-isoDPP monomers were prepared upon condensation of two equivalents of ethylarylacetates with one equivalent of oxalic acid bis(arylimidoyl)dichlorides according to a method described by Langer et al. Polymers were prepared upon palladium-catalyzed coupling reactions. Deeply colored polymers with molecular weights up to 22 kDa were obtained. The polymers are soluble in common organic solvents. They exhibit broad absorption bands with maxima between 400 and 500 nm, the absorption coefficients being in the range of 104 L/mol cm. The fluorescence is only weak. Band gaps of phenyl-substituted isoDPP polymers are in the range of 2 eV, while those of thienyl-substituted isoDPP polymers are at about 1.5 eV. Cyclic voltammetry indicates quasireversible oxidation behavior. The polymers might be useful for electronic applications, as dyes and colorants.

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Surface Structure and Crystallization Behavior of a High Mobility n-Type Semiconducting Polymer

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We study the surface structure and crystallization behavior of the thiophene-based semiconducting copolymer, poly([*N,N′*-bis(2-octyldodecyl)-11 naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl] -*alt*-5,5′-(2,2′-12 bithiopene)), P(NDI2OD-T2), using amplitude modulation atomic force microscopy (AFM). In particular, we combine tapping mode AFM height and phase images with maps of amplitude-phase-distance (APD) curves. From a map of APD curves, the tip indentation into the soft (compliant) amorphous surface layer is measured. This spatial information serves as depth coordinate for reconstructing high resolution cross sections and 3D depth profiles of the top 10 nm of the specimen. Furthermore, the shape of the unperturbed (true) surface and the thickness of the amorphous top layer are determined. With this depth profiling technique we discovered that the entire surface of 40-nm-thin films of P(NDI2OD-T2) is covered by a soft amorphous layer. Its thickness depends on the annealing conditions and in our case is about 5 nm. Furthermore we report on recrystallization-induced changes of the surface structure after annealing above the melting point and after long-term storage at ambient temperature. We discuss the possible impact of the surface structure, the amorphous surface layers, and the recrystallization processes on the electronic properties and the performance of thin-film electronic devices.

Spherical polyelectrolyte brushes as "nanoreactor" for well-defined Crystalline TiO_2 Nanoparticles

Yan Lu, Matthias Ballauff

Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

TiO_2 nanomaterials have received much attention recently because of their photocatalytic activity, high chemical stability and possible applications in solar cells.[1] Moreover, mesoporous TiO_2 networks with high surface area are of particular interest for a number of applications.[2] Colloidal latex particles have been used for the preparation of hollow TiO_2 spheres or continuous macroporous TiO_2 structures. However, all as- prepared TiO_2 composites prepared in this way by a sol-gel approach are amorphous. The latex particles act only as a template for the macroporous structure and calcination is required to achieve sufficient crystallinity.[3]

Here we demonstrate that spherical polyelectrolyte brushes (SPB) particles may serve as well-defined nanoreactors for the direct generation of crystalline anatase TiO_2 nanoparticles at room temperature.[4,5] Thus, composite particles of a polymeric carrier and crystalline TiO_2 in a well-defined modification can be obtained without any further heat treatment. The SPB particles consist of a solid PS core from which long anionic polyelectrolyte chains are densely grafted.[6] Tetraethylorthotitanate (TEOT) is hydrolyzed in the presence of brush particles in a controlled manner leading to the formation of well-dispersed TiO_2 nanoparticles (d = 4 ~12 nm). Wide-angle X-ray scattering demonstrates that anatase nanoparticles with high crystallinity have been generated at room temperature, no additional heat treatment is necessary. In addition, the as-prepared TiO_2 nanocomposites exhibit an excellent colloidal stability. The photocatalytic activity for the degradation of dye RhB under UV irradiation of the composite particles can be dramatically enhanced after deposition of metal nanoparticles on it. [7] Finally, calcination of the composite particles leads to a macroporous scaffold of anatase nanoparticles, which are thermally stable against collapse. Possible applications, as e.g. for solar cells, are discussed. [8]

