

CPP 31: Poster: Polymer Dynamics

Time: Wednesday 17:30–19:00

Location: Poster C

CPP 31.1 Wed 17:30 Poster C

Semidilute Polymer Solutions under Shear Flow — •CHIEN-CHENG HUANG, ROLAND G. WINKLER, and GERHARD GOMPPER — Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich

In shear flow, polymers exhibit remarkably large conformational fluctuations due to tumbling motion, i.e., a polymer stretches and recoils in the course of time. In the average, a polymer is aligned, which implies shear thinning at sufficiently large shear rates. To characterize the conformational, dynamical, and rheological properties of semidilute polymer solutions under shear flow, we performed novel mesoscale hydrodynamic simulations combining molecular dynamics simulations and the multiparticle collision dynamics (MPC) approach. At equilibrium, the dependence of the radius of gyration and the zero-shear viscosity on the polymer concentration is in agreement with scaling predictions. The alignment, shear viscosity, and tumbling time are determined for various concentrations and shear rates. In the dilute limit, these quantities are functions of the Weissenberg number only and are in agreement with available analytical theories. Above the overlap concentration, additional density effects are obtained, which cannot be accounted for by the Weissenberg number.

CPP 31.2 Wed 17:30 Poster C

Dynamics of Diblock Copolymers in patterned thin films — •MARIANNE HECKMANN¹, MARCUS MÜLLER², and BARBARA DROSSEL¹ — ¹Institut für Festkörperphysik, TU Darmstadt — ²Institut für Theoretische Physik, Georg-August-Universität Göttingen

We investigate the ordering process of symmetric diblock copolymers which are confined between two hard walls. One of the walls has a stripe pattern with stripes that attract the A-component of the copolymer while the opposite wall is neutral. We use dynamic self-consistent field theory in order to describe the ordering of the melt. We are interested in the time until the system is perfectly ordered into perpendicular oriented lamellae and the structures which occur during the ordering process. We present results for different distances between the stripes at the walls in a two-dimensional system for systems with two or three stripes.

CPP 31.3 Wed 17:30 Poster C

Viscoelastic rheology of Polymer dispersed Liquid Crystals — •MARCEL ROTH¹, CHRIS GRIGORIADIS², DORIS VOLLMER¹, GEORGE FLOUDAS², and GÜNTER K. AUERNHAMMER¹ — ¹Max Planck Institute for Polymer Research, Polymer Physics, 55128 Mainz, Germany — ²University of Ioannina, Department of Physics, 45110 Ioannina, Greece

Polymer dispersed liquid crystals consist of nematic liquid crystalline droplets embedded in a polymer matrix. Applications as optical diodes are manifold and also include curved modules.[1] A thorough understanding of the mechanical properties of these devices is essential.

For composites of linear PMMA and 4 cyano-4'-biphenyl (5CB) phase separation is induced by cooling through the isotropic-nematic transition. This process is accompanied by a change from a viscous fluid into an elastic network. We employed rheometry and dielectric spectroscopy (DS) to follow the PMMA and 5CB dynamics, respectively. In rheology, all data could be reduced to a single master curve via time-temperature-superposition, irrespective of initial mixing ratios. This behavior relies on two facts: Firstly, 5CB acts as a plastifier for PMMA and thusly speed up the polymer segmental dynamics. Secondly, the phase separation strictly follows the equilibrium PMMA-5CB phase diagram. DS on the other hand, probes mainly the 5CB dynamics and revealed that a part of 5CB molecules does not crystallize in the presence of PMMA. The speed-up of the dynamics of these molecules is in accord with the restricted rotational diffusion model.

