

## Supplementary Materials: Redox-Responsive Crosslinked Mixed Micelles for Controllable Release of Caffeic Acid Phenethyl Ester

DLS/ELS measurements revealed that single polymer micelles do not exist in the sample of mixed micelles. The determined diameter of mixed micelles (38 nm) is between  $D_h$  of the two single copolymer micelles (Table S1). The same tendency is found for zeta potential values (Table S1). The zeta potential of mixed micelles is -22 mV, while the single polymer micelles have zeta potential of -33 mV ( $PAA_{13}$ -*b*- $PCL_{35}$ -*b*- $PAA_{13}$ ) and -0.6 mV ( $PEO_{113}$ -*b*- $PCL_{35}$ -*b*- $PEO_{113}$ ), respectively. We have established that mixed micelles, comprising a nonionic and an ionic block, exhibit single zeta-potential value, unlike the mixture of two pre-formed single-polymer micelles (self-assembled separately and then mixed) [1]. Thus, our results are direct proof that only mixed micelles were formed from the  $PEO_{113}$ -*b*- $PCL_{35}$ -*b*- $PEO_{113}$ / $PAA_{13}$ -*b*- $PCL_{35}$ -*b*- $PAA_{13}$  blend at the reported experimental conditions.

**Table S1.** Dynamic and electrophoretic light scattering data and critical micelle concentrations of single copolymer and mixed copolymer micelles.

Copolymers	Hydrodynamic diameter (nm)	Zeta potential (mV)	Critical micelle concentration (g L <sup>-1</sup> )
$PAA_{13}$ - <i>b</i> - $PCL_{35}$ - <i>b</i> - $PAA_{13}$	$86 \pm 3$	$-33 \pm 3$	0.063
$PEO_{113}$ - <i>b</i> - $PCL_{35}$ - <i>b</i> - $PEO_{113}$	$26 \pm 1$	$-0.6 \pm 0.1$	0.090
$PEO_{113}$ - <i>b</i> - $PCL_{35}$ - <i>b</i> - $PEO_{113}$ / $PAA_{13}$ - <i>b</i> - $PCL_{35}$ - <i>b</i> - $PAA_{13}$ (molar ratio 3:1)	$38 \pm 2$	$-22 \pm 3$	0.078

[1] Kamenova K, Haladjova E, Grancharov G, Kyulavska M, Tzankova V, Aluani D, et al. Co-assembly of block copolymers as a tool for developing novel micellar carriers of insulin for controlled drug delivery. *Eur Polym J.* **2018**, *104*, 1–9.