CPP 58: Gels, Polymer Networks and Elastomers III

Time: Friday 11:30–13:00 Location: ZEU/0255

CPP 58.1 Fri 11:30 ZEU/0255

X-ray induced structural changes in supramolecular polymer networks — •Niels C. Giesselmann[1,2], Yasothaa Thavayogarajah[3], Mostafa Ahmadi[3], Sebastian Seiffert[3], and Katrin Amann-Winkel[1,2] — [1]Institute of Physics, Johannes Gutenberg University, Mainz, Germany — [2]Max Planck Institute for Polymer Research, Mainz, Germany — [3]Institute of Chemistry, Johannes Gutenberg University, Mainz, Germany

Supramolecular polymer networks consist of non-covalently crosslinked macromolecules. Such transient links can be established through functionalized polymer building blocks. An interesting property of this group of materials is their ability to self-heal mechanical damage. We observed polymer networks made of star-shaped four-arm PEG building blocks with metal-complexing end groups. Due to their transient binding, the building blocks diffuse through the polymer network in a process that is not yet understood in detail. In this study, we employed both X-ray scattering in order to probe the structure of the network on the molecular as well as the macromolecular level. This way, we hope to better understand the mechanical and self-healing properties of these polymer networks. We report the emergence of structural changes in dependence of the X-ray flux that futhermore persist when measuring far away from the initially illuminated area. This effect can be explained by the affected molecules spreading throughout the sample by means of the transient binding dynamics mentioned above.

CPP 58.2 Fri 11:45 ZEU/0255

Deciphering the photopolymerization-induced nanostructure and interface formation for submicron additive manufacturing — •Shouzheng Chen[1,2,3], Yufeng Zhia[2], Lixing Li[1], Sarathlal Koyiloth Vayalil[2], Rolf A.T.M. van Benthem[4], Johan F.G.A Janssen[5], Mats K. G. Johansson[6], Peter Müller-Buschbaum[1], and Stephan V. Roth[2,6] — [1]TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — [2]DESY, Hamburg — [3]MLZ, TUM, Garching, Germany — [4]TU/e, Eindhoven, the Netherlands — [5]Covestro (Netherlands) B.V., Geleen, the Netherlands — [6]Department of Fibre and Polymer Technology, KTH, Stockholm, Sweden

UV-curing is widely used in additive manufacturing due to its controllable spatiotemporal characteristics. In submicron additive manufacturing, the involvement of solvents and limitations on film thickness complicate the precise regulation of nanostructures and interlayer interface. By using grazing incidence small angle X-ray scattering (GISAXS) and employing the oligomer (urethane dimethacrylate, UDMA)/monomer (2-ethylhexyl acrylate, 2-EHA) based resin system, we quantify the heterogeneous distribution of UDMA- and 2-EHA-rich nanodomains (around 23 nm and 13 nm in radii, respectively) in the cured system. Combining Bornagain, we reveal the buried "frozen" nano-wrinkles at interlayer interfaces(cones with radius of 70 nm, slope angle of 18°) induced by solvent and constraint stress synergistically. Our findings offer deeper insights for high precision submicron additive manufacturing.

CPP 58.3 Fri 12:00 ZEU/0255

From real polymers to random graphs: percolation thresholds in associative polymer solutions — •Xinxiang Chen, Lennart Hebestreit, and Friederike Schmid — Johannes Gutenberg-University Mainz, Mainz, Germany

Multivalent reversible crosslinking is ubiquitous in soft matter and biomolecular condensates, yet their sol-gel transitions often deviate from the classical Flory-Stockmayer picture due to chain conformations, intrachain binding, and loop formation. Here, we develop a unified framework combining molecular dynamics simulations with random-graph and random-geometric-graph approaches to quantitatively link real polymer architectures to abstract network models. For single- and two-component reversible polymers with one-to-one specific binding, we determine gel points from topological connectivity and find percolation thresholds substantially higher than Flory-Stockmayer predictions. By comparing spatially unconstrained random graphs with spatially correlated random geometric graphs, we show that intrachain binding and loops markedly reduce the effective interchain bonding needed to form an infinite cluster. Meanwhile, the theoretical results of the generating function and the Lagrange inversion further yield cluster size distributions and giant cluster fractions. Our work demonstrates how spatial correlations and polymer conformations fundamentally reshape reversible network formation, offering a unified topological and physical perspective on reversible gels and biomolecular condensates.

