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Phase behavior of thermo- and photoresponsive diblock copolymers for non-invasive schizophrenic switching

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Stimuli-responsive diblock copolymers (DBCPs) have gathered considerable interest for uptake, transport and release processes due to their property alteration upon exposure to external stimuli, such as temperature and light. In this study, DBCPs consisting of two thermoresponsive blocks, each with lower critical solution temperature (LCST) behavior and coil-to-globule transitions at the respective cloud points (CPs) are investigated in aqueous solutions. These are PNIPAM and azopyrazole (AzPy) functionalized PNDMAM. Upon exposure to UV light, the CP of the PNIPAM is expected to remain unchanged, while the CP of AzPy-PNDMAM may be tuned. This way, the DBCPs can be switched completely non-invasively and are expected to form unimers, (inverse) micelles, and aggregates in dependence on temperature. Here, we present the temperature-dependent phase behavior of a series of DBCPs with various block lengths and AzPy contents and in different isomeric states of the latter. Synchrotron small-angle X-ray scattering (SAXS) reveals that the DBCPs are expanded chains below the first CP and are collapsed at temperatures above, forming large aggregates without an intermediate micellar phase. Switching the photoactive group by UV irradiation does not have significant effect on this behavior.

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