CPP 29 POSTER: Polymer physics

Zeit: Dienstag 16:30–18:30 Raum: Poster TU D

CPP 29.1 Di 16:30 Poster TU D

PEGylated Membranes - A SANS study on brushes and mushrooms — •Beate Klösgen[1], Kell Mortensen[2], and Lise Arleth[3] — [1]University of Southern Denmark, Phys. Dept. and MEMPHYS, Odense, Denmark — [2]The Danish Polymer Center, Risø, Denmark — [3]Royal Veterinary and Agricultural University, Frederiksberg, Denmark

Polyethylene glycol (PEG) polymers tethered to lipids were proposed as shielding layers against immune system recognition in so-called stealth liposome formulations. Each polymer is anchored into lipid membrane vesicles that might serve as a nano-vial for membrane embedded hydrophobic or for encaged hydrophilic drugs. The highly polar polymers are assumed to form a loose aqueous PEG layer along the (inner and) outer membrane surface of the hosting vesicle, similar to the glykocalix of a cell. The membrane itself shall still be acessible by small diffusing molecules. We present some details of the polymer packing and its conformational changes as extracted from the analysis of SANS experiments. Results were obtained from suspensions of extruded SUVs (small unilamellar vesicles) that varied in the average amount of polymer that had been anchored into the bilayer sheets, in the number of monomers in the linear polymer chain, and in the average size/curvature of the hosting vesicles.

CPP 29.2 Di 16:30 Poster TU D

The Antibiotic Peptide KLA1 Induces Fluctuating Membrane Pores — •Dennis Kim[1,2], Margitta Dathe[3], Sergej Bezrukov[4], Thomas Hauss[5], Silvia Dante[5], and Beate Klösgen[2] — [1]La Jolla Bioengineering Institute, La Jolla, USA — [2]University of Southern Denmark, Odense, Denmark — [3]Institute of Molecular Pharmacology, Berlin, Germany — [4]NICHD, Bethesda MD, USA — [5]Hahn-Meitner Institute, Berlin, Germany

Antimicrobial peptides constitute the first natural line of defense against pathogens in animals and plants. During the last decade, thousands of these AMPs have been isolated from their natural sources or designed de novo with the goal of creating another generation of antibiotics to counter increasingly resistant bacteria. The effect of a synthetic antimicrobial peptide, KLA1, on a lipid model bilayer was studied by a combination of methods including cryo-TEM, SANS, conductivity experiments, and micromechanical deformation studies by micropipet aspiration. Experiments were done on small unilamellar vesicles (SUVs), planar membrane stacks, black lipid membranes (BLMs), and giant unilamellar vesicles (GUVs). Results are presented and discussed with respect on different models for induction of membrane lysis. Our system seems to represent an example for the toroidal pore model that involves the spontaneous formation of transitory membrane holes. Such pores fluctuate, and their formation and stability are governed by local defect induced modulations of the elsehow continuous bending elastic properties of the membrane.

CPP 29.3 Di 16:30 Poster TU D

Frequency dependence of mechanical properties of thin polymer films — •Michael Holzwarth, Andreas Kleiner, Martin Hinz, Alexander Gigler, Sabine Hild, and Othmar Marti — Department of Experimental Physics, University of Ulm, 89069 Ulm, Germany

It is well known from measurements on bulk polymer samples that their mechanical properties reveal a certain frequency dependence. These materials have already been investigated on a nanometer scale with AFM techniques such as force-distance-curves at low frequencies (1 Hz) and Pulsed-Force Mode at higher frequencies (1 kHz). The aim of our work is to investigate the frequency-dependent behaviour in the intermediate range. We use AFM cantilevers to perform nanoindentations on thin films of PMMA (Polymethylmethacrylate) spin-coated on a silicon substrate. Force-distance-curves are evaluated to reveal the mechanical properties of the polymer. The remanent depth of the indentations will be shown as a function of frequency and maximum applied load.

CPP 29.4 Di 16:30 Poster TU D

Mechanics of flat freestanding membranes — •Ingo Dönch, G. Bogdanovic, V. Bosio, M. Nolte, B. Schöler, A. Fery, and H. Möhwald — MPI of Colloids and Interfaces 14176 Golm

Lab on a chip applications demand for miniaturization of existing technologies for sensing physical solution properties like hydrostatic or osmotic pressure. In this context, membrane sensors are promising, since they can be scaled down without change of concept.

We have to developed a novel technique that allows to transfer ultrathin polyelectrolyte multilayer membranes onto substrates with holes of diameters between several microns and several 100s of microns. The compliance of the resulting membrane patches is depending only on the thickness of the membrane and the radius of the covered hole. It can be described with simple continuum mechanical models. We can directly probe the compliance of the membranes with AFM and compare our findings to these predictions.

Since the thickness of the multilayers can be controlled on the nm level, the compliance of the membranes can be precisely controlled and varied over orders of magnitude. Additionaly, the PE-membranes are semi-permeable, which makes them sensitive to osmotic pressure differences. Thus they are promising elements for future micro-scale membrane sensors.

CPP 29.5 Di 16:30 Poster TU D

Strain induced compression of smectic layers in free-standing liquid crystal elastomer films — •Victor Aksenov[1], Jürgen Bläsing[1], Martin Rössle[2], Ralf Stannarius[1], and Rudolf Zentel[2] — [1]Univesity Magdeburg, Institute of Experimental Physics — [2]University of Mainz, Institute of Organic Chemistry

Liquid crystal elastomers (LCEs) combine rubber elasticity and anisotropic liquid crystal properties. Conventional rubber materials are isotropic and have a Poisson ratio equal to 1/2. If the stress of smectic A LCEs is in the smectic layer plane, a Poisson ratio close to 1 has been observed parallel to the smectic layer, and zero perpendicular to it [1].

The smectic LCE investigated here behaves as a conventional rubber. Optical reflectometry shows that stretching of the free standing films with smectic layers parallel to the film surface causes the change of the optical thickness of the film. Small angle X-ray scattering measurements confirm that strain leads to smectic layer compression. The measured Poisson ratio is close to 1/2.

[1] E. Nishikawa and H. Finkelmann, Macromol. Chem. Phys. 200, 312 (1999).

CPP 29.6 Di 16:30 Poster TU D

Mikromechanische und optische Untersuchungen an dünnen Schichten aus Seidenproteinen — •Uwe Spohn[1], Frauke Junghans[1], Stefan Schulze[1], Udo Conrad[2], Andreas Heilmann[1] und Uwe Spohn[1] — [1]Fraunhofer Institut für Werkstoffmechanik Halle, D-06120 Halle, Heideallee 19 — [2]Institut für Pflanzengenetik und Kulturpflanzenforschung, D-06466 Gatersleben, Corrensstr. 3

Durch Spincoating und Casting wurden Schichten aus Seidenproteinen mit Dicken zwischen 50 nm und 10 Mikrometern auf Glassubstraten abgeschieden. Durch das Lösungsmittel lassen sich die mechanischen Eigenschaften solcher Schichten variieren. Die Spinnenseiden wurden durch Expression aus Tabakpflanzen [1] gewonnen. Die Morphologie der Schichten wurde durch Rasterelektronenmikroskopie, Environmental Scanning Microscopy (ESEM) und durch AFM untersucht. Durch AFM wurden die Schichtdicken bestimmt. Bei sehr dünnen Schichten kann deren Dichte mit einer Quarzmikrowaage bestimmt werden. Die Schichten wurden sowohl FT-IR- als auch UV-VIS spektroskopisch charakterisiert. Sowohl die AFM als auch die ortsaufgeloeste UV-VIS Spektroskopie ermoeglichen Aussagen über die Homogenitaet und die Menge der abgeschiedenen Spinnenseidenproteine. Mit einer Quarzmikrowaage wird der komplexe Elastizitaetsmodul von Proteinschichten durch akustische Netzwerkanalyse bestimmt. Untersucht wurde der Einfluß der Temperatur und der Luftfeuchtigkeit

[1] J. Scheller, K.-H. Guehrs, F. Grosse, U. Conrad, Nature biotechnology 19 (2001) 573 ff.

CPP 29.7 Di 16:30 Poster TU D

Internal Order in Polyelectrolyte Multilayers — •Manesh Gopinadhan[1], Jens-Uwe Günther[1], Heiko Ahrens[1], Roland Steitz[2], and Christiane A. Helm[1] — [1]Angewandte Physik, Universität Greifswald, 17487 Greifswald — [2]Hahn-Meitner Instiut Berlin, 14109 Berlin

Polyelectrolyte multilayer fabrication by consecutive adsorption of polyanions and polycations proved to be a versatile method for a broad range of applications. Multilayers were prepared by consecutively adsorbing poly(allylamine) hydrochloride (PAH) and polystyrene sulfonate (PSS) from aqueous KCl solution (1 Mol/L) at different temperatures, approaching the precipitation temperature at 55°C. Thus, the film thickness can be increased by up to 70%. With neutron reflectivity measurements on multilayers with every second PSS layer deuterated, the layer interdigitation is probed. Up to 35°C, the film/air roughness as determined by X-ray reflectivity and the internal roughness per bilayer thickness determined by neutron reflectivity increase linearly with the layer thickness. On further increase of the preparation temperature, the internal roughness increases more than the polyelectrolyte bilayer thickness, proving large interdigitation caused by local polyelectrolyte coils.

CPP 29.8 Di 16:30 Poster TU D

The Internal Interface of a Homogeneous Compressed PEE-PEO Diblock-Copolymer Monolayer — •Alexander Wesemann[1], Heiko Ahrens[1], Roland Steitz[2], Stephan Förster[3], and Christiane A. Helm[1] — [1]Angewandte Physik, Uni Greifswald, 17487 Greifswald — [2]Stranski-Laboratorium, TU Berlin, 10623 Berlin — [3]Physikalische Chemie, Uni Hamburg, 20146 Hamburg

Amphiphilic block copolymers consisting of a fluid hydrophobic (Poly ethyl ethylene, PEE) and a hydrophyilic (Polyethyleneoxide, PEO) block form monolayers at the air/water interface. With X-ray and neutron reflectivity the density profile of $PEE_{432}PEO_{484}$ is investigated. It was found that the polymer adsorption layer consists of a homogeneous PEE and a homogenous PEO block, which can be compressed by a factor of three. The PEE thickness increases inversely proportional to the molecular area, and the PEO brush follows roughly the scaling law predicted for a brush in a good solvent. However, the stretching of the two blocks roughens the PEE-PEO interface, causing a transition from a PEO-monolayer adsorbed to a hydrophobic interface (0.8-1.1 nm thick) to a PEO/PEE/water interfacial layer of 3nm thickness. This transition of the interfacial layer highlights the rich phase behavior of amphiphilic block copolymers, which resembles that of lipids and non-ionic surfactants.