[1] D. Coates, J. Mater. Chem., 1995, 5, 2063 - 2072

CPP 31.4 Wed 17:30 Poster C

Probing macroscopic viscosity on a sub-nm scale in polymers — •MARKUS SELMKE, SUBHASIS ADHIKARI, and FRANK CICHOS — Universität Leipzig, Exp. Physik I, mona

Well known are the results from hydrodynamics for the viscous drag spheres experience upon translation and rotation in a continuous

medium. For each mode of Brownian motion in the respective degrees of freedom a diffusion equation may be setup with the well established diffusional parameters of the Stokes-Einstein Relation (SER) and the Debye-Stokes-Einstein Relation (DSER). Our recent results show for the first time that these relations accurately predict the measured rotational diffusion time constants of sub-nm sized single fluorescent probe molecules in the complex environment of a glass-forming polymer (PMA) close to its glass transition temperature. Dielectric spectroscopy however does not and shows a different temperature dependence of relaxation times. Simulations of log-normal distributed time-traces of time-constants which describe normal rotational diffusion explain the observed distributions of relaxation parameters that are used to fit the individual molecules' dynamics. No spatial heterogeneity needs to be assumed, the system seems ergodic. The Synthesis of dual-labeled bola-polymers will enable the probing of this spatially homogeneous but dynamically heterogeneous system in more detail. First results from the synthesis are promising. An extension of the far-field two-point microrheology to near-field nano-rheology has been devised in theory and will give access to both the complex shear modulus as well as insight into hydrodynamics on nm length scales.

CPP 31.5 Wed 17:30 Poster C

Stimuli Responsive Polymer Carpets — •IHSAN AMIN¹, MARIN STEENACKERS², NING ZHANG², ANDRÉ BEYER¹, RAINER JORDAN^{2,3}, and ARMIN GÖLZHAUSER¹ — ¹Physik supramolekularer Systeme, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany — ²Wacker Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany — ³Professur für Makromolekulare Chemie, Department Chemie, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany

We developed an innovative strategy to fabricate freestanding polymeric membranes. An experimentally very easy method has been employed, by combining nanosheets and self-initiated photografting and photopolymerization (SIPGP). The composite films consist of a 1 nm thin crosslinked monolayer of biphenylthiol providing outstanding mechanical properties to the layer on which a soft and stimuli responsive 10-300 nm thick polymer brush layer is grafted, forming so-called polymer carpets. These polymer carpets exhibit remarkable properties (optical, wetting) combining extreme thinness, mechanical stability, robustness, flexibility and unprecedented chemical sensitivity. The membrane thickness as well as its mechanical and chemical properties can be tuned precisely by varying the monomer and polymerization time. Moreover, polymer carpet layers buckle and unbuckle reversibly by applying an external (chemical) stimulus. This unprecedented reversible and fast conformational change is visible with the naked eye and could be applied for the development of new and advanced sensors, displays and micromechanical systems.

CPP 31.6 Wed 17:30 Poster C

single molecule study on heterogeneous dynamics of polymer PMA close to glass transition temperature — •SUBHASIS ADHIKARI, MARKUS SELMKE, and FRANK CICHOS — Molecular Nanophotonics, Institute of Experimental Physics I, University of Leipzig, 04103 Leipzig, Germany

In the study of glassy polymer systems there has been a long debate about the nature of heterogeneity of the material. There exist essentially two pictures of spatial and dynamic heterogeneities. Recent experiments on single dye molecules in glassy glycerol suggest mainly a spatial heterogeneity, where each molecule shows a different dynamics. In this presentation we present recent results on this issue by analyzing the rotational diffusion of PDI dye molecule in glassy polymer PMA at both, the ensemble and the single molecule (SM) level close to T_g. From our SM measurements in vacuum in the temperature range (T_g+13K to T_g+22K) we obtain a broad distribution of rotational relaxation times of different individual molecules at a given temperature and the rotational correlation function of a single molecule is well fitted by a stretched exponential decay. The mean of the relaxation time distribution fits perfectly the temperature dependent shear viscosity data. A wealth of new information on the heterogeneous dynamics and structure is further expected from an extension of two point microrheology to SM optical studies based on fluorescence resonance energy transfer (FRET). We have therefore synthesized bi-labeled (Alexa488 & Alexa546) polystyrene polymer and have been characterized by absorp-

tion and emission spectra. First SM FRET measurements are reported.

