

## CPP 23: Polymer Dynamics

Time: Wednesday 9:30–12:45

Location: H48

## Invited Talk

CPP 23.1 Wed 9:30 H48

**On the dynamics of polymers in nanocomposites and under confinement** — ●DIETER RICHTER — Jülich Centre for Neutron Science and Institute for Solid State Research, Research Center Jülich, D-52425 Jülich, Germany

Confinement effects in polymer melts may lead to unusual properties. This concerns both, the chain conformation as well as chain dynamics that may be altered due to the surface interactions and changes of topology. In my presentation I will display neutron scattering data, addressing length and time scales from the single monomer to the entanglement network and beyond. These experiments reveal the basic relaxation rates related to monomeric friction, the intermediate scale Rouse dynamics as well as the entanglement controlled dynamics. Polymer nanocomposites have been investigated at various compositions using filler particles smaller and larger than the polymer size. I will discuss the effects of the filler size and concentration on the polymer conformation as well as on the dynamics on the various important length scales. The effect of confinement was also studied on well defined porous alumina samples which were filled with polyethylene oxide (PEO). Thereby the chain dimensions were much larger or smaller than the lateral pore size  $D$ . While for the long chains an expanded entanglement network is observed, the confinement seems to have a weaker effect on the short chains. In particular we do not observe any corset effect as proposed by NMR relaxometry.

## Topical Talk

CPP 23.2 Wed 10:00 H48

**From simple liquids to polymers: Dynamics revealed by field cycling  $^1\text{H}$  NMR** — AXEL HERRMANN, AZZA ABOU ELFADL, ROMAN MEIER, DANUTA KRUK, VLADIMIR N. NOVIKOV, and ●ERNST A. RÖSSLER — Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

We apply field cycling NMR to study the crossover from glassy through Rouse to reptation dynamics in series of different linear polymers (PB, PDMS, PPO, PI) with molecular weight  $M$  ranging from the low- $M$  limit (simple liquid) to the high- $M$  limit. Dispersion data of the spin-lattice relaxation time  $T_1(\omega)$  are transformed to the susceptibility representation  $\chi''(\omega\tau_s) = \omega/T_1$ , and using frequency-temperature superposition master curves  $\chi''(\omega\tau_s)$  ( $\tau_s :=$  segmental correlation time) are constructed which reflect spectral contributions from glassy as well as polymer specific dynamics. We are able to cover six decades at  $\omega\tau_s < 1$  allowing to monitor in detail the emergence of polymer specific relaxation contributions. Transforming the master curves into the time domain yields the segmental reorientational correlation function which we follow over six decades in amplitude. From this the order parameter as well as bond-vector correlation function are derived. Comparison with theoretical predictions by the tube-reptation model as well as renormalized Rouse theory reveals significant discrepancies whereas good agreement is found with Monte Carlo simulations. We conclude that the crossover to entanglement dynamics appears to be highly protracted. This is confirmed by accompanying measurements of dielectric normal mode spectra.

CPP 23.3 Wed 10:30 H48

**Bond-correlation functions determined in MD simulations of entangled polymer melts** — ●HENDRIK MEYER — Institut Charles Sadron, CNRS UPR22, 67034 Strasbourg, France

The polymer dynamics of entangled bead-spring chains is analysed based on large scale molecular dynamics simulations. As found in previous studies, the predicted power law regimes of mean-square displacements attributed to Rouse-motion in the tube (cross-over from  $t^{0.5}$  to  $t^{0.25}$ ) are only well developed beyond  $Z \geq 10$  entanglements per chain. Similar power law regimes are present for bond time-autocorrelation functions ( $P_1 \propto t^{-0.5}$  and  $t^{-0.25}$ ). NMR experiments measure a correlation function proportional to the second Legendre polynomial  $P_2$  of the bond correlations, which is found to be proportional to the square of  $P_1$  only for flexible chains, whereas a slower time decrease is found for chains with a small angular potential. Clear evidence is found that the terminal relaxation time increases stronger than predicted by reptation theory for  $Z > 5$ . We critically compare this finding with theories of contour length fluctuations, often invoked as the main explanation of this slowing down.

