Electronic Supplementary Information for:

Cylindrical nanocapsules from photo-cross-linkable core-shell bottlebrush copolymers

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Fig. S1 ¹H NMR spectra (d_6 -DMSO) of poly(GM)₂₀₀ (A) before and (B) after hydrolysis.



Fig. S2 ¹H NMR spectra (CDCl₃) of (A) poly(GM)₂₀₀, (B) poly(GM₂₀₀-g-LA₃₆) and (C) RAFT modified poly(GM₂₀₀-g-(LA-TC)₃₆).



Fig. S3 ¹H NMR spectra (CDCl₃) of bottlebrush copolymers poly(GM-*g*-LA-*g*-(S/CMA)) from Table 1.



Fig. S4 SEC traces of (A) poly(GM)₂₀₀, (B) poly(GM₂₀₀-g-LA₃₆) and (C) poly(GM₂₀₀-g-(LA-TC)₃₆).



Fig. S5 TEM analysis of a photo-cross-linked bottlebrush copolymer poly(GM-g-LA-g-(S/CMA)).

Control experiments for PLA degradation

Control experiments were utilized to provide unambiguous identification of signals in the FTIR spectra and confirm that complete degradation of the PLA core was achieved. For this purpose, the PLA block of the uncross-linked bottlebrush copolymer poly(GM-g-LA-g-(S/CMA)) was degraded under the conditions mentioned in the experimental section. Complete PLA degradation was corroborated by the disappearance of the PLA methine signals at 5.2 ppm in the ¹H NMR spectrum (Fig. S3). Additionally, the integrated areas under the aromatic and 4-methylcoumarin signals did not change after the degradation, suggesting the shell layer was not affected by the utilized conditions.



Fig. S6 ¹H NMR spectrum (CDCl₃) of uncross-linked poly(GM-*g*-LA-*g*-(S/CMA)) (A) before and (B) after PLA degradation.



Fig. S7 FTIR characterization of (A) uncross-linked poly(GM-*g*-LA-*g*-(S/CMA)) bottlebrush copolymer, (B) after PLA degradation and (C) after coumarin dimerization under 365 nm UV irradiation.

In the FTIR spectrum of the uncross-linked poly(GM-*g*-LA-*g*-(S/CMA)), the bottlebrush precursor polymer showed a strong carbonyl stretch around 1730 cm⁻¹, which was attributed to both conjugated coumarin lactone and methyl methacrylate ester groups (Fig. S4). Also, there was a small shoulder around 1757 cm⁻¹, which was attributed to the PLA carbonyl stretch. After PLA degradation, the carbonyl stretch peak was narrower and the shoulder at 1757 cm⁻¹ disappeared, as expected due to the complete degradation of the PLA core. After coumarin dimerization, the double bond stretch at 1614 cm⁻¹ shifted to 1624 cm⁻¹ suggesting the successful dimerization of 4-methylcoumarin units. Most importantly, the carbonyl stretch peak ended up with a shoulder at 1757 cm⁻¹, which corresponds to non-conjugated coumarin lactone ester peaks. The control experiments demonstrated that if the sequence of events was reversed (applying first PLA degradation, then UV irradiation to the precursor polymer), the FTIR spectrum obtained (Fig. S4) completely matched with the nanocapsule FTIR spectrum (Fig. 7).



Fig. S8 SEC traces of (A) uncross-linked poly(GM-g-LA-g-(S/CMA)) bottlebrush copolymer, (B) after PLA degradation.

Experimental Details

PLA degradation of uncross-linked bottlebrush copolymer poly(GM-g-LA-g-S/CMA) using methanolic NaOH (Control experiment 1): Uncross-linked bottlebrush copolymers (3 mg) were dissolved in 1,4-dioxane (1 ml). Methanolic sodium hydroxide ($60:40 \text{ H}_2\text{O}:MeOH$, 0.5 M, 30μ l) was then added to the above solution dropwise under stirring. The mixture was left to stir for 2 h at room temperature. To quench the reaction, HCl solution (0.5 M, 50μ l) was added. The obtained polymer was precipitated in methanol.

Coumarin dimerization of the poly(S/CMA) random copolymer (Control experiment 2): After PLA degradation of uncross-linked bottlebrush polymer poly(GM-g-LA-g-S/CMA), the remaining poly(S/CMA) branches in solution (1 mg/mL chloroform) were exposed to $\lambda = 365$ nm UV light (Intensity = 600 mW cm⁻²) for 2 hours in a glass vial. The solvent was evaporated and the sample was used for IR analysis.



Fig. S9 UV-Vis spectra of poly(GM-g-LA-g-(S/CMA)) bottlebrush copolymer (A) after photodimerization upon 365 nm irradiation (B) after photo-cleavage upon 254 nm irradiation. The concentration used for the analysis was 0.1 mg/mL in chloroform.



Fig. S10 SEC traces of poly(GM₂₀₀-*g*-LA₃₆-*g*-(S₉₀/CMA₃₇)) (A) before and (B) after photo-cleavage upon 254 nm irradiation.



Fig. S11 Expanded FTIR spectra of (A) poly(GM-g-(LA-TC)), (B) poly(GM-g-LA-g-(S/CMA)) bottlebrush copolymer, (C) after shell photo-cross-linking under 365 nm UV irradiation and (D) after PLA degradation.