

Supporting Information to the paper:

Dual Stimuli-Responsive Multicompartment Micelles from Triblock Terpolymers with Tunable Hydrophilicity

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Modification of BTD Triblock Terpolymers

Hydrolysis of the PtBMA Block

Figure S1 shows FTIR spectra of the B₈₀₀T₂₀₀D₂₈₅ terpolymer before and after hydrolysis of the PtBMA block. The obtained results are in good agreement with the literature, *e.g.* for PS-*b*-PMAA diblock copolymers.¹ The complete disappearance of the characteristic double band for the *tert*-butyl group at 1392 and 1367 cm⁻¹ indicates a successful hydrolysis of the PtBMA compartment. Additionally, the absorption bands of the ester moieties of the PtBMA and PDMAEMA blocks at 1723 cm⁻¹ (C=O stretching vibration) and at 1248 and 1139 cm⁻¹ (C–O–C stretching vibration) decrease and are slightly shifted after hydrolysis of PtBMA to PMAA. This indicates that the ester moieties of PDMAEMA are still intact after treatment under acidic conditions.

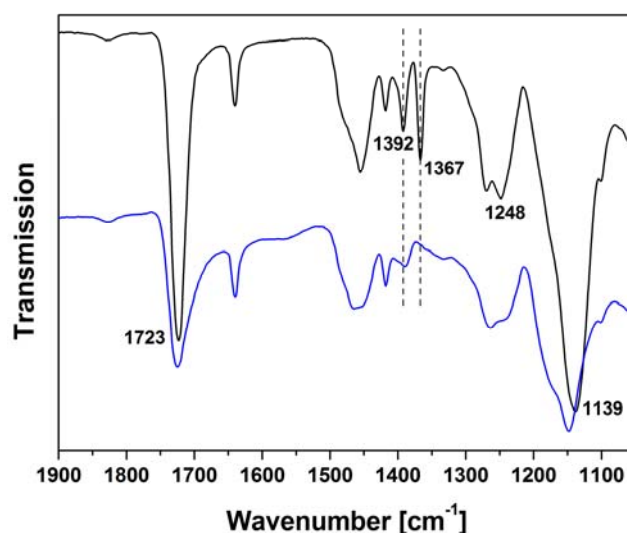


Figure S1. FTIR spectra of B₈₀₀T₂₀₀D₂₈₅ (black line) and B₈₀₀MAA₂₀₀D₂₈₅ (blue line).

In addition, the hydrolysis of the *Pt*BMA block of $B_{800}T_{200}D_{85}$ was monitored by $^1\text{H-NMR}$ in 1,4-dioxane- d_8 . Figure S2 shows the corresponding spectra before and during hydrolysis. Before hydrolysis (Figure S2A), all peaks have been assigned to the protons *a* to *h* of the terpolymer. The hydrolysis can be followed via the decrease of the signal at 1.42 ppm which corresponds to the protons *c* of the *tert*-butyl group of *Pt*BMA. By comparing the integral of this signal to that of the methine protons *a* of PB from 5.3 to 5.6 ppm in the spectra A to D of Figure S2, the relative intensity of the *tert*-butyl signal at different reaction times is calculated (Figure S3).

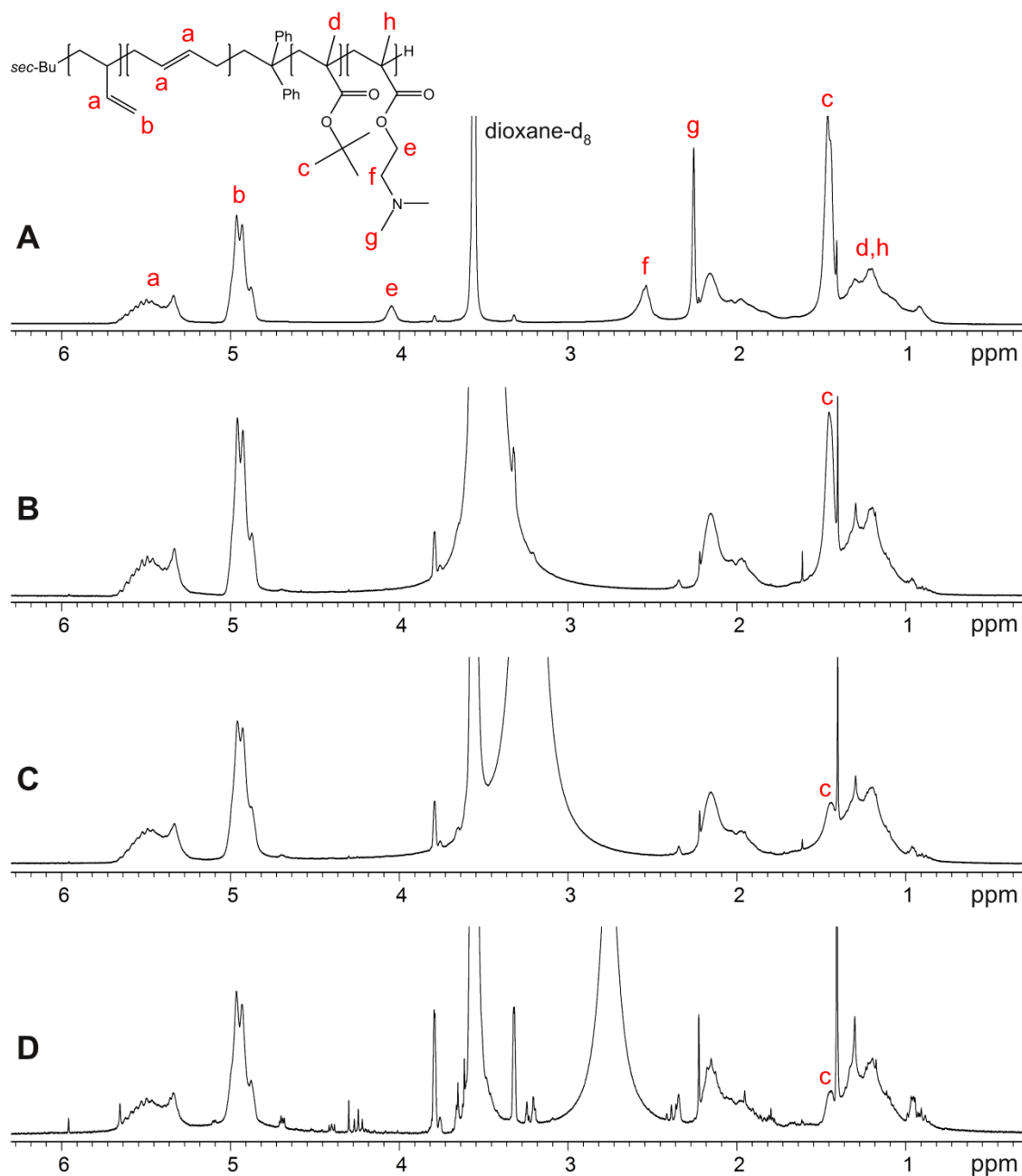


Figure S2. $^1\text{H-NMR}$ spectra of the hydrolysis of the *Pt*BMA block of $B_{800}T_{200}D_{85}$ in 1,4-dioxane- d_8 at different reaction times; before hydrolysis (A), after 3 h (B), 8.5 h (C), and 24 h (D).

Figure S3 shows that after 24 hours under these conditions the signal of the *tert*-butyl group is reduced to ~9 %, indicating almost complete hydrolysis of the *Pt*BMA block. As the signal discussed between 1.4 and 1.5 ppm in Figure S2D could also result from aliphatic protons of the polymeric backbone, the actual degree of hydrolysis might even be higher.

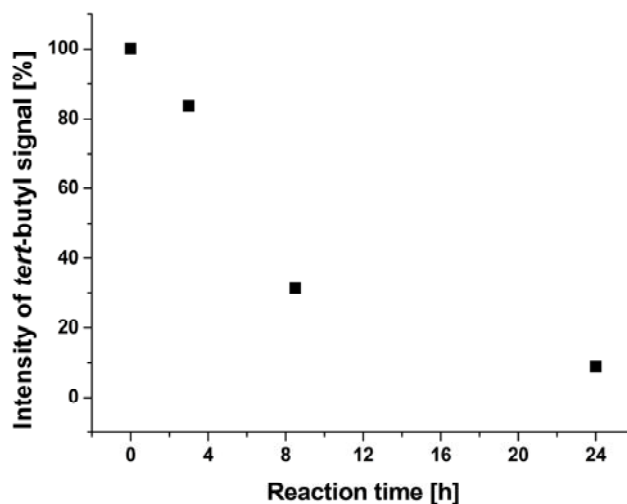


Figure S3. Intensity of the *tert*-butyl signal of *Pt*BMA at different reaction times for the hydrolysis of B₈₀₀T₂₀₀D₈₅, calculated from ¹H-NMR spectra in Figure S2.

Quaternization of the PDMAEMA Block

Figure S4A and B show enlarged regions of the FTIR spectra of B₈₀₀T₂₀₀D₂₈₅ and B₈₀₀MAA₂₀₀Dq₂₈₅. In Figure S4A, a broad absorption band between 3700 and 3300 cm⁻¹ is observed for B₈₀₀MAA₂₀₀Dq₂₈₅. It originates from O–H stretching vibrations of PMAA after hydrolysis and increases upon quaternization, as it overlaps with stretching vibrations of the generated ammonium groups. After quaternization, a change in the absorption peaks at 2822 and 2770 cm⁻¹, corresponding to C–H stretching vibrations of the –N(CH₃)₂ groups of PDMAEMA, occurs, indicating the successful methylation of the amino moieties.² Additionally, the absorption band of the antisymmetric deformation of –CH₃ substituents on the amino groups is shifted from 1456 to 1478 cm⁻¹ (Figure S4B).

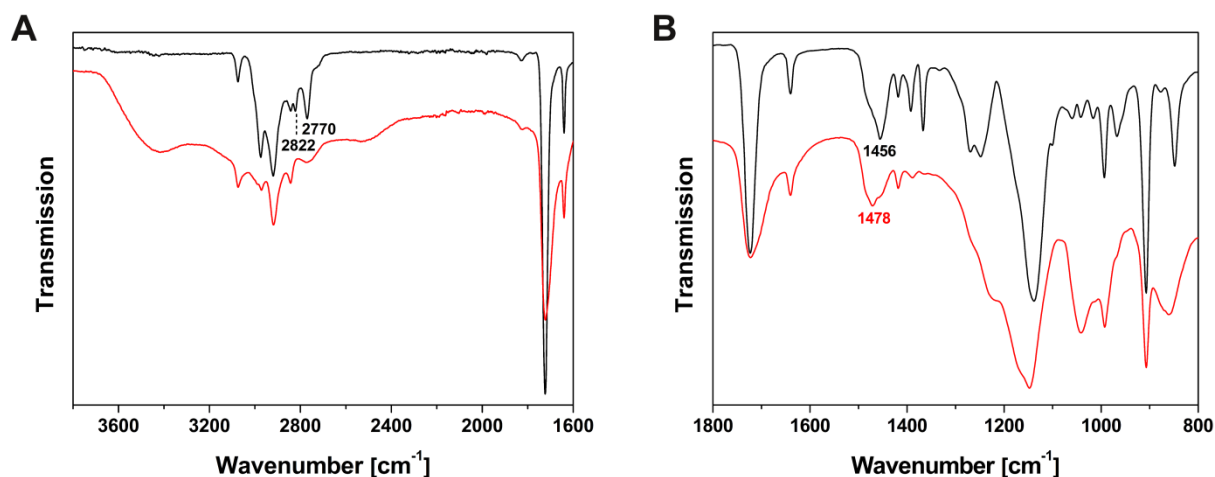


Figure S4. FTIR spectra of B₈₀₀T₂₀₀D₂₈₅ (black line) and B₈₀₀MAA₂₀₀Dq₂₈₅ (red line).

Solution Characteristics of Micellar Aggregates

For all micellar aggregates prepared in this work, a spherical shape is indicated by DLS measurements through the extrapolation of the decay rate $\Gamma_{q \rightarrow 0} = 0$, shown exemplarily for B₈₀₀MAA₂₀₀Dq₂₈₅ at pH 10 in Figure S5A. The size of the micelles at the concentrations used here ($c \sim 0.5$ g/L) corresponds in good approximation to the dimensions at infinite dilution. This is confirmed by the extrapolation of the hydrodynamic radius $\langle R_h \rangle_{z, c \rightarrow 0}$, shown exemplarily for B₈₀₀MAA₂₀₀Dq₂₈₅ at pH 10 in Figure S5B.

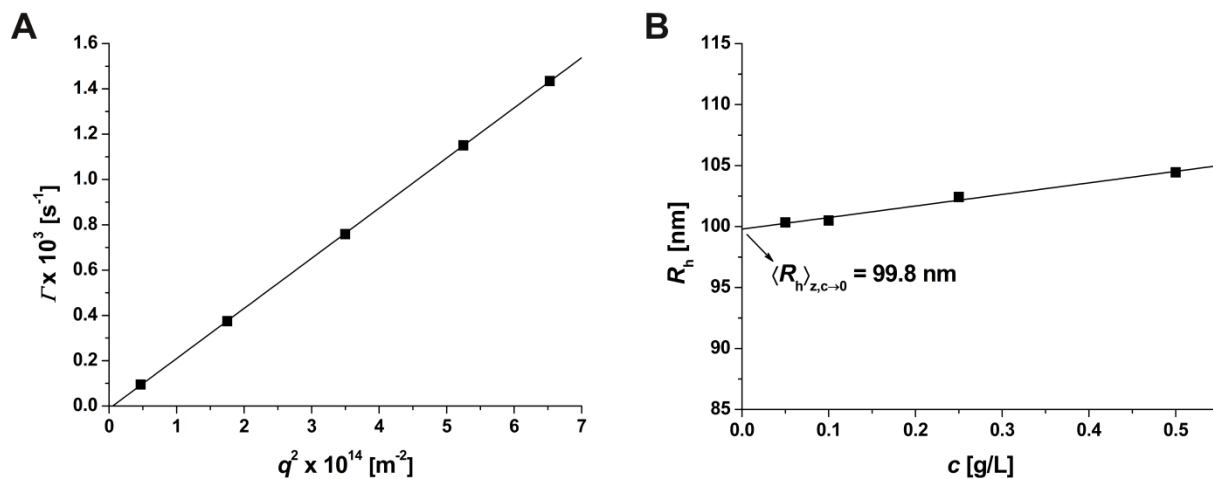


Figure S5. Γ versus q^2 for B₈₀₀MAA₂₀₀Dq₂₈₅ in pH 10 buffer solution ($c = 0.05$ g/L) (A); R_h versus c for B₈₀₀MAA₂₀₀Dq₂₈₅ at $\theta = 90^\circ$ (B).

References

- 1 G. J. Wang and D. Y. Yan, *J. Appl. Polym. Sci.*, 2001, **82**, 2381-2386.
- 2 D. Roy, J. S. Knapp, J. T. Guthrie and S. Perrier, *Biomacromolecules*, 2008, **9**, 91-99.