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[2] J. Lee, M. C. Orilall, S. C. Warren, M. Kamperman, F. J. Disalvo, U. Wiesner, Nature Mater., 2008, 7, 1.
[3] W. S. Choi, H. Y. Koob, W. T. S. Huck, J. Mater. Chem., 2007, 17, 4943.
[4] Y. Lu, M. Hoffmann, R. Sai Yelamanchili, A. Terrenoire, M. Schrinner, M. Drechsler, M. Möller, J. Breu, M. Ballauff, Macro. Chem. Phys. 2009, 210, 377.
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[6] M. Ballauff, Prog. Polym. Sci., 2007, 32, 1135.
[7] Y. Lu, T. Lunkenbein, J. Preussner, S. Proch, J. Breu, R. Kempe, M. Ballauff, Langmuir 2010, 26, 4176.
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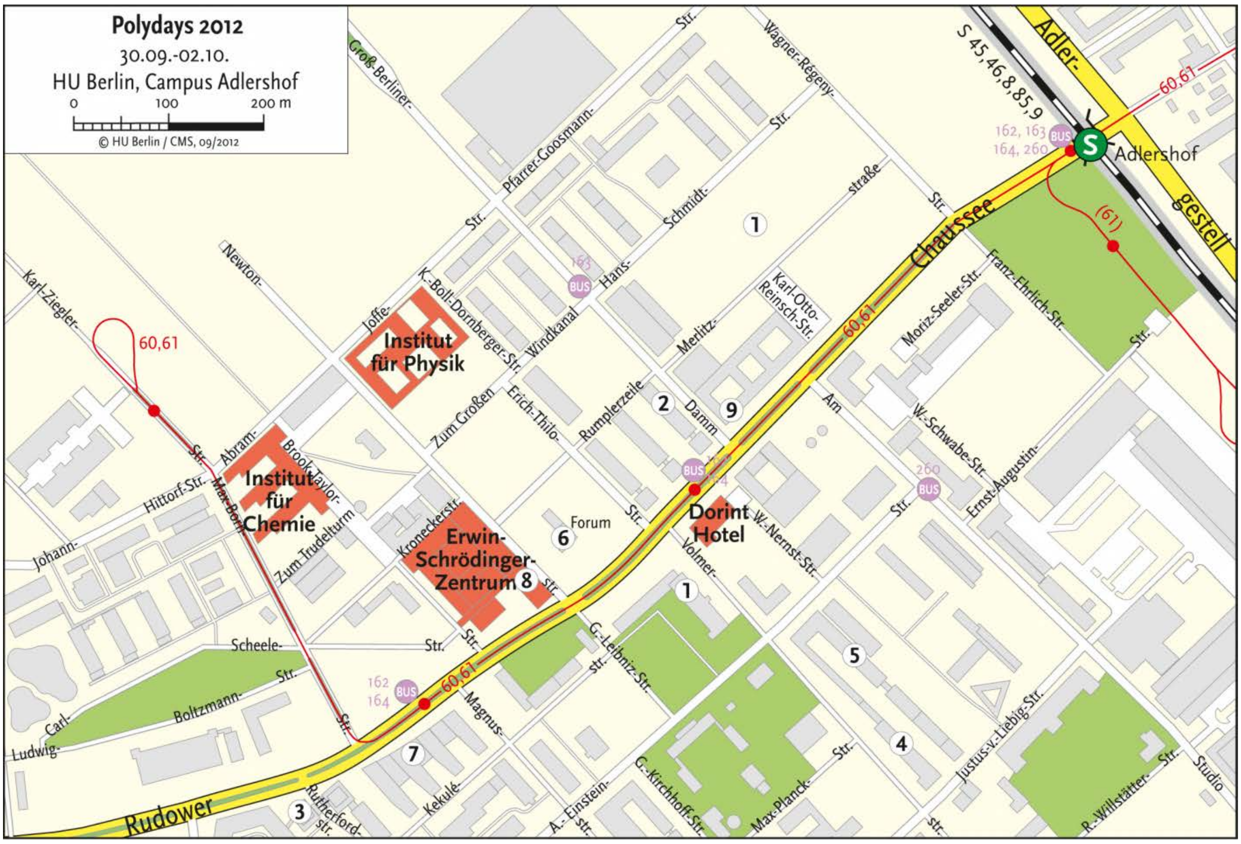
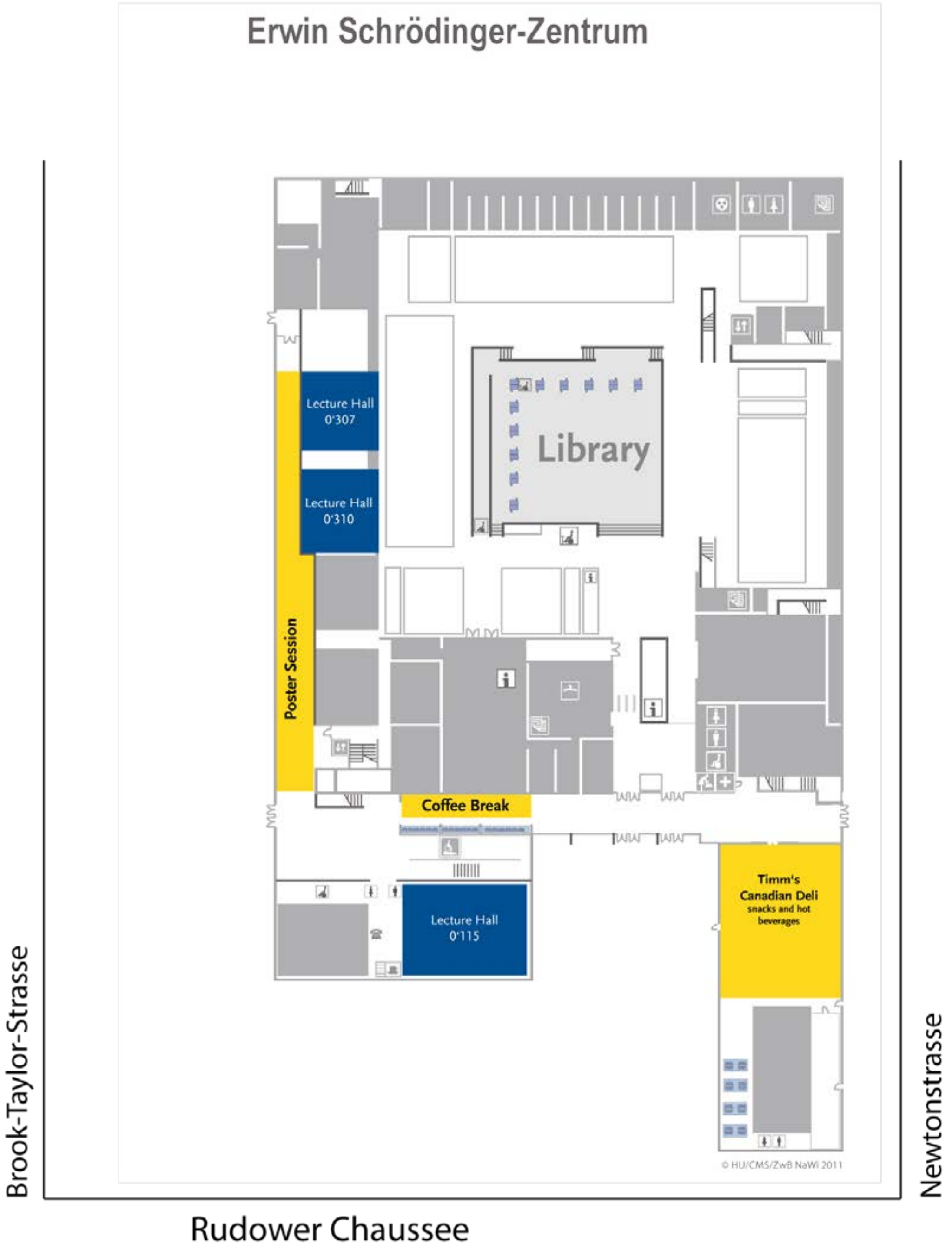
Area map:



Lunch locatios Adlershof:

① WISTA Mensa ABR, Eingang Volmerstraße 2
② Jouis Nour (Bio-Mensa), Groß-Berliner Damm (Entrance), Rudower Chaussee 14
③ IGZ "Die Hummel", Rudower Chaussee 29
④ UTZ "Steinkauz", Volmerstraße 9
⑤ Bistro "Sonnenschein, Volmerstraße 7b
⑥ Esswirtschaft, Rudower Chaussee 24
⑦ Mensa "Oase", Johann Neumann-Haus, Rudower Chaussee 25
⑧ Tim‘s Canadian Deli, Erwin Schrödinger-Zentrum
⑨ Subways, Rudower Chaussee 12b

Site plan:


Erwin Schrödinger-Zentrum
Lecture Hall 0'307
Lecture Hall 0'310
Library
Poster Session
Coffee Break
Lecture Hall 0'115
Timm's Canadian Deli snacks and hot beverages
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Rudower Chaussee

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Polydays 2012: Polymers and Light

Sunday, September 30

16:30-21:00

Guided Tour
(Deutsches Technikmuseum Berlin)

and Boat Trip

Monday, October 1

Registration from 8:00
0’101

Opening 9:00- 9:15
0’115

Plenary Talk 9:15-10:00
High resolution imaging technology for microelectronics
C. Grant Willson, University of Texas at Austin

Coffee Break 10:00-10:30

Plenary Talk 10:30-11:15
0’115
Lessons from nature about solar light harvesting: A little bit of coherence?
Gregory D. Scholes, University of Toronto

Plenary Talk 11:15-12:00
0’115
THz Spectroscopy: A Novel Experimental Tool to Study Water Network Dynamics
Martina Havenith, Ruhr-Universität Bochum

