

CPP 26: Polymer Dynamics

Time: Wednesday 10:30–11:45

Location: ZEU 160

CPP 26.1 Wed 10:30 ZEU 160

Local mobilities and chain end effects in non-entangled polymer melts - a molecular dynamics simulation study — ●DIDDO DIDDENS^{1,2} and ANDREAS HEUER^{1,2} — ¹Institut für physikalische Chemie, Universität Münster, Corrensstraße 30, 48149 Münster, Germany — ²NRW Graduate School of Chemistry, Corrensstraße 36, 48149 Münster, Germany

The dynamics of a polymer chain in a dense, non-entangled melt can be well described by the Rouse model. Within this model, the chain is composed of a series of Brownian beads connected by harmonic springs, where each bead is characterized by a uniform friction coefficient imposed by the surrounding chains. However, when probing the bead's mean square displacement, the chain ends move faster than the central monomers for topological reasons, and the chain ends have on average more intermolecular neighbors.

Using a newly developed method [1] we study the dependence of the local chain dynamics on the bead position by direct determination of the local friction coefficient. In this way, the Rouse assumption of uniform friction coefficients along the entire chain and specifically at the chain end is tested for an all-atom MD simulation of a poly(ethylene oxide) (PEO) melt. In particular, the interplay of the surroundings of a given monomer and the friction coefficient is discussed. Furthermore we analyze whether the forward-backwards dynamics of the monomers is compatible with the predictions of the Rouse model.

[1] D. Diddens, M. Brodeck, A. Heuer, EPL 91 (2010) 66005

CPP 26.2 Wed 10:45 ZEU 160

Short time dynamics of medium length molecules — ●HUMPHREY MORHENN¹, SEBASTIAN BUSCH¹, DIETER RICHTER², and TOBIAS UNRUH³ — ¹Technische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz and Physik Department E13, 85747 Garching, Germany — ²Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — ³Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

The description of transport mechanisms in molecular liquids is a challenging task. Especially the mechanism of molecular self-diffusion in liquids of organic medium-chain molecules is not fully understood yet. TOF-QENS experiments were performed on a polyethylene melt ($n\text{-C}_{100}\text{H}_{202}$), and a polydimethylsiloxane melt (PDMS, molecular weight approx. 17,250). Both chains are long enough to show gaussian chain statistics in their conformations so that it was possible to check the validity of the Rouse model on this time and length scale. It could be shown that the simple Rouse model cannot describe the TOF-QENS data satisfactorily but respecting a reduced local chain flexibility by a mode dependent friction coefficient the Rouse model can surprisingly reproduce the experimental data of PE down to $t = 1$ ps.

CPP 26.3 Wed 11:00 ZEU 160

Coarse-grained modelling of the spreading of droplets on reactive substrates — ●MURAT MULAYIM and MARCUS MULLER — Institut für Theoretische Physik, Georg-August-Universität, Göttingen, Germany

We study, by molecular simulation, the statics and dynamics of chemi-

cally driven running polymer droplets. The polymer melt is composed of 10-bead chains and described with coarse-grained potentials that retains the main properties of the chains. The substrate is modelled by two layers of a FCC lattice, having density $\rho_s = 2\sigma^{-3}$. The temperature was held constant with a Dissipative Particle Dynamics thermostat that locally conserves momentum and thus leads to hydrodynamic behaviour on long time and length scales. A self-produced wettability is gradient generated under the droplet via changing the type of substrate atoms depending on their spatial position and with a pre-defined probability. Parameters (reaction rate) for observing running polymer droplets in MD simulations are identified and the velocity profile and dissipation mechanisms in the quasi steady-state is presented.

CPP 26.4 Wed 11:15 ZEU 160

Temperature dependent single molecule rotational dynamics in PMA — ●SUBHASIS ADHIKARI, MARKUS SELMKE, and FRANK CICHOS — Molecular Nanophotonics Group, Inst. of Expt. Phys. I, Univ. of Leipzig, 04103, Leipzig, Germany

Temperature dependent measurements of the rotational diffusion of single dye molecules in the polymer poly(methyl acrylate) (PMA) are presented and compared to shear viscosity data and numerical simulations of the rotational diffusion process. It is found that single molecule rotational diffusion very accurately follows the Debye-Stokes-Einstein predictions for the shear viscosity without any additional parameter. We employ a simple model of dynamic changes of the rotational speed of a single molecule. This dynamic heterogeneity model is based on a Gaussian distribution of activation energies in a VFTH (Vogel-Fulcher-Tammann-Hesse) type temperature dependence of the polymer viscosity. The simulations explain all experimental details concerning the stretched exponential single molecule relaxation dynamics and the related distributions. They also reveal that the observed distributions are related to the intrinsic physical properties of the polymer but do in general not reflect the instantaneous spread of local viscous properties.

CPP 26.5 Wed 11:30 ZEU 160

Polymer dynamics under uniaxial mechanical stress — UTE BÖHME and ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden

The influence of uniaxial mechanical stress on the dynamics in semicrystalline polymers has been studied using low-field NMR. While in elastomers a monotonic change of the polymer dynamics, a time-dependent behaviour is found for semicrystalline materials. Under mechanical stress there is creep of the polymer chains, which results in a rearrangement of the crystallites. Though not change in the degree of crystallinity has been found, DSC shows better quality of the crystallites, which is a clear indication of rearrangement of the polymer chains. Low-field NMR using permanent magnets in a Halbach arrangement permit in-situ NMR experiments during stretching. The example of poly(propylene) shows an initial shortening of the transverse relaxation time, which is followed by a prolongation. In a stress-relaxation experiment the stress required to keep a constant elongation decreases exponentially. The transverse relaxation time returns to its initial value with a comparable time constant.