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Permeation of a polymer chain through nanopores – timescales and mechanism — ●SARA MARLEEN HELLENKAMP, ANDREAS HEUER, and MONIKA SCHÖNHOF — Institute of Physical Chemistry, University of Münster, Corrensstr. 28/30, 48149 Münster, Germany

We investigate the permeation of polymers through the nanoporous wall of hollow capsules, in particular the correlation between polymer molecular weight and exchange time. In a previously analysed system consisting of polyelectrolyte multilayer capsules and poly(ethylene glycol) as probe molecules two scaling regimes were identified [1]. In a theoretical study, a scaling law was derived and confirmed by Monte Carlo simulations, where the polymer is represented as a Rouse chain [2].

In the present study, we combine experiments of chain permeation by diffusion time dependent Pulsed Field Gradient NMR diffusion studies with Monte Carlo Simulation of a polymer chain threaded through a nanopore. The simulations are a first step to understand the whole mechanism of polymer permeation through a nanopore. We investigate the correlation between the exchange time and several parameters, in particularly the chain length and the wall thickness. The final goal of this study is to identify general laws governing chain permeation.

[1] R. Choudhury, P. Galvosas, M. Schönhoff, J. Phys. Chem. (2008)

[2] J. L. A. Dubbeldam, A. Milchev, V.G. Rostiashvili, T.A. Vilgis, Cond. Mat. (2007)

CPP 31.8 Wed 17:30 Poster C

Monte Carlo Study of Semiflexible Star-Branched Polymers in Good Solvents — ●GANNA BEREZOVSKA and ALEXANDER BLUMEN — Theoretical Polymer Physics, University of Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany

We study the influence of the excluded volume on the local properties of regular semiflexible 3- and 4-arm star polymers in a good solvent, by performing simulations in the framework of the bond fluctuation model. Stiffness is introduced through a bending potential between successive bond vectors and we focus in our investigation on the bond vector correlation functions. In agreement with the partially stretched, freely rotating chain arms model proposed by Guenza et al. [1] the stiffness of the arms becomes larger when approaching the core, but the influence of the core and the correlations between the arms decrease with increasing chain stiffness. Within the same arm the bond vectors show long range correlations which obey power law decays.

[1] M. Guenza, M. Mormino, A. Perico, Macromolecules, 24, 6168, (1991).

CPP 31.9 Wed 17:30 Poster C

Force-induced conformational changes in single polymer chain — ●ALEXANDER GERSTMAYR, MASOUD AMIRKHANI, and OTHMAR MARTI — Institute of Experimental Physics, Ulm University

During the last decade, conformational properties of macromolecules and its response to an external stimulation have received many attention from various disciplines of scientists. In this work an external stimulation is applied to a single chain of polymer and in-situ atomic force microscopy (AFM) is performed to study the conformational change of the polymer's chain. We used different gas environments and an electric field to stimulate conformational change and chain rotation. The polymer's chain has an extended form in the presence of water vapor and a globule form in the presence of ethanol. We applied torque to the polymer's chain by a uniform electric field that causes an orientation of the chain.

CPP 31.10 Wed 17:30 Poster C

Spectral Diffusion Probing Nanoscale Fluctuations — ●STEFAN KRAUSE, DANIELA TÄUBER, and CHRISTIAN VON BORCZYKOWSKI — Center for Nanostructured Materials and Analysis, Chemnitz University of Technology D-09107 Chemnitz, Germany

Since the first single molecule experiments spectral diffusion is known to occur for almost every single emitter. The reason for this photo-physical phenomenon can either be related to intrinsic changes of the conformation of a single molecule which is in most cases not rigid but exhibits different states or to changes of the surrounding environment and the resulting reorientation of environmental dipoles. Thus spectral fluctuations can at one hand give insight into the dynamic process of conformational changes and at the other hand probe dynamical pro-

cesses in condensed matter on the nanometer scale. Here we present results of our investigation on various types of single molecule in different environments such as polymers and on SiO₂ surfaces. We use a homebuilt confocal laser scanning microscope and spectroscopy setup to detect spectral dynamics. The extracted data are analysed and interpreted with a model very similar to that used for two dimensional spatial diffusion processes revealing clear correlations between the types of environment and the degree of spectral fluctuations.

