

CPP 33: Polymer Dynamics

Time: Thursday 9:30–12:30

Location: C 264

Topical Talk

CPP 33.1 Thu 9:30 C 264

Neutron Scattering Studies on Self-Healing Model Polymers — ●ANA RITA BRÁS¹, JESSALYN CORTESE², CORINNE SOULIÉ-ZIAKOVIC², FRANÇOIS TOURNILHAC², JÜRGEN ALLGAIER¹, WIM PYCKHOUT-HINTZEN¹, ANDREAS WISCHNEWSKI¹, LUDWIK LEIBLER², and DIETER RICHTER¹ — ¹Forschungszentrum Jülich, JCNS-1/ICS-1, D52425 Jülich, Germany — ²Matière Molle et Chimie, ESPCI-CNRS (UMR7167), France

Supramolecular polymers are an increasingly important class of polymers, where designed intermolecular interactions allow a specific tailoring of polymer properties. One of the most recent additions to this field are self-healing polymers, which base on the hydrogen-bonding interaction of groups on parts of the molecules. Neutron scattering measurements were performed on recently synthesized model systems, using DNA-inspired end-groups like Thymine-1-acetic acid, Diaminotriazine and 2-aminoethyl-imidazolidone with properties closer to natural materials. The backbone was polypropylene(glycol) and polyethylene(glycol) based polymer, respectively. The end-functionalization allowed going from one to three reactive sites, shifting the association equilibrium to bonding. Both Small Angle Neutron Scattering and Neutron Spin-Echo allowed to quantitatively access the assembly process thus probing the hydrogen-bonding association mechanism. Results of these measurements will be presented. For the first time such an association process was observed on quasielastic neutron scattering time scale.

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Orientation autocorrelation function of the 2nd Legendre polynomial for Rouse chains with fixed ends — ●SEMION STEPANOW and KAY SAALWÄCHTER — Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, D-06099 Halle, Germany

We have calculated the autocorrelation function of the 2nd Legendre polynomial of the segmental orientation for a Rouse chain with fixed ends. This function is relevant for nuclear magnetic resonance (NMR) measures of chain dynamics in polymer networks [1] and entangled melts [2], for which a chain with fixed ends represents the simplest model for the time range from the segmental relaxation time up to the onset of cross-link or tube constraints. The time-dependent part of the ACF is given by $c_1 t^{-1/2} + c_2 t^{-1}$. It thus deviates from free-Rouse result $\sim t^{-1}$, and compares favorably with experimental data [1,2].

[1] K. Saalwächter, A. Heuer, *Macromolecules* 39 (2006) 3291[2] A. Herrmann, V. N. Novikov, and E. A. Rössler, *Macromolecules* 42 (2009) 2063; F. Vaca Chavez, K. Saalwächter, *Phys. Rev. Lett.* 104 (2010) 198305

CPP 33.3 Thu 10:15 C 264

Viscoelastic hydrodynamic interactions explain anomalous CM diffusion in polymer melts — ●HENDRIK MEYER, JEAN FARAGO, and A.N. SEMENOV — Institut Charles Sadron, CNRS, 67034 Strasbourg, France

Contrary to common belief, hydrodynamic interactions in polymer melts are *not screened* beyond the monomer length and are important in transient regimes. We show that viscoelastic hydrodynamic interactions (VHI) lead to anomalous dynamics of a tagged chain in an unentangled melt at $t < t_N$, the Rouse time. The center-of-mass (CM) mean-square displacement is enhanced by a large factor increasing with chain length. We develop a theory of VHI-controlled chain dynamics yielding a negative CM velocity autocorrelation function which agrees with our molecular dynamics simulations without any fitting parameter. It is shown that Langevin friction strongly affects the short- t CM dynamics, also captured by our theory. All results apply also to entangled melts for times shorter than the entanglement time. Transient VHI effects thus provide the dominant contribution to the subdiffusive CM motion universally observed in simulations and experiments. [*Phys. Rev. Lett.* 107, 178301 (2011)]

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Origin of the β -relaxation in Poly(ϵ -caprolactone) — ●BJÖRN KÜTTICH, CHRISTINA LEDERLE, and BERND STÜHN — TU Darmstadt, Experimentelle Physik kondensierter Materie

Broadband Dielectric Spectroscopy is a simple but highly informative measuring method to study polymer dynamics in the bulk as well as

under confinement on a large timescale. By analysing the observable dielectric relaxations it is possible to investigate cooperative phenomena like the α -process and also much faster local chain dynamics.

