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What high pressure can teach us about block copolymer micelles with a thermoresponsive shell

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In dilute aqueous solution, diblock copolymers with a hydrophobic and a thermo-responsive block self-assemble into core-shell micelles. Here, we present the self-assembly behavior of the diblock copolymer PMMA-*b*-PNIPAM consisting of a short hydrophobic poly(methyl methacrylate) and a long thermoresponsive poly(*N*-isopropylacrylamide) block. Synchrotron small-angle X-ray scattering reveals that, below the cloud point CP, spherical micelles are formed, having a PMMA core and a hydrated PNIPAM shell. Above the CP, the micellar shell dehydrates and contracts, and the micelles form aggregates [1]. Applying pressure to an aqueous micellar solution of PMMA-*b*-PNIPAM is a tool to alter the hydration behavior of the PNIPAM block [2]. We find that not only the value of the CP, but also the transition behavior depends on pressure [3]. The pressure-induced alteration of the properties of the micellar shell and the correlation between the micelles allows investigating the relation between these effects.

References

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- [2] Papadakis, C. M.; Niebuur, B.-J.; Schulte, A. Thermoresponsive Polymers under Pressure with a Focus on Poly(*N*-isopropylacrylamide) (PNIPAM). *Langmuir* **2024**, 40, 1.
- [3] Alvarez Herrera, P. A., Papadakis, C. M. et al. Effect of Pressure on the Micellar Structure of PMMA *b* PNIPAM Diblock Copolymers in Aqueous Solution. *Macromolecules* **2024**, 57, 10263.

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