**Supporting Information to the paper:**

# Stimuli-Responsive Micellar Interpolyelectrolyte Complexes – Control of Micelle Dynamics *via* Core Crosslinking

by Eva Betthausen, Markus Drechsler, Melanie Förtsch, Dmitry V. Pergushov, Felix H. Schacher, and Axel H. E. Müller

## Interpolyelectrolyte Complex Formation with BMANaDq Precursor Micelles

*Complexation with Poly(sodium 4-styrenesulfonate)*

In addition to all complexation reactions with commercially available PSSNa with a broad molecular weight distribution, IPEC formation was carried out with a narrowly distributed PSSNa ($M_n$ = 20 000 g/mol, PDI = 1.02). The IPECs were prepared at pH 10 and $Z_{-/+}$ = 1 using the non-crosslinked BMANaDq micelles as precursors. The cryo-TEM micrograph of the resulting micellar IPECs in Figure S1 shows a broadening of the micellar size distribution comparable to the complexation with commercial PSSNa.

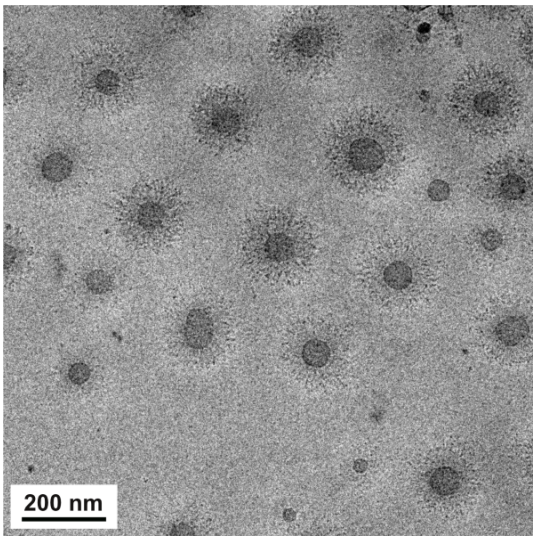


**Figure S1: Cryo-TEM micrograph of micellar IPECs from BMANaDq precursor micelles and narrowly distributed PSSNa in aqueous solution at pH 10 and $Z_{-/+}$ = 1.**

*Complexation with Poly(sodium acrylate)*

Prior to IPEC formation with PANa-*b*-PNIPAAm diblock copolymers, experiments were carried out using a PANa homopolymer. For this purpose a commercially available PANa

with a molecular weight of $M_w$ = 1 250 000 g/mol was used. The non-crosslinked BMANaDq precursor micelles were mixed with PANa at pH 10 and $Z_{-/+}$ = 1 and the resulting micellar IPECs were analyzed by DLS and cryo-TEM (Figure S2). Both methods show a broadening of the micellar size distribution upon IPEC formation, probably due to rearrangements of the micellar cores as observed during the complexation with PSSNa. Again, the micellar IPECs at $Z_{-/+}$ = 1 remain water-soluble. Also here, we assume that overcharging effects are present, as the PANa used is of extremely high molecular weight. Thus, the complexation with PANa might again lead to the formation of "loops" and "trails" and, thus, structures with a negative net charge. The micellar IPECs with PANa exhibit a hydrodynamic radius of $\langle R_h \rangle_z$ = 99 nm.