Poly(ϵ -caprolactone) (PCL) is a polymer widely used in engineering and medical engineering. The latter especially because of its biodegradability. Despite of its wide application area, the basic principles of the polymer's dynamics are not yet fully understood. There are only few publications existent in which the mechanic and dielectric relaxations of PCL were investigated. Notably the reasons for the observed dielectric β -relaxation are discussed controversially.

Our experiments are now suited to clarify the reasons for the reported dielectric β -relaxation in bulk PCL. The experiments show a linear dependency of the relaxation strength of the β -relaxation from the amount of water inside the polymer. Furthermore they suggest that this relaxation is completely due to the dynamics of water molecules strongly bound to the PCL by hydrogen bonds which act as small side chains. The comparison to the dynamics of polyamides is in our view ineligible, because PCL lacks the possibility to build intra- or interchain hydrogen bonds in the absence of water molecules.

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Excitation Dynamics in Donor-Acceptor Copolymers — ●B. GIESEKING¹, B. JÄCK¹, E. PREIS², S. JUNG², M. FORSTER², U. SCHERF², C. DEIBEL¹, and V. DYAKONOV^{1,3} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, D-97074 Würzburg — ²Macromolecular Chemistry and Institute for Polymer Technology, Bergische University of Wuppertal, D-42097 Wuppertal — ³Bavarian Centre for Applied Energy Research (ZAE Bayern), D-97074 Würzburg

Recently the efficiency of organic bulk heterojunction solar cells could be significantly increased by using donor-acceptor type copolymers in the active device layer. Nevertheless only little is known about the elementary processes following photoexcitation of these materials.

Here we present an in-depth study of the excitation dynamics in the copolymer PCDTBT. By carrying out comparative steady state absorption and photoluminescence (PL) measurements on PCDTBT and its building blocks we assign the two prominent absorption bands to two spatially separated co-monomer units on the polymer chain coupled by an efficient energy transfer process. The relaxation dynamics investigated by time-resolved PL spectroscopy are dominated by a redshift of the spectrum while adding PC₇₀BM results in an efficient PL quenching. We find no evidence for a direct decay pathway from the higher energy band of the donor towards the acceptor. Our findings indicate that effective coupling between copolymer building blocks leading to the energy transfer between comonomer units governs the photovoltaic performance of the blends.

15 min break**Topical Talk**

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Shear inversion of polymer-brush bilayers with embedded colloids — ●TORSTEN KREER¹ and ANDRE GALUSCHKO² — ¹Leibniz-Institut fuer Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden — ²Institut fuer Theoretische Physik, Georg-August Universitaet, 37077 Goettingen

Based on a recent scaling approach to describe the shear motion of polymer-brush bilayers at constant velocity, the response of bilayers with colloidal inclusions to highly non-stationary inversion processes is discussed by means of molecular dynamics simulations and scaling theory. Bilayers with a simple (dimeric) solvent reveal an overshoot for the shear stress, while simulations of dry brushes without explicit solvent molecules fail to display this effect. For the first time, it is demonstrated that mechanical instabilities can be controlled by the inclusion of macromolecular structures, such as colloids of varying softness. A characteristic time for conformational and collective responses under highly non-stationary shear is introduced. It can be expressed in terms of the equilibrium properties of the bilayer.

