

## CPP 40: Polymer and Molecular Dynamics, Friction and Rheology

Time: Tuesday 10:45–12:45

Location: ZEU 255

CPP 40.1 Tue 10:45 ZEU 255

**Exploring the Properties of Ionomers Through the Use of Coarse Grained Molecular Dynamic Simulations** — ●NICHOLAS MICHELARAKIS<sup>1</sup>, KONSTANTINOS GKAGKAS<sup>2</sup>, and FRAUKE GRÄTER<sup>1</sup> — <sup>1</sup>Heidelberg Institute for Theoretical Studies, Heidelberg, Germany — <sup>2</sup>Toyota Motor Europe NV/SA, Zaventem, Belgium

The mechanical and structural properties of the Nafion membrane in the core of a Proton Exchange Membrane Fuel Cell (PEMFC) are controlled by the molecular interactions within the Nafion molecules and with the dispersion solvent. The effect of the dispersion solvent on the Nafion membrane assembly process, and on the final Nafion membrane properties (structural morphology, water/solvent content, ion exchange capacity, membrane stability), remains an area of intense study. Here we present a non-equilibrium Coarse Grained Molecular Dynamics method, based on the MARTINI force field, for calculating the dynamic shear viscosity of the Nafion 'ink' used in PEMFC membrane printing; a trait closely correlated to the properties of the final Nafion membrane. In this method, two stationary walls are introduced in the simulation box. A pulling force along the z-axis is then applied to the bottom wall allowing for the simulation of a Couette flow. Using water as an initial test-case we demonstrate that this method has the ability to accurately predict the dynamic shear viscosity of this solvent. This is subsequently extended to a collection of other solvents and Nafion solutions, simulated under PEMFC printing conditions, indicating that this approach has the ability to recapitulate the dynamic viscosity values calculated experimentally.

CPP 40.2 Tue 11:00 ZEU 255

**Polymer electrolytes: how do they react upon application of an external electric field?** — ALINA WETTSTEIN, DIDDO DIDDENS, and ●ANDREAS HEUER — Inst. Phys. Chemie, WWU Muenster, Germany

Polymer electrolytes are of utmost relevance for many applications of lithium ion batteries. Close to the electrodes they are exposed to high electric fields. Here we present extensive molecular dynamics simulations of a standard polymer electrolyte (poly(ethylene oxide) with a lithium salt) for different applied electric fields up to a few Volt per nanometer. We observe a prominent dependence of structural and dynamical properties on the electric field, reflecting nonlinear effects. It is shown that studying the field dependence allows one to characterize the motional mechanisms for the lithium transport in these electrolytes. Furthermore, several key questions can be answered: (1) Does the strong increase of the mobility upon increasing electric field result from the corresponding change of structural features? (2) Is it possible to identify the underlying reasons for structural field dependencies? Finally, the results are compared with corresponding experimental studies of the same system [1].

[1] M. Rosenwinkel and M. Schönhoff, *J. Electrochem. Soc.* 166, A1977-A1983 (2019).

**15 min. break**

CPP 40.3 Tue 11:30 ZEU 255

**dynamics of ring on polymer in polyrotaxane investigated by quasi-elastic neutron scattering and MD simulation** — ●KOICHI MAYUMI<sup>1</sup>, YUSUKE YASUDA<sup>1</sup>, TAKESHI YAMADA<sup>2</sup>, KAZUSHI FUJIMOTO<sup>3</sup>, SUSUMU OKAZAKI<sup>3</sup>, HIDEAKI YOKOYAMA<sup>1</sup>, and KOHZO ITO<sup>1</sup> — <sup>1</sup>The University of Tokyo, Chiba, Japan — <sup>2</sup>CROSS, Ibaraki, Japan — <sup>3</sup>Nagoya University, Aichi, Japan

We study molecular dynamics of polyrotaxane (PR), composed of alpha-cyclodextrins (CDs) and a poly(ethylene glycol) (PEG) axis chain, in solution by means of quasi-elastic neutron scattering (QENS) measurements and full-atomistic molecular dynamics (MD) simulations [1]. From the QENS experiments on PR with hydrogenated PEG (hPR) and that with deuterated PEG (dPR), we separately estimated the translational diffusion coefficients of CD and PEG monomers in PR solutions. For further analysis, we performed full-atomistic MD simulations on PR solutions. By analyzing the simulation results, we succeeded for the first time in observing and quantifying the sliding motion of CD along PEG chain. The sliding diffusion coefficient is formulated by a combination of Brownian diffusion term and Arrhenius-like jump diffusion term with an energy barrier along the axial chain.

[1] Y. Yasuda, Y. Hidaka, Y., K. Mayumi, T. Yamada, K. Fujimoto, S. Okazaki, H. Yokoyama, K. Ito, *J. Am. Chem. Soc.*, 141, 9655 (2019).

CPP 40.4 Tue 11:45 ZEU 255

**Local polymer chain mobility under shear** — BENJAMIN KOHN<sup>1</sup>, ROLAND VOGEL<sup>1</sup>, PETRIK GALVOSAS<sup>2</sup>, and ●ULRICH SCHELER<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V — <sup>2</sup>Victoria University of Wellington

The NMR transverse relaxation T2 is sensitive to the slow motion of polymer chain segments. In entangled polymers at least two components are observed, a short one for chain segments with restricted motion due to entanglements and a longer component originating from the more free chain segments. Here the effect of external shear in a Searle cell as used in rheological experiments is studied. For short polymer chains little effect of shear is observed while for high molecular weight with clear signs of entanglement both components become longer. This is indicative of longer chain segments between entanglements, which results from loss of entanglements or rearrangement resulting in longer chain segments between entanglements. A new experimental setup permits measuring NMR relaxation under oscillatory shear varying both amplitude and frequency. The resulting strain-rate dependence shows that the prolongation of the relaxation time indicating longer chain segments between entanglements starts at a strain of at least 100 for entangled PDMS. The combination of PFG NMR with NMR imaging in the same setup allows to measure flow pattern. At the turning point of the oscillation for low-viscosity fluids a counterflow is observed.