CPP 29.9 Di 16:30 Poster TU D

Patterning in Azobenzene Polymer Films — •Knut Morawetz[1], Burkhars Stiller[1], Thomas Geue[2], Marina Saphiannikova[1], and Ullrich Pietsch[1] — [1]Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam — [2]Paul Scherrer Institute, ETH Zurich, Switzerland

Thin azobenzene polymer films show a interesting property namely the optically induced material transport. The physical mechanism underlying this phenomenon has not yet been thoroughly understood. Nevertheless this effect enables to inscribe different structures onto the film surface including one- and two-dimensional periodical structures. Typical size of such structures is about one micrometer, i.e. it is comparable with a wavelength of the laser used for optical excitation. In this study we have measured mechanical properties of the one- and two-dimensional gratings with a high lateral resolution. It was used force-distance curves and pulse force mode of the atomic force microscope. We also report on the generation of considerably finer structures with a typical size of 100 nm, which were inscribed onto the polymer surface by an optical pen (by the cantilever of a scanning near-field optical microscope). Such kind of inscription does not only open new possibilities for applications but also gives a deeper insight into the physical fundamentals of the optically induced material transport.

CPP 29.10 Di 16:30 Poster TU D

Investigation of Thermal Treated Surface Relief Gratings by Means of Atomic Force Microscopy and Diffraction Measurements — •Stefan Katholy[1], Knut Morawetz[1], Burkard Stiller[2], and Ullrich Pietsch[1] — [1]Universität Potsdam, Institut für Physik, STAN, Am Neuen Palais 10. 14469 Potsdam — [2]Universität Potsdam, Institut für Physik, PWM, Am Neuen Palais 10. 14469 Potsdam

Thin Spin Coating films of polymers with photochromic azobenzene side chains are of great interest for optical data storage systems. These gratings are prepared under ambient conditions by illumination of the films with actinic light (488nm). The E/Z isometrization of the azochomophoric groups causes a remarkable mass transport of film material, leading to a periodic change of the film thickness, the so called surface relief grating (SRG) [1,2]. The E/Z isomerization changes also the optical properties of the material, i.e. the refractive index [2]. For special applications it is of prior interest to generate a periodic lateral variation of the optical properties. The aim of this work was to find optimal preparation conditions for films, which have a periodic variation of refractive index, but with a smooth surface (so called density gratings). These films are prepared by thermal annealing of SRG gratings. The quality of the obtained density gratings depends on the properties of the polymer, the inscription conditions of the SRG grating and the subsequent annealing process.

[1] J. Barrett, L. Rochon, A. Natansohn, J. Chem. Phys., 109 (1998), p.1505 [2] U. Pietsch Phys. Rev. B 66 (2002), pp.155430-1

CPP 29.11 Di 16:30 Poster TU D

Structuring of polyelectrolytes in liquid nanofilms — •Dan Qu[1], Helmuth Möhwald[1], and Regine v. Klitzing[1,2] — [1]MPI f. Kolloid- und Grenzflächenforschung — [2]Institut f. Physikalische Chemie, CAU Kiel

It has been predicted by theories that semi-dilute polyelectrolyte solutions form mesh-like network structures in bulk. The mesh size depends on both the concentration and the charge density of the polyelectrolyte. Experiments from both light scattering and free-standing films show characteristic length scales within the bulk, corresponding to the mesh size. In the current work, we have investigated the effect of charge on the structural forces in aqueous, salt-free, semi-dilute solutions of partially charged Polyacrylamide sulfonate (PAMPS) with different charge fractions f, using a colloidal probe AFM. The period of the found oscillatory forces give hints for the existence of Manning condensation, but the decay of the forces doesn't. Results from conductivity measurements confirm this point of view, showing that the actual conductivity of the solutions is between that predicted by Manning condensation with fixed, immobile, condensed ions and that of total free counter ions, indicating that the condensed ions are not perfectly fixed on the polymer chains and are mobile to a certain degree.

CPP 29.12 Di 16:30 Poster TU D

A Novel Method for Determining Thickness of Self-Assembled Monolayers — •Saju Pillai, Sabine Hild, and Othmar Marti — Department of Experimental Physics, University of Ulm, Ulm, Germany, D-89069

Usually, thickness of a completely formed monolayer has been achieved using Ellipsometry as the silanes are covalently bonded to the substrate through Si-O-Si bond. However we could develop an easy and convenient method to determine the thickness of a completely formed monolayer by employing a 'selective dissolution' method combined with atomic force microscope(AFM). Especially we studied monolayer formation and growth mechanism of octadecylsiloxane obtained using octadecyltrimethoxysilane(OTMS). OTMS exhibits a monolayer growth through an island expansion process similar to octadecyltrichlorosilane, but with a slow growth rate. The average height of islands, surface coverage, contact angle and RMS roughness increase with OTMS adsorption time in a consecutive manner. The 'selective dissolution' method was extended to determine the monolayer thickness of various silanes with different C-chain lengths. The samples were analyzed and characterized in both Pulsed Force Mode and Tappingmode in a custom built and commercially available AFMs.

CPP 29.13 Di 16:30 Poster TU D

Formation of Large PEE-Domains in $PEE_{212} - PEO_{112}$ Diblock Copolymer Monolayers: Shift of the PEO-Desorption Transition — •Alexander Wesemann[1], Heiko Ahrens[1], Stephan Förster[2] und Christiane A. Helm[1] — [1]Angewandte Physik, Uni Greifswald, 17487 Greifwald — [2]Physikalische Chemie, Uni Hamburg, 20146 Hamburg

$PEE_{212} - PEO_{112}$ diblock copolymer monolayers are studied at the air-water interface. At large molecular areas, with X-ray reflectivity PEE domains are observed, which are partly immersed into the water. The domain thickness increases on compression (28 to 40 Å). With off-specular X-ray reflectivity, an average domain radius of 750 Å is found, but there are also smaller domains. Due to the space constraints, most PEO-blocks form a brush beneath the PEE domains. Only a few PEO-blocks form a corona surrounding the domains and adsorb flatly onto the air-water interface. When the domain area fraction is 95%, the onset of the PEO desorption transition is found at the typical pressure of 9 mN/m. Yet, it occurs at $6\mathring{A}^2$/EO-monomer, 50 % of the value found usually. Apparently, the thickness of the PEE-domains is determined by the forces from the two interfaces, not by the PEO-block.

CPP 29.14 Di 16:30 Poster TU D

Heating of Elastomer Surfaces after Plasma Fluorination — •T. Meyer — Universiät Osnabrüeck, Fachbereich Physik, Barbarastr. 7, D-49069 Osnabrück, Germany

For many industrial applications, i.e. in the printing-industrie, hydrophobic HNBR-Elastomer surfaces are necessary. In this work the thermal stability of these surfaces will be investigated. HNBR (Hydrated Nitril Butadien Rubber) was treated by a 2.45 GHz microwave CF$_4$-Plasma in order to incorporate fluorinated functional groups. The consequences of subsequent heating treatments after fluorination were investigated by a combination of angle-resolved XPS and measurements of the surface free energy (contact angle γ_s), over a temperature range from 100°C to 240°C. After the CF$_4$ plasma treatments, the incorporation of CF$_x$ groups at the surface of HNBR induces a decrease of the γ_s value. Further thermal treatments lead to modifications of the chemical surface composition and of γ_s. The most important changes concern a significant increase of the surface free energy, where the contribution of the dispersive component is the most affected, and a decrease of the Fluor/Carbon ratio. The loss of fluorine is caused by chain scission in the polymer and is accompanied by a surface oxidation, as revealed by an increasing O 1s XPS-peak intensity.

CPP 29.15 Di 16:30 Poster TU D

Temperature and thickness regulated domain spacings in thin films of a cylinder forming diblock copolymer — •Larissa Tsarkova, Armin Knoll, Robert Magerle und Georg Krausch — Physikalische Chemie II, Universität Bayreuth

Recent research on thin films of asymmetric block copolymers has demonstrated deviations from the bulk behavior due to confinement and surface field effects [1]. With scanning force microscopy (SFM) we study the phase behavior in thin films of a polystyrene-*block*-polybutadiene copolymer. Long range microdomain ordering as well as terrace formation was achieved by thermal annealing in vacuum. With the home made software [2] performing quantitaive processing of SFM images we analyze the cylinder spacings within the terraces and at transition film thickness (steps). We demonstrate systematic changes in the lateral domain spacing induced by a variation of the annealing temperature and the film thickness. Both results suggest novel routes to tune and control the microdomain dimensions on a nanometer scale without changing the composition of the polymer film. [1] A. Knoll, *et al.*, PRL, 89, 035501 (2002).[2] A. Knoll, Ph.D. Thesis, Universität Bayreuth, Germany (2003).

CPP 29.16 Di 16:30 Poster TU D

Dielektrisch behinderte Entladungen - eine wirkungsvolle Methode zur Oberflächenmodifikation — •Ingrid Graz[1], Reinhard Schwödiauer[1], Siegfried Bauer[1], Hermann Gruber[2] und Christoph Romanin[2] — [1]Physik weicher Materie, Inst. F. Experimentalphysik, J. Kepler Universität Linz, Altenbergerstraße 69, 4040 Linz, Austria — [2]Inst. F. Biophysik, J. Kepler Universität Linz, Altenbergerstraße 69, 4040 Linz, Austria

Die Behandlung mit Plasma ist eine Standardmethode zur Oberflächenmodifikation. Dielektrisch behinderte Entladungen bieten eine einfache und effektive Möglichkeit zur Erzeugung von Nichtgleichgewichts-Plasmen (speziell energiereiche Elektronen): Im Luftspalt zwischen zwei Elektroden, von denen zumindest eine mit einem Dielektrikum bedeckt ist, werden durch Anlegen von Hochspannung Mikroentladungen gezündet. Diese Entladungen erzeugen nun ein kaltes Plasma im Luftspalt, das zur Modifikation von Oberflächen benutzt werden kann. Im Speziellen wurde durch dielektrisch behinderte Entladungen die Benetzbarkeit von Polymerfolien erhöht. Der Vorteil des Verfahrens besteht im sehr einfachen experimentellen Aufbau, da der Prozess bei Atmosphärendruck stattfindet.

