

CPP 58: Polymer Dynamics II

Time: Friday 9:30–11:15

Location: ZEU 114

Invited Talk

CPP 58.1 Fri 9:30 ZEU 114

Probe Rheology with Neutron Scattering — ●WIM PYCKHOUT-HINTZEN — Jülich Centre for Neutron Science (JCNS-1) and Institute for Complex Systems (ICS-1), Forschungszentrum Jülich, Germany

An improved understanding of the nonlinear rheology of complex mixtures of polymers with different architectures for e.g. processing applications is a formidable task and one of today's challenges in polymer science. Therefore, blends of model branched and linear polymers with strongly dispersed time scales were investigated with time-dependent small angle neutron scattering after a fast uniaxial step strain and quenched after different relaxation times. A hyperbranched structure of second generation, dilutely dispersed in linear homopolymer matrices of different length acted thereby like sensitive probes for structurally, not yet firmly established features of the tube model for bi-disperse melts. We show that the equilibration time of the linear matrix determines the size of the fluctuations that the outer and inner arms of the branched probe experience. Within a random phase approximation treatment, accounting for different degrees of freedom inherent to the broad time scales and the hierarchical relaxation scheme, the observed loss of anisotropy with time is described in terms of two parameters only, namely the tube diameter and the fraction of relaxed arms of the minority component. The scattering data reveal the underlying mechanisms, which cannot be extracted from but determine the macroscopic flow properties. This information is a prerequisite to quantify the nonlinear viscoelasticity for the strategic blending of mixed architectural systems.

CPP 58.2 Fri 10:00 ZEU 114

Network structure and entanglement effects in saturated and unsaturated acrylonitrile elastomers — ●PATRICK STRATMANN^{1,2}, FRANK FLECK^{1,2}, and MANFRED KLÜPPEL^{1,2} — ¹Deutsches Institut für Kautschuktechnologie e.V. — ²Eupener Straße 33, 30519 Hannover

Differently cross-linked, saturated and unsaturated acrylonitrile elastomers (HNBR, NBR) are investigated regarding their entanglement contributions in uniaxial stress strain measurements. Our main focus lies on the assessment of the *non affine* tube model and *slip tube* model in analysing the mechanical data, whereby the influence of entanglement contributions on the fitted topological constraint modulus and crosslink modulus are considered. Conclusions on the validity or invalidity of specific tube theories cannot be drawn without careful consideration of the network microstructure, which determines the entanglement density. Rheological investigations of the viscoelastic response show a difference in the plateau modulus between the nitrile rubber and the hydrogen nitrile rubber due to different entanglement densities. The analysis of the stress strain and rheological data are compared. The *non affine* tube model, which has been extended to consider finite chain extensibility, delivers excellent fits to the measured stress strain data and fair correlations with the estimated entanglement density from the measured plateau modulus.

CPP 58.3 Fri 10:15 ZEU 114

Local Dielectric Spectroscopy to detect Dynamic Heterogeneity and Phase Separation Kinetics in Miscible Poly(vinyl acetate)/Poly(ethylene oxide) Blends — TOMAS P. CORRALES¹, DAVID LAROZE², GEORGE ZARDALIDIS³, GEORGE FLOUDAS³, HANS-JÜRGEN BUTT¹ und ●MICHAEL KAPPL¹ — ¹MPI for Polymer Research, Mainz, Germany — ²Instituto de Alta Investigación, Universidad de Tarapacá, Arica, Chile — ³Department of Physics, University of Ioannina, Ioannina, Greece

We employed atomic force microscopy based local dielectric spectroscopy (LDS) to analyze the miscible blend composed of poly(vinyl acetate) (PVAc) and poly(ethylene oxide) (PEO). The two homopolymers have very different relaxation times and glass temperatures, which give rise to dynamic heterogeneity in their blends. The aim was to study the dynamic heterogeneity in films as a function of the film thickness. Measurements of the local blend composition at the nanoscale show that LDS is indeed sensitive to the dynamic heterogeneity. In thin films, phase segregation of the homopolymers occurs due to heterogeneous nucleation and crystallization of PEO. We were able to follow the kinetics of phase demixing by detecting the change in local composition of blends including depletion zones of PEO in the PVAc/PEO blend around the

PEO crystals via LDS spectra. These results open new possibilities for studying surface segregation in polymer blends, local variation in polymer concentration, and interdiffusion at polymer-polymer interfaces as a function of annealing temperature with LDS.