CPP 31.11 Wed 17:30 Poster C

Electric Field Induced Alterations of Block Copolymer Domain Spacings — ●CHRISTIAN W. PESTER, HEIKO G. SCHOBERTH, and ALEXANDER BÖKER — Lehrstuhl für Makromolekulare Materialien und Oberflächen and DWI an der RWTH

We investigate the effects of direct current electric fields on a concentrated lamellar polystyrene-*b*-polyisoprene (SI) block copolymer system in toluene by using synchrotron small angle X-ray scattering (SAXS). Measurements were performed in a home-built capacitor with parallel gold electrode geometry at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. As previously shown, electric fields are able to align bulk copolymer morphologies, whereas increasing field strengths lead to both sub-nanometer size variations of SI block copolymer lamellae in the phase separated regime, as well as to alteration of correlation hole scattering lengths in the mixed state. In this work we were able to show, that the sensitivity ($\Delta L/E$) of the SI copolymer chains towards the electric field varies strongly with the temperature of the system, and a shift in the order-disorder transition temperature regime occurs. Furthermore, non-Gaussian behavior of SI-chains in the phase separated regime was discovered, as various field strengths deform the present lamellae to different degrees. Above T_{ODT} Gaussian behavior is adopted, and, due to the lack of morphology based pre-alignment of the polymer chains, their sensitivity towards the electric field increases. In this state chains themselves can be influenced and deformed away from their Gaussian state.

CPP 31.12 Wed 17:30 Poster C

Micromechanics of Thin Films of Elastomeric Polypropylene — ●MARTIN NEUMANN¹, MECHTILD FRANKE¹, ANDREAS SCHOBEL², and ROBERT MAGERLE¹ — ¹Chemische Physik, TU Chemnitz, D-09107 Chemnitz — ²WACKER-Lehrstuhl für Makromolekulare Chemie, TU München, D-85747 Garching

We present a micro-tensile testing setup that allows imaging with scanning force microscopy (SFM) the deformations within the microstructure of approximately 1 μm thick polymer films. This allows correlating directly the micromechanical behavior of a polymeric specimen with its macroscopic stress-strain behavior. In elastomeric polypropylene, a semicrystalline polymer with only 12% crystallinity, we image the deformation behavior of individual crystalline lamellae upon straining and relaxation. Our data shows a large variety of phenomena: bending, kink formation and fragmentation of individual lamella, fixed branching angles between lamellae, as well as locally auxetic behavior of certain crystal complexes. The stress-strain behavior is viscoelastic with elastic moduli in the range between 0.2 to 2 MPa and two relaxation time constants of about 10 s and 300 s, similar as measured for macroscopic specimens.

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Glassy dynamics in nanometer thin layers of polystyrene — ●EMMANUEL U. MAPESA¹, MARTIN TRESS¹, MICHAEL ERBER², KLAUS-JOCHEN EICHHORN², BRIGITTE VOIT², ANATOLI SERGHEI³, and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Germany — ²Leibniz Institut für Polymerforschung, Dresden, Germany — ³University of Amherst, USA

Glassy dynamics in nanometer (5 nm - 200 nm) thin layers of polystyrene are studied by Broadband Dielectric Spectroscopy and spectroscopic Ellipsometry. For the dielectric measurements *two* types of sample arrangements were applied using either evaporated metal or doped silicon counter electrodes, the latter being accomplished with nanostructured highly insulating silica spacers. In both cases - within the experimental accuracy of ± 2 K - *no* change in the mean relaxation rate *and* in the width of the relaxation time distribution function is observed. Coinciding results are obtained by the ellipsometric measurements.