## 15 min. break

CPP 23.4 Wed 11:00 H48

**The role of the intermolecular magnetic dipole-dipole interaction in low frequency proton NMR in polymer melts.** — ●NAIL FATKULLIN<sup>1</sup>, ANVAR GUBAIDULLIN<sup>1</sup>, SIEGFRIED STAPP<sup>2</sup>, and RAINER KIMMICH<sup>3</sup> — <sup>1</sup>Kazan State University, Kazan 420008, Tatarstan, Russia — <sup>2</sup>Technische Universität Ilmenau, Dept. Technical Physics II, 98684 Ilmenau, Germany — <sup>3</sup>University of Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany

The different contributions to the dynamic magnetic dipole-dipole correlation function, which is responsible for proton NMR phenomena like the spin-lattice relaxation, the free induction decay, the solid echo, etc., are analyzed. For the anisotropic tube-reptation model the relative weight of the intra-molecular contribution in the time dependent magnetic dipole-dipole correlation function should progressively increase with time, corresponding to lower resonance frequency, compared to the intermolecular contribution. For the isotropic n-Renormalized Rouse model the situation is opposite: with increasing of time/decreasing frequency the relative weight of the intermolecular contribution progressively increases and may eventually dominate. Theoretical estimations and analyses of published experimental results, connected with proton NMR spin-lattice relaxations in polymer melts, directly show that at times longer than and at frequencies below the regime, neglecting the intermolecular contributions to proton NMR phenomena in polymer melts, as had been done in the majority of scientific papers, is incorrect.

CPP 23.5 Wed 11:15 H48

**Multiple quantum NMR observation of reptation and constraint release in polymer melts** — ●FABIAN VACA CHAVEZ and KAY SAALWAECHTER — Institute of Physics, Martin-Luther-University Halle-Wittenberg, Halle (Saale), Germany

In his seminal paper, de Gennes [1] propose a qualitative explanation of the polymer melts dynamics, far above the entanglement molecular weight  $M_e$ , in terms of a reptative, snake-like motion of the chain through a mesh of fixed topological constraints (entanglements) set by the other chains. Here we show results from  $^1\text{H}$  multiple quantum (MQ) NMR on a benchtop spectrometer [2], probing the validity of the tube model of polymer dynamics, which combines the reptation concept with the Rouse theory for unentangled chains. This fixed-tube model is insufficient for the quantitative description of actual mechanical data, and ongoing discussions focus on including dynamics of the tube itself, caused by contour-length fluctuations (CLF), arising from chain-end motions of the test chain, or constraint release (CR), arising from matrix chain motions. We also observe characteristic deviations from the tube model predictions up to high molecular weights, and show that CR processes are responsible for modified chain modes faster than actual reptation. Our results extend previous observations by neutron spin-echo spectroscopy (NSE), whose limited dynamic range poses limitations to the study of well-entangled systems.

[1] P. G. de Gennes, *J. Chem. Phys.*, 55, 572 (1971). [2] K. Saalwächter, *Progr. NMR Spectrosc.*, 51, 1 (2007).

CPP 23.6 Wed 11:30 H48

**Atomistic molecular dynamics simulations of polybutadiene at graphite: slowing down of orientation relaxations in confinement vs. bulk system** — ●LEONID YELASH<sup>1</sup>, PETER VIRNAU<sup>1</sup>, WOLFGANG PAUL<sup>2</sup>, and KURT BINDER<sup>1</sup> — <sup>1</sup>Institut für Physik, Johannes-Gutenberg Universität Mainz — <sup>2</sup>Institut für Physik, Martin-Luther-Universität Halle-Wittenberg

A nanoscopic thin polybutadiene film confined between two graphite surfaces is studied using molecular dynamics simulations. Polymer is described with an united atom model incl. Lennard-Jones, bending and torsion interactions[1]. The crystalline surface is modeled by several layers of graphite atoms placed at their crystallographic positions[2]. Our previous study has shown that the confinement affects the statics as well as the dynamics. E.g., gyration radius calculated perpendicular to the surface decreases strongly near the surface showing that the whole molecules prefer to orient parallel to the surface. The mean square displacement shows a preferred lateral diffusion of polymer; the diffusion perpendicular to the surface is significantly slowed

down.

Here we report results of our recent analysis of the MD data for the orientation relaxations of specific chemical bonds ( $\alpha$ -,  $\beta$ -, and double-bonds) present in polybutadiene as well as dielectric relaxation in bulk and confined systems. Such relaxation functions can be obtained experimentally, e.g., from NMR measurements[3].

