

CPP 29: Polymer Networks and Dynamics III: Mechanical Properties

Time: Tuesday 14:00–16:00

Location: ZEU 250

CPP 29.1 Tue 14:00 ZEU 250

Tuning the Properties of Polymer Films by Manipulating the Preparation Pathways — ●SIVASURENDER CHANDRAN, RISHAB HANDA, and GÜNTER REITER — Experimental Polymer Physics Group, Physikalisches Institut, Universität Freiburg, Freiburg, Germany

Polymer thin films take a central stage in various technological fronts ranging from polymer electronics to responsive biological surfaces. As a consequence, the ability to tune the properties of polymer films is of crucial importance. Here, through controlled manipulation of preparation pathways, we show that the final properties of pristine polymer films viz., the amount of residual stresses, elastic modulus and work for deformation, quantifying the film stability, can be tuned by orders of magnitude. Further, by identifying a normalized preparation parameter characterizing the non-equilibrium nature of polymer thin films, we deduced simple scaling relations between relaxation time and film stability with the amount of preparation induced residual stresses. Our experiments provide simple strategies for manipulating the lifetime of non-equilibrium states and hence for tuning the properties of polymer films.

CPP 29.2 Tue 14:15 ZEU 250

Analysis of entanglement effect on deformed polymer melts in non-linear viscoelastic regime — ●HSIAO-PING HSU and KURT KREMER — Max Planck Institute for Polymer Research

Dynamics of polymer melts are strongly affected by the entanglement effect due to the topological constraints between chains in melts both in linear and non-linear viscoelastic regime. Starting from the fully equilibrated and highly entangled bead-spring chains in melts we deform the melts by isochoric uniaxial-elongation with fixed strain rate. The strain rate is chosen such that it is fast compared to the global relaxation but slow compared to the local relaxation on the scale of the tube diameter. We study the dynamic and static properties, and the topological structures of strongly deformed polymer melts during the relaxation process in detail by molecular dynamics simulations using the package ESPResSo++. Through the primitive path analysis (PPA), the entanglement points are identified according to the curvature along the primitive path of chains. We show that the distribution of entanglement points of polymer melts becomes inhomogeneous, and the tension forces along the original and primitive paths in the stretching direction are equivalent.

CPP 29.3 Tue 14:30 ZEU 250

What controls the structure, and the linear and non-linear rheological properties of dense, dynamic supramolecular polymer networks? — ●KLAUS SCHRÖTER¹, TINGZI YAN¹, FLORIAN HERBST², WOLFGANG H. BINDER², and THOMAS THURN-ALBRECHT¹ — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg — ²Institut für Chemie, Martin-Luther-Universität Halle-Wittenberg

Telechelic polyisobutylenes with different functional groups and a series of molecular weights were investigated by means of small angle x-ray scattering and rheology. All samples form a dense, dynamic network of interconnected micelles resulting from aggregation of the functional groups and leading to viscoelastic behavior. The dynamic character of this network manifests itself in the appearance of terminal flow at long timescales. While the elastic properties are distinctly molecular weight dependent, the terminal relaxation time is controlled by the functional end groups. The yielding properties under large deformation during startup shear experiments can be understood by a model of stress activation of the dynamic bonds. Stress relaxation experiments help to separate the non-linear response into two contributions: a fast collapse of the network and a slow relaxation, happening on the time scale of the terminal relaxation. The latter is also shown to control self-healing of the collapsed structure.

CPP 29.4 Tue 14:45 ZEU 250

Re-association dynamics of supramolecular transient networks — ●BARBARA GOLD, WIM PYCKHOUT-HINTZEN, JÜRGEN ALLGAIER, ANDREAS WISCHNEWSKI, and DIETER RICHTER — JCNS-1, Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Straße, 52428 Jülich

Supramolecular polymers form an emerging class of smart materials bearing novel motifs such as shape memory or self-healing. Those are introduced by re-associating groups. However, a fundamental understanding of the underlying physical processes is still missing, inhibiting the design of tailor-made applications.

We present a multiple methods investigation of the dynamics of entangled supramolecular polyisoprene networks with the objective, to decipher the so far unexplained gross discrepancy between transient bond life times and rheological relaxation due to the supramolecular stickers. Information on the association constant of the functional H-bonding groups is revealed by FTIR spectroscopy while SANS measurements show a homogenous supramolecular melt. In the common temperature range the H-bond lifetime (dielectric α^* -process) and the rheological relaxation differ by two orders of magnitude in time.

Within the concept of a compact random walk, where the random walker (opened sticker) undergoes multiple returns to its starting point, we quantitatively understand this so far unexplained discrepancy: The bond dissociation gives rise to the dielectric response. However, for mechanical relaxation, the association with a new partner, taking place only after multiple returns to the original binding partner, is relevant.

