CPP 49: Polymer and Molecular Dynamics, Friction and Rheology

Time: Friday 11:30–13:00 Location: H39

CPP 49.1 Fri 11:30 H39

Molecular Mobility and Physical Aging in Polymers of Intrinsic Microporosity (PIM-1) Revisited: A Big Glassy World — •Farnaz Emamverdi, Martin Böhning, and Andreas Schönhals — Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

Polymers of Intrinsic Microporosity (PIMs) are promising candidates for the active layer in gas separation membranes because of their high permeability and reasonable permselectivity. However, PIMs suffer from a decrease in performance with time due to physical aging. The initial microporous structures approach a denser state via local rearrangements, leading to a reduction of the permeability. Hence a characterization of the molecular mobility in these materials can provide valuable information about physical aging. In this work, the dielectric behavior of PIM-1 films and their behavior upon heating (aging) were revisited during different heating/cooling cycles in a broad temperature range between 133 K and 523 K. In addition, the obtained results were compared with data of samples that were annealed at ambient temperatures for different time. Multiple dielectric processes were observed like different relaxations due to local fluctuations and a Maxwell-Wagner-Sillars polarization effects due to the microporosity. The temperature dependence of the rates of all the processes follows the Arrhenius law where the estimated activation energy depends on the process. The influence of the thermal history on the processes is discussed in detail.

CPP 49.2 Fri 11:45 H39

Orientation approach to the light-induced surface relief gratings formation in azopolymer materials — •Nina Tverdokhleb, Bharti Yadav, and Marina Saphiannikova — Leibniz-Institut für Polymerforschung Dresden e. V., PF 120411, 01005 Dresden

The phenomenon of azopolymer deformation giving rise to surface relief gratings (SRG) under the influence of polarized light was discovered two and a half decades ago. Despite the numerous different theoretical approaches to this effect, an accurate representation that would interpret all peculiarities of this phenomenon is absent. At present, the light-induced orientation of polymer backbones looks like the most promising explanation [1]. With help of this orientation approach and the finite element modeling software ANSYS, we simulate the viscoplastic formation of sinusoidal protrusions produced by the applied light-induced stress on the thin azopolymer films. We explain the difference in SRG height for irradiation with various interference patterns. It is found that the mechanical boundary conditions have a crucial impact on the output. The results of our viscoplastic modeling are in good agreement with recent experiments [2]. [1] B. Yadav et al. J. Phys. Chem. B 122 (2019) 2001-2009. [2] B. Yadav, N. Tverdokhleb et al. Macromol. Mater. Eng. (2022) 2100990.

CPP 49.3 Fri 12:00 H39

Measuring Volume Exclusion on Single Polymer Chains Diffusing in Solution — •Tobias Thalheim and Frank Cichos — Peter Debye Institute for Soft Matter Physics, Leipzig University, Germany

Excluded volume effects in single polymer chains occur due to long-range interactions of distant segments in the chain which cannot pass through each other entailing a strong influence of the static as well as the dynamic behavior of the polymer. Various theoretical descriptions were thus devised to incorporate these effects in the interpretation of experimental outcomes. A theory by Schäfer and Krüger incorporating this real-polymer phenomenon predicts a distribution function which describes the total segment density about an individual polymer's center of mass. This distribution function augments the picture of an ideal Gaussian chain by correction functions that account for volume exclusion and which were derived in the framework of renormalization groups. Although this permits the assessment of the role of volume exclusion for single chains in contrast to usual accesses via scaling theories or ensemble measurements, this theory has never been tested before. We report on experiments including two types of freely-diffusing double-stranded DNA molecules that utilize Schäfer's and Krüger's theory to investigate these effects. We show that for short λ-DNA molecules volume exclusion is of minor importance, whereas long T4-DNA molecules exhibit prominent volume exclusion. Furthermore, we employ a thermophoretic trapping method to test this theory on single compressed polymers subjected to a virtual harmonic potential.