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Real and apparent effects on glassy dynamics in thin polymer layers — ●MARTIN TRESS¹, EMMANUEL U. MAPESA¹, ANATOLI

SERGHEI², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Germany — ²University of Amherst, USA

Numerous studies report changes of glassy dynamics in thin polymer layers. A careful investigation of the preparative factors reveals that remaining solvent can act as plasticizer and annealing in presence of oxygen or water vapour may cause chain breaking and hence chemical degradation. Furthermore physical aging has to be considered. Additionally to these effects on glassy dynamics there is an apparent effect which arises from the fact that the measured net impedance of a sample is influenced by interfacial effects. Analytical and numerical analysis of a simple layer model show that oxide layers at the interfaces of the electrodes can have strong impact on the dielectric net function of the sample, especially in the case of thin films. Based on an analysis of these real and apparent effects it is found that the molecular dynamics in thin polymer layers is *not* altered down to thicknesses of 5 nm.

CPP 31.15 Wed 17:30 Poster C

Group-specific Motion of Single Perylene Bisimide Molecules at Interfaces — •DANNY KOWERKO¹, STEFAN KRAUSE¹, RICHARD BÖRNER², and CHRISTIAN VON BORCZYKOWSKI¹ — ¹Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz — ²Institut für Physik, Universität zu Lübeck 23538 Lübeck, Ratzeburger Allee 160

The motion of single organic molecules is often used as probe for the dynamics in heterogeneous media like polymers. Therefore rotational and conformational fluctuations are analysed with single molecules spectroscopy techniques, providing information on the mobility of the local environment of the molecule. Restricted mobility of the molecule itself can be enforced by functional groups. Here we demonstrate on a single molecule level how perylene bisimide molecular (conformational and rotational) dynamics are changed upon adsorption to SiO₂ or quartz glass surfaces. A recently developed multi-parameter single molecule detection set-up allowing for rapid parallel determination of 3-D orientation, spectrum and lifetime is used to demonstrate (pyridyl) group-specific adsorption of PBI to the surfaces and how this fact restricts conformation and orientation dynamics.

CPP 31.16 Wed 17:30 Poster C

Relaxation processes of ABA type block copolymers due to chemical confinement — •MORITZ SCHWABE and KONRAD

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It was shown that block copolymers can have an additional relaxation mode, which is localized in the temperature range between the γ -relaxation and a softening of the system. This mode is discussed as a flipping of new short segments, produced by additional hydrogen bonds (chemical confinement). [1] In this work we systematically determined ABA-block copolymers with dynamic-mechanical analysis to their relaxation modes with a main focus on a chemical confinement due to hydrogen bonds. We could identify three different relaxation modes, whereby two modes seemed to depend on the length of the inner B-block and one of the outer A-blocks. We thank the SFB 602 and the GRK 782 for financial supporting. [1] J. Hachenberg, B. Steisel, U. Nergui, D. Bedorf, M. Buback, K. Samwer, International journal of materials, 2008, 99, 5, 502-506

CPP 31.17 Wed 17:30 Poster C

Dynamics and Morphology of Different Poly(alkylene oxide)s — •CHRISTINE GERSTL¹, GERALD JOHANNES SCHNEIDER¹, JÜRGEN ALLGAIER¹, ANGEL ALEGRIA², JUAN COLMENERO^{2,3}, and DIETER RICHTER¹ — ¹Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — ²Centro de Fisica de Materiales, Apartado 1072, 20080 San Sebastian, Spain — ³Donostia International Physics Center, Apartado 1072, 20080 San Sebastian, Spain

Poly(alkylene oxide)s (PAOs) form a homologous series of type-A polymers with side groups of varying length. Since the PAOs poly(ethylene oxide) and poly(propylene oxide) are known for a long time and have been studied extensively, the higher homologues are ideally suited to probe the influence of side chains on the dynamics of a polymer.

We will present the results of temperature dependent neutron diffraction experiments on four different PAOs with side chain lengths ranging from CH₂CH₃ (poly(butylene oxide)) to (CH₂)₉CH₃ (poly(dodecene oxide)). Furthermore, the chain conformation studied by neutron small angle scattering (SANS) will be shown and also compared to literature values of other side chain polymers.

Moreover, the relaxation behaviour of the whole polymer chain as well as the segmental dynamics, which were investigated by means of broadband dielectric spectroscopy and neutron backscattering are presented and compared to theoretical predictions.