Beehive-like Aggregates from ABC Miktoarm Star Terpolymers

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Polymer architecture plays an important role in the development of novel aggregation forms and bulk morphologies. Going from linear triblock terpolymers to ABC miktoarm star terpolymers more complex micellar aggregates and micro-phase separated structures are obtained. This is a consequence of the fact that the three chemically differing polymer chains are connected at one point.
We developed a modular route for the synthesis of ABC miktoarm star terpolymers consisting of polybutadiene, poly(2-vinylpyridine) and poly(*tert*-butyl methacrylate) (BVT). By quaternizing the poly(2-vinylpyridine) arm and transferring the polymer into water unique beehive-like aggregates are formed (Figure 1). Starting with the quaternized miktoarm star terpolymer (BVqT) in dioxane, structural evolution from micelles with an ionic core to big compartmentalized aggregates takes place during the dialysis against water. A complete inversion of the solubility of the respective block seems to be the key factor for the development of this complex structure as dialysis from dioxane to methanol to water leads to ill defined aggregates.

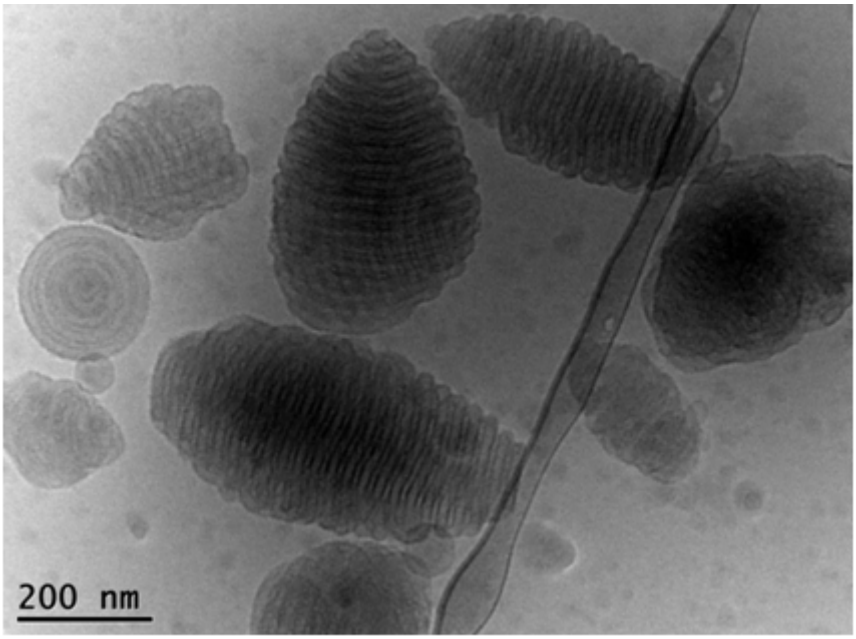

Figure 1. Cryo-TEM of aggregates of the quaternized BVqT star terpolymer in water

The quaternized poly(2-vinylpyridine) serves as the stabilizing corona whereas the insoluble polybutadiene and poly(*tert*-butyl methacrylate) form alternating rings with uniform dimensions. The obtained structures are stable for some days to weeks and can additionally be stabilized by photocrosslinking of the polybutadiene block. Furthermore the precipitate of the aged samples consist of particles which retain the initial shape of the merged original aggregates but with a more complex phase separated core. This precipitate can be embedded in a resin and the respective cuts are interesting candidates for TEM tomography.