

SUPPORTING INFORMATION FOR: Micellar Drug Delivery Vehicles formed from Amphiphilic Block Copolymers Bearing Photo-Cross-linkable Cyclopentenone Side Groups

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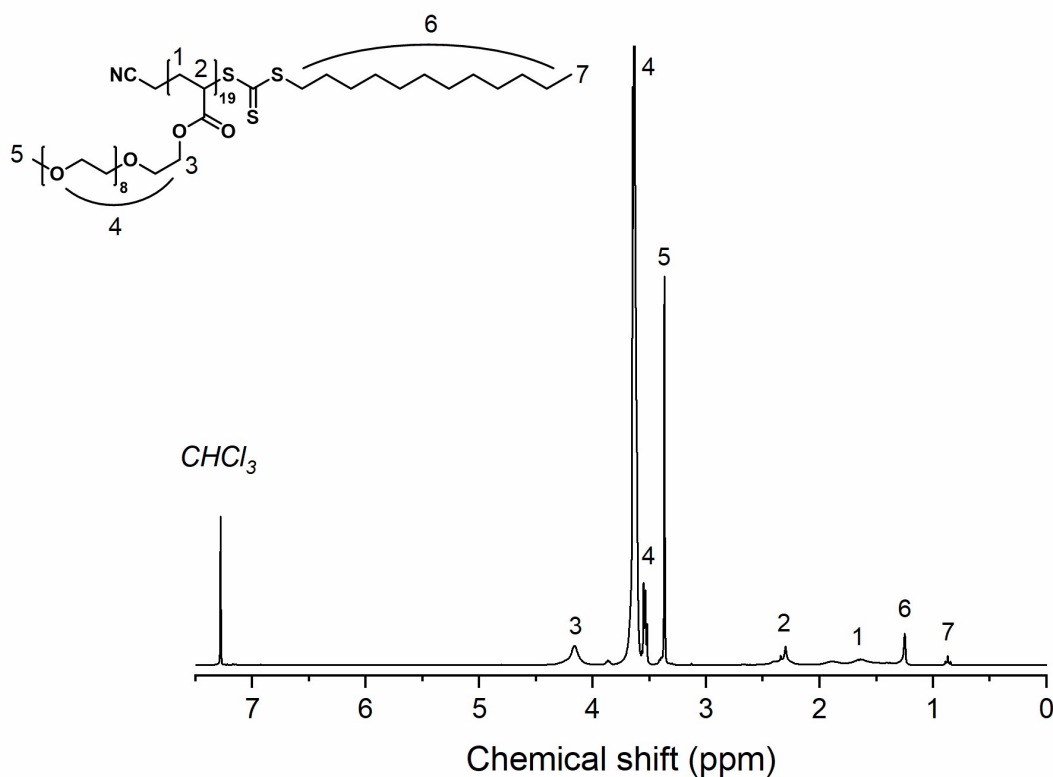


Figure S1. Assigned ¹H NMR spectrum of POEGA₁₉ macro RAFT agent.

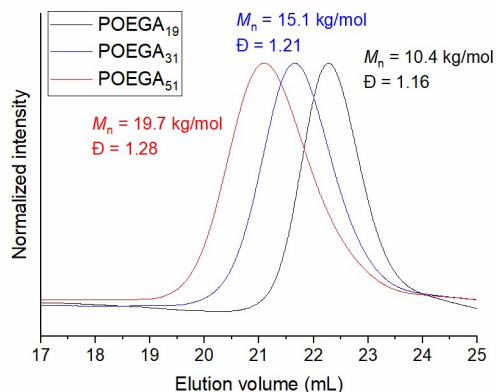


Figure S2. Overlay of the GPC traces of POEGA macro-RAFT agents using DMF containing 6 g/L AcOH and 0.035 mol/L LiCl as the eluent and a refractive index detector.

Table S1. GPC results of the synthesized block copolymers.

Polymer	$M_{n, GPC}$ (g/mol)	\bar{D}
POEGA ₁₉	10.4	1.16
POEGA ₁₉ -HB ₁₆	5.8	1.61
POEGA ₁₉ -HB ₃₇	5.6	1.63
POEGA ₁₉ -HB ₅₀	6.8	1.46
POEGA ₃₁	15.1	1.21
POEGA ₃₁ -HB ₁₇	8.5	1.84
POEGA ₃₁ -HB ₃₈	10.1	2.27
POEGA ₃₁ -HB ₄₉	9.4	1.59
POEGA ₅₁	19.7	1.28
POEGA ₅₁ -HB ₁₅	14.9	1.71
POEGA ₅₁ -HB ₃₂	10.7	2.07
POEGA ₅₁ -HB ₄₇	13.8	1.96

The eluent that was used was DMF containing 6 g/L AcOH and 0.035 mol/L LiCl. Molecular weights are given relative to poly(methyl methacrylate) standards using a refractive index detector.

