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Supporting Information

Well-defined hyperstar copolymers based on a thiol-yne hyperbranched core and a poly(2-oxazoline) shell for biomedical applications

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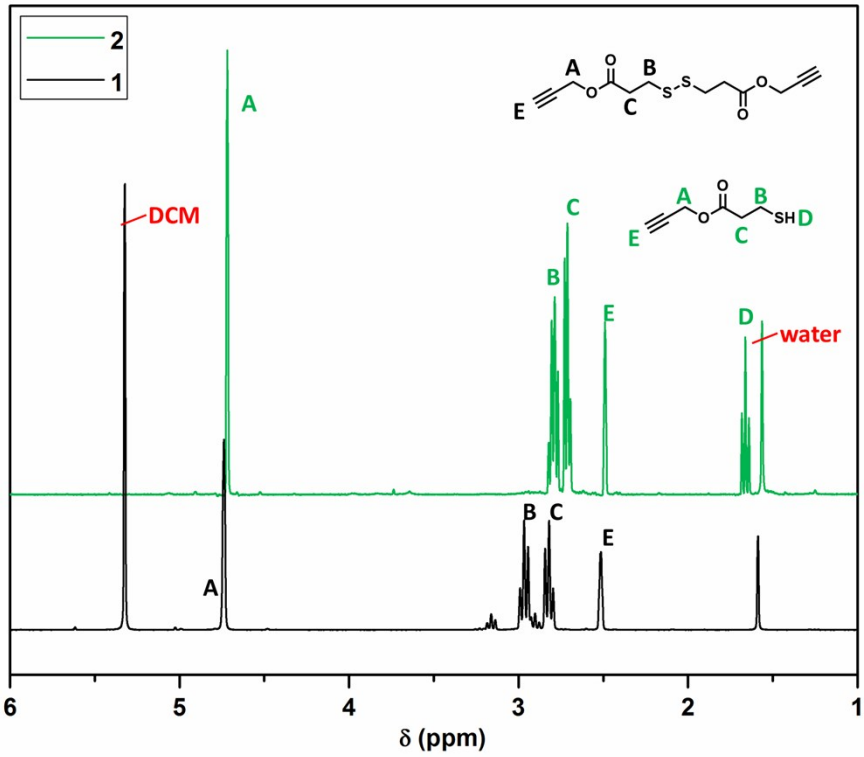


Figure S1: NMR spectra of oxidized thiol-yne monomer precursor (**1**) and PYMP (**2**). Peaks at 2.8 and 3.2 in the spectrum of **1** are associated to unreacted starting material which is removed upon purification after reduction.

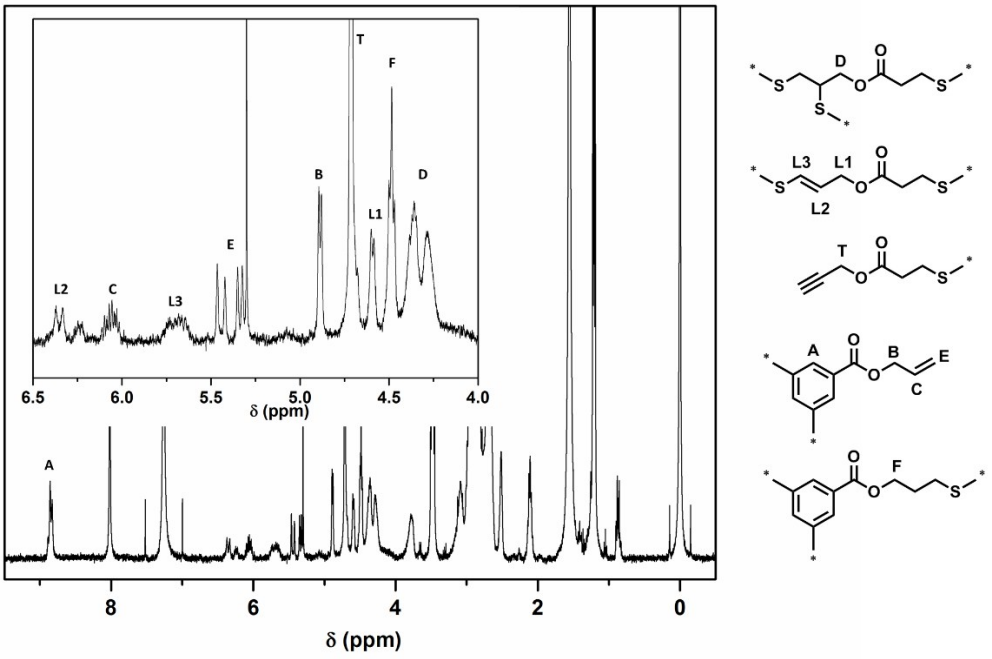


Figure S2: NMR spectrum of hyperbranched polymer poly(PYMP) (**3**).