CPP 58.4 Fri 10:30 ZEU 114

Structure and Dynamics of Supramolecular Polymers by Neutron Scattering — ●ANA R. BRÁS, MARGARITA KRUTYEVA, CLAAS HÖVELMANN, WIEBKE ANTONIUS, JÜRGEN ALLGAIER, WIM PYCKHOUT-HINTZEN, ANDREAS WISCHNEWSKI, and DIETER RICHTER — Forschungszentrum Jülich, JCNS-1/ICS-1, D52425 Jülich, Germany

Supramolecular polymers allow a specific tailoring of polymer properties. A recent addition are self-healing polymers, displaying hydrogen-bonding interaction. The conformation and dynamics of self-healing model telechelic polymers, consisting of polypropylene glycol (PPG) end-functionalized with hydrogen-bonded associating groups was investigated by means of Small Angle Neutron Scattering (SANS) and Neutron Spin Echo (NSE) spectroscopy. SANS in deuterated toluene confirmed a linear conformation of the studied system. The scattering data were examined using an RPA model approach, usually applied to pure polymer systems. It revealed a reasonable description of the SANS data. More, it underlined the importance of chemical interactions between the components. NSE performed under the same conditions, revealed that the dynamics slowed down upon association. The NSE data were analyzed in terms of a modified Zimm model for polymer dynamics in solution taking into account an additional internal friction originating from the hydrogen-bonded groups. It was unambiguously proven that dynamic neutron scattering is probing the association by H-bonding mechanism. For the first time such an association process in solution was observed by quasielastic neutron scattering. Supported by DFG-SPP1568.

CPP 58.5 Fri 10:45 ZEU 114

Passive and active microrheology of a polymer melt studied by molecular dynamics simulation — ●ANJA KUHNHOLD and WOLFGANG PAUL — Institute of Physics, Martin-Luther-University Halle-Wittenberg

The rheological behaviour of a material is determined by the relaxation of its stress autocorrelation [1]. In simulation studies the stress tensor can explicitly be calculated and serves as a reference for the microrheological results, that are based on the behaviour of suspended particles [2]. The system under study is the well established bead-spring polymer melt model [3] including one or two nanoscopic particles.

Passive microrheology yields linear response properties of the polymer melt by looking at the thermal motion of the nanoparticles. From the mean squared displacement of the nanoparticles the complex modulus $G^*(\omega)$ of the melt is determined by using a generalized Stokes-Einstein equation. The results are in very good agreement to the stress autocorrelation results. With regard to hydrodynamic effects, a more complete form of the analysis is discussed [4].

[1] M. Vladkov, J.-L. Barrat, *Macromol. Theory Simul.* **15**, 252 (2006).

[2] T. G. Mason, *Rheol. Acta* **39**, 371 (2000).

[3] C. Bennemann et al., *Phys. Rev. E* **57**, 843 (1998).

[4] A. Erbas et al., *Eur. Phys. J. E* **32**, 147 (2012).

CPP 58.6 Fri 11:00 ZEU 114

A Highly Parallelizable Monte Carlo Method For Simulating Polymeric Systems — ●CHRISTOPH JENTZSCH¹, RON DOCKHORN¹, MARCO WERNER¹, and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden, Germany — ²TU-Dresden, Institut für theoretische Physik, Germany

We show a new variant of the Bond Fluctuation Model (BFM), a coarse grained algorithm to simulate polymer systems. Our model is based on a bcc lattice instead of a simple cubic lattice used for the original BFM. This leads to a modified set of bond vectors, as well as larger moves. The algorithm allows for a very efficient parallelization which is based in subdividing the bcc lattice in two disjunct sublattices. By implementing our algorithm on a consumer graphic card, we gain an upspeed of about two orders of magnitude as compared to the CPU-implementation. We compare our model with the original BFM for dense polymer melts with respect to static and dynamic properties.

We conclude that this model is applicable to simulate all quantities and polymeric systems as the original BFM does, but with a significant upspeed.