Lunch 12:00-13:30

Sessions 13:30-15:00

Solar I 0’307	**Characterization I** 0’310
Silvia Janietz	Friedrich Kremer
Dieter Neher	Michael Maskos
Kay Saalwächter	Nikolaus Ernsting

Coffee Break 15:00-15:30

Sessions 15:30-17:00

Solar II 0’307	**Characterization II** 0’310
Rudolf Zentel	Andreas Thünemann
Michael Jäger	Jens Weber
Kamalakannan Kailasam	Sebastian Seiffert

Short oral presentation of selected posters 17:10-18:00
0’115

Poster Session 18:00-19:00
BBQ 19:00-21:00

Tuesday, October 2

Gerhard Kanig-Lecture 9:00-10:00
0’115
Electroactive polymers in energy conversion
Jean M. J. Frechet,
King Abdullah University of Science and Technology

BVP Awards 10:00-10:30
0’115
Kurt Ueberreiter-Award: Jing Cui
Georg Manecke-Award: Daniel Zehm

Coffee Break 10:30-11:00

Plenary Talk 11:00-11:45
0’115
Azo polymers for bio-surface switching and the photo-mechanical effect
Christopher J. Barrett, McGill University Montreal

Plenary Talk 11:45-12:30
0’115
Advanced molecular design of functional materials
Takuzo Aida, University of Tokyo

Lunch 12:30-13:45

Plenary Talk 13:45-14:30
0’115
Exploring structure and function of natural polymeric materials with synchrotron radiation
Peter Fratzl, Max Planck Institute of Colloids and Interfaces

Sessions 14:30-16:00

Solar III 0’307	**Lithography** 0’310
Uwe Bunz	Bernd Strehmel
Michael Sommer	Armin Gölzhäuser
Stefan Schiller	Christian Neuber

Coffee Break 16:00-16:30

Sessions 16:30-18:00

Optomechanics 0’307	**Display** 0’310
Andreas Fery	Peter Strohriegl
Svetlana Santer	Hartmut Krüger
David Bléger	Joachim Stumpe

Sessions Mo, October 1, 13:30-15:00

Solar I 0’307

Silvia Janietz	Tailor-made absorber polymers for efficient organic solar cells
Dieter Neher	Charge generation and extraction in polymer-based solar cells
Kay Saalwächter	NMR investigations of crystallinity and supramolecular organization in polymers for photovoltaics applications

Characterization I 0’310

Friedrich Kremer	Infrared - transition moment orientational analysis
Michael Maskos	Characterization of shape switching of polymers induced by light
Nikolaus Ernsting	Oscillation of DNA recognition observable on fluorescence shift?

Sessions Mo, October 1, 15:30-17:00

Solar II 0’307

Rudolf Zentel	Blockcopolymer - nanocrystal hybrids for optoelectronic applications
Michael Jäger	Modular polymer-based architectures for efficient multiple charge-separation: Redox-active polymers and decoration with luminescent ruthenium complexes
Kamalakannan Kailasam	Polymeric heptazine networks for photocatalytic water splitting

Characterization II 0’310

Andreas Thünemann	Polymer characterization using hard X-rays for revealing solution and solid state structures
Jens Weber	Characterization of nanoporous polymers by X-ray scattering
Sebastian Seiffert	Smart Microgel Capsules and Model Colloids Tailored by Photocrosslinking in Droplet-Based Microfluidics

Sessions Tue, October 2, 14:30-16:00

Solar III 0’307

Uwe Bunz	Use of alkene metathesis for the synthesis of pentacene-containing materials
Michael Sommer	Conjugated polymers via step growth and chain growth polymerizations
Stefan Schiller	Defined nanostructured & supramolecular precision biopolymer architectures as photonic building blocks

Lithography 0’310

Bernd Strehmel	Ultrafast photopolymers for lithographic printing applications
Armin Gölzhäuser	Carbon nanomembranes engineered from molecular monolayers
Christian Neuber	Tailored star block copolymer architecture for high performance chemically amplified resists

Sessions Tue, October 2, 16:30-18:00

Optomechanics 0’307

Andreas Fery	Correlation between local pressure and fluorescence in mechanoresponsive polyelectrolyte brushes
Svetlana Santer	Polymer films with optically controlled shape and actuation on a nanometer scale
David Bléger	Photo-shrinkable rigid-rod polymers as building blocks for photodynamic materials

Display 0’310

Peter Strohriegl	Lithographic patterning of semiconducting polymers
Hartmut Krueger	Polymers as universal matrix for highly efficient phosphorescent OLEDs and display applications
Joachim Stumpe	Active and passive polarization elements for LC Displays