# CPP 23: Polymer Dynamics

Time: Wednesday 9:30–13:00 Location: H39

**Invited Talk** CPP 23.1 Wed 9:30 H39
**Polymers, rings and pores: A neutron scattering study** —
•Andreas Wischnewski — Jülich Centre for Neutron Science JCNS-1 and Institut for Complex Systems ICS-1, Forschungszentrum Jülich, Germany

Polymers are one of the most important and fascinating soft matter materials both from the fundamental point of view as well as with respect to their wide range of applications. Industrial processing, design, fabrication and application depends to a large extend on the understanding of the rheological properties on a microscopic level. Neutron scattering is a powerful tool to access the microscopic characteristics of polymeric systems and has already significantly contributed to the understanding of the static and dynamic properties of polymers with different architectures and in different, complex environments. Recently, ring polymers have attracted ample interest both from simulation experts and experimentalists. The absence of chain ends, which determine the dynamics of linear chains and in particular branched polymers, allows to examine fundamental aspects of polymer theory. Neutron spin echo spectroscopy reveals significant differences in ring dynamics compared to the linear counterpart. In particular rings cannot build up easily the tube confinement as known from long linear chains. In contrast to that, polymers in nano-pores are subject to a stronger topological confinement as compared to the bulk system if a surface-polymer interaction is present. Neutron scattering studies combined with complementary techniques are presented.

CPP 23.2 Wed 10:00 H39
**The collapse transition of poly(2-oxazoline) gradient copolymers - a multistep process** — Sebastian Jaksch[1], Konstantinos Kyriakos[1], Jianqi Zhang[1], Isabelle Grillo[2], Anita Schulz[3], Rainer Jordan[3], and •Christine M. Papadakis[1] — [1]TU München, Physik-Department, Physik weicher Materie, Garching — [2]Institut Laue-Langevin, Grenoble — [3]TU Dresden, Department Chemie, Professur für Makromolekulare Chemie

Thermoresponsive poly[(*iso*-propyl-2-oxazoline) (P*i*PrOx) polymers in aqueous solution exhibit a strong change in solubility and chain conformation when heated above their cloud point (CP). The CP decreases strongly upon insertion of few hydrophobic monomers.

We investigated poly[(*iso*-propyl-2-oxazoline)-*grad*-(*n*-nonyl-2-oxazoline)] (P[*i*PrOxNOx]$_{grad}$) gradient copolymers with a varying fraction of NOX moieties. In temperature-resolved SANS experiments, we have found a two-step collapse and aggregation behavior of the gradient copolymers at the cloud point which is not present in the homopolymer [1]. Time-resolved SANS allowed us to monitor the structural evolution of the aggregates when rapidly heating the solutions from below the CP to different temperatures above. We found that, the higher the target temperature, the more pronounced is the collapse. Moreover, the aggregates present in the intermediate regime are stable and do not transform into those found at higher target temperatures.

[1] S. Salzinger, S. Jaksch, C.M. Papadakis et al., *Colloid Polym. Sci.* **290**, 385 (2012).

CPP 23.3 Wed 10:15 H39
**Local, global and collective dynamics in a short polymer system.** — •Humphrey Morhenn[1,2], Sebastian Busch[3], and Tobias Unruh[2] — [1]Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) and Lehrstuhl für Funktionale Materialien, Technische Universität München, Germany — [2]Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [3]Department of Biochemistry, University of Oxford, United Kingdom

The *n*-alkane $C_{100}H_{202}$ is an oligomer on the edge of being a polymer. Although its chains are shorter than the entanglement length and long enough to show Gaussian chain statistics, the Rouse model fails to predict the chain dynamics. Detailed quasielastic neutron scattering experiments and extensive molecular dynamics simulations were performed, providing complementary pictures on the molecular motions. Three distinct relaxation processes on the pico- to nanosecond time regime were separated, eventually leading to molecular self-diffusion. Two relaxations were found to correspond to local torsional and global rotational motions of single molecules, whereas a third, intermediate

relaxation can be explained by intermolecular collective motions. Taking these contributions into account a physical model describing molecular self-diffusion is being developed.