CPP 49.4 Fri 12:15 H39

Dynamics in polymer-fullerene blends for photovoltaic applications studied with quasielastic neutron scattering — •Dominik M. Schwaiger[1], Wiebke Lohstroh[2], and Peter Müller-Buschbaum[1,2] — [1]TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — [2]MLZ, TU München, 85748 Garching

In organic photovoltaics, donor - acceptor bulk heterojunctions are often used as active layer due to their superior performance compared to e.g. planar structured devices. In this optically active polymer layer, photons are absorbed, excitons are created, subsequently dissipated at a material interface and hence free charges are provided. A promising low-bandgap electron donor material is the conjugated polymer PTB7 that is often used in combination with the fullerene derivate PCBM. Besides a large number of studies on structure and electrical properties, the level of knowledge about dynamics in this system is very limited. We investigated films of PTB7, PCBM and different blends of these two, prepared out of chlorobenzene solutions. Quasielastic neutron scattering experiments were performed to determine hydrogen dynamics on a pico- to nanosecond timescale. In addition, two well established techniques for performance enhancement in organic photovoltaics, namely the addition of DIO to the casting solution and a methanol posttreatment of the active layer, are applied and their influence on the polymer dynamics is investigated.

CPP 49.5 Fri 12:30 H39

Equilibration of free-standing films of highly entangled polymer melts — •Hsiao-Ping Hsu and Kurt Kremer — Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

Equilibrating confined and free-standing films of highly entangled polymer melts is a challenge for computer simulations. We approach this problem by first studying polymer melts based on a soft-sphere coarse-grained model confined between two walls. The distance of the walls is compatible with the simulation box of bulk melts in equilibrium, while periodic boundary conditions in the directions parallel to the walls are kept. Then we successively insert more fine grained polymer representations until the underlying microscopic details of the bead-spring model are reached. Tuning the wall potential, the monomer density of confined polymer melts in equilibrium is kept at bulk melt density even near the walls. Switching to another recently developed variant of the bead-spring model we can study melts at zero pressure [1] and study free-standing polymer films [2]. Furthermore, this also allows us to study free-standing films under strain and analyze the influence of entanglements on the local film morphology.

[1] H.-P. Hsu, K. Kremer, J. Chem. Phys. 150, 091101 (2019); 150, 159902 (2019).

[2] H.-P. Hsu, K. Kremer, J. Chem. Phys. 153, 144902 (2020); 156, 019901 (2022).

CPP 49.6 Fri 12:45 H39

Liquid flow through nanoporous media: non-linear response and blocking — •Roya Ebrahimi Viand[1] and Felix Höfling[1,2] — [1]Department of Mathematics and Computer Science, Freie Universität Berlin, Germany — [2]Zuse Institute Berlin, Germany

Directed fluid flow is a major transport mechanism in porous media that can either be generated by pumps or emerge in response to a pressure gradient. The pressure-flow relation and how it depends on the structure and geometry of the medium is investigated by non-equilibrium molecular dynamics (NEMD) simulations of a flow of dense liquids through regular bead packings as a model for nanoporous medium. Upon decreasing the porosity, we find a significant non-linear response. The linear permeability varies over two orders of magnitude and vanishes beyond a critical porosity. Our simulations further exhibit a substantial increase in temperature inside the porous medium, which we attribute to the local balance of energy fluxes using fluid mechanical conservation laws. Finally, we show that a recent NEMD approach based on the adaptive resolution simulation (AdResS) tech-

nique can help to decrease the required simulation volume considerably [1,2]. This simulation approach is expected to be highly applicable for research on flow in porous as well as biological media.

[1] R. Ebrahimi Viand et al., J. Chem. Phys. 153, 101102 (2020)
[2] R. Klein, R. Ebrahimi Viand et al., Adv. Theory Simul. 4, 2100071 (2021)