CPP 54: Gels, Polymer Networks and Elastomers II

Time: Friday 9:30–11:15 Location: ZEU/0255

Invited Talk CPP 54.1 Fri 9:30 ZEU/0255

NMR-based molecular rheology and structural characterization of model gels — •Kay Saalwächter and Bidit Lamsal — Institut für Physik - NMR, Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Germany

Low-resolution proton NMR holds great potential for the routine assessment of the relation between the NMR-detected monomer-level mobility and the relevant physical properties of polymer-based materials. In elastomers and gels, multiple-quantum (MQ) NMR allows for the precise measurement of residual dipolar couplings (RDCs) among the monomer protons, which reflects the conformational space of the highly mobile network chains. In this way, not only the average network chain length but also structural inhomogeneities become accessible. In model networks made by end-linking of star polymers, we can go as far as quantifying connectivity motifs in gels made by heterocomplementary [1,2] and homocomplementary coupling reactions [3], either in one-component [1,3] or amphiphilic co-networks [2].

While the measured RDC is consistently found to be proportional to the gels' elasticity modulus [3], the absolute-level interpretation of the measured average RDC to predict the modulus remains a challenge. We here report on recent experiments performed on a variety of PEO-based model gels to elucidate the effects of solvent on local conformational fluctuations, thermodynamic aspects (solvent quality) and the inhomogeneity of the gels.

[1] Macromolecules 44, 9666 (2011); [2] Macromolecules 55, 6573 (2022); [3] Macromolecules 57, 3058 (2024)

CPP 54.2 Fri 10:00 ZEU/0255

Characterization of the deformation and fracture of tough double-network hydrogels — •Eric Euchler[1], Sitao Wang[2], Konrad Schneider[1], and Sven Wiessner[1,3] — [1]Leibniz-Insititut für Polymerforschung Dresden, Dresden, Germany — [2]Leibniz-Insititut für Polymerforschung Dresden, Dresden, Germany — [3]TUD Dresden University of Technology, Dresden, Germany

Double-network hydrogels (DNHs) feature two interpenetrating networks: a stiff, densely crosslinked first network that carries the load at low strain, and a flexible, loosely crosslinked second network that remains deformable under high strain, offering mechanical properties comparable to elastomers and soft load-bearing biological tissues. Additionally, a yielding phenomenon accompanied by necking of the sample can be observed. This necking zone forms under uniaxial tension and grows with continued loading, which is associated with the fracture of the first network. In this contribution, new insights into the mechanical deformation and damage behavior are given by advanced characterization approaches.

CPP 54.3 Fri 10:15 ZEU/0255

The Role of Connectivity Defects in Governing the Rheology and Microstructure of tPEG Networks — •Sayam Bandyopadhyay[1,2], Sebastian Seiffert[3], and Arash Nikoubashman[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Germany — [2]Institut für Theoretische Physik, Technische Universität Dresden, Germany — [3]Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Germany

We utilized coarse-grained molecular simulations to examine how connectivity defects influence tetra-PEG (tPEG) polymer networks. Both homoleptic and heteroleptic systems were studied, with noncovalent end-group bonds modeled by an inverted Gaussian potential to control valency. Defects were introduced either by deactivating functional end groups or by deviating from ideal stoichiometry in heteroleptic mixtures. Post-gelation structure was quantified using structure factors, radial distribution functions of attractive beads, and internal loop statistics. Network dynamics and molecular mobility were assessed through mean-square displacements of individual tPEG molecules and through bond lifetimes. Our results show that defects enhance loop formation and substantially increase star-polymer mobility. As a consequence, networks with higher defect concentrations exhibit lower viscosity and faster stress relaxation. We also discuss the system's shear response simulated using a mesoscale solvent with hydrodynamic interactions to probe loop and link interconversion kinetics. These findings provide a molecular level understanding of how defects control the structure, dynamics, and mechanical properties of tPEG networks.