CPP 23.4 Wed 10:30 H39
**Selective Solid-State NMR Investigations of Polymer Dynamics** — Ute Böhme, Anastasia Vyalikh, and •Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V.

NMR relaxation provides information on the molecular dynamics over a wide range of correlation times. To achieve spectral resoltion in solid polymers high-resolution solid-state NMR based on CRAMPS (combined multipulse and rotation spectroscopy) has been applied. The spectral resolution permits to resolve different components in copolymers and mixtures in proton NMR spectra. The sensitivity in the proton spectra will permit the study of thin films as well. Selective swelling of single components which is accompanied by enhanced segmental dynamics has been observed in both spn-spin-relaxation (T2) and spin-lattice relaxation in the rotating frame (T1rho). Spectral resolution permits the identification of the components and assignments of their local mobility.

CPP 23.5 Wed 10:45 H39
**Studies of entangled polymer dynamics by NMR: validity of tube model variants and nanoparticle effects** — •Filipe Furtado[1], Joshua Damron[1], Marie-Luise Trutschel[1], Mansi Agarwal[2], Charles Zukoski[2], and Kay Saalwächter[1] — [1]Institut f. Physik-NMR, Martin-Luther-Univ. Halle, Deutschland — [2]University of Illinois at Urbana-Champaign, USA

The validity of fixed-tube model remains a matter of intense debate. Ongoing discussions include the dynamics of the tube itself and of contour-length fluctuations (CLF) and constrained release (CR) effects. Suitable NMR experiments [1] were used to investigate CR effects by probing the dynamics of diluted protonated polybutadiene (PB) chains in matrices of deuterated (NMR-invisible) high molecular weight PB chains. Such dilution experiments have been reported to be subject to a bias due to interchain correlations in NMR T1 relaxation experiments [2], but these effects have been shown to not significantly affect our experiments. CLF was investigated on deuterated pseudotriblock copolymers (2H-1H-2H). Furthermore, we hereby present the first NMR experiments clearly confirming the recently predicted nanoparticle effect on chain disentanglement [3] on a molecular scale by monitoring the influence of polyhedral oligomeric silsesquioxanes (POSS) on the disentanglement time of polyethyleneoxide melts.
[1] F. V. Chávez et al., Phys. Rev. Lett., 2010, 104, 198305
[2] A. Herrmann et al., Macromolecules, 2012, 45, 6516
[3] Y. Li et al., Phys. Rev. Lett., 2012, 20121, 09, 118001

CPP 23.6 Wed 11:00 H39
**Deformation Dynamics of Thin Stretched Polymer Films** —
•Stefan Krause, Martin Neumann, Melanie Bibrach, Robert Magerle, and Christian von Borczyskowski — Fakultät für Naturwissenschaften, TU Chemnitz, D-09107 Chemnitz

The fluorescence of polymer embedded reporter molecules reacts very sensitive on environmental changes such as mechanical stress. Especially polarization effects of these fluorophores allow for the spatial and temporal observation of the deformation within drawn polymer films while the utilization of ultra sensitive force sensors enables to measure the global mechanical deformation behaviour of the polymer film. We report on fluorescence (single molecule) microscopy, atomic force and mechanical force investigations of thin films of viscoelastic polymethylacrylate (PMA). The films are stretched using a micro tensile testing setup. Simultaneously, perylenediimide dyes functionalized with different side chains were embedded in the film and report via their molecular dynamics changes within their local environment.

