Contribution ID: **15** Type: **Talk**

All-in-one "schizophrenic"self-assembly of orthogonally tuned thermoresponsive diblock copolymers

Tuesday 10 December 2019 13:40 (25 minutes)

Smart, fully orthogonal switching was realized in a diblock copolymer system with variable trigger-induced aqueous self-assembly. The polymers are composed of nonionic and zwitterionic blocks featuring lower and upper critical solution temperatures (LCSTs and UCSTs). In the system investigated, diblock copolymers from poly(N-isopropyl methacrylamide) (PNIPMAM) and a poly(sulfobetaine methacrylamide), variation of the molar mass of the latter block shifts its UCST above the LCST of the PNIPMAM block in a salt-free condition. Successive thermal switching results in "schizophrenic"micellization, in which the roles of the hydrophobic core block and the hydrophilic shell block are interchanged [1]. Adding salt, the UCST is shifted below the LCST of the PNIPMAM block by adding small amounts of a salt, thus inverting the pathway of switching. Small-angle neutron scattering was used to verify that this orthogonal switching by electrolyte addition results in two switching scenarios between the two types of micelles, namely (i) via an insoluble state or (ii) via a molecularly dissolved state. The versatile and tunable self-assembly offers manifold opportunities, for example, for smart emulsifiers or for sophisticated carrier systems.

[1] N. S. Vishnevetskaya, C. M. Papadakis et al., Macromolecules 49, 6655 (2016), 50, 3985 (2017) and 51, 2604 (2018), Langmuir 35, 6441 (2019). C. M. Papadakis, P. Müller-Buschbaum, A. Laschewsky, Langmuir 35, 9660 (2019).

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Session Classification: Soft Matter

Track Classification: Soft Matter