CPP 29.17 Di 16:30 Poster TU D

Simple, tunable nano- and micro-periodic surfaces in poly(dimethyl siloxane) — •Arnaud Chiche, Joao T. Cabral, and Christopher M. Stafford — NIST Polymers Division, Gaithersburg, MD (United States)

We report a simple methodology to generate periodic structures in poly(dimethyl siloxane) surfaces. The technique requires only a conventional surface treatment (ultraviolet and/or plasma exposure) and simultaneous mechanical deformation of an elastomeric membrane. Sinusoidal surface modulations, with tunable amplitude and frequency, in the nano- and micrometer range, are readily obtained. The limitations and potential of this technique are discussed in detail, as well as the oxidation mechanism and kinetics particularly in the case of a plasma treatment. Finally, we demonstrate that complex periodic topologies are induced under multi-axial deformation. Applications of this inexpensive methodology include stamps for soft lithography and surface patterning.

CPP 29.18 Di 16:30 Poster TU D

Collective description of polymer blends in the presence of a surface — •Semjon Stepanow and Andrei Fedorenko — Martin-Luther-Universität Halle, Fachbereich Physik, D-06099

We consider the polymer blend composed of two different homopolymers in the presence of the surface. Using the random phase approximation we derive the effective surface Hamiltonian, and study the interplay between the surface and the bulk behaviour of mixture of polymers, which have different affinities to the surface. Additionally, we consider the compressible polymer melt near the attractive surface, and study the mononer density profile and the surface concentration of adsorbed polymers using the concept of effective potentials.

CPP 29.19 Di 16:30 Poster TU D

In-situ time-resolved grazing-incidence small-angle X-ray scattering: A tool to study reorientational processes in thin diblock copolymer films — •C.M. Papadakis[1], P. Busch[2], D.-M. Smilgies[2], D. Posselt[3], and M. Rauscher[4] — [1]Physikdepartment E13, TU München — [2]Cornell University, Ithaca NY, USA — [3]Roskilde University, Denmark — [4]MPI for Solid State Research, Stuttgart

Diblock copolymers in the melt spontanously self-organize into mesoscopically ordered structures. This makes them attractive candidates as templates for the patterning of surfaces. In order to understand the structure formation and the response to outer stimuli, it is important not only to know the surface structure (readily available by atomic force microscopy), but also the structure within the film.

Grazing-incidence small-angle X-ray scattering (GISAXS) offers the possibility to simultaneously gain information on the structures normal to the film surface and on lateral structures. In addition, the short measuring times make time-resolved in-situ measurements on samples in solvent vapor possible. We will present our results on lamellar polystyrene-polybutadiene diblock copolymer films, where we have found an unexpected change of the lamellar orientation as a function of block copolymer molar mass as well as significant changes upon solvent vapor treatment.

CPP 29.20 Di 16:30 Poster TU D

Modification and imaging of surface charges on polymers using atomic force microscopy — •Andreas Kleiner[1], Sabine Hild[1], Othmar Marti[1], Armin Knoll[2], Bernd Gotsmann[2], Urs Dürig[2], and Johannes Windeln[2] — [1]Dept. of Experimental Physics, University of Ulm, 89069 Ulm — [2]IBM Research GmbH, Zurich Research Laboratory, CH-8803 Rüschlikon

The atomic force microscope (AFM) is widely used to investigate and modify mechanical properties of thin polymer films. Different static and dynamic modes like force curve measurements, Pulsed Force Mode or intermittent contact techniques apply certain amounts of normal and lateral forces to the sample. This implies the possibility to create surface charges, similar to the macroscopic contact electrification of insulators. These charges can be imaged in the 'Surface Potential' or 'Kelvin Probe Force' mode of the AFM. The quantity of charge depends on parameters like contact time, force or velocity. By an additional tip voltage during contact, the amount and polarity of the surface charges can be influenced. The long-term stability of these charges, measured on different polymers, will be also shown in this work.

CPP 29.21 Di 16:30 Poster TU D

SFM characterization of single polymer chains in controlled environments: effect of tip adhesion and chain swelling — •Wei Zhuang[1], Christof Ecker[1], Paolo Samorí[2], and Jürgen P. Rabe[1] — [1]Department of Physics, Humboldt University Berlin, Newtonstrasse15, 12489 Berlin — [2]Instituto per la Sintesi Organica e la Fotoreattività, C.N.R. Bologna, via Gobetti 101, 40129 Bologna, Italy

Isolated slightly hydrophilic chains of poly(isocyanodipeptides) (PIC) adsorbed on mica were studied by Tapping Mode SFM in an atmosphere controlled both with respect to the relative humidity (RH) and the presence of CHCl3 vapor. SFM revealed that the apparent average chain height increases with decreasing RH, leading to the highest value at RH = 0. This is due to both a minimization of the capillary forces between the SFM tip and the hydrophilic substrate surface and a collapse of the side chains in poor solvent. In a saturated CHCl3 vapor atmosphere the chain heights increase up to twice this value, which is close to the polymer diameter measured by powder X-ray diffraction. This indicates that the PIC chains are solvated by CHCl3 molecules, causing the swelling of the single polymers. Additional experiments on an alkylated dendronised polymer revealed that the swelling of the chains occurs also on HOPG.

CPP 29.22 Di 16:30 Poster TU D

16k by 16k imaging to study the long range morphology of thin polymer films — •Alexander Schmatulla and Othmar Marti — Universität Ulm Abt. Experimentelle Physik Albert-Einstein-Allee 11 89081 Ulm

We will show an AFM image with 256 million pixels of a thin polymer film. Aim is to study the longe range morphology of grafted polymers, phase transitions and left-, right distribution of the sidechains with nm resolution.

CPP 29.23 Di 16:30 Poster TU D

Polymer adhesion at surfaces — •Alexander Schmatulla[1], Igor Potemkin[2], Alexei Khokhlov[2], and Othmar Marti[1] — [1]Abt. Experimentelle Physik Albert-Einstein-Allee 11 89081 Ulm — [2]Abt. Polymer Physik Albert-Einstein-Allee 11 89081 Ulm

Several methods, like force spectroscopy or optical tweezers, have been developed to analyse the mechanical properties of single polymer chains, like DNA, PE, PMMA. In the case of graft copolymers with long side chains, parameters like the length, orientation with respect to the backbone and density can influence the micro structure and the mechanical properties of the entire macromolecule. For such polymers, the properties of the side chains are interesting, too. However, the mechanical properties of the single side chain of graft polymers are still unknown. First aims of this project are to prepare brushed copolymers on different surfaces and to detect the backbone and the side chains in tapping mode. The next step will be to measure the mechanical behavior of the side chains: a suitable measurement apparatus to determine these properties is our custom-built differential AFM. Also using the Digital Pulsed Force Mode allows to detect the forces necessary to pull-off the side chains from the surfaces by digitalizing the complete trajectory of the tip and successively converting the acquired data into an array of force vs. distance curves.

CPP 29.24 Di 16:30 Poster TU D

Cavity growth in soft adhesives — •Arnaud Chiche, Josef Dollhofer, and Costantino Creton — ESPCI, Paris (France)

We have studied the growth of cavities in a SIS based soft adhesive layer submitted to a hydrostatic stress, in a flat-probe geometry (tack). We have shown that cavity growth occurs from lack of interfacial contact during the bonding process, due to the elastic properties of the adhesive material. These initial flaw sizes have been varied through the change of both probe and adhesive surface roughness. This size appears to be a critical parameter for the cavitation process. The growth of large enough flaws is not affected by their size and appears to be controlled by a local stress criterion that depends on the elastic properties of the material. On the other hand the growth of small flaws becomes extremely size sensitive: the smaller is the initial defect, the higher is the stress it eventually grow, always above the previous criterion. The expansion then appears to be controlled by the amount of available elastic energy, consistent with the observed sensitivity to the adhesive layer thickness. These new experimental results are consistent with a model we developed based on the assumption that potential flaw size effect results on its surface energy.

CPP 29.25 Di 16:30 Poster TU D

Influencing factors on the adhesion of elastomeres — •Martin Kitsche[1], Wolfram Hild[1], Norbert Kendziorra[2], Gert Heinrich[3], and Juergen A. Schaefer[1] — [1]TU Ilmenau, Institut für Physik und ZMN, Postfach 100565, 98694 Ilmenau — [2]Continental AG, Jädekamp 30, 30419 Hannover — [3]Leibniz-Institut für Polymerforschung, Hohe Straße 6, 01069 Dresden

Adhesion has been a topic of research for a long time. However, it is not well understood in detail. Due to their unique properties and various conformations, elastomeres are very important for many industrial sectors. The relation between the adhesion mechanisms and the associated characteristics of friction and wear of elastomeric components is still unexplained although it is essential for many technical applications. Former investigations in this field do not pay enough attention to viscoelastic properties of the material.

In the investigations presented here we studied the influence of normal force, detachment velocity, Youngs-modulus of rubber samples (natural, isoprene and styrene-butadien rubber) and the roughness of the counter sample (glass and perspex) on the pull-off force. It was found that the viscoelastic properties have a significant influence on the measured pull-off forces in dynamic loading. Another finding is the decrease of pull-off forces with increasing roughness. This decrease is steeper with higher Youngs-modulus and corresponds to the results of Fuller and Tabor.