**15 min. break**

CPP 23.7 Wed 11:30 H39
**Dynamics of Regular Hyperbranched Polymers** — •Florian Fürstenberg, Maxim Dolgushev, and Alexander Blumen — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str.3, D-79104 Freiburg, Deutschland

Theoretical investigations of hyperbranched polymers are enjoying growing attention. Up to now, analytic work focused on regular fully-flexible hyperbranched polymers such as dendritic structures. Here we investigate the dynamics of semiflexible dendrimers of arbitrary functionality $f$ and generation $g$. We focus on the solution of the corresponding Langevin equations which can be formulated in an analytic form[1]. Moreover, we show that the corresponding diagonalization problem can be drastically simplified by using a complete set of eigenmodes, which is similar to the set for fully-flexible dendrimers known from the literature[4,5]. Another advantage of our diagonalization scheme is that it provides automatically the eigenvalues' degeneracies[4]. The presented scheme for dendrimers paves the way for theoretical investigations of more complex polymeric architectures[5].

[1] M Dolgushev and A. Blumen, J. Chem. Phys. **131**, 044905 (2009).
[2] C. Cai and Z.Y. Chen, Macromolecules **30**, 5104 (1997).
[3] A. A. Gurtovenko, D.A. Markelov, Y.Y. Gotlib, and A. Blumen, J. Chem. Phys. 119, 7579 (2003).
[4] F. Fürstenberg, M. Dolgushev, and A. Blumen, J. Chem. Phys. **136**, 154904 (2012).
[5] F. Fürstenberg, M. Dolgushev, and A. Blumen, submitted.

CPP 23.8 Wed 11:45 H39
**Unwinding polymer globules under stretching force: A Monte Carlo study** — ●Christoph Jentzsch[1,2], Marco Werner[1,2], and Jens-Uwe Sommer[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden, Germany — [2]Technische Universität Dresden, Germany

We investigate linear polymer chains under poor- and non-solvent conditions using the bond fluctuation model with explicit solvent. By implementing many-body effects implicitly, this model allows for free diffusion of polymer globules under non-solvent conditions on the same time scale as in good solvent while keeping the computational effort low as compared to off-lattice calculations. We analyze static and dynamic properties of polymer globules in poor solvent. We further calculate the force acting on chain ends, when they are fixed at a given distance. Our results for the force-extension curve are qualitatively in good agreement with recent experiments and with numerical results using a self-consistent field approach. For distances slightly larger than the globule diameter, we observe a tadpole regime where one stretched part of the chain is in equilibrium with a single residual globule. The force necessary to form a stable tadpole conformation as function of solvent quality can be understood using scaling arguments based on the thermal blob size. For increasing distances, we observe a decay of the tadpole into smaller globules and stretched chain parts. Here, the stretching force shows a local minimum and a quantitative explanation for the observed shape of the force-extension curve remains a challenge. For larger distances a cross-over to a strongly stretched chain behavior is found.

CPP 23.9 Wed 12:00 H39
**Translocation of macromolecules with different architectures through polymer brush covered microchannels** — ●Irina Neratova[1], Torsten Kreer[1], and Jens-Uwe Sommer[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany — [2]Technische Universität Dresden, Institut für Theoretische Physik, Zellescher Weg 17, D-01069, Dresden, Germany

Polymer brush covered channels have attracted a lot of attention in recent years for both engineering and biomedical applications. They play an important role in the design of novel microfluidic devices, the control of targeted drug delivery, stabilization of colloids, and lubrication. Although the equilibrium properties of polymer brushes are well understood, many non-equilibrium phenomena have not been studied to date. One example is the translocation of macromolecules through a brush covered microchannel.

In this study, Molecular Dynamics simulations are employed to investigate the influence of the architecture of macromolecules on their ability to pass through a brush covered channel. The properties of linear and star polymers embedded in the microchannel are studied in thermodynamic equilibrium and within Poisseuille flows of various strengths. It is shown that, in equilibrium, a linear macromolecule diffuses faster than a polymer star of the same molecular weight. On the other hand, a pressure gradient may be regarded as a driving force for faster motion of the star polymer.