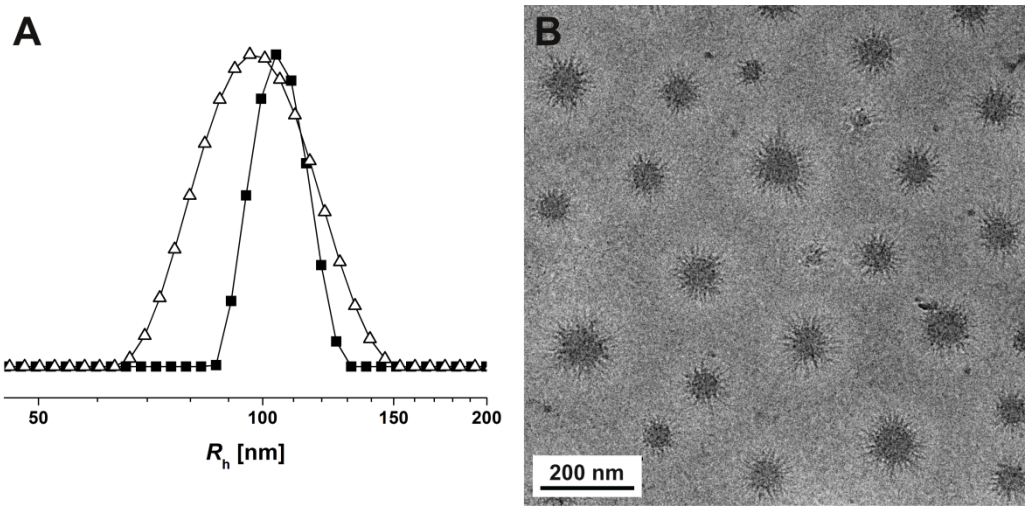


**Figure S2: Intensity-weighted DLS CONTIN plots for BMANaDq precursor micelles in aqueous solution at pH 10 (−■−, $\langle R_h \rangle_z$ = 107 nm, PDI = 0.06) and micellar IPECs with PANa at $Z_{-/+}$ = 1 (−△−, $\langle R_h \rangle_z$ = 99 nm, PDI = 0.10) (A); cryo-TEM micrograph of micellar IPECs from BMANaDq and PANa at $Z_{-/+}$ = 1 (B).**

*Complexation with Bis-Hydrophilic PANa-b-PNIPAAm Diblock Copolymers*

In addition to core-crosslinked micellar IPECs with a PNIPAAm corona obtained through complexation with bis-hydrophilic PANa-*b*-PNIPAAm diblock copolymers, comparable IPECs with non-crosslinked cores were prepared. The IPEC formation was carried out at pH 10 by mixing BMANaDq precursor micelles and $ANa_{27}NIPAAm_{150}$ at $Z_{-/+}$ = 1. The DLS CONTIN plot and a cryo-TEM micrograph of the resulting micellar IPECs are shown in Figure S3. The hydrodynamic radius decreases ($\langle R_h \rangle_z$ = 97 nm) as compared to the precursor micelles ($\langle R_h \rangle_z$ = 107 nm), but nearly coincides with the size found for IPECs with PANa, which can be explained by the collapse of the PDMAEMAq corona upon interpolyelectrolyte complexation. Since the non-crosslinked BMANaDq micelles were used as precursors, again

a broadening of the micellar size distribution upon IPEC formation is observed both in the DLS CONTIN plot and the cryo-TEM micrograph.