[1] Smith, G.D., and Paul, W., *J. Phys. Chem. A*, 102, 1200 (1998); Krushev, S., *Diss. Mainz* 2002. [2] Steele, W.A., *Surf. Sci.*, 36, 317 (1973). [3] Saalwächter, K., *Prog. NMR Spec.*, 51, 1 (2007)

CPP 23.7 Wed 11:45 H48

**Understanding the Origin of Dynamical Heterogeneities in Polymer Blends** — •DIDDO DIDDENS<sup>1,2</sup>, ANDREAS HEUER<sup>1,2</sup>, and MARTIN BRODECK<sup>3</sup> — <sup>1</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, 48149 Münster, Germany — <sup>2</sup>NRW Graduate School of Chemistry, Corrensstraße 36, 48149 Münster, Germany — <sup>3</sup>Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Polymer blends composed of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) have been the focus of many investigations such as neutron scattering or NMR experiments. Within this polymer blend both components have greatly different glass transition temperatures, so that the low- $T_g$  compound (PEO) moves in a random, nearly frozen environment imposed by the high- $T_g$  compound (PMMA), leading to strong dynamical heterogeneities within the PEO dynamics. One common approach to model the dynamics of the PEO chains is the phenomenological Random-Rouse Model, in which the random environment imposed by the slow PMMA component is modelled by a Rouse chain with different friction coefficients on each bead.

Here we discuss the merits and limitations of the Random-Rouse Model for a simulated PEO/PMMA blend. By using a recently developed method to determine local mobilities in polymeric systems, we can check the different assumptions of this model. Moreover, the length-scale dependence of the retardation of the PEO dynamics in the blend compared to the homopolymer was studied.

CPP 23.8 Wed 12:00 H48

**Investigation of structural heterogeneities of porous diblock copolymer membranes by single particle tracking** — •CHANDRASHEKARA R. HARAMAGATTI<sup>1</sup>, DOMINIQUE ERNST<sup>1</sup>, FELIX SCHACHER<sup>2</sup>, MATHIAS ULBRICHT<sup>3</sup>, AXEL H. E. MÜLLER<sup>2</sup>, and JÜRGEN KÖHLER<sup>1</sup> — <sup>1</sup>Experimental Physics IV, University of Bayreuth, 95440, Bayreuth, Germany — <sup>2</sup>Macromolecular Chemistry II, University of Bayreuth, 95440, Bayreuth, Germany — <sup>3</sup>Technical Chemistry II, University of Duisburg-Essen, 45117, Essen, Germany

We study the structural heterogeneity of porous diblock copolymer membranes employing single particle tracking. The membranes were prepared by non solvent induced phase separation (NIPS) methods. Information on the thickness and pore sizes of the membranes is known

from scanning electron microscopy. Fluorescent polystyrene beads were used as fluorescent particles and the spatial position of which was monitored with sub-diffraction limited accuracy. The diffusion behavior of these particles provides information of the structural properties of the membranes.

CPP 23.9 Wed 12:15 H48

**Dynamics in thin polymer films probed by single molecule fluorescence microscopy at high temperatures** — •BENTE FLIER, MORITZ BAIER, JOHANNES HUBER, DOMINIK WÖLL, STEFAN MECKING, and ANDREAS ZUMBUSCH — Fachbereich Chemie, Universität Konstanz, Universitätsstraße 10, 78457 Konstanz, Germany

Wide-field fluorescence microscopy is a versatile technique for the investigation of single molecule dynamics. We use this technique for the analysis of dynamical properties of thin polymer films in the vicinity of the glass transition temperature. In this contribution we present first results of high temperature single molecule studies above 400 K of polystyrene and poly butyl methacrylate films with thicknesses between 10 nm and 100 nm. For single molecule measurements fluorescent dyes are either covalently bound to the polymer chains or used as probes of free volume. The measurements yield the temperature dependence of the diffusion coefficients which can be explained by free-volume theory. Compared to bulk techniques, however, the single molecule approach allows for an investigation of diffusional heterogeneities.

CPP 23.10 Wed 12:30 H48

**Dynamics of semiflexible treelike polymeric networks** — •MAXIM DOLGUSHEV and ALEXANDER BLUMEN — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Deutschland

Extending the generalized Gaussian structure model[1] we study the dynamics of treelike networks, in which we include stiffness using mean-field restrictions on the bonds' orientations. We proceed by using the Bixon-Zwanzig-model[2] and also the maximum entropy principle[3]. For semiflexible treelike networks both approaches turn out to be equivalent[4]. The dynamics of semiflexible treelike polymers obeys Langevin equations, which we succeeded in deriving analytically[4]. This allows us to determine straightforwardly the dynamical characteristics relevant to mechanical and dielectric relaxation[4,5].

[1] A. A. Gurtovenko and A. Blumen, *Adv. Polym. Sci.*, 182, 171 (2005).

[2] M. Bixon and R. Zwanzig, *J. Chem. Phys.*, 68, 1896 (1978).

[3] R. G. Winkler, L. Harnau, P. Reineker, *J. Chem. Phys.*, 101, 8119 (1994).

[4] M. Dolgushev and A. Blumen, *J. Chem. Phys.*, 131, 044905 (2009).

[5] M. Dolgushev and A. Blumen, *Macromolecules*, 42, 5378 (2009).