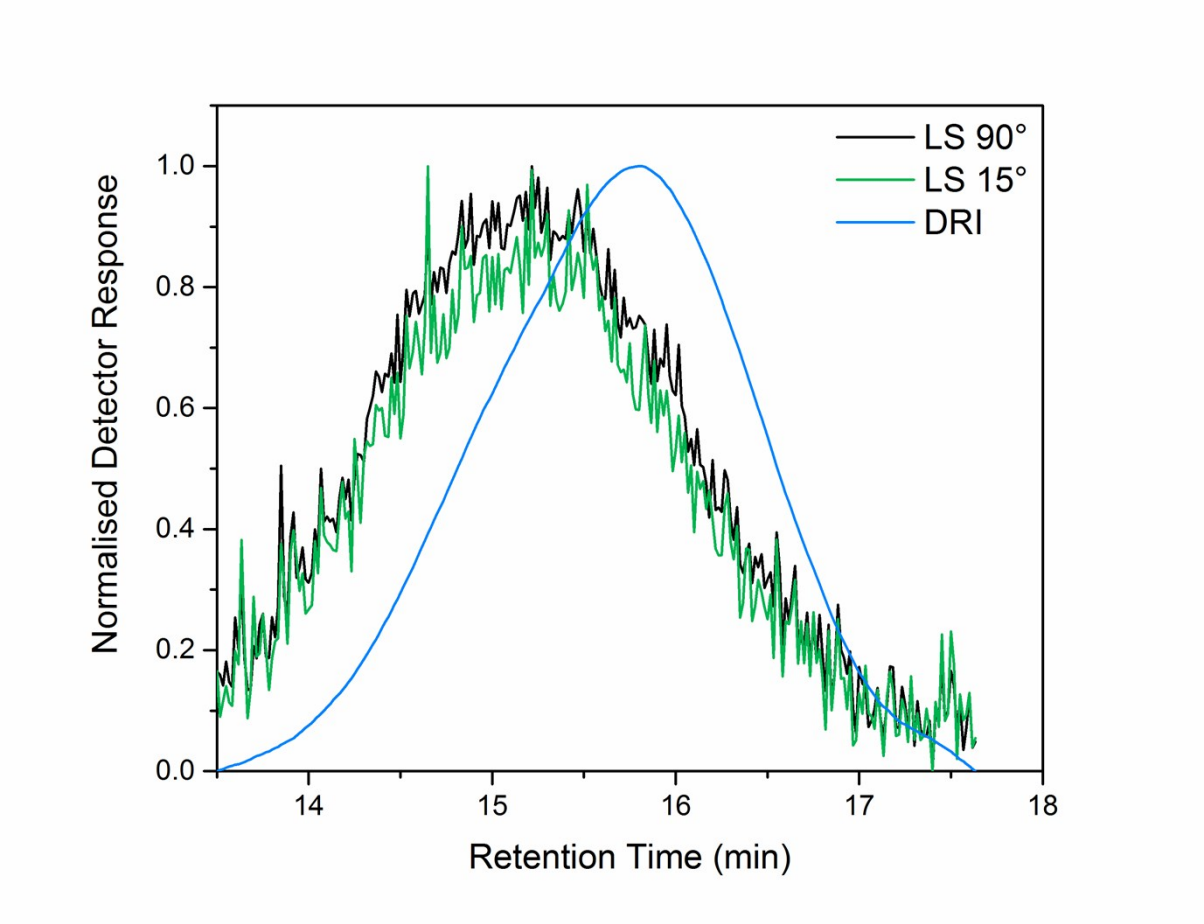


Figure S3: Multi-detector SEC chromatograms for hyperbranched polymer **(3)** by slow monomer addition to multifunctional alkene core.

