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Injectable hydrogels from thermoresponsive tri- and tetrablock terpolymers investigated using scattering methods

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Thermogels are an exciting class of stimuli-responsive materials with many promising applications ranging from the medical field to additive manufacturing. The mechanical properties in the gel state strongly depend on the architecture of the polymer [1].

Here we address an ABC triblock terpolymer and a BABC tetrablock terpolymer consisting of the hydrophilic oligo(ethylene glycol) methyl ether methacrylate (OEGMA, A), the hydrophobic *n*-butyl methacrylate (BuMA, B), and the thermoresponsive di(ethylene glycol) methyl ether methacrylate (DEGMA, C). The results from dynamic light scattering (DLS) on dilute solutions indicate that the hydrodynamic radii of the micelles formed by both, ABC and BABC, increase strongly above 25 ℃, and the solutions feature a cloud point, i.e. aggregation of the micelles sets in. By synchrotron small-angle X-ray and neutron scattering (SAXS/SANS), we found that the triblock terpolymers ABC form spherical core-shell micelles, that transform into cylinders at high temperatures. In contrast, the core-shell micelles formed by the BABC tetrablock terpolymers stay spherical and form small fractal aggregates at higher temperatures, that become more compact upon further heating.

[1] A. P. Constantinou, B. Zhan et al., *Macromolecules*, 2021, *54*, 1943.

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