CPP 23.10 Wed 12:15 H39
**A Simulation Study of the Lithium Transport Mechanism in Ternary Polymer Electrolytes – The Critical Role of the Segmental Mobility** — ●Diddo Diddens and Andreas Heuer — Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster

Polymer electrolytes – typically consisting of PEO and a lithium salt such as LiTFSI – are promising candidates for light-weighted but powerful energy storages. However, at ambient temperatures, the conductivity of most polymer electrolytes is still too low for an efficient technological use. Among several other remedies, the incorporation of an ionic liquid (IL) seems to be a fruitful improvement of these materials. Here, it was observed that depending on the ratio of PEO ether oxygens to lithium ions, the lithium diffusion coefficient significantly increases with the IL concentration or, alternatively, is roughly constant [Passerini *et al.*, *Electrochim. Acta*, 2012]. In order to unravel the microscopic scenario giving rise to these observations, we use MD simulations in combination with a Rouse-based analytical transport model, which has originally been devised for classical polymer electrolytes. It turns out that the mobility of the PEO segments plays a decisive role for the precise value of the macroscopic lithium diffusion constant due to the cooperative motion of the lithium ions with the polymer segments. For the latter, two opposing effects are present in the ternary systems: the slowing-down due to the coordinating lithium ions and the plasticizing effect of the IL. Thus, for the design of novel battery materials, one should ensure that the latter effect dominates.

CPP 23.11 Wed 12:30 H39
**Multi-scale Modelling of Phase Inversion Membranes** — ●Richard J Broadbent, James S Spencer, Andrew G Livingston, Arash A Mostofi, and Adrian P Sutton — Imperial College London, United Kingdom

It is expected that by 2025 two-thirds of the world's population will live in countries with water supply problems[1]. Separation processes account for 40-70% of capital and operating costs in industry[2]. Membrane technology is expected to be key to addressing both these issues. Organic solvent nano-filtration membranes are widely used by industry.

Understanding and predicting the performance of nano-filtration membranes remains unsolved and is an area in which theory and simulation is yet to have a major impact. One of the challenges for the development of accurate and predictive models of the structure of polymer membranes is that they must span multiple length- and time-scales: the membranes are manufactured over a period of seconds from chemicals which diffuse on a picosecond time scale; the pores within the membranes are often less than a nanometer in size, while the polymers they are made from are often almost a micrometer long. By combining Density Functional Theory, Molecular Dynamics and Monte Carlo methods it is possible to capture all these key scales and advance our understanding of this important technology.

[1] http://www.un.org/ecosocdev/geninfo/sustdev/waterrep.htm
[2] Jimmy L. Humphrey and George E. Keller II. Separation Process Technology. New York, McGraw-Hill, 1997.

CPP 23.12 Wed 12:45 H39
**Interplay of morphology and rheology during foaming of block copolymers of polystyrene and poly(methyl methacrylate)** — Golda Louis Chakkalakal[1], ●Ulrich A. Handge[1], Ulla Vainio[2], and Volker Abetz[1] — [1]Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany — [2]Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg

Porous and cellular polymers are technologically used in a variety of applications, e.g. in lightweight applications or for acoustic and thermal insulation. Furthermore, porous polymers with an open-cell structure can be used as membranes for microfiltration purposes. If a block copolymer is chosen for preparation of a porous or cellular polymer, then the phenomenon of microphase-separation yields an additional degree of freedom to prepare nanostructured materials. In this study, we systematically investigate the influence of morphological and rheological properties on the preparation of foams of polystyrene (PS)-b-poly(methyl methacrylate) block copolymers. The foams were prepared using the technique of batch foaming with carbon dioxide as blowing agent. The analysis of rheological data reveals that molecular weight and morphology strongly influence the complex modulus and the creep compliance. The solution of carbon dioxide in PS-b-

PMMA block copolymers leads to a reduction of the glass transition temperature of the PS and the PMMA phase. Generally, foaming of PS-b-PMMA block copolymers with a cylindrical morphology leads to foams with a lower density than the foams with a lamellar morphology.