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Self-assembly of thermo- and photo-responsive diblock copolymers

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Stimuli-responsive diblock copolymers (DBCPs) have gathered considerable interest for uptake, delivery and release processes due to their property tunability upon exposure to external stimuli, such as temperature and light. In this study, DBCPs comprising PNIPAM as the thermoresponsive block and azopyrazole (AzPy) functionalized PNDMAM as the photo-responsive block are expected to feature dual lower critical solution temperature (LCST) behavior with coil-to-globule transitions at the respective cloud points (CP). At this, the CP of the PNIPAM is expected to remain unchanged, while the other CP may be altered by exposure to UV light. This way, the system can be switched fully externally from unimers to micelles or inverse micelles and aggregates. Here, we present the temperature-dependent phase behavior of PNIPAM-*b*-P(NDMAM-*co*-AzPyNDMAM) with different degrees of polymerization and AzPy contents in different isomeric states of the latter. Dynamic light scattering (DLS) revealed that both BCPs exhibit a cloud point (CP2) and a subsequent clearing point (CP1) in both their *trans*- and *cis*-state. Furthermore, in the *cis*-state, the CPs are slightly shifted, while the aggregates are significantly larger than in the trans-state.

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