CPP 54.4 Fri 10:30 ZEU/0255

Assembling a true Olympic gel from >16,000 combinatorial DNA rings — Sarah K. Speed[1,2], Yu-Hsuan Peng[1,2], Azra Atabay[1,2], Krishna Gupta[1,2], Toni Müller[3,4], Carolin Fischer[5], Ilka Hermes[6], Jens-Uwe Sommer[3,4,7], Michael Lang[3], and •Elisha Krieg[1,2] — [1]Division of Polymer Biomaterials Science, Leibniz Institute of Polymer Research Dresden, Germany — [2]Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Germany — [3]Division of the Theory of Polymers, Leibniz Institute of Polymer Research Dresden, Germany — [4]Institute for Theoretical Physics, Technische Universität Dresden, Germany — [5]B CUBE - Center for Molecular Bioengineering, Technische Universität Dresden, Germany — [6]Division of Physical Chemistry and Physics of Polymers, Leibniz Institute of Polymer Research Dresden, Germany — [7]Cluster of Excellence Physics of Life, Technische Universität Dresden, Germany

Olympic gels consist of a three-dimensional network of mechanically interlocked cyclic molecules providing unique mechanical properties. We report the successful assembly of a true Olympic gel from a library of DNA rings comprising more than 16,000 distinct molecules. Each of these rings contains a unique sequence domain that can be enzymatically activated to produce reactive termini that favor intramolecular cyclization. Results are shown on the genetic, mechanical, and structural characteristics of the material by next-generation sequencing, oscillatory rheology, large-scale computational simulations, atomic force microscopy, and cryogenic electron microscopy.

CPP 54.5 Fri 10:45 ZEU/0255

On the symmetry breaking between gelation and network degradation — •Michael Lang — Division of the Theory of Polymers, Leibniz Institute of Polymer Research Dresden, Germany

Recent experiments indicate that there is a possible symmetry breaking between gelation and network degradation processes in contrast to the predictions of percolation models and classical mean field models. We analyze this problem by large scale computer simulations and mean field modeling in order to avoid possible problems of the experimental setup. The modeling is generalized to capture the main effects of cyclization and composition fluctuations on the gelation process. Both our modeling and the simulation data confirm the existence of the symmetry breaking already for systems above the overlap threshold. This indicates some general problems of the percolation approach for modeling polymer networks.

CPP 54.6 Fri 11:00 ZEU/0255

Crosslinking Mechanisms of Alginate-based Graft Copolymers with Thermoresponsive Side Chains — •Wenqi Xu[1], Sofia-Falia Saravanou[2], Yefan Song[1], Yandong Wang[1], Joachim Kohlbrecher[3], Constantinos Tsitsilianis[2], and Christine M. Papadakis[1] — [1]TUM School of Natural Sciences, Soft Matter Physics Group, Garching, Germany — [2]University of Patras, Greece — [3]PSI, Villigen, Switzerland

Alginates are naturally occurring, non-toxic polysaccharides which have seen extensive use in biomedicine. Here, we investigate an alginate-based graft copolymer, namely alginate-g-P(NIPAM$_{94}$-co-NtBAM$_6$), where a random copolymer of N-isopropylacrylamide (NIPAM) and N-*tert*-butyl acrylamide (NtBAM) is grafted onto a sodium alginate backbone [1]. While introducing thermoresponsive PNIPAM enables temperature-induced gelation, the hydrophobic comonomer NtBAM regulates the transition temperature and the mechanical properties of the hydrogel. The structure and the gelation mechanisms of the copolymers are studied in aqueous solutions using small-angle neutron scattering (SANS). At this, contrast matching of the backbone and the side chains was used to obtain selective information. The SANS data show strong forward scattering above the transition temperature of PNIPAM, which is attributed to the collapse of the side chains, resulting in hydrophobic globules which act as nodes of the hydrogel network.

[1] K. Safakas, C. Tsitsilianis. *Int. J. Mol. Sci.* **2021**, 22(8), 3824.