CPP 58.4 Fri 12:15 ZEU/0255

From Champagne Fizzling to Confined Polymer: Natural and Artificial Bubble Nucleation — •Carlos Arauz-Moreno[1,2], Keyvan Piroird[2], and Elise Lorenceau[1] — [1]Université Grenoble Alpes, CNRS, LIPhy, F-38000 Grenoble, France — [2]Saint-Gobain Research Paris, F-93360 Aubervilliers, France

Bubbles dazzle the senses when pouring a Champagne glass. However, there is a hidden trick to this elegant experience: natural nucleation sites, such as tartrate crystals from washing or cellulose fibers from drying, or artificial sites, like crenels in the flute, are used to trigger bubble nucleation by lowering the energy barrier required to grow a bubble; otherwise, Champagne wouldn't bubble at all. By using a model system of viscoelastic polyvinyl butyral (PVB), we show that the concepts of natural and artificial nucleation from Champagne equally apply to confined viscoelastic polymers. Our experimental results show that water vapor, which tends to aggregate inside the PVB matrix in the form of clusters, escapes in copious amounts from the polymer bulk when the latter is heated and decompressed (e.g., at 140°C, dP=1bar). However, bubbles may only form at naturally trapped fibers, dust speckles, or in artificial crenels on the glass surface. The number of natural nuclei is apparently and counterintuitively inversely proportional to the applied temperature. Moreover, bubbles can take on different shapes and sizes because coalescence does not occur. Finally, we investigated how the growth rate of bubbles is impacted by whether nucleation is natural or artificial, revealing a clear distinction between the two: the growth rate in the former is global while in the latter is local.

CPP 58.5 Fri 12:30 ZEU/0255

Steric Origins of Microgel Thermoresponsiveness Revealed by All-Atom Polymer Simulations — •Jannis Krüger[1], Letizia Tavagnacco[2], Emanuela Zaccarelli[2], and Thomas Hellweg[1] — [1]Physical and Biophysical Chemistry, Bielefeld University, Germany — [2]Department of Physics, Sapienza University of Rome, Italy

Microgels based on N-isopropylacrylamide (NIPAM) are well established in soft matter science due to their thermoresponsive swelling behavior. Dynamic light scattering (DLS) reveals a sharp decrease in the hydrodynamic radius at a characteristic volume phase transition temperature (VPTT), which occurs around 34°C. In our previous work[1] we observed that by adding a non-thermoresponsive comonomer such as N-tert-butylacrylamide (NtBAM), this transition broadens in temperature until it disappears at high molar contents. The VPT is typically interpreted in terms of hydrophilicity or hydrophobicity; however, the steric demand of chemical substituents is often overlooked. In this work, we compare DLS measurements with all-atom molecular dynamics simulations of NIPAM and NtBAM polymer chains in water, to show how subtle differences, like replacing an isopropyl with a tert-butyl group, substantially affects the coil-globule transition of polymers in water, thereby providing deeper insights into the molecular origin of the broadening and lowering of the VPTT in real microgels.

[1] J. Krüger, S. Kakorin, and T. Hellweg, Colloid Polym. Sci. 303, 1815 (2024).

CPP 58.6 Fri 12:45 ZEU/0255

Photo-responsive microgels as model systems with tunable crosslinking density — •Dominik Wöll and Christian Metzen — Institute of Physical Chemistry, RWTH Aachen University

Functional microgels have powerful applications due to their specific structure, which can quickly respond to external stimuli such as temperature, pH, ionic strength, solvent composition, and light. We synthesized double-responsive poly(N-isopropylacrylamide) (PNIPAM) microgels that react to both light and temperature. The light responsiveness is achieved by the addition of photoswitchable trans-azobenzene (Azo) units that crosslink with the corresponding β-cyclodextrin (β-CD) units copolymerized into the microgel. Irradiation with light causes switching from trans-Azo to cis-Azo and thus opening of the crosslink. With the wavelength of light, and the corresponding photostationary state, the crosslinking density in these microgels can be precisely controlled with light. This model system allows us to investigate the influence of crosslinking density on the structure and properties of microgels.