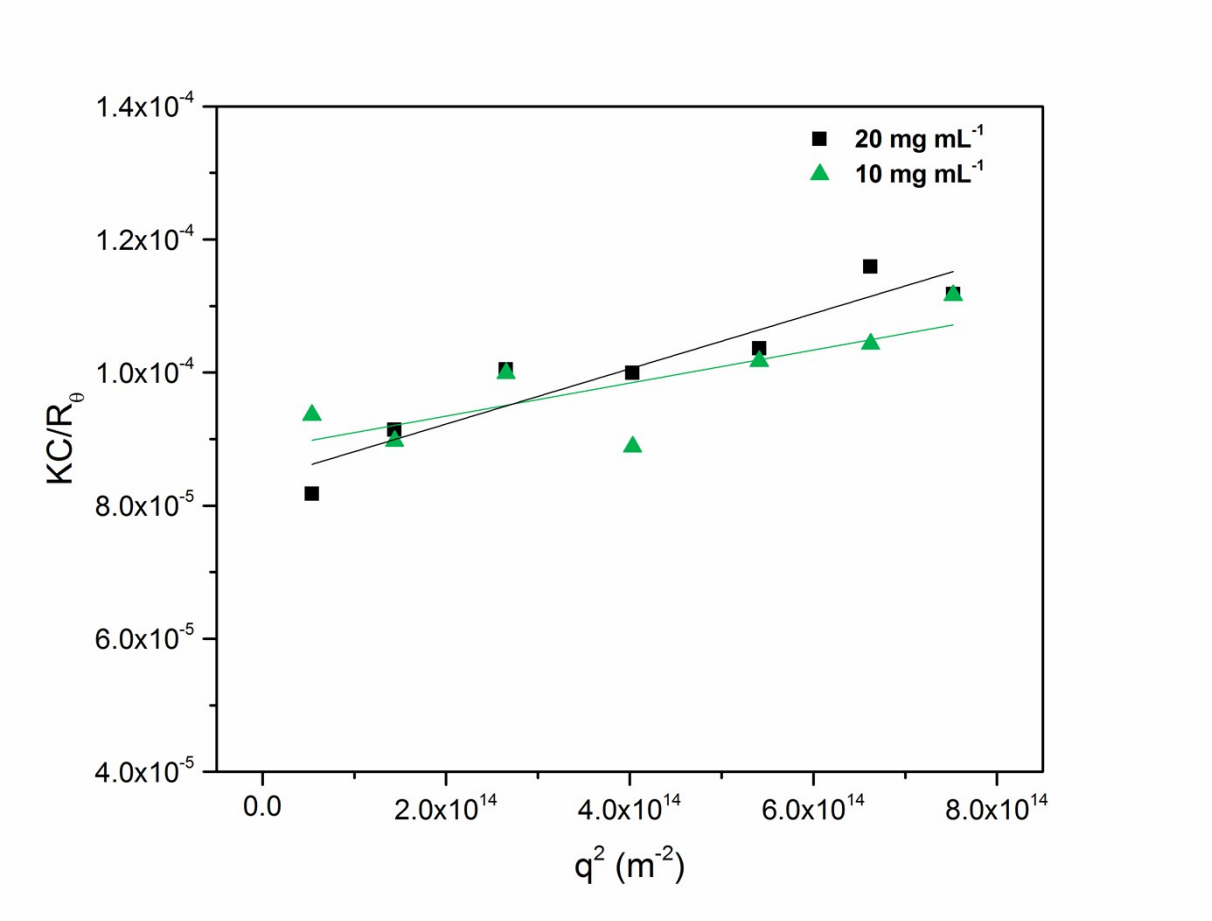


Figure S4: Evolution of KC/R of **3** in DMF as a function of q^2 obtained by light scattering.

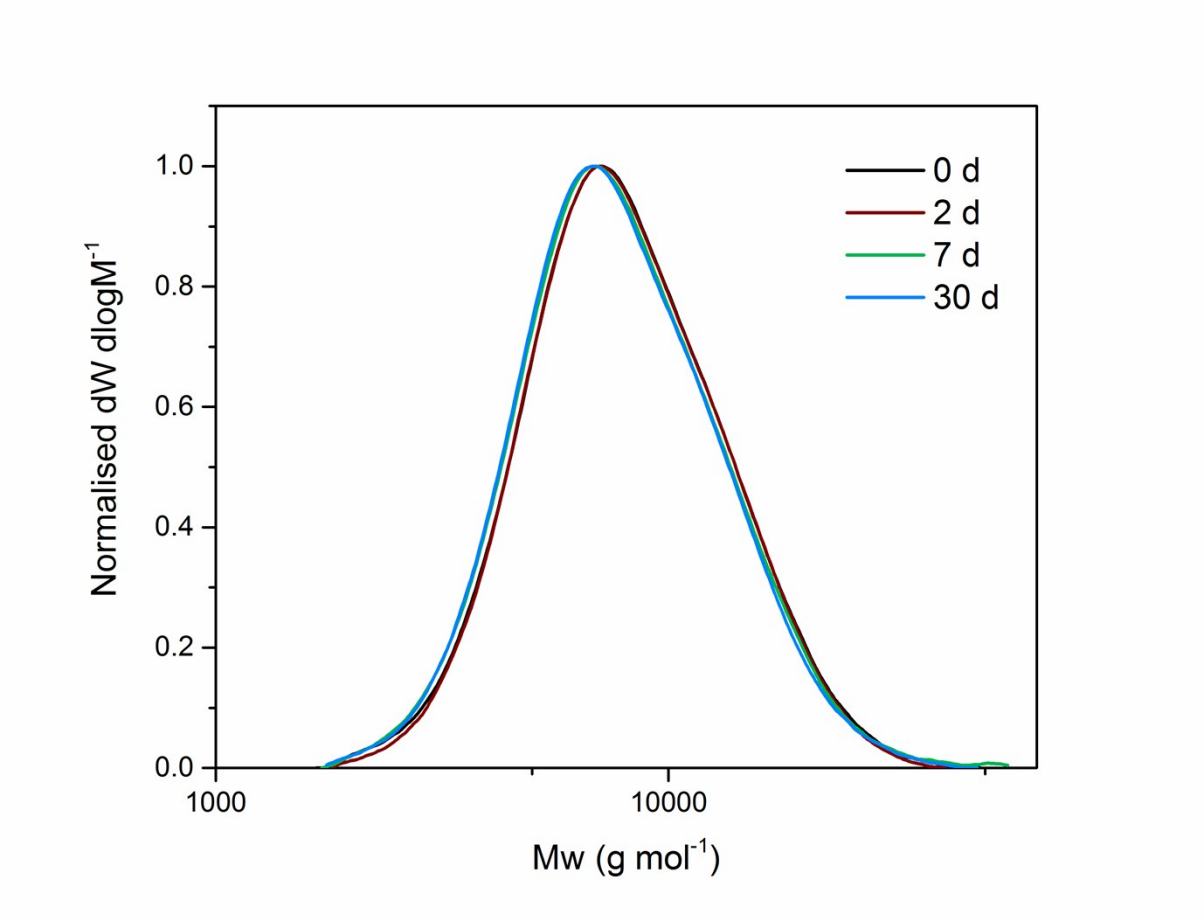


Figure S5: SEC traces of poly(PYMP) (**3**) stored in DMF at a concentration of 20 mg mL^{-1} at -20°C in dependence of the time.