CPP 29.26 Di 16:30 Poster TU D

High Sensitive AC-calorimeter for Nanometer Sized Samples — •Heiko Huth, Alexander Minakov, and Christoph Schick — Universität Rostock, Institut für Physik, Universitätsplatz 3, Rostock 18051

For nanogram samples and films in the μm... nm range standard calorimetric methods are mostly not applicable. To overcome these limitations one can measure with high heating and cooling rates. This is realized by the use of chip calorimeters. These calorimeters use thin film techniques to avoid large addenda heat capacities. With the use of small samples this results in possible heating rates up to 100,000 K/s. These chip calorimeters can also be used to measure frequency dependent heat capacity. We use a standard vacuum gauge from Xensor Integration, NL, as an AC-Calorimeter. On a thin membrane of silicon-nitride a small heater is placed with the hot junctions of a thermopile around. The sample is placed on the heater in case of small samples or spread over the whole sensor using spin coating in case of thin films. In this case only the heated area is of interest. The achieved high sensitivity gives us the possibility to measure samples below one nanogram or heat capacities below 1 nJ/K. Choosing the right experimental conditions a frequency range between about 1 Hz and 1 kHz is accessible.

CPP 29.27 Di 16:30 Poster TU D

Photoelectron spectroscopy and microscopy on magnetic nano particles embedded into block copolymers — •O. Seifarth[1], Y. Burkov[1], D. Schmeisser[1], A. Sydorenko[2], R. Kremek[2], and M. Stamm[2] — [1]Brandenburg Technical University, 03046 Cottbus, Konrad Wachsmann Allee 17 — [2]Institut für Polymerforschung, 01069 Dresden, Hohe Strasse 6

The formation of metallic nano particles stored in thin films of block copolymers has been investigated by means of synchrotron radiation based photoemission spectroscopy (PES) and microscopy (PEEM). Empty channels in poly(styrene-block-4-vinylpyridine) copolymer with diameters of tens of nanometers filled with CrO_2, Cr_2O_3 and Ni provide ideal bases for performing electron spectroscopy with energy and lateral resolution on magnetic nano particles. We present UPS, XPS, NEXAFS spectra and PEEM images on and off the C 1s, Cr 2p, Ni 2p resonances and discuss the geometric and electronic structure of such compounds. The synchrotron radiation was delivered from the U49/2 beamline at BESSY II.

CPP 29.28 Di 16:30 Poster TU D

Conductivity and Gassorption Properties of Carbon Nanotubes Polycarbonate Nanocomposites — •Andreas Schoenhals, Martin Boehning, Ning Hao, and Harald Goering — Fderal Institute for Materials Reserach and Testing, Department VI.3, Unter den Eichen 87, D-12205 berlin

Nanocomposites of Polycarbonate with different concentrations of multiwalled carbon nanotubes (MWCNT) are investigated by dielectric spectroscopy in a broad frequency and temperature rang. The influence of the temperature and the concentration of the MWCNT on the conductivity are discussed. This includes a investigation of the influence of a thermal annealing on the properties of the nanocomposites revealed by dielectric spectroscopy and gas sorption measurements as well.

CPP 29.29 Di 16:30 Poster TU D

An Analytical Derivation of the Polarisation P(t) in Organic Molecular Aggregates — •Annetraud Scheuing and Peter Reineker — Theoretische Physik, Universität Ulm, D-89069 Ulm

We start with a Hamiltonian which comprises onsite, transfer and generalized Hubbard electron-electron-interactions plus a linear electron-phonon-interaction. In principle any number of sites i and excitations ν are allowed. Specializing to the dimer problem, we derive a matrix equation for the Eigenstates and Eigenvectors, which has to be solved numerically. Regarding the general electronic sub-Hamiltonian coupled to an electric field H_F, the expression for the polarisation $P(t)$ is derived analytically. For numerical evaluation of $P(t)$ the lowest Eigenvalue and

Eigenstates of the matrix equation have to be used.

CPP 29.30 Di 16:30 Poster TU D

Unexpected mechanical properties in reactiv polymer nanocomposites as seen by Brillouin spectroscopy — •R. Bactavatchalou[1,2,3,4], C. Gilow[1,2], J. Baller[1,3], R. Sanctuary[1,3], D. Rouxel[1,4], W. Possart [2], and J.K. Krüger[1,2,3,4] — [1]Laboratoire Européen de Recherche Universitaire Saarland-Lorraine (LERUSL) — [2]Universität des Saarlandes, Saarbrücken, Germany — [3]Université du Luxembourg, Luxembourg — [4]Université de Nancy I, France

The mechanical properties of polymers can strongly be modified by filling the polymer with nanoparticles of different materials. In reactiv polymer systems, the nanoparticles are present during the polymerisation and due to their big surface, they can cause by surface catalytic reactions additionnal morphologies. These specific interactions between nanoparticles and the matrix may cause great modifications of the phenomological properties of the nanocomposites. For example, the impact resistance and the elastic modulus can increase simultaneously, whereas normally these physical quantities evolve in opposite directions. The mechanical investigations are performed with Brillouin spectroscopy, which is of special interest because the involved acoustic wavelenght may become of the order of the interparticle distance.

CPP 29.31 Di 16:30 Poster TU D

The interaction between single colloids with and without grafted DNA as measured by optical tweezers — •Kati Kegler, Christof Gutsche, Mathias Salomo, and Friedrich Kremer — Institute for Experimental Physics I, University of Leipzig, Linnestr. 5, 04103, Leipzig, Germany

Optical Tweezers (OT) are extraordinary microscopic tools with nanometer resolution in 3-D space and sub pico newton - resolution in force. They are used to measure the interaction potential between single pairs of colloids grafted with (genetically engineered) DNA of varying length (base pairs (bp), 1000 bp, 2000 bp and 4000 bp). The interaction forces are measured in two dimensions - parallel and perpendicular to the axis between the two colloids. This enables one to measure the effective thickness of the DNA layer and its elastic properties.

CPP 29.32 Di 16:30 Poster TU D

The interaction between single colloids with and without grafted DNA as measured by optical tweezers — •Christof Gutsche, Kati Kegler, Mathias Salomo, and Friedrich Kremer — Institute for Experimental Physics I, University of Leipzig, Linnestr. 5, 04103, Leipzig, Germany

Optical tweezers are commonly used to study a wide variety of flow phenomena. With their extraordinary resolution in space (2 nm) and force (1 pN) they became an irreplaceable tool with a broad spectrum of applications. Within our cooperation we focused our interest on the analysis of the interaction potential between single pairs of colloids. Special emphasis is given to the change of the surrounding medium, but as well the influence of the particle size will be studied.

CPP 29.33 Di 16:30 Poster TU D

Swelling and Plasticization in Glassy Polymer/Gas-Systems - Combined Examination of Experimental and Modelling Results — •Ole Hoelck[1], Martin Boehning[1], Martin Siegert[2], and Matthias Heuchel[2] — [1]Bundesanstalt fuer Materialforschung und -pruefung (BAM VI.3), Unter den Eichen 87, 12200 Berlin — [2]GKSS Forschungszentrum Geesthacht GmbH, Inst. f. Chemie, Kantstrasse 55, 14513 Teltow

Swelling and plasticization of glassy polymers upon sorption of gas molecules affects several application relevant properties as well as the general stability and reliability of the polymer matrix. This joint research project of experimental evaluation and molecular modelling aims at the convergence of boundary conditions of both, experiment and simulation, to enable a comparison and complementary analysis of their results, in order to gain a deeper understanding of the phenomena on the molecular level. Presented results - focussed on the polysulfone/carbondioxide-system - concerning corresponding changes in physical properties of simulation and experiment are subjected to interpretation in terms of the site-distribution model as well as other phenomenological gas transport models.

CPP 29.34 Di 16:30 Poster TU D

Upgrade of the BW4 beamline at HASYLAB/DESY — •Stephan V. Roth, Ralph Döhrmann, Martin Dommach, and Rainer Gehrke — HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany

Small-angle X-ray scattering is a versatile method to investigate mesoscopic correlations in bulk matter and thin films. The beamline BW4 is designed to extend this range to the ultra SAXS (USAX) regime [1,2]. Here, maximum resolvable length scales can be extended near 1μm upto several micrometers in grazing incidence geometry (GIUSAX) [3]. The scientic field ranges from deformation in polymer-based materials to thin film investigations in polymer and colloid science [2,4,3]. In an ongoing development program at HASYLAB the beamline BW4 has been refurbished. We will present the upgrade the BW4 beamline, including e.g. a dedicated SAXS position, the installation of new detectors and beam monitoring equipment. Furthermore we will focus on available sample environments like GISAXS cells, stretching and heating devices.

[1] R. Gehrke, *Rev. Sci. Instrum.* **63**, 455, (1992)
[2] R. Gehrke et al., *Rev. Sci. Instrum.* **66** , 1354 (1995)
[3] P. Müller-Buschbaum et al., Europhys. Lett. **42**, 517 (1998)
[4] N. Stribeck et al., *Macromol. Chem. Phys.* **203**, 636 (2002)

CPP 29.35 Di 16:30 Poster TU D

Energy Dispersive Small Angle X-Ray Scattering — •Tushar Sant, Wolfram Leitenberger, Tobias Panzner, and Ullrich Pietsch — Institute of Physics, University of Potsdam, Am Neuen Palais 10, D-14469 Potsdam, Germany.

Small Angle X-ray Scattering is well known technique for characterizing polymers, colloids and biological samples. The characterization is usually done with angular-dispersive set-ups. We are developing the energy dispersive SAXS set-up with the incident synchrotron beam in the range $4<E<30$KeV at BESSY bending magnet beamline. We recorded the whole diffracted energy spectrum at a fixed angular position of the detector. The feasibility of energy dispersive technique was already proved by our group in the fields like Grazing incidence diffraction and X-ray reflectivity. We used a silicon drifted diode detector with energy resolution of about 250 eV. We investigated the similarity between angular dispersive and energy dispersive techniques on several samples. The main advantage of such a set up is that the whole spectrum appears simultaneously and it can be used for the analysis of the sample on a time scale of minutes. On the other hand, this also requires the exact knowledge of the background and energy dependent absorption properties of the system, which is also discussed.

