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Dehydration of thermoresponsive molecular brushes with block or random copolymer side chains

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Molecular brushes with thermoresponsive copolymer side chains have attracted attention for drug delivery purposes because of their elongated shape and their versatility. In the present work, two molecular brushes having copolymer side chains composed of poly(propylene oxide) (P) and poly(ethylene oxide) (E) are studied in aqueous solution. The side chains are either a diblock (PbE) or a random copolymer (PrE). Their structures, dehydration and aggregation behavior around the cloud point, Tcp, are investigated using small-angle neutron scattering (SANS) at KWS-1, MLZ [1].

At 25 ℃, the brushes are elongated and feature a core-shell structure with a polymer-rich core and a water-rich shell. Upon heating to Tcp, PbE dehydrates only weakly, and the shell shrinks slightly. Above Tcp, large aggregates from strongly interpenetrating brushes are formed, which is due to the high mobility of the still rather hydrated side chains. In contrast, PrE undergoes a rod-to-disk shape transformation along with a severe decrease of the water content, already before aggregation sets in at Tcp. Above, the PrE brushes form small aggregates from loosely connected brushes, which is a result of the low side chain mobility. Thus, the choice of the side chain architecture not only allows control of the inner structure and shape, but also of the transition behavior.

[1] J.-J. Kang, C. M. Papadakis et al., *Macromolecules* **53**, 4068 (2020)

Primary author: KANG, Jia-Jhen (Physik-Department, Technische Universität München)

Co-authors: JUNG, Florian A. (Physik-Department, Technische Universität München); KO, Chia-Hsin (E13, Physik-Department, Technische Universität München.); SHEHU, Kaltrina; BARNSLEY, Lester (Jülich Centre for Neutron Science); KOHLER, Fabian (Physik-Department, Technische Universität München); Prof. DIETZ, Hendrik (Physik-Department, Technische Universität München); Dr ZHAO, Junpeng (Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation); Dr PISPAS, Stergios (Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation); PAPADAKIS, Christine (Technische Universität München, Physik-Department, Fachgebiet Physik weicher Materie)

Presenter: KANG, Jia-Jhen (Physik-Department, Technische Universität München)

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