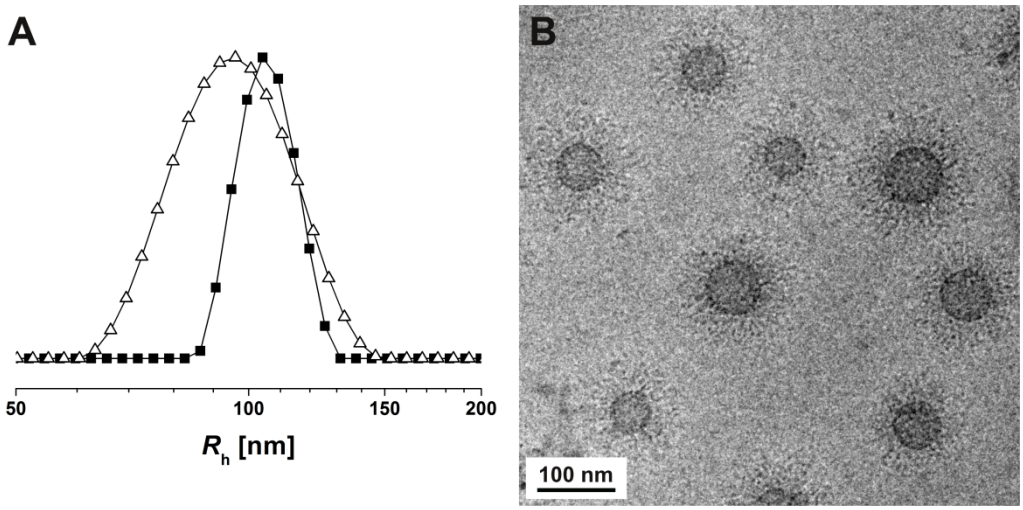


**Figure S3: Intensity-weighted DLS CONTIN plots for BMANaDq precursor micelles in aqueous solution at pH 10 (−■−, $\langle R_h \rangle_z$ = 107 nm, PDI = 0.06) and micellar IPECs with $ANa_{27}NIPAAm_{150}$ at $Z_{-/+}$ = 1 (−△−, $\langle R_h \rangle_z$ = 97 nm, PDI = 0.10) (A); cryo-TEM micrograph of micellar IPECs from BMANaDq and $ANa_{27}NIPAAm_{150}$ at $Z_{-/+}$ = 1 (B).**

The thermo-responsive properties of these structures were investigated *via* turbidity measurements ($c$ ~ 0.3 g/L) and temperature-dependent DLS measurements (Figure S4). In both cases, a cloud point of 36 °C could be obtained. A further increase in temperature resulted in the precipitation of the IPEC particles.

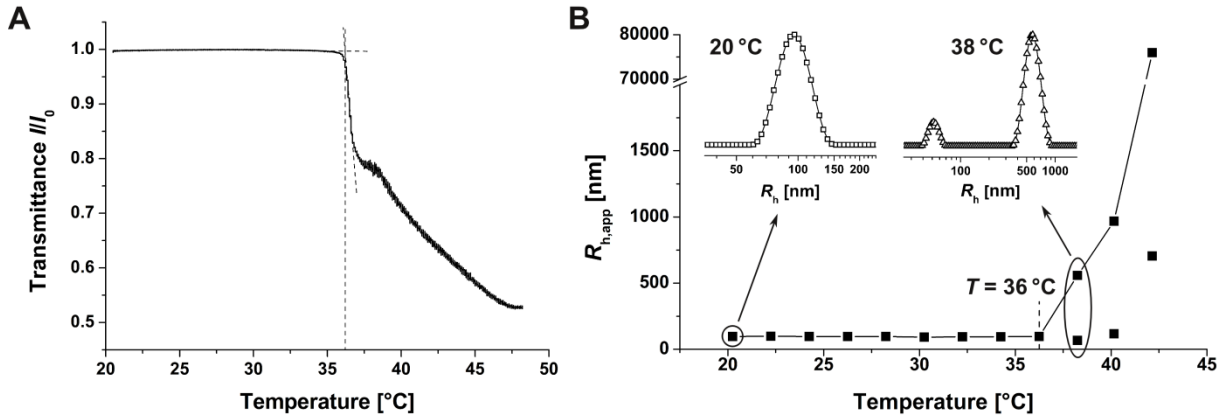


**Figure S4: Cloud point determination for micellar IPECs from BMANaDq precursor micelles and $ANa_{27}NIPAAm_{150}$ at $Z_{-/+}$ = 1 in aqueous solution at pH 10 *via* turbidity measurements ($c$ ~ 0.3 g/L) (A); dependence of hydrodynamic radius of micellar IPECs on the temperature as determined by DLS (B); the insets show intensity-weighted DLS CONTIN plots for the micellar IPECs at different temperatures; 20 °C (−□−, $\langle R_h \rangle_z$ = 97 nm, PDI = 0.10) and 38 °C (−△−, $R_{h,app}$ = 68 nm and 553 nm); the onset of aggregation is highlighted at 36 °C.**