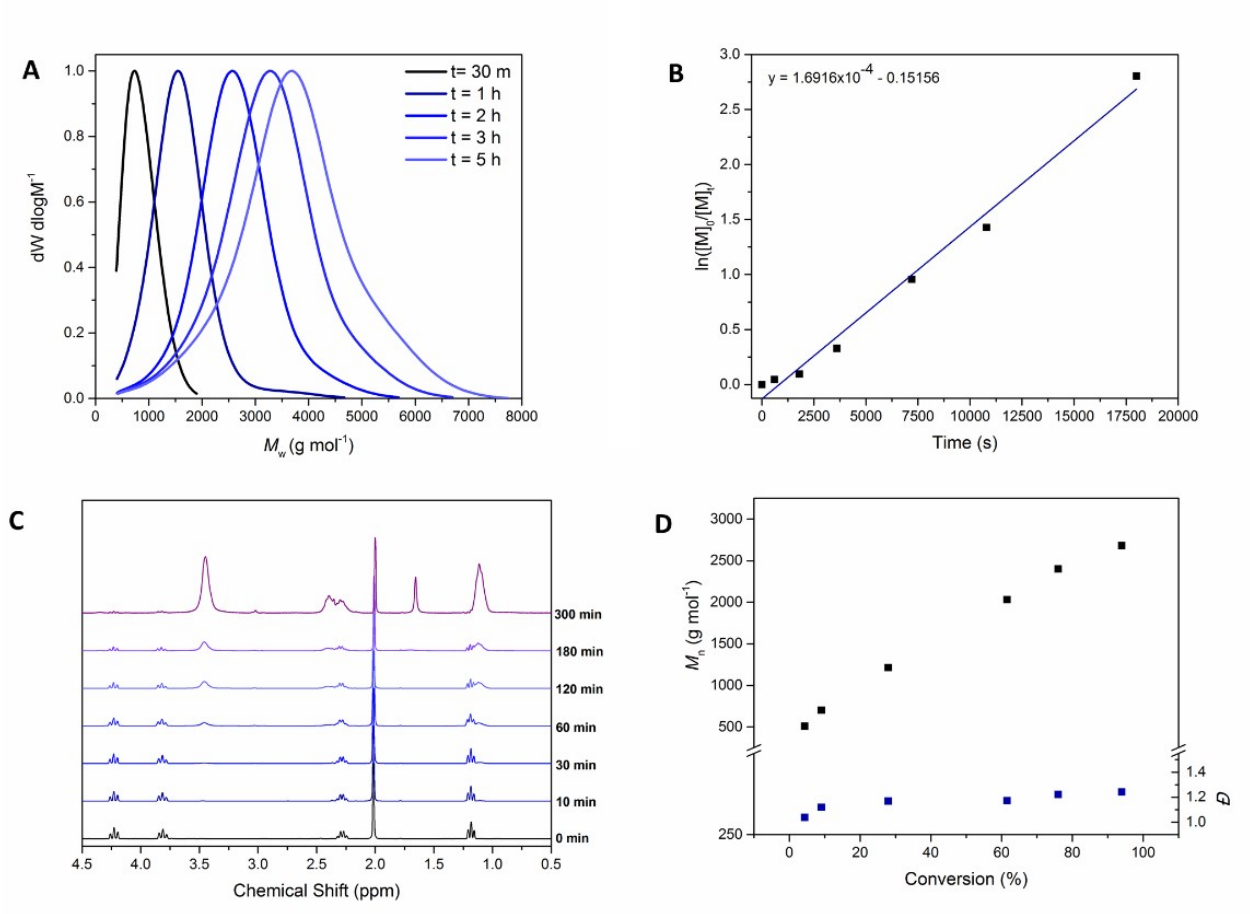


Figure S6: Kinetic studie of the polymerization of EtOx in Acetonitrile at 78˚C. A) SEC traces of kinetic samples, B) Semi-logarithmic plot of the evolution of conversion over time, C) ^{1}H-NMR spectra of kinetic samples measured in $CDCl_3$, D) Molar mass (black) and Dispersity (blue) as a function of conversion.