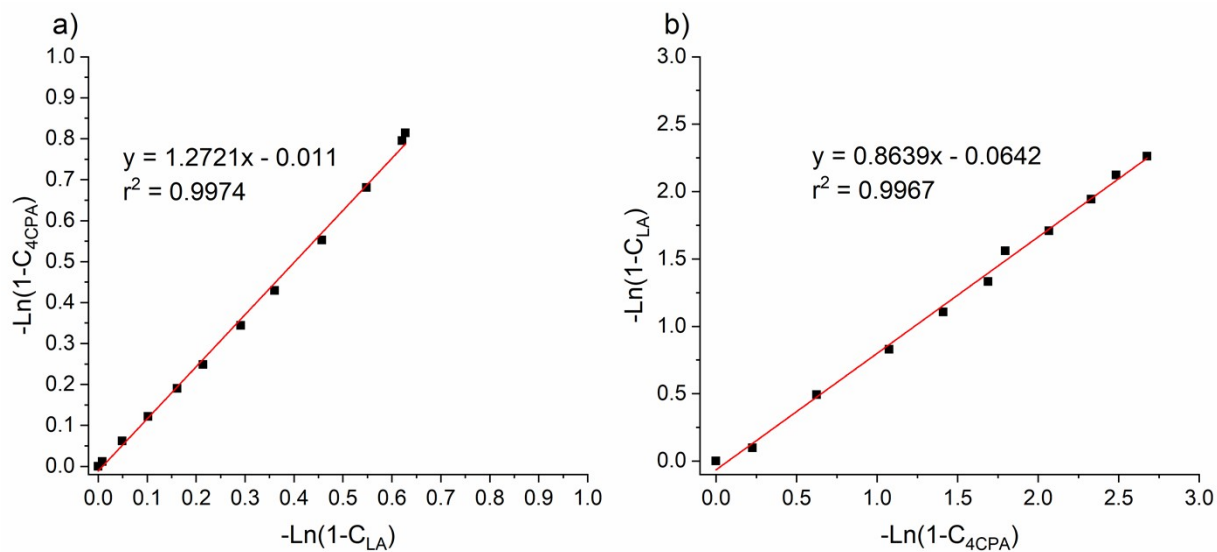


Figure S3. Jaacks plots of the copolymerization of 4CPA with LA. a) Excess 4CPA and b) excess LA.

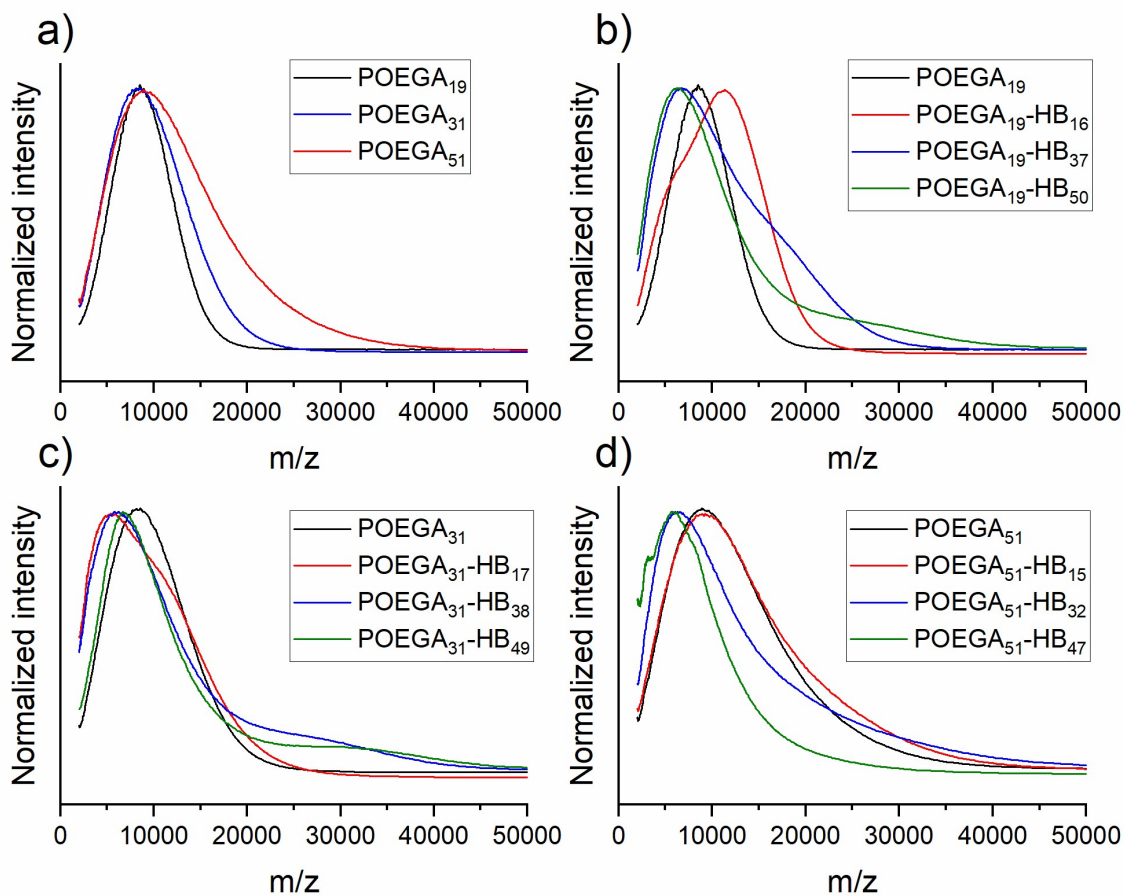


Figure S4. MALDI-ToF-MS spectra of a) POEGA macro-RAFT agents, b) POEGA₁₉ block copolymers, c) POEGA₃₁ block copolymers, and d) POEGA₅₁ block copolymers.