CPP 29.36 Di 16:30 Poster TU D

Folding Channels in Coarse-Grained Heteropolymer Models — •Stefan Schnabel, Michael Bachmann, and Wolfhard Janke — Institut für Theoretische Physik, Universität Leipzig, Augustusplatz 10/11, 04109 Leipzig, Germany

We investigated versions of the AB model [1,2], being off-lattice models for heteropolymers, with multicanonical simulations. The heteropolymers consist of hydrophobic (A) and hydrophilic (B) monomers. Nonbonded pairs of these monomers interact via specific Lennard-Jones potentials. In particular, AA contacts are favored to force the formation of a hydrophobic core. We study the complexity of the free energy landscape by comparing the equilibrium conformations with the folded state in terms of a structural overlap parameter [3]. This parameter is expected to act as a suitable system parameter allowing the identification of conformational transitions and can be used to identify folding channels of these heteropolymers.

[1] F. H. Stillinger, T. Head-Gordon, and C. L. Hirshfeld, Phys. Rev. E 48, 1469 (1993).
[2] A. Irbäck, C. Peterson, F. Potthast, and O. Sommelius, J. Chem. Phys. 107, 273 (1997).
[3] M. Bachmann, H. Arkin, and W. Janke, preprint (2004).

CPP 29.37 Di 16:30 Poster TU D

Evidence of pre-crystalline order in super-cooled polymer melts revealed from dielectric spectroscopy — •Andreas Wurm, Ragab Soliman, and Christoph Schick — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18051 Rostock

Existence and formation of pre-ordered structures as the initial step of polymer crystallization are discussed controversially. Most of the findings and interpretations are based on scattering experiments, which test small density differences between the assumed precursors of the crystals and the surrounding melt. Contrary relaxation experiments are probing motions in the sample and are therefore independent on density contrast. During crystallization material is transformed from the liquid to the solid state. Consequently, motions (fluctuations) typical for a liquid become impossible and do not longer contribute to the measured relaxing signal. For pre-ordered structures we expect changes in mobility too because of the changes in conformation on pre-ordering.

We have studied the complex dielectric permittivity of polycaprolactone (PCL) during non-isothermal and isothermal crystallization in the frequency range from 0.01 Hz to 10 MHz. At high frequencies the expected result was obtained - a decrease of permittivity with decreasing amorphous fraction during crystallization. This was confirmed by a simultaneous SAXS and dielectric experiment. At lower frequencies pronounced effects in ϵ' are observed before changes in crystallinity can be detected.This strongly supports the idea of pre-order in the polymer melt before the formation of crystals.

CPP 29.38 Di 16:30 Poster TU D

Melting and reorganization of poly(ethylene terephthalate) on fast heating (1000 K/s) — •Christoph Schick, Alexander Minakov, and Dmitry Mordvintsev — Universität Rostock, Institut für Physik, 18051 Rostock

For poly(ethylene terephthalate) (PET) and other polymers the origin of the multiple melting peaks observed in differential scanning calorimetry (DSC) curves is still controversially discussed. This is due to the difficulty to investigate the melting of the originally formed crystals exclusively. Recrystallization is a fast process and most experimental techniques applied so far do not allow fast heating in order to prevent recrystallization totally. Developments in thin-film (chip) calorimetry allow scanning rates as high as several thousand Kelvin per second. We utilized a chip calorimeter based on a commercially available vacuum gauge, which is operated under non-adiabatic conditions. The calorimeter was used to study the melting of isothermally crystallized PET. Our results on melting at rates as high as 2700 K/s give clear evidence for the validity of a melting-recrystallization-remelting process for PET at low scanning rates (DSC). At isothermal conditions PET forms crystals, which all melt within a few dozens of K slightly above the isothermal crystallization temperature. There is no evidence for the formation of different populations of crystals with significantly different stability (melting temperatures) under isothermal conditions.

CPP 29.39 Di 16:30 Poster TU D

Crystallization of Two-Dimensional Off-Lattice Lennard-Jones Polymers — •Anna Kallias, Michael Bachmann, and Wolfhard Janke — Institut für Theoretische Physik, Universität Leipzig, Augustusplatz 10/11, 04109 Leipzig

We investigate thermodynamic properties of stiff off-lattice polymers in two dimensions by means of Metropolis Monte Carlo simulations. The non-bonded monomers interact via a Lennard-Jones potential with equilibrium distance equal to the bond length. We study in detail the crystallization of these polymers below the collapse transition temperature. Peaks in the measured end-to-end distance distribution as well as in the radial distribution function are uniquely identified with distances on the expected triangular crystal lattice. For comparison, we discuss the differences of the thermodynamic behavior and the crystallization induced by extending the model by an additional bending rigidity [1]. The limited applicability of Metropolis simulations for these polymers at low temperatures is discussed by analyzing acceptance rates and autocorrelations.
[1] F. H. Stillinger and T. Head-Gordon, Phys. Rev. E **52**, 2872 (1995).

CPP 29.40 Di 16:30 Poster TU D

High precision light attenuation measurementsas a tool for studying the initial stagesof polymer crystallization — •Jens Fritsch, Werner Stille, and Gerd Strobl — Physikalisches Institut, Albert-Ludwigs-Universität Freiburg 79104 Freiburg, Germany

Investigating the crystallization kinetics of polymers, a variety of experimental approaches are applied. Although based on different properties there is not much difference in the sensitivity of all these methods. Reliable data are only obtained over a dynamic range of one to two orders of magnitude. Searching for an experimental tool with a higher sensitivity we found that measurements of the light attenuation coefficient can have a much larger dynamic range. We achieve the higher sensitivity with a self constructed measuring device which uses a modulated laser light source together with lock-in signal detection. For a data evaluation during the initial stages of polymer crystallization known relationships describing the dependance of the linear attenuation coefficient on the radius and the index of refraction of the growing objects can be used. We now are able to observe the crystallization process of polymers samples over a dynamic range of about four orders of magnitude and will report first results obtained for poly(ethylene-co-octene)s, s-polypropylene and poly(epsilon-caprolactone).

CPP 29.41 Di 16:30 Poster TU D

Temperature dependent mechanical properties of polyelectrolyte shells — •Renate Müller, Nils Elsner, and Andreas Fery — Max Plank Institute of Colloids and Interfaces, Science Park Golm, 14424 Potsdam

Polyelectrolyte multilayer capsules, that are produced by template assisted self assembly, are interesting either as biomimetic systems or for applications in encapsulation (drug delivery). In this context, the mechanical properties of the capsules are an important quantity, since they limit mechanical stability, behaviour in flow and adhesive properties. We have in the past established a combination of colloidal probe AFM technique as a force spectroscopy method and the RICM (reflectance interference contrast microscope) to directly investigate the compliance of individual microcapsules and derive elastic constants of the capsule wall material from the measurements. Here we focus on the effect of temperature on polyelectrolyte multilayer mechanics: Certain polyelectrolyte systems react towards temperature changes by shrinking and increasing their wall thickness. These changes are not reversible at return to room temperature. Thus capsules with varying wall thickness can be produced by different annealing times from the same starting batch in a simple manner. We can directly quantify how these shape changes are connected to changes in capsule compliance and additionally, we have investigated the dependency of the compliance on temperature by measurements during the annealing process.

CPP 29.42 Di 16:30 Poster TU D

Konzentrationsinhomogenitäten in aus homogener binärer Polymerschmelze gewachsenen Sphärolithen — •Bernd-J. Jungnickel und Jieping Liu — Deutsches Kunststoff-Institut, D-64289 Darmstadt

Die Kristallisation einer Komponente in homogen geschmolzenen Polymermischungen erfordert weitreichende Diffusion der kristallisierenden Spezies hin zur und der anderen weg von der Kristallisationsfront. Es entwickeln sich unter bestimmten Bedingungen entsprechend weitreichende und zuweilen starke Konzentrationsinhomogenitäten sowohl in der Restschmelze als auch im Innern der wachsenden Kristallaggregate. Sie schlagen sich in einer entsprechenden zeitlichen Veränderung der Kristallisationskinetik nieder wie auch in einer von der Mitte zum Rand der Sphärolithe hin sich ändernden Kristallmorphologie, z.B. der Lamellentwistperiode oder der Kristallmodifikation. Diese Konzentrationsinhomogenitäten können mit geeigneten experimentellen Verfahren, u.a. mit Infrarotmikroskopie oder EDX-Analyse an einem Rasterelektronenmikroskop abgebildet werden. Wir berichten über entsprechende Experimente an PVDF-Sphärolithen, die in einer Mischung mit PMMA gewachsen sind. Es zeigt sich, dass an der Sphärolithoberfläche ein Konzentrationssprung entsteht, der ein Vielfaches der ursprünglichen Mischungszusammensetzung betragen kann.

CPP 29.43 Di 16:30 Poster TU D

Influence of Angular Potentials on the Crystallization of Model Polymer Chains — •Hendrik Meyer, Thomas Vettorel, and Jörg Baschnagel — CNRS, Institut Charles Sadron, 67083 Strasbourg, France

A simplified polymer model appeared to be extremely efficient for the study of polymer crystallization in molecular dynamics simulations [1]. Our model goes one step further than usual united-atom models and resumes all atoms of a monomer into one sphere. We present here the influence of different simulation parameters, and in particular of the angular potential.

We characterized the melt at a reference temperature and looked for correlations with the crystallization temperature determined during continuous cooling. For most quantities as persistence length, radius of gyration or relaxation times, no trivial correlation can be found, except for the fraction of stretched tt conformations in the melt: the higher this fraction, the easier is the crystallization and thus the higher the temperature where ordering starts.

[1] H. Meyer and F. Müller-Plathe, J. Chem. Phys. 115 (2001) 7807; Macromolecules 35 (2002) 1241.

CPP 29.44 Di 16:30 Poster TU D

Physical Aging in Complex Systems — •Trichy R. Gopalakrishnan, Adnan Javed, and Mario Beiner — FB Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany

We have investigated the influence of quenching and physical aging on the dynamics of nanophase-separated polymers with long alkyl groups in the side chain. These materials show two different relaxation processes with typical features of a dynamic glass transition: (i) The conventional α relaxation at high temperatures and (ii) a polyethylene-like glass transition α_{PE} related to cooperative motions in alkyl nanodomains with a typical dimension of 1-2nm formed by aggregated alkyl groups. Quenched samples and samples annealed between both glass transition temperatures are studied by shear measurements and dielectric spectroscopy. It is shown that the α_{PE} process is amplified in rapidly quenched samples and that annealing slightly below the conventional glass transition temperature reduces the intensity of the α_{PE} process in shear data significantly. Indications for an additional localized dynamics within the alkyl nanodomains are reported. A speculative picture describing the findings based on differences in the contraction of immobile main chains and liquid-like alkyl groups below the conventional glass temperature where the main chains freeze-in is discussed.