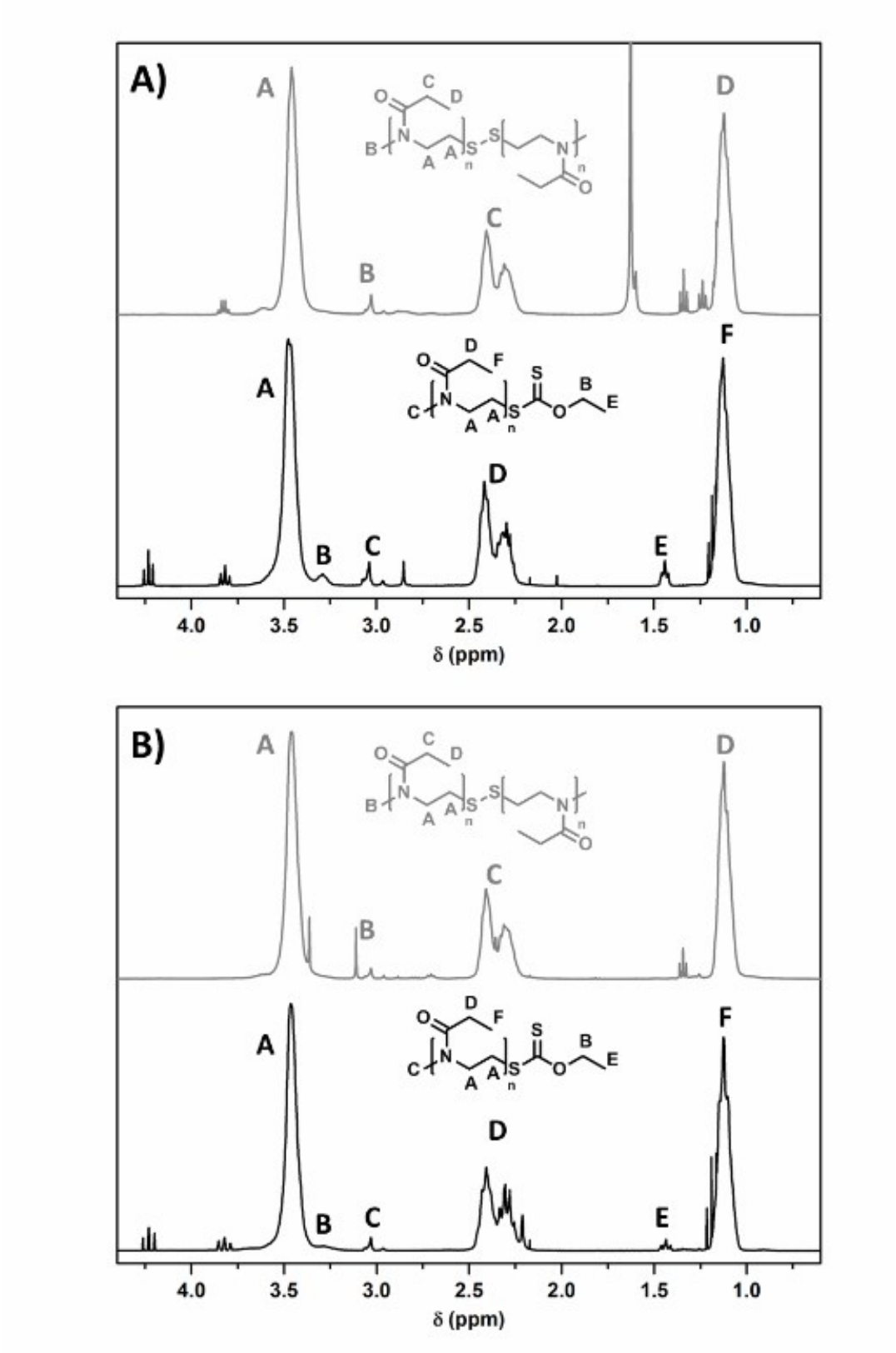


Figure S7: NMR spectra ($CDCl_3$) of PEtOx after termination using ethyl xanthate and after aminolysis having a DP of 23 (**4** (black), **6** (grey)) (A) or 42 (**5** (black), **7**(grey)) (B).

