On the packing parameter for non-equilibrium systems: Narrow-disperse frozen micelles from triblock terpolymers

S. Prévost¹,²*, A. Boschetti de Fierro³, D. Fierro², Y. Talmon⁴, V. Abetz³ and M. Gradzielski¹

¹Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany
²Helmholtz-Zentrum-Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
³Helmholtz-Zentrum-Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany
⁴Technion - Israel Institute of Technology, 32000 Haifa, Israel
*e-mail: prevost.sylvain@gmail.com

Multi-block copolymers attract steadfast interest due to their bringing together smart functionalities and polymorphism. Inter-block interactions lead to the formation of nanodomains with the capacity for selective encapsulation while block-solvent interactions promote self-assembly with a rich variety of structures. The many degrees of freedom (length, chemistry and reactivity, crystallinity, solvophilicity, sequential order of the blocks) allows for a tailored control of all properties at a reasonable cost, naturally bringing such nanocontainers under the spotlight for widespread industrial applications.

Well-defined triblock terpolymers consisting of poly(styrene) (S), poly(butadiene) (B) – possibly catalytically hydrogenated in poly(ethylene) (E), and poly(ethylene oxide) (EO) have been synthesized by living anionic polymerization [1]. The S block is glassy while E and EO are crystallizable. The B block could even be used further for cross-linking [2]. The overall block-copolymers have masses of ca. 100-200 kg mol⁻¹. Having previously studied the complex microdomain geometries in bulk and films, we present here the formation of rather monodisperse micelles in water, in a freezing state after “quenching” a polymer-dioxane solution. The aggregate size is perfectly linearly dependent on expectations from the packing parameter model, despite the non-equilibrium of the system. The technique allows for reproducible micelles with aggregation numbers ranging from a few tens to several hundreds, with the dioxane-water mixing method as an additional tuning parameter based on perceived solvent quality.

(left) cryo-TEM image; (center) small angle neutron scattering for B₁₉₀₀₀S₃₄₀₀₀EO₃₇₀₀₀ and 2 methods of preparation (solvent quality); (right) linear relation between the micellar volume and the copolymers blocks sizes for a given solvent quality.