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Effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution

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Amphiphilic diblock copolymers feature self-assembly behavior in aqueous solution. In particular, poly(methyl methacrylate)-b-poly(N-isopropylacrylamide) (PMMA-b-PNIPAM) forms core-shell micelles upon heating above the cloud point of PNIPAM (Tcp) [1]. Previously, it was found that pressure strongly affects the dehydration extent of PNIPAM homopolymers in aqueous solution [2].
Here, we present the effect of pressure on the micellar structure of PMMA-b-PNIPAM in aqueous solution by small-angle neutron scattering (SANS). In temperature-resolved experiments, we find that the micellar shell strongly dehydrates above Tcp at atmospheric pressure. In contrast, at 75 MPa, it remains hydrated, and the micelles form highly correlated aggregates. We also characterized the micellar structure in a pressure-resolved experiment at 31.8 ℃. We find that, after crossing the co-existence line, the micellar shell appreciably shrinks, despite it remains partially hydrated. Thus, pressure is a tool to modify the micellar structure and the aggregation behavior of the micelles.
[1] C.H. Ko, C.M. Papadakis et al., Macromolecules. 2021, 54, 384.
[2] B.-J. Niebuur, C. M. Papadakis et al., ACS Macro Lett. 2017, 6, 1180.

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