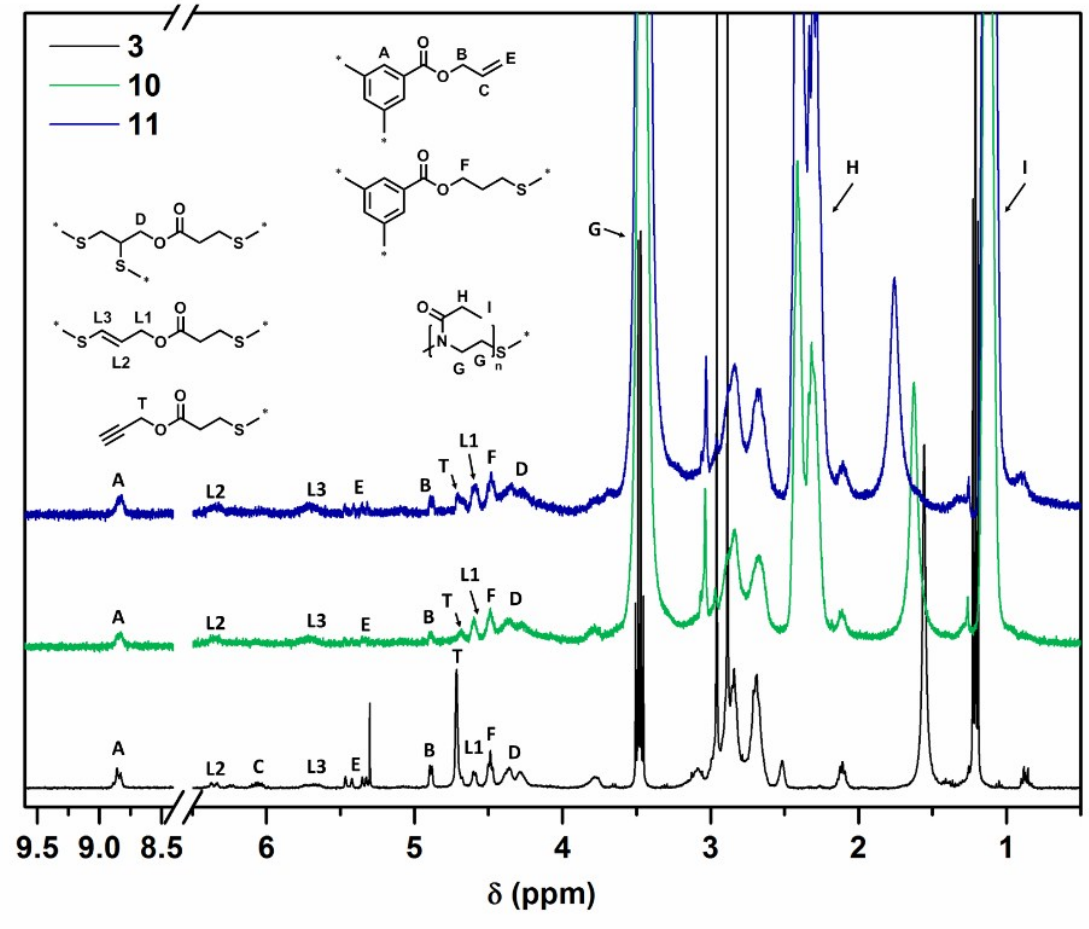


Figure S8: ^{1}H-NMR spectra of poly(PYMP) (**3**) as well as hyperstar copolymer (**10**, **11**) in $CDCl_3$.

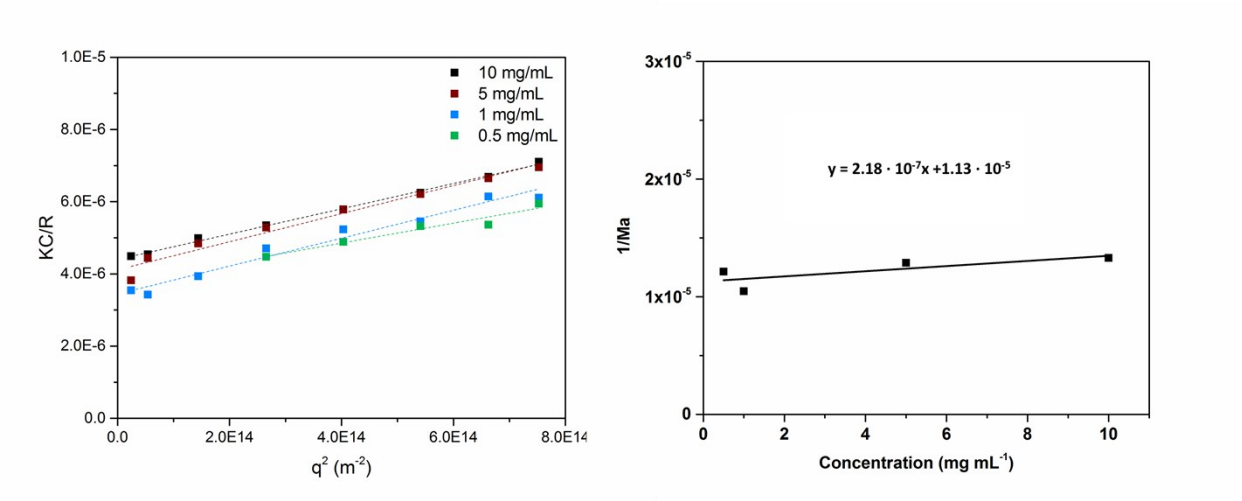


Figure S9: Evolution of KC/R of **10** in DMF as a function of q² and concentration obtained by light scattering.

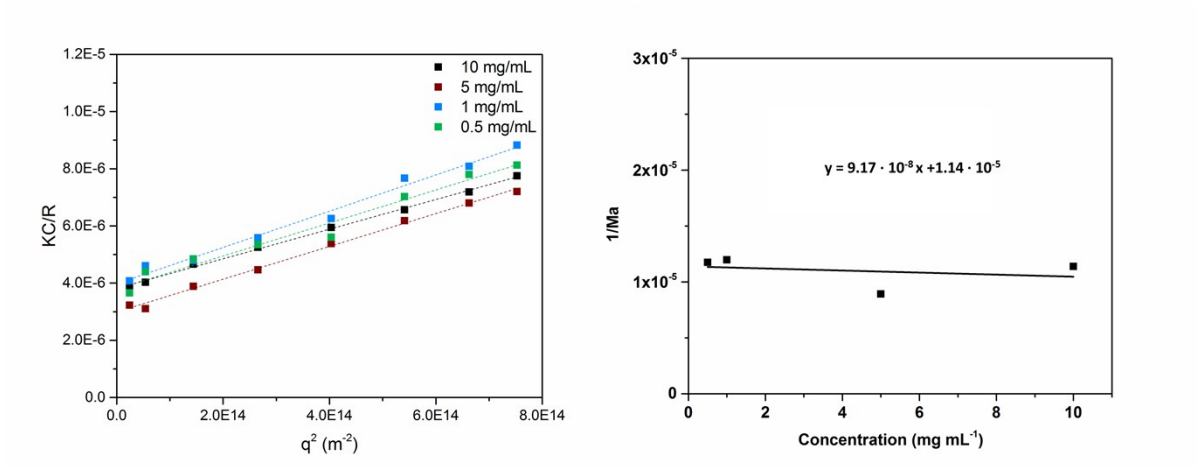


Figure S10: Evolution of KC/R of **11** in DMF as a function of q² and concentration obtained by light scattering.

