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## The Topology of Polymer Brushes Determines Their Nanoscale Hydration

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By utilizing time-of-flight neutron reflectometry (ToF-NR) under different relative humidities, we demonstrate that grafted polymer brushes constituted by hydrophilic cyclic macromolecules exhibit more compact conformation with lower roughness compared to linear brush analogues, due to the absence of dangling chain ends extending at the interface. [1] In addition, due to increased interchain steric repulsions, cyclic brushes feature larger swelling ratio and increased solvent uptake with respect to their linear counterparts presenting the same composition and comparable molar mass. Moreover, the two topologies exhibit differences in ageing, upon repetitive runs of swelling/drying trials.

To correlate the equilibrium swelling ratios as a function of relative humidity for different topologies a new form of the Flory-like expression for equilibrium thicknesses is proposed. The relative humidity represents the chemical potential balance between brush and surrounding environment. The Flory-like expression, which has been successfully utilized so far for thin polymer films, breaks down for the cyclic brush. Additional topological contributions need to be taken into account in this expression, in order to rationalize differences reflected in swelling ratios and solvent content between the linear and cyclic polymer brush topologies.

[1] A. Vagias et al., in preparation

**Primary authors:** VAGIAS, Apostolos (Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich); NELSON, Andrew (ANSTO); WANG, Peixi (Workgroup Polymer Interfaces, TUM Department of Physics, Technical University of Munich); REITENBACH, Julija; GEIGER, Christina (Technical University of Munich, Chair of Functional Materials); Dr KREUZER, Lucas (MLZ (FRM II, TUM)); SAERBECK, Thomas (Institut Laue-Langevin); CUBITT, Robert (Institut Laue-Langevin); Prof. BENETTI, Edmondo Maria (Dr.); MÜLLER-BUSCHBAUM, Peter (TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany)

**Presenter:** VAGIAS, Apostolos (Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich)

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