CPP 29.45 Di 16:30 Poster TU D

Side Chain Crystallization in Microphase-Separated Poly(styrene-octadecylmethacrylate) Copolymers — •E. Hempel, H. Budde, S. Höring, and M. Beiner — FB Physik & FB Chemie, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany

The crystallization behavior of two microphase-separated poly(styrene-*b*-octadecylmethacrylate) block copolymers with lamellar and cylindrical morphology is studied by DSC. The findings are compared with results for a polyoctadecylmetharcylate (PODMA) homopolymer. The situation in the block copolymers is characterized by the occurrence of a confined side chain crystallization in small PODMA domains surrounded by a glassy polystyrene phase. The strength of confinement effects depends significantly on the block copolymer morphology. In cylindrical PODMA domains with a diameter of about 10nm strong confinement effects are observed: The degree of crystallinity is 50% reduced and the crystallization kinetics is slowed down. The crystallization behavior of PODMA lamellae with a thickness of about 10nm is less affected and similar to the situation in the homopolymer. There are experimental arguments supporting one-dimensional growth in PODMA cylinders: The Avrami coefficients change from $n \approx 3$ for the homopolymer and PODMA lamellae to $n \approx 1$ for PODMA cylinders. A change from heterogeneous to homogeneous nucleation having similar consequences seems to be unlikely since the undercooling for the PODMA cylinders is tiny ($T_m - T_c < 1\text{K}$). This value is smaller than those for the PODMA homopolymer and homogenously nucluated alkanes. A speculative picture explaning the different crystallization behaviors of PODMA lamellae and cylinders is discussed.

CPP 29.46 Di 16:30 Poster TU D

Dynamic Structure Factor of Constrained Polymer Chains — •Strauch Michael and Straube Ekkehard — University of Halle, Department of Theoretical Physics, D-06099 Halle, GERMANY

The poster presents investigations concerning the analytical calculation and numerical simulation of the dynamic structure factor $S_{\mathbf{q}}(t)$ of polymer chains.

The dynamic structure factor for a network of chains with fixed end-to-end distances is calculated strictly analytically. This calculation was first done for the equilibrium end-to-end distance R. An integration over distributions of end-to-end vectors in the network gives an estimation of the influence of chain localisation on $S_{\mathbf{q}}(t)$. – In agreement with plausible considerations, the dynamic structure factor of the network reaches a finite plateau value rather than zero for long times because the correlations between chain segments do not completely vanish.

Additionally, an extension of a model originally introduced by de Gennes is studied. In the original model, the dynamic behaviour of the chain is calculated as a one-dimensional, longitudinal diffusion along the primitive path being described as a *random walk*. The effect of including transverse fluctuations is studied.

CPP 29.47 Di 16:30 Poster TU D

Hydrodynamic effects: polymers modelled by small world networks — •Mircea Galiceanu and Alexander Blumen — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany

We investigate on polymers in the form of small world networks (SWN) the influence of hydrodynamic effects using the Zimm model, with a preaveraged Oseen tensor. The monomers (beads) are connected by harmonic springs and they are subjected to external fields. A SWN realization starts from a N-monomer ring, whose pairs of beads are randomly connected, with probability p, by additional links. Varying p from 0 to 0.5 we consider the averaged mean square displacement of the polymers, the storage and the loss moduli, $G'(\omega)$ and $G''(\omega)$.

In the Zimm model, as in the Rouse model [1], changes in structure are evident in an intermediate (time or frequency) domain; even very small but nonvanishing p lead to changes from the $p = 0$ case. Furthermore, the long time domain is reached earlier by structures with more crosslinks (higher p).

[1] S. Jespersen, I. Sokolov and A. Blumen, J.Chem.Phys. 113, 7652, (2000).

CPP 29.48 Di 16:30 Poster TU D

Confinement, Fluctuations, and the Order-Disorder Transition in Diblock Copolymer Melts — •Alfredo Alexander-Katz[1,2] and Glenn H. Fredrickson[1] — [1]Materials Research Laboratory, University of California, Santa Barbara, CA, 93106, USA — [2]Department fuer Physik, Ludwig-Maximilians-Universitaet, Theresienstr. 37, D-80333 Munich, Germany

Using field-theoretic simulations, we study the effects of confinement and fluctuations in the location of the order-disorder transition (ODT) for a diblock copolymer system. Specifically, we consider a melt of copolymers confined between two neutral hard walls separated by a distance L. For this system, it is found that confinement induces a shift in the ODT which depends on the strength of the fluctuations (dominated by the length of the copolymers), as well as on the width of the slit. The shift in the ODT due to fluctuations presents a minimum when the slit width is comparable to the unperturbed size of the polymer. Also, we present results on the structure of the disorder phase close to the ODT which exhibits non-trivial oscillations in the composition fluctuations.

CPP 29.49 Di 16:30 Poster TU D

Determination of Pyroelectric Coefficient in Polyethylene Terephthalate — •Francisco Camacho González, Axel Mellinger, and Reimund Gerhard-Multhaupt — Department of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany

The current measured in a thermally stimulated discharge (TSD) experiment shows the contribution of dipoles and free carriers. To discern between dipoles and free carriers in Polyethylene Terephthalate (PETP), cycles of thermally stimulated polarization current (TSPC) and thermally stimulated current (TSC) were performed. Experimental results show the presence of a bimodal peak with two maxima around 202 and 212 K, which are related to the dipoles. Charge contribution shows also a bimodal peak with maxima at 202 and 218 K. In order to learn more about the dipole contribution, the pyroelectric coefficient was determined. To measure small pyroelectric coefficients, experimental results from PETP samples under two different conditions were analyzed using the fast fourier transform (FFT). In the first case, where the sample was charged at 383 K under 26 V/μm and a partial TSD was performed, a pyroelectric coefficient of around 60 nC/m^{2}K was determined. In the second case, coefficients of about 6 nC/m^{2}K were obtained exposing a sample to a low electric field (1 V/μm).

CPP 29.50 Di 16:30 Poster TU D

Adaptive Coarse-Graining Molecular Dynamics Scheme — •Matej Praprotnik, Luigi Delle Site, and Kurt Kremer — Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D 55021 Mainz, Germany

We present a new adaptive coarse-graining technique for efficient multiscale molecular dynamics (MD) simulations. The new approach is tailor-made for studying molecular systems that require in some regions an atomistic resolution but otherwise involve length and time scales that are difficult to capture by the conventional atomistic MD simulation. Our method allows an on-the-fly interchange between a given molecule's atomistic and coarse-grained level of description, enabling to reach large length and time scales while spatially retaining atomistic details of the system. The efficiency of our approach is illustrated on the model system of a four-particle pyramid molecular liquid. In this model system the simulation box is divided into two regions: one containing only atomistically resolved four-particle pyramid molecules, the other containing only one-particle coarse-grained molecules. Molecules can freely move between regions while changing their level of resolution accordingly. It is shown that this system has the same statistical properties as the corresponding fully atomistically resolved system at the same physical conditions.

CPP 29.51 Di 16:30 Poster TU D

Polymer Crystallization studied on the Nanometer Scale in 3D — •Nicolaus Rehse, Sabine Marr, Sabine Scherdel und Robert Magerle — Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth

Semi-crystalline polymers often form extremely different morphologies depending on the crystallization parameters (*i.e.*cooling rate, crystallization temperature). We have studied semi-crystalline polypropylene films which were prepared via solvent casting and afterwards melted and recrystallized on a heating stage. The crystallization process was followed with *in-situ* tapping mode scanning force microscopy (TM-SFM) to monitor the crystal growth. Individual crystallites were then investigated with nanotomography. This technique is based on TM-SFM and a subsequent etching process, where the topmost 5-8 nanometers of the sample are removed. The resulting SFM images are stacked and aligned to give a three-dimensional material distribution of the sample. We aim to compare the resulting structures qualitatively using morphological measures and learn more about the processes that lead to different morphologies.

CPP 29.52 Di 16:30 Poster TU D

Using NMR in studies of the kinetics of polymer crystallisation — •Christopher Hertlein[1], Kay Saalwächter[2], and Gert Strobl[1] — [1]Fakultät für Mathematik und Physik, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — [2]Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier Str. 31, 79104 Freiburg, Germany

In our work we investigated the crystallization kinetics of several semicrystalline polymers using proton-NMR relaxation experiments. As crystallization of a polymer goes along with a solidification of the material and therefore with a substantial increase in dipolar coupling among the protons, NMR is a suitable method due to its sensitivity to dipolar couplings. The materials under investigation were poly(ethylene-co-octene), poly-(ε-caprolactone) and syndiotactic polypropylene.

Different parts of registered NMR decay curves could be related to a melt, a crystalline phase and non-crystalline regions with a reduced mobility. The decay curve measured at the very beginning of the crystallization process represents the melt. Scaling the melt-curve with a time-dependent calculated factor representing the remaining melt fraction, and substracting it from each curve, we obtained for all times the decay curves of the non melt-like parts of the sample. Usually the crystal contribution to the curves could be identified and the development of the crystallinity with time determined. A comparison with results obtained by small- and wide-angle X-ray scattering and dilatometry indicate a formation of crystals out of regions with a reduced mobility.

CPP 29.53 Di 16:30 Poster TU D

Molecular Mobility in Polycarbonate / Silsesquioxane based Nanocomposites. — •Ning Hao, Martin Boehning, and Andreas Schoenhals — Federal Institute for Materials Research and Testing, Unter den Eichen 87, Department VI.3, D-12205 Berlin

Polycarbonate base nanocomposites are prepared by disperse phenethyl substituted polyhedral oligomeric silsesquioxane particles into the host polymer matrix. The sample film are formed by solution casting under room temperature. Further investigation methods confirm a good compatibility of such particles inside polymer bulk phase. The molecular mobility of the nanocomposites are investigated by broadband dielectric relaxation spectroscopy. The main effect is a plasticisation of the segmental dynamics where the localized Fluctuations are only weakly influenced. The shift of the dynamic glass transition temperature is compared with that measured by DSC. Also gas transport measurements (permeation, sorption) are reported.

