

CPP 4: Focus: The Physics of Adaptive Polymer Networks

organized by Regine von Klitzing (TU Darmstadt) und Christian Holm (Universität Stuttgart).

Adaptive polymer networks and gels represent soft materials with dimensional stability and viscoelasticity, which can assume different states due to changes in environmental conditions. This makes them promising candidate materials for a variety of applications, such as membranes for separation techniques or perm-selective membranes, and sensors and actuators. A particularly versatile class of adaptive gels are amphiphilic networks, which combine components that swell selectively in different media. The investigation of these amphiphilic co-networks represents a topic of high current relevance in polymer sciences, which has been coordinated in Germany by the research group FOR2811 since 2019 (www.for2811.uni-mainz.de).

Time: Tuesday 10:00–12:45

Location: H3

Invited Talk

CPP 4.1 Tue 10:00 H3

Adaptable amphiphilic co-networks: structure and properties in relation with multi-quantum NMR — ●MICHAEL LANG¹, REINHARD SCHOLZ¹, LUCAS LÖSER², CAROLIN BUNK¹, FRANK BÖHME¹, and KAY SAALWÄCHTER² — ¹Leibniz-Institut für Polymerforschung, Hohe Straße 6, 01069 Dresden, Germany — ²Martin-Luther-Universität Halle-Wittenberg, Institut für Physics - NMR Group, Betty-Heimann-Str. 7, 06120 Halle, Germany

Amphiphilic co-networks made by the hetero-complementary coupling of four arm star polymers are an interesting model system to understand the physics of adaptive co-networks and currently the focus of the DFG research unit FOR2811 in which we participate. We analyze these model networks in different states (preparation in co-solvent, swollen state, and "switched" states where one type of polymer is swollen and the other collapsed) with large scale Monte-Carlo simulations and experiments. We discuss the degree of swelling, the scattering function, chain extensions, etc. of these model systems briefly. A particular focus is put on data and models regarding proton multiple-quantum NMR. After a brief tutorial on what can be analyzed with this method, we sketch analytical models for NMR order parameters in a particular state and compare with the available simulation or experimental data in these states. This analysis provides useful information on the time average local properties of individual network strands including the strain distribution of network strands. Such information is hardly accessible with alternative methods and allows even for the analysis of cyclic network defects under appropriate conditions.

Invited Talk

CPP 4.2 Tue 10:30 H3

Adaptive networks through supramolecular interactions — ●ILJA VOETS — Department of Chemical Engineering and Chemistry & Institute for Complex Molecular Systems, Eindhoven University of Technology

Supramolecular interactions offer a powerful tool to modulate self-assembly pathways to generate dynamic materials with adaptive properties. In this lecture I will showcase two versatile, supramolecular approaches to generate adaptive, polymer-based materials, based on electrostatically driven co-assembly of ionic-neutral block copolymers and on amphiphilic copolymers equipped with suitable motifs, such as C3-symmetrical discotics based on benzene-1,3,5-tricarboxamide (BTAs), encoded to form one-dimensional helical 'stacks'. I will discuss the structure and properties of the micellar and fibrillar objects that these materials form in dilute aqueous solution, and of the transient networks which emerge at elevated concentrations. Recent efforts and insights in e.g. polyelectrolyte complexation out-of-equilibrium, strain stiffening, high resolution optical imaging and templated polymerization will be addressed. In future, these concepts may be exploited to further custom-tailor gels towards a desired structure and associated mechanical response.

15 min.break

CPP 4.3 Tue 11:15 H3

Chain connectivity of tetra-PEG - tetra-PCL amphiphilic end-linked polymer model networks — ●LUCAS LÖSER¹, CAROLIN BUNK², FRANK BÖHME², and KAY SAALWÄCHTER¹ — ¹Inst. f. Physik - NMR, Martin-Luther-Universität Halle-Wittenberg — ²Leibniz-Institut f. Polymerforschung Dresden e.V., Hohe Str. 6, Dresden

A new approach for the synthesis of model-like amphiphilic co-networks is introduced, and their structure analysed by static 1H time-domain

nuclear magnetic resonance (NMR) methods. A novel approach of hetero-complementary end-linking [1] of two well-defined tetra-armed polyethylene glycol (PEG) stars based on Sakai et al. [2] is used and modified in a way, that amphiphilic gels are obtained. We link PEG stars with a hydrophobic poly- ϵ -caprolactone star (tetra-PCL) terminated with an oxazinone group, resulting in the formation of an amphiphilic network. By using static 1H-1H multi-quantum-NMR, as initially performed by Lange et al. [3], we show that our method is capable of distinguishing different chain species in the swollen PEG-PCL networks, allowing quantification of network connectivity defects arising from the end-linking reaction of A4- and B4-type stars, as well as accurate quantification of inelastic material. The parameter space of the synthesis is explored and changes in microscopic network structure are studied depending on polymer concentration and different temperature programs during synthesis. [1] Jakisch et al. ; *Macromol. Chem. Phys* 2017, 219 [2] Sakai, T. et al.; *Macromolecules* 2008, 41 [3] Lange, F. et al.; *Macromolecules* 2011, 44

CPP 4.4 Tue 11:30 H3

Microscopic and macroscopic mechanical properties of amphiphilic model co-networks — ●NORA FRIBICZER¹, KEVIN HAGMANN², CAROLIN BUNK³, SEBASTIAN SEIFFERT¹, REGINE VON KLITZING², and FRANK BÖHME³ — ¹Department of Chemistry, Johannes Gutenberg University Mainz, D-55128 Mainz — ²Institute for condensed matter physics, Technische Universität Darmstadt, D-64289 Darmstadt — ³Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden

Amphiphilic polymer gels are composed of both hydrophilic and hydrophobic polymers, which makes their mechanical properties dependent on environmental conditions such as the solvent polarity. In this work, we present both a microscopic and macroscopic perspective of these properties using indentation atomic force microscopy and oscillatory shear rheology. With this, we aim to get a rational understanding of the interplay between the environmental conditions and the resulting mechanical properties in the bulk material and at the interface.