CPP 29.5 Tue 15:00 ZEU 250

Friction between ring polymer brushes — ●JAROSLAW PATUREJ^{1,2} and AYKUT ERBAS³ — ¹Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany — ²Institute of Physics, University of Szczecin, 70451 Szczecin, Poland — ³Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

Friction between ring polymer brush bilayers sliding past each other at melt densities is studied using extensive coarse-grained molecular dynamics simulations and scaling arguments, and the results are compared to the friction between bilayers of linear polymer brushes. We show that for a velocity range spanning over three decades, the frictional forces measured for ring polymer brushes are smaller in comparison to the corresponding friction in the case of linear brushes. In the linear-force regime, the weak inter-digitation between ring brush layers as compared to linear brushes leads also to a lower number of binary collisions between the monomers from opposing brushes. At high velocities, where the thickness of the inter-digitation between bilayers is on the order of monomer size regardless of brush topology, stretched segments of ring polymers adopt the double-stranded conformation.

CPP 29.6 Tue 15:15 ZEU 250

Loss of entanglement or shear-induced ordering in polymer melts — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

The transverse NMR relaxation T₂ is most suited to investigate polymer chain dynamics. In polymers commonly at least two components are observed, which are attributed to the entangled and free polymer chain segments respectively. In the present study different polysiloxane melts with a narrow molecular-weight distribution have been used. Under shear in a Couette cell one commonly assumes shear-induced ordering, which would result in restricted degrees of freedom and hence a shortened T₂. However in most cases a prolonged T₂ has been observed under shear, which can be explained by either a loss of entanglements or an increased mesh size between entanglements based on a local crowding of entanglements. A shortened T₂ as signature of shear-induced ordering is observed only for short-chain polymers, which exhibit a single exponential decay, indicative of the absence of entanglements. That implies that the loss of entanglements is the process dominating the local polymer dynamics, while shear-induced ordering happens as well for entangled polymers.

CPP 29.7 Tue 15:30 ZEU 250

Mechanical response of soft materials at the nanoscale and the moving-surface model — ●PER-ANDERS THOREN, RICCARDO BORGANI, DANIEL FORCHHEIMER, and DAVID B. HAVILAND — Nanos-structure Physics, KTH Royal Institute of Technology, Stockholm, Sweden

The Atomic Force Microscope (AFM) is ideal for characterization of surfaces and interfaces at the nano-scale. Despite many different measuring techniques, understanding the interaction between the AFM

tip and the surface of soft materials is challenging. In most cases a Hertzian contact-mechanics model is used, where only the elastic deformation of an indented surface is considered. This approach might be justified for stiff samples, but not for soft viscoelastic materials. We present a dynamic model of both the cantilever and the soft viscoelastic surface[1]. The strong adhesion force and finite relaxation of the surface gives rise to distinct features in the oscillation amplitude dependence of the cantilevers dynamic force quadratures[2]. These dynamic force curves are easily obtained from multi-frequency AFM measurements without assuming a particular interaction model, and they separately reveal the conservative and dissipative character of the tip-surface interaction. Numerical simulation of our nonlinear moving-surface model compares extremely well to the measured force quadratures, allowing us to extract the relaxation time of the viscoelastic surface.

[1] D.B. Haviland *et al.* *Soft Matter*, 12, 619 (2016).

[2] D. Platz *et al.* *Beilstein J. Nanotechnol.* 4, 45-56 (2013).

CPP 29.8 Tue 15:45 ZEU 250

Determination of biases in equilibrium free-energy estimations from single-molecule unbinding experiments — THOMAS UTZIG¹, PHILIPP STOCK^{1,2}, LAILA MORENO OSTERTAG¹,

and ●MARKUS VALTNER^{1,2} — ¹Max-Planck-Institut fuer Eisenforschung GmbH, Duesseldorf, Germany — ²TU Bergakademie Freiberg, Freiberg, Germany

The capabilities of Atomic Force Microscopes to probe bond rupture at a molecular level are widely appreciated. These measurements are carried out unidirectional under non-equilibrium conditions. Jarzynski's equality (JE) has proven useful to relate the work obtained along these events to the underlying free energy of the unfolding or unbinding process. It has been also pointed out that the free energies can be biased due to finite sampling of work trajectories and dominance of rare events. Here, we present an experimental approach to quantify and correct errors arising from application of JE to single-molecule unbinding at interfaces. In particular we probe the amine/gold bond as a function of the linker's length which is used to immobilize the amine on a flat surface. With increasing linker length we observe an increase in the average work spent on unfolding and bond rupture. Also interaction energies calculated using JE increase if longer linkers are used. Our data demonstrate that the energy stored within the stretched molecule influences single molecule experiments. Further we show how these influences can be quantified, providing important design aspects for single-molecule AFM experiments.