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Rigid vs flexible polyelectrolytes: Structural forces and rheology in nm scale volume — ●CAGRI ÜZÜM and REGINE V. KLITZING — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Strasse des

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In this contribution, flexible and rigid polyelectrolytes (i.e. NaPSS and DNA) in aqueous medium are compared with respect to two small scale dynamic parameters. First, the existence and dynamics of oscillatory structural forces in confinement were studied by colloidal probe AFM. In accord with theoretical calculations, structural forces are suppressed with increasing chain rigidity, presumably due to a longer chain reorientation time in the confinement [1].

Second parameter is the newly introduced micro-viscosity, which corresponds to the viscosity in nm scale volumes. It was measured by an AFM microcantilever [2]. While the solutions of flexible chains have nearly the same micro-viscosity as the bulk, rigid chains have significantly lower ones as compared to the bulk viscosity. Possible reasons for this significant difference are addressed.

[1] Kleinschmidt, F.; Stubenrauch, C.; Delacotte, J.; von Klitzing, R. and Langevin, D. J. Phys. Chem. B, (2009), 113, 3972-3980

[2] Boskovic, S.; Chon, J.; Mulvaney, P. and Sader, J. J. Rheol., (2002), 46, 891-899

CPP 33.8 Thu 12:00 C 264

Time-Humidity-Superposition Principle in Conductivity Spectra of Ion-Conducting Polymers — CORNELIA CRAMER¹, SOUVIK DE^{1,2}, and MONIKA SCHÖNHOF¹ — ¹Institute of Physical Chemistry, University of Muenster, Corrensstraße 28/30, 48149 Münster, Germany — ²Graduate School of Chemistry, University of Muenster, Corrensstraße 28/30, 48149 Münster, Germany

We analyze the scaling properties of the ac conductivity spectra of ion-conducting polyelectrolyte complexes (PEC) of different compositions. PEC are composed of cationic poly(diallyldimethyl ammonium chloride)(PDADMAC) and anionic poly(sodium 4-styrene sulfonate) (NaPSS) and pressed into dry, solid pellets. Frequency-dependent spectra were taken at ambient temperature but at different relative humidities.

Enhanced humidity increases the long range transport (dc conductivity) as well as the local motions, characterised by the onset of conductivity dispersion. Even more, the complete spectral shape of spec-

tra taken at different humidity can be superimposed to a mastercurve. Thus, for the first time, we report on a scaling principle for conductivity spectra termed 'time-humidity-superposition principle' in analogy with the well-known time-temperature-superposition principle. This model-free scaling holds for different materials over several decades in frequency. It implies that the hydration is activating ion motion over short and long distances in a similar, general way, a concept so far only established for thermal energy.

(1) Cramer, De, Schönhoff Phys. Rev. Lett. 107, 028301 (2011)

CPP 33.9 Thu 12:15 C 264

Lithium transport mechanism in ternary mixtures of polymer electrolytes and ionic liquids - a molecular dynamics simulation study — DIDDO DIDDENS^{1,2} and ANDREAS HEUER^{1,2} — ¹Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Germany — ²Graduate School of Chemistry, Münster, Germany

Electrolytes based on mixtures of lithium salts and poly(ethylene oxide) (PEO) are important candidates for modern lithium ion batteries. Unfortunately, in case of the common binary electrolytes like PEO/lithium-bis(trifluoromethane sulfonimide) (LiTFSI), the ionic conductivity is still too low for an efficient technological use. Here, the incorporation of room temperature ionic liquids (RTILs) into these materials promises a significant improvement, as the ionic conductivity is increased about an order of magnitude at room temperature, thus making them an ideal compromise between solid and liquid electrolytes.

Motivated by these experimental findings, we study the underlying microscopic transport mechanisms of the lithium ions by means of MD simulations. We find that these mechanisms are qualitatively the same as already observed in a previous study for PEO/LiTFSI. When adding ionic liquid into the electrolyte, the characteristic time scale of one of the mechanisms, namely the cooperative motion with the PEO segments, is reduced significantly. Therefore, it is possible to describe the lithium dynamics by a Rouse-based analytical transport model that has been developed for binary polymer electrolytes.