Next to the investigation of the mechanical properties under good and bad solvent conditions, we put special emphasis on the characterization of the gelation process during network formation. By variation of concentration and temperature the reactivity and network topology can be controlled due to the use of an innovative bi-functional coupling agent which connects the hydrophilic tetra-PEG and the hydrophobic tetra-PCL. Monitoring the network formation using shear rheology allows for determination of the respective gel points, which coincide with results obtained from nuclear magnetic resonance spectroscopy.

Invited Talk

CPP 4.5 Tue 11:45 H3

Tunable self-assembled hydrogels from block copolymers with thermoresponsive and pH-responsive blocks — ●CHRISTINE M. PAPADAKIS¹, FLORIAN A. JUNG¹, and CONSTANTINOS TSITSILIANIS² — ¹Physics Department, Technical University of Munich, Garching, Germany — ²Department of Chemical Engineering, University of Patras, Greece

Pentablock terpolymers with thermoresponsive end blocks and a pH-responsive middle block form hydrogels in aqueous environment. By altering the stability of the crosslinks and the degree of bridging, the responsivities afford numerous possibilities to tune the mechanical properties. Small-angle neutron scattering revealed the underlying mesoscopic structures in dependence on temperature and the pH value [1]. The thin film geometry allows studying the microphase-separated structures in the dry state and during swelling in the vapor of water

or organic solvents in situ using grazing-incidence small-angle X-ray scattering. The results reveal the role of the dielectric properties of the solvent for microphase separation and hydrogel formation [2].

[1] C. Tsitsilianis et al., *Macromolecules* **2018**, *51*, 2169. F. A. Jung et al., *Macromolecules* **2019**, *52*, 9746. M. M. S. Lencina, et al., *ACS Appl. Polym. Mater.* **2021**, *3*, 819.

[2] F. A. Jung et al., *Macromolecules* **2020**, *53*, 6255.

CPP 4.6 Tue 12:15 H3

Structural characterization of covalently connected amphiphilic star polymer conetworks — ●REINHARD SCHOLZ¹, LUCAS LÖSER², KAY SAALWÄCHTER², CAROLIN BUNK¹, FRANK BÖHME¹, and MICHAEL LANG¹ — ¹Leibniz Institut für Polymerforschung, 01005 Dresden, Germany — ²Institut für Physik - NMR, Martin-Luther Universität Halle-Wittenberg, 061120 Halle, Germany

Polymer networks consisting of complementary four functional stars of poly ethylene glycol (PEG) and poly caprolactone (PCL) were synthesized via covalent coupling of complementary end groups. The equilibrium swelling in various solvents revealed either compatibility of both polymer components with good solvents for both components like in toluene, or a reduced swelling in solvents like THF or water, representing selective solvents for the PEG component only. Complementary X-ray scattering studies allowed to assign the structure factor to a swollen conetwork (in toluene), or to a swollen PEG component connecting embedded clusters of PCL (in THF or water). These experimental results were accompanied by simulations of network formation as a function of polymer concentration during preparation, and subsequent swelling in a cosolvent or a selective solvent. The calculated structure factor arising from the simulated model networks reveals a typical length scale for the size and distance of the PCL clusters, in

reasonable agreement with the dependence of the observed scattering intensity on wave vector.

CPP 4.7 Tue 12:30 H3

From four-arm block copolymers to electrostatically cross-linked gels — ●PETER JOHANNES MONS¹, NORA FRIBICZER², DAVID BEYER³, FELIX HELMUT SCHACHER¹, SEBASTIAN SEIFFERT², and CHRISTIAN HOLM³ — ¹Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-University Jena, D-07743 Jena — ²Department of Chemistry, Johannes Gutenberg-University Mainz, D-55128 Mainz — ³Institute for Computational Physics, University of Stuttgart, D-70569 Stuttgart

Reversibly electrostatically cross-linked polymer networks composed of oppositely charged four-armed star block copolymers feature favorable properties such as environmentally sensitive viscoelasticity and selective permeability. In this work, we present different double hydrophilic star-shaped block copolymers with oppositely charged polyelectrolytes that can form electrostatically cross-linked gels. A new class of reversible double hydrophilic or amphiphilic networks can be synthesized based on these gels.

The four-armed copolymers consist of a PEG-core block extended with sulfonated polystyrene or N,N-dimethylaminopropyl acrylamide (DMAPAA). The sulfonated polystyrene block carries a permanent anionic charge whereas the DMAPAA block carries a permanent cationic or pH-tunable charge. The gel formation upon mixing these block copolymers was verified by shear rheology, which showed a high dependence of the gel strength on the presence of counterions. Coarse-grained molecular dynamics simulations support the picture of well-gelated networks and give insight into the molecular conformations.