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Effect of architecture in thermoresponsive hydrogels from PEG-based terpolymers

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The lower critical solution temperature (LCST) polymers have attracted great interest in the biomedical sectors, as they are water-soluble at room temperature, while they can form a gel at body temperature. Under the appropriate conditions, thermoresponsive polymers may form a 3D network, namely a thermoresponsive gel [1] with the mechanical properties in the gel state strongly depending on the architecture of the polymer [2]. Here we address an ABC triblock terpolymer and a BABC tetrablock terpolymer consisting of the hydrophilic oligo(ethylene glycol) methyl ether methacrylate with an average Mn of 300 g mol–1 (OEGMA, A), hydrophobic n-butyl methacrylate (BuMA, B), and thermoresponsive di(ethylene glycol) methyl ether methacrylate (DEGMA, C). Visual observation shows that ABC has a wider gelation region compared to BABC. The results from dynamic light scattering (DLS) on dilute solutions show that the hydrodynamic radii Rh of the micelles formed by both, ABC and of 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 scattering (SAXS), it was found that, ABC and BABC form elongated and spherical micelles, respectively. Forward scattering attributed to large aggregates is observed at temperatures above the cloud point for both terpolymers.

References
[1] A. P. Constantinou et al., Polym. J. 2016, 78, 366.
[2] A. P. Constantinou, B. Zhan et al., Macromolecules, 2021, 54, 1943.

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