CPP 40.5 Tue 12:00 ZEU 255

**The instability onset behavior of viscoelastic Taylor-Couette flow as a combined function of flow geometry and rheological parameters: purely elastic versus thermo-elastic instabilities** — ●REZA GHANBARI<sup>1,3</sup> and BAMIN KHOMAMI<sup>1,2</sup> — <sup>1</sup>MRAIL (Material Research and Innovation Lab), Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, USA — <sup>2</sup>Sustainable Energy and Education Research Center (SEERC), University of Tennessee, Knoxville, USA — <sup>3</sup>Present: Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland

Linear stability analysis of Taylor-Couette flow (TCF) of dilute polymer solutions has been performed by using prototypical constitutive equations for polymeric solutions, namely, the Oldroyd-B & the FENE-P models. The hydrodynamic stability characteristics of the flow in the presence & absence of thermal effects & in the limit of vanishing fluid inertia have been determined using an eigenvalue analysis. Particular attention has been paid to determine the instability onset conditions as a function of fluid thermal sensitivity & gap ratio. We observed a reduction in the critical Weissenberg (Wic) for the instability onset as the gap ratio & fluid thermal sensitivity are enhanced. In particular, under non-isothermal conditions, Wic was reduced by almost an order of magnitude for all gap ratios. Our results suggest that recent experimental observations of purely elastic turbulence in the TCF at order (1) Wi were not performed under isothermal conditions. Hence, this new flow state should be labeled as thermo-elastic turbulence.

CPP 40.6 Tue 12:15 ZEU 255

**Rheological and diffusion properties of solutions of polyethersulfone and poly(N-vinyl pyrrolidone) for membrane fabrication** — ●ULRICH A. HANDGE<sup>1</sup>, OLIVER GRONWALD<sup>2</sup>, MARTIN WEBER<sup>2</sup>, JOACHIM KOLL<sup>1</sup>, CLARISSA ABETZ<sup>1</sup>, BIRGIT HANKIEWICZ<sup>3</sup>, and VOLKER ABETZ<sup>3</sup> — <sup>1</sup>Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Max-Planck-Strasse 1, 21502 Geesthacht, Germany — <sup>2</sup>BASF SE, Advanced Materials & Systems Research, Performance Polymer Blends & Membranes RAP/OUB, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany — <sup>3</sup>University of Hamburg, Institute of Physical Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Membranes of polyethersulfone (PESU) and poly(N-vinyl pyrrolidone) (PVP) are commonly used for ultrafiltration applications. We investigate the rheological and diffusion properties of solutions which are used for membrane fabrication via a non-solvent induced phase separation

process. The polymer solutions are composed of PESU and PVP as well as a mixture of the solvent N-methyl-2-pyrrolidone (NMP) and the non-solvent glycerol. In this work, the influence of glycerol is studied. The addition of glycerol leads to a larger viscosity, a larger average relaxation time and a stronger tendency of demixing. The increase of viscosity is explained by the increase of the monomeric friction coefficient with increasing glycerol concentration. Dynamic light scattering data reveal the existence of two diffusive processes with different time scales in the presence of glycerol. This result is discussed taking into account the phase behaviour of the solution and the solvent quality.

CPP 40.7 Tue 12:30 ZEU 255

**Impact of hydrogen bonding strength on the structure and dynamics of supramolecular PEO** — •ANA BRÁS<sup>1</sup>, ANA ARIZAGA<sup>1</sup>, UXUE AGIRRE<sup>1</sup>, MARIE DORAU<sup>1</sup>, PATRICIA BACH<sup>1</sup>, JUDITH E. HOUSTON<sup>2,3</sup>, AUREL RADULESCU<sup>3</sup>, MARGARITA KRUTEVA<sup>4</sup>, and ANNETTE M. SCHMIDT<sup>1</sup> — <sup>1</sup>UzK, Cologne, Germany — <sup>2</sup>ESS, Lund, Sweden — <sup>3</sup>FZJ, Garching, Germany — <sup>4</sup>FZJ, Jülich, Germany

In this work we investigate supramolecular poly(ethylene oxide) (PEO)

oligomers at the entanglement molar mass (Me) with different hydrogen bonding end groups, such as diaminotriazine (Dat) and thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy). Small angle scattering and rheology were combined to study the influence of different end-groups association strength as Upy is highly self-associative in comparison to the heterocomplementary pair Thy/Dat. Results on the structure provide insight into the underlying molecular mechanisms and reveal that while Upy-terminated chains phase segregate, forming network-like systems, the Thy/Dat pair-terminated system self-assemble to linear chains, thereby increasing the effective chain length. Moreover, rheological measurements also reveal differences in the viscoelastic response as Upy-terminated chains exhibit an extended rubbery plateau, typical of networks, and the pair Thy/Dat presents a Newtonian fluid behaviour. Remarkably, albeit both systems show end-group association, different hydrogen bonding species influence the type of associates. Acknowledgements: DFG for a research grant (BR5303) and Prof. Dr. D. Richter, Prof. Dr. R. Strey and Dr. Wim Pyckhout-Hintzen for fruitful discussions.