CPP 29.54 Di 16:30 Poster TU D

Exciton dynamics in molecular rings — •PETER REINEKER[1], CHRISTOPH WARNS[1], and IVAN BARVIK[2] — [1]Department of Theoretical Physics, University of Ulm, 89069 Ulm, Germany — [2]Institute of Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

We investigate the relation between the exciton transfer regime and the optical properties of ring molecular systems.

We simulate the influence of the coupled coherent and incoherent exitonic energy transport on the optical line shape of the rings.The influence of the bath is described by (fast) colored dichotomic Markov processes with short time constants for the decay of theircorrelation functions.The colored dichotomic Markov processes leading to transfer integral fluctuations are correlated between nearest neighboring sites.

The exciton transfer and the optical line shape of the molecular ring is investigated in dependence of the parameters of the stochastic processes.

CPP 29.55 Di 16:30 Poster TU D

Dynamic Theory of Vibronic Spectra of Charge Transfer Excitons — •Ivan J. Lalov[1], Christoph Supritz[2], and Peter Reineker[2] — [1]Faculty of Physics, Sofia University, Sofia 1164, Bulgaria — [2]University of Ulm, Department of Theoretical Physics, 89069 Ulm

The vibronic spectra of Charge Transfer Excitons (CTE) in a molecular one-component or alternatively ordered two-component chain are treated in the framework of dynamic approach. The model introduces two mechanisms of coupling between CTEs and vibrational quanta: 1) the shift of equilibrium positions of nuclei in ionized donor or acceptor; 2) the change of the vibrational frequency in the ionized molecule. This model allows to generalize the simple CTEs Hamiltonian and the vibronic Hamiltonian of Frenkel excitons. The linear optical susceptibility is calculated in the vibronic region (one CTE + one vibrational quantum). The double splitting of vibronics of CTEs was analyzed: a) the splitting connected with the location of the intramolecular vibration - on the donors or on the acceptors; b) the splitting connected with the symmetry of the vibronic spectra (in degenerate case). The general structure of the vibronic spectra of CTE is established. It contains structureless absorption lines, which correspond to two-particle bands and Lorentz-type lines of one-particle states, which correspond to bound propagation of the CTE and phonon.

CPP 29.56 Di 16:30 Poster TU D

Energy transfer and trapping in light harvesting polymers — •ANTONIO VOLTA[1], ALEXANDER BLUMEN[1], AUREL JURJIU[1], and THORSTEN KOSLOWSKI[2] — [1]Theoretische Polymerphysik, Universität Freiburg, Hermann Herderstr. 3, D-79104 Freiburg, Germany — [2]Institut für Physikalische Chemie, Universität Freiburg, Albertstr. 23a, D-79104 Freiburg, Germany

The energy transfer over polymers (such as in photosynthesis) is a topic of much interest; the subject is interdisciplinary and combines physics with biology and chemistry. In the present theoretical work we deal with light harvesting polymers (antennae) over which an energy transfer takes place from the periphery to a reactive center. The model is based on continuous time random walks (CTRWs) over dendrimers and over regular hyperbranched fractals (RHFs). We compute, thanks to analytical methods which avoid direct diagonalizations, the average probability of occupation of the starting point of the motion [1], as a function of time, for very large structures. We find clear differences between fractal (RHF) and non-fractal (dendrimer) structures.

[1] A. Blumen, A. Volta, A. Jurjiu, and Th. Koslowski; J. Luminescence, in press

CPP 29.57 Di 16:30 Poster TU D

A program package for the development of reactive bond-order potentials — •Paul Erhart and Karsten Albe — TU Darmstadt, Institut für Materialwissenschaft, Petersenstraße 23, 64287 Darmstadt

The bond-order formalism due to Abell, Tersoff and Brenner has turned out to be a very successful and reliable scheme for the development of reactive interatomic potentials. In the past, parameterizations for a number of systems have been generated including pure metals and semiconductors as well as metal-carbides and group IV, III-V and II-VI compound semiconductors. We have developed the program package PONTIFIX/PINGUIN which provides a simple interface for the generation of new parameterizations. It comprises two modules: PONTIFIX can be run from the command line and contains the core functionality of the package; PINGUIN provides a graphical interface based on the GTK library which allows to run PONTIFIX interactively. The underlying principle has been successfully employed in a number of foregoing studies. The user is requested to provide a set of data comprising the cohesive energies and bond lengths for a number of structures and at least one complete set of elastic constants for one of these structures. Based on the weights given to each of these properties the code optimizes the parameter set(s) using the Levenberg-Marquardt least-squares minimization algorithm. The program allows to fit several parameter sets simultaneously. Recently, PONTIFIX has been applied in the development of bond-order potentials for W-C and Zn-O. The PONTIFIX/PINGUIN program package is freely accessible for researchers in academic environments.

CPP 29.58 Di 16:30 Poster TU D

Optical Absorption in Dendrimers — •Christoph Supritz, Andreas Engelmann, and Peter Reineker — University of Ulm, Department of Theoretical Physics, 89069 Ulm

Dendrimers are highly branched molecules which are expected to be useful for example as efficient artificial light harvesting systems in nanotechnological applications.

There are two different classes of dendrimers: compact dendrimers with constant distance between neighbouring branching points throughout the macromolecule, and extended dendrimers where this distance increases from the system periphery to the center. We investigate the linear absorption spectra of these dendrimer types and the transport of excitation energy inside them using the Frenkel exciton concept.

To take into account the electron phonon interaction we introduce a heat bath that interacts with the excitons in a stochastic manner. In addition, for the energy transport we assume the dendrimer core to be connected to a randomly modulated decay channel (trap).

CPP 29.59 Di 16:30 Poster TU D

Globular Structures of Helix-Coil Copolymers: A SCFT Treatment — •Christian Nowak, Vakhtang Rostiashvili, and Thomas Vilgis — Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz

A general self-consistent field theory to describe the conformational behavior of a single helix-coil copolymer is constructed. The helices are modeled by stiff rods which are connected to flexible, coil-like spacer chains. The short ranged interactions between the individual segments are modeled by Flory-Huggins type parameters. In addition, an orientation dependent Maier-Saupe like interaction between the helices is introduced to account for ordering of the helices along the copolymer.

The use of a grand canonical formulation becomes necessary since each segment may undergo a microscopic transition between helix state and coil state. Hence the distribution of helix lengths is not fixed but determined by equilibrium conditions.

Due to the competing entropic and energetic contributions the model shows a transition between open structures and globular states which in turn affects the formation of helices. Therefore the theory can be used as a rather general model to describe the hydrophobic collapse and formation of helix bundles in proteins.

CPP 29.60 Di 16:30 Poster TU D

Merging of diffusion and relaxation times in concentrated polystyrene/toluene solutions near the glass transition — •Philipp Schleiffer, Jürgen Rauch, and Werner Köhler — Physikalisches Institut, Universität Bayreuth

Diffusion of polystyrene in toluene has been investigated by both dynamic light scattering and transient holographic gratings. Approaching the glass transition by increasing the concentration or lowering the temperature, the α-relaxation emerges on the experimental timescale. The relaxation time of the α-relaxation shows a stronger concentration and temperature dependence than the mutual mass diffusion time and is not q-dependent. It is not clear how the two timescales of the interdiffusion process and the α-relaxation merge. Long-time observations are not easily feasible, since the experimental method is subject to fluctuations on the timescale of seconds. These fluctuations can partly be overcome by proper stabilization techniques.

CPP 29.61 Di 16:30 Poster TU D

Reorientation of the Microdomains in Concentrated Block Copolymer Solutions using AC/DC Electric Fields — •Kristin Schmidt[1], Heiko Zettl[1], Frank Schubert[1], Helmut Hänsel[1], Franz Fischer[2], Thomas M. Weiss[3], Alexander Böker[1], and Georg Krausch[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany — [2]Lehrstuhl für Kristallographie, Universität Bayreuth, D-95440 Bayreuth, Germany — [3]European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France

We investigate the microdomain structure of concentrated block copolymer solutions exposed to an electric field by time-resolved synchrotron small-angle X-ray scattering (SAXS). As a model system, we use a polystyrene-b-polyisoprene block copolymer dissolved in toluene. We study the mechanism of reorientation of block copolymers with different microdomain structures (lamellar and cylindric) using a DC field.

Depending on the polymer concentration and the initial degree of order we identify two different microscopic mechanisms which dominate the orientation process, i.e. *nucleation and growth of domains* and *grain rotation*.

In addition, we study the frequency dependence of the reorientation of our block copolymer systems in AC electric fields. For example, we find reorientation at 150 Hz, which allows us to exclude any influence of migration of ions in the block copolymer solutions.

CPP 29.62 Di 16:30 Poster TU D

Counterion-Condensation Transition at Charged Polymers — •Ali Naji[1,2] and Roland R. Netz[1,2] — [1]Physics Department, Technical University Munich, James Franck Strasse, D-85748 Garching, Germany — [2]Physics Department, Ludwig Maximilian University, Theresienstrasse 37, D-80333 Munich, Germany

Charged polymeric systems are in many cases influenced by electrostatistic effects induced by neutralizing counterions present in the solution. A particular example is the so-called counterion-condensation process at charged extended polymers, which can trigger such striking phenomenon as aggregation of like-charged polymers in the DNA condensates and actin bundles. Counterion condensation emerges as a threshold process, i.e. counterions condense around the chains when the linear charge density of polymers exceeds a certain threshold; below that threshold, counterions diffuse away into the solution. Our chief goal is to examine the statistical properties of the counterion-condensation process near the threshold point for the model system of counterions at a charged cylinder (cylindrical cell model). It is shown that this threshold process is in fact characterized by a set of scaling relations for "order parameters"(as well as other thermodynamic quantities), which will be determined using a novel Monte-Carlo sampling method and also using the standard mean-field (Poisson-Boltzmann) theory. Our results for the scaling exponents indicate that the threshold counterion condensation is described by the mean-field universality class in both two and three spatial dimensions, and thus contrast previous speculations that it belongs to the Kosterlitz-Thouless phase transition class.

CPP 29.63 Di 16:30 Poster TU D

Linear-dendritic amphiphilic block copolymers in solution and in Langmuir-Blodgett films — •Sofiya Raleva[1], Bernd Stühn[1], Ahmed Sayeed[1], Holger Kautz[2], and Holger Frey[3] — [1]Instutute of Solid State Physics, Technical University Darmstadt, D-64289 Darmstadt — [2]Department of Chemistry and Chemical Engineering, Eindhoven University, 5600 Eindhoven, The Netherlands — [3]Institute of Organic Chemistry, Johannes Gutenberg University, D-55128 Mainz

A new type of linear-hyperbranched surfactant has been prepared by ring-opening multibranching polymerization of glycidol onto an end functional poly(propylene oxide) (PPO) macroinitiator. A hyperbranched, highly hydrophilic polyglycerol block is obtained as the polar segment of the structure. In this work we have studied the structure formation of these polymers in water and in thin films. Due to their unique architecture these amphiphiles are able to form well-defined micelles in water. SAXS in Kratky geometry was used to determine the structure factor as well as the form factor of the micelles formed in aqueous solution. Langmuir-Blodgett films were deposited from chloroform and methanol solutions at room temperature onto silicon substrate at different surface pressures. The thickness, interface roughness and electron density variation perpendicular to the surface of the so deposited layers were determined using specular X-ray reflection. In all cases we find well-separated hydrophobic and hydrophilic smooth layers. The hydrophilic layer shows a density profile, depending on the degree of polymerization of the hyperbranched block. We discuss the results with respect to the copolymer architecture and the hydrophilic/hydrophobic balance.

CPP 29.64 Di 16:30 Poster TU D

Phase transitions of a single homopolymer chain from Monte Carlo simulations — •Federica Rampf, Wolfgang Paul, and Kurt Binder — Institut für Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany

The coil-globule transition of homopolymer chains has been studied since a long time. It is connected with the vanishing of the second virial coefficient for the effective interactions between the monomers of the chain and typically described theoretically using a truncated virial expansion. A more recent finding was that even simple, flexible homopolymer models can exhibit a first-order phase transition of the globular structure into an ordered phase.

Using an adaption of the Wang-Landau sampling method we determine the density of states for flexible polymer chains of the bond-fluctuation lattice model including attractive neighbour interactions. Analysis of the specific heat obtained from the density of states clearly reveals two distinct phase transitions. The one at the lower temperature develops into a δ-like singularity with increasing chain length exhibiting the first-order nature of this transition. A finite size scaling of the transition temperatures reveals that they agree in the thermodynamic limit. The effects of anchoring the chain on a neutral surface and confining it with another neutral surface are also discussed.

CPP 29.65 Di 16:30 Poster TU D

Effect of spatial confinement on polyelectrolyte conformation — •Daniel H. Rapoport, Dan F. Anghel, Helmuth Möhwald, and Regine v. Klitzing — Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Golm, Germany

Intermolecular forces between polyelectrolytes in aqueous solutions govern a great number of important phenomena: From the folding and targeting of proteins in cells to the rheology of modern water based paints. One particular question of interest is the behaviour of polyelectrolytes, when put inside a geometrically confined environment, such as a pore or a slit.

Free standing foam films, which are essentially an ultrathin slab (5-100 nm) of surfactant solution provide a unique tool for pursuing this question. When adding polyelectrolytes to the solution, raising the gas pressure in a sealed chamber excerts very defined forces onto the molecules in solution. This way, force oscillations have been measured, which were attributed to structural forces between the polyelectrolytes.

One advantage of free standing foam films over other ways of confining the solutes, is the easy allowance for a combination with optical methods, such as fluorescence spectroscopy. In order to gain insight on a mlolecular level, rather than an integral behaviour, we have labeled poly(acrylic acid) with pyrene fluorescent probes. Upon film formation an increase of the excimer emission intensity can be observed at the expense of monomer fluorescence.

CPP 29.66 Di 16:30 Poster TU D

Determination of the Overlap Concentration of Polymers in a Good Solvent using Fluorescence Correlation Spectroscopy (FCS) — •Ute Lippert[1], Heiko Zettl[1], Alexander Böker[1], Holger Schmalz[2], Axel H. E. Müller[2], and Georg Krausch[1] — [1]Physikalische Chemie II, Universität Bayreuth — [2]Makromolekulare Chemie II, Universität Bayreuth

For polymer solutions the dilute and concentrated regime is well investigated by light scattering, rheology and fluorescence recovery after photo bleaching. The crossover concentration between the dilute and semi-dilute regime and the properties of solutions in the semi-dilute regime are less investigated. This concentration range is difficult to assess with the above mentioned methods. Here, we use fluorescence correlation spectroscopy to determine the diffusion behavior of single polymer chains in solution. We are able to assign the crossover between dilute and semi-dilute for molecular weights in the range of 4 kg/mol to 1500 kg/mol. We find a scaling law for the dependence of the overlap concentration on molecular weight in agreement with theoretical predictions.

CPP 29.67 Di 16:30 Poster TU D

The influence of constraint release on the reptation process: NSE study and comparison to simulation — •M. Zamponi[1], A. Wischnewski[1], M. Monkenbusch[1], L. Willner[1], D. Richter[1], A. Likhtman[2], B. Farago[3], and G. Kali[3] — [1]Forschungszentrum Juelich, 52425 Juelich — [2]University of Leeds, Leeds LS2 9JT, GB — [3]Institut Laue-Langevin, 38042 Grenoble, France

The dynamics of long entangled polymer melts is well described by the reptation model, where the topological confinement is modeled by a virtual tube confining a given chain. However, with decreasing molecular weight reptation limiting processes such as contour length fluctuations and constraint release have to be taken into account. The latter process describes the loss of confinement due to the relaxation of the chains building the tube. To explore the role of the surrounding chains on the confinement a systematic study with neutron spin echo (NSE) spectroscopy has been performed on polyethylene melts. A few labeled long chains of fixed length have been put into successively shorter matrix chains to follow the onset of constraint release. Whereas long chains in a matrix of the same molecular weight display the constrained motion in the tube, with decreasing length of the matrix chains a gradual loss of confinement and transition to Rouse dynamics has been observed. In the limit of the lowest molecular weight matrix the long labeled chains show free Rouse motion. So far there is no full theoretical description of the dynamic structure factor including the effect of constraint release, but a new simulation concept based on the slip-links model gives a good description of the NSE data over the full range of matrix molecular weights.

CPP 29.68 Di 16:30 Poster TU D

Chain Ordering and Diffusion in Polymer Networks: New Insights by Low-Field Proton NMR and FCS — •Kay Saalwächter, Felix Kleinschmidt, and Giorgio Modesti — Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Str. 31, D-79104 Freiburg, Germany

We have recently developed a new approach to ^{1}H multiple-quantum NMR, which yields qualitatively new information on chain ordering, dynamics, and heterogeneities in polymer networks. The technique can be implemented on simple low-field NMR spectrometers without compromise in data quality [1], and has been applied to investigations of filler effects in technical elastomers and the swelling process of model networks. In the latter case, substantial chain-order heterogeneities have been found to develop on swelling, thus challenging established models [2]. Here, our most recent results on details of the chain dynamics in natural rubber are reported, where we have also found substantial deviations from accepted model predictions. We further study the influence of swelling heterogeneities on diffusive transport in model networks by fluorescence correlation spectroscopy (FCS) and pulsed field-gradient NMR.

[1] K. Saalwächter, *J. Am. Chem. Soc.* **125** (2003) 14684.

[2] K. Saalwächter et al., *Macromolecules* **37** (2004) 8556.

CPP 29.69 Di 16:30 Poster TU D

Order Phenomena in s-PP Crystallization? — •Andreas Maus and Kay Saalwächter — Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Stefan Meier Str. 31, D-79104 Freiburg, Germany

We report on the crystallization behavior of syndiotactic polypropylene (s-PP), where the kinetic is highly influenced by the thermal history of the sample, primarily the temperature of the melt prior to cooling to the crystallization temperature, as was shown by dilatometry [1]. In our NMR experiments the isothermal crystallization process was observed via the analysis of the transverse relaxation function measured by applying a modified CPMG pulse sequence, including a magic-echo-sandwich (MSE) for quantitative evaluation of the crystallinity. In our measurements we reproduced this so called memory effect (self seeding) which occurs in many polymers, and could resolve subtler differences in the crystallization kinetics. Possible causes of the memory effect, which are assumed to be related to local order phenomena, are investigated using static ^{1}H multi quantum (MQ) and relaxation experiments.

[1] B. Heck, G. Strobl, Colloid Polym. Sci, 282, 511-513 (2004)

CPP 29.70 Di 16:30 Poster TU D

Diffusion in Networks Studied by Fluorescence Correlation Spectroscopy — •Giorgio Modesti[1], Boris Zimmermann[2], Michael Boersch[2], and Kay Saalwächter[1] — [1]Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Str. 31, D-79104 Freiburg, Germany — [2]Institut für Physikalische Chemie, Universität Freiburg

The aim of our work is to establish FCS and confocal microscopy as new tools to study local structure and dynamics in polymers. Here, we study dye diffusion through poly(dimethylsiloxane) networks swollen to different degrees in organic solvents. A comparative analysis of solvent diffusion in the same network studied by NMR is also shown. For the FCS diffusion experiments, nonpolar dyes were dissolved in octane at low concentration and introduced into the networks.

Our results show that dye diffusion is influenced by the topological structure of the network and becomes slower when the crosslinking density increases. Especially, by comparison with the diffusion behaviour of equivalent solutions of linear PDMS we always observe a higher obstruction effect. In addition, we observed that the same dye dissolved in different solvents has a different relative diffusivity in networks at comparable degrees of swelling, indicating an unexpected solvent dependence of the obstruction effect of the network chains.

Confocally scanned intensity images further reveal the existence of micron-sized heterogeneities. These were previously observed by other groups, and we here try to establish a correlation with the spatially resolved diffusivities.