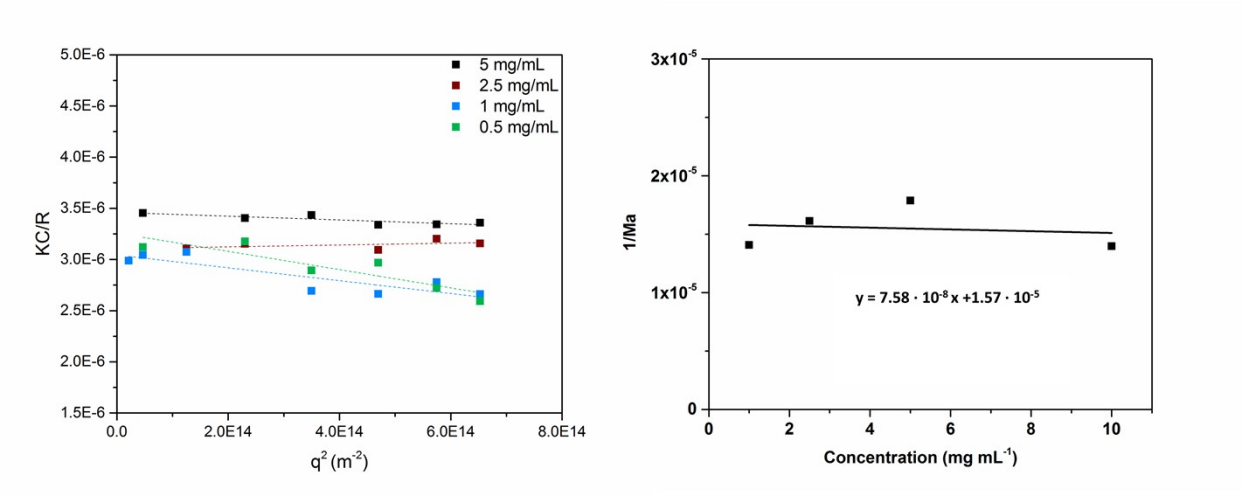


Figure S11: Evolution of KC/R of **10** in water as a function of q² obtained by light scattering.

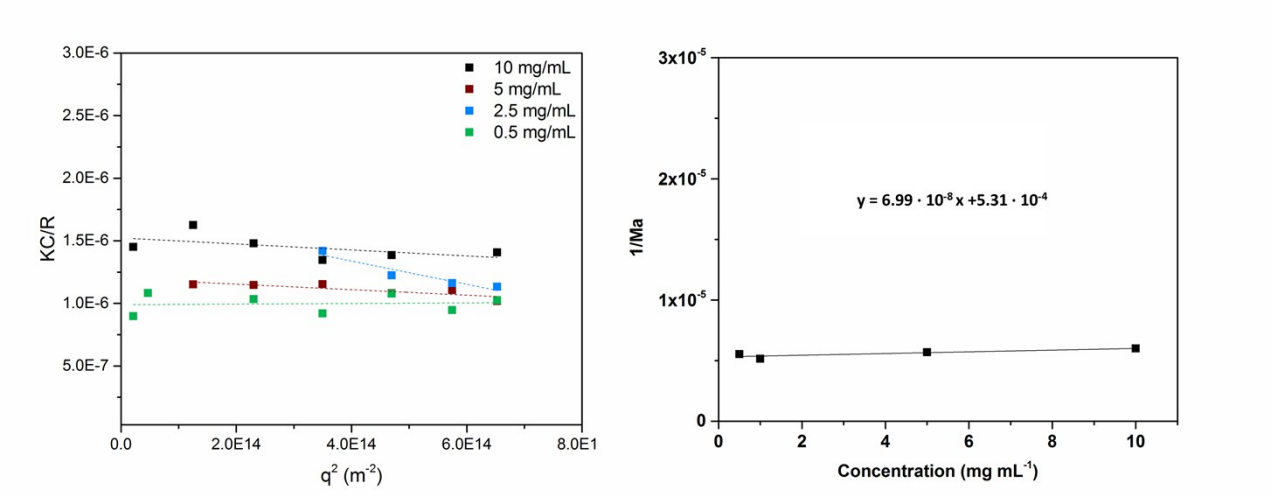
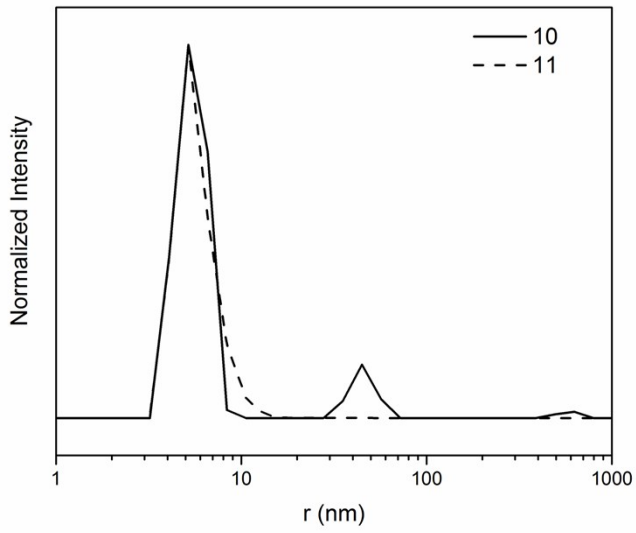


Figure S12: Evolution of KC/R of **11** in water as a function of q² obtained by light scattering.



Hyperstar	z-average (r, nm)	PDI
10	8	0.252
11	5	0.166

Figure S13: DLS data of hyperstars **10** and **11** in water. The graph shows the intensity distribution.

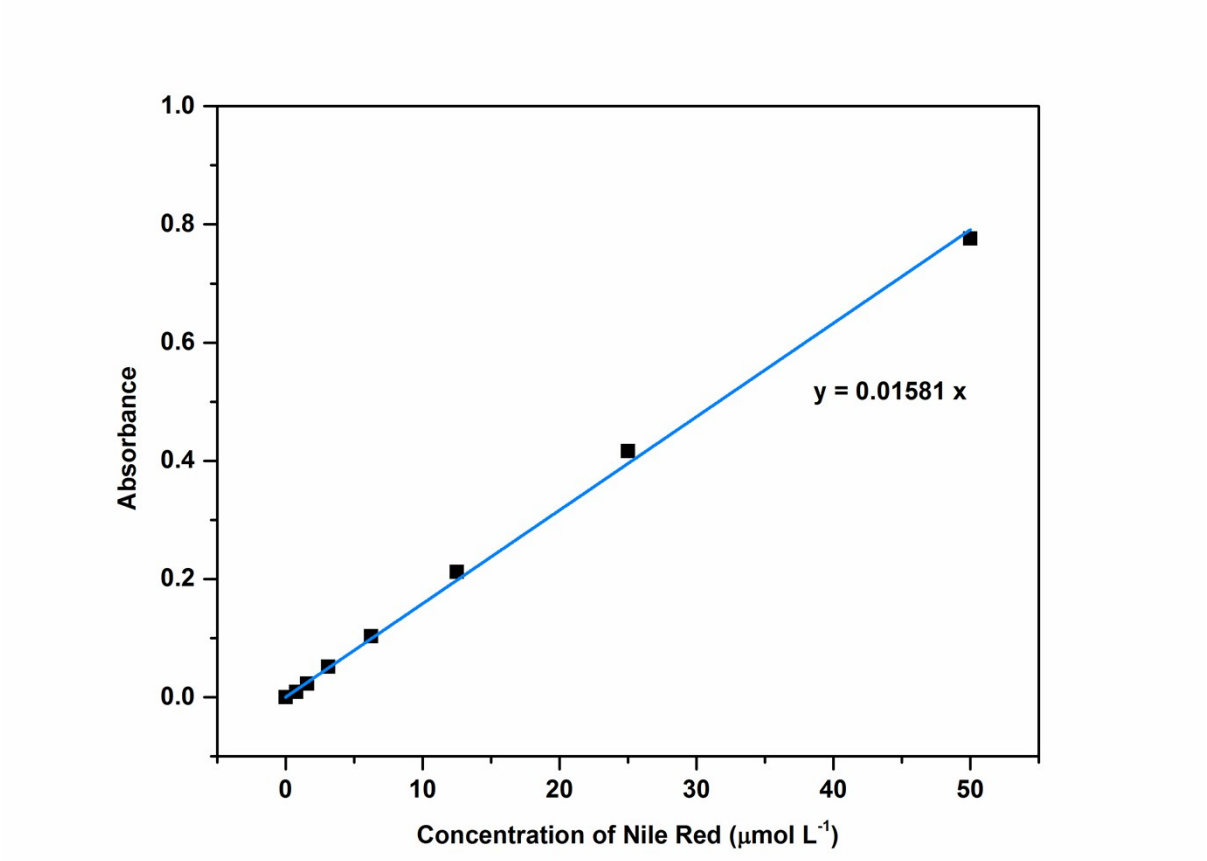


Figure S14: Calibration of the concentration dependent absorbance intensity of nile red in THF at a wavelength of 520 nm.

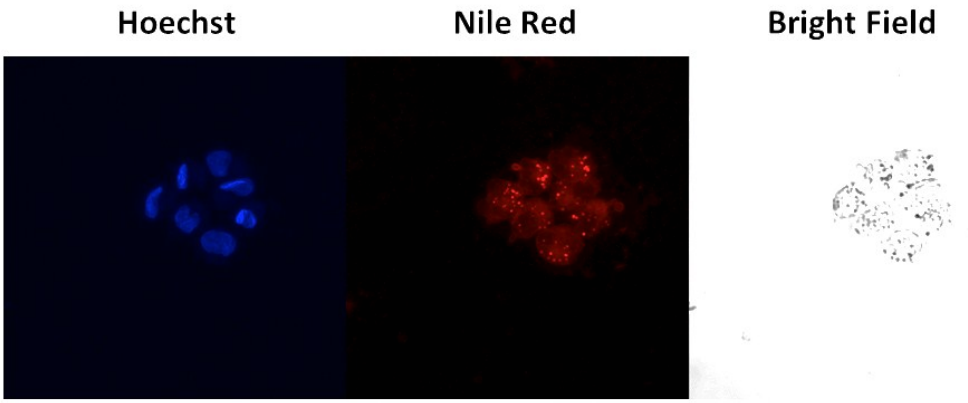


Figure S15: Confocal images of A2780 human ovarian carcinoma cells treated with nile red loaded hyperstars (**10**) for 2 h at 37˚C at a concentration of 0.1 mg mL^{-1}. Nuclei were stained using Hoechst 33258.