

SUPPLEMENTARY INFORMATION

Hydrolytic stability of 8armPEG10k-maleimide

To demonstrate that the determined pseudo-first-order rate constants (k_{obs}) are independent from the concentration of the starting material, 5 mg, 10 mg, and 20 mg of 8armPEG10k-maleimide were dissolved in 2 mL of 50 mM phosphate buffer (pH 7.4). The samples were placed in a Kontron UVIKON[®] 941 spectrophotometer (Kontron Instruments S.p.A, Milan, Italy) equipped with a temperature-controlled cell changer; 10 mm quartz cuvettes were used. The decrease in the absorbance at 299 nm (UV maximum of 8armPEG10k-maleimide) was monitored for 1200 min at 37 °C. All measurements were performed in triplicate. Assuming that the pH of the buffered solutions does not change during hydrolysis (constant OH⁻ concentration), pseudo-first-order kinetic models were least-squares fitted to the experimental data to determine the hydrolysis rate constants (k_{obs}) and half-lives ($t_{1/2}$) of 8armPEG10k-maleimide. The plateau value was shared between all groups and k_{obs} was set greater than zero. The results are presented in Figure S1 and Table S1.

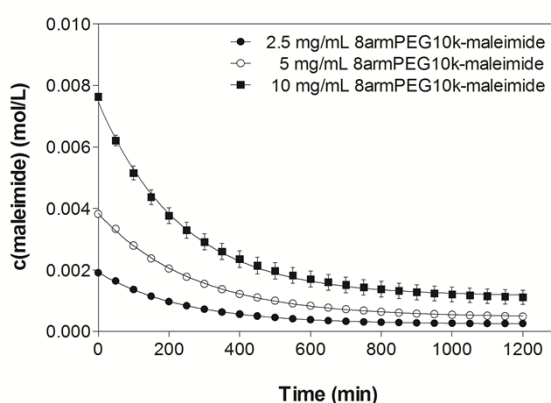


Figure S1: Hydrolytic stability of 8armPEG10k-maleimide at 37 °C and pH 7.4. The experimental data is indicated by symbols; the solid lines represent the least-squares fits of pseudo-first-order kinetic models. The experiments were carried out in triplicate and the results are presented as means \pm standard deviations.

Table S1: Pseudo-first-order rate constants (k_{obs}) of the ring-opening hydrolysis and half-lives ($t_{1/2}$) of 8armPEG10k-maleimide at 37 °C in 50 mM phosphate-buffer, pH 7.4 as a function of the polymer concentration.

c (polymer) (mg/mL)	c (maleimide) (mol/L)	k_{obs} (s⁻¹)	$t_{1/2}$ (min)	$3 \cdot t_{1/2}$ (days)	R^2
2.5	0.001909	$7.06 \cdot 10^{-5}$	164	0.3	0.9972
5.0	0.003818	$6.38 \cdot 10^{-5}$	181	0.4	0.9990
10.0	0.007637	$7.04 \cdot 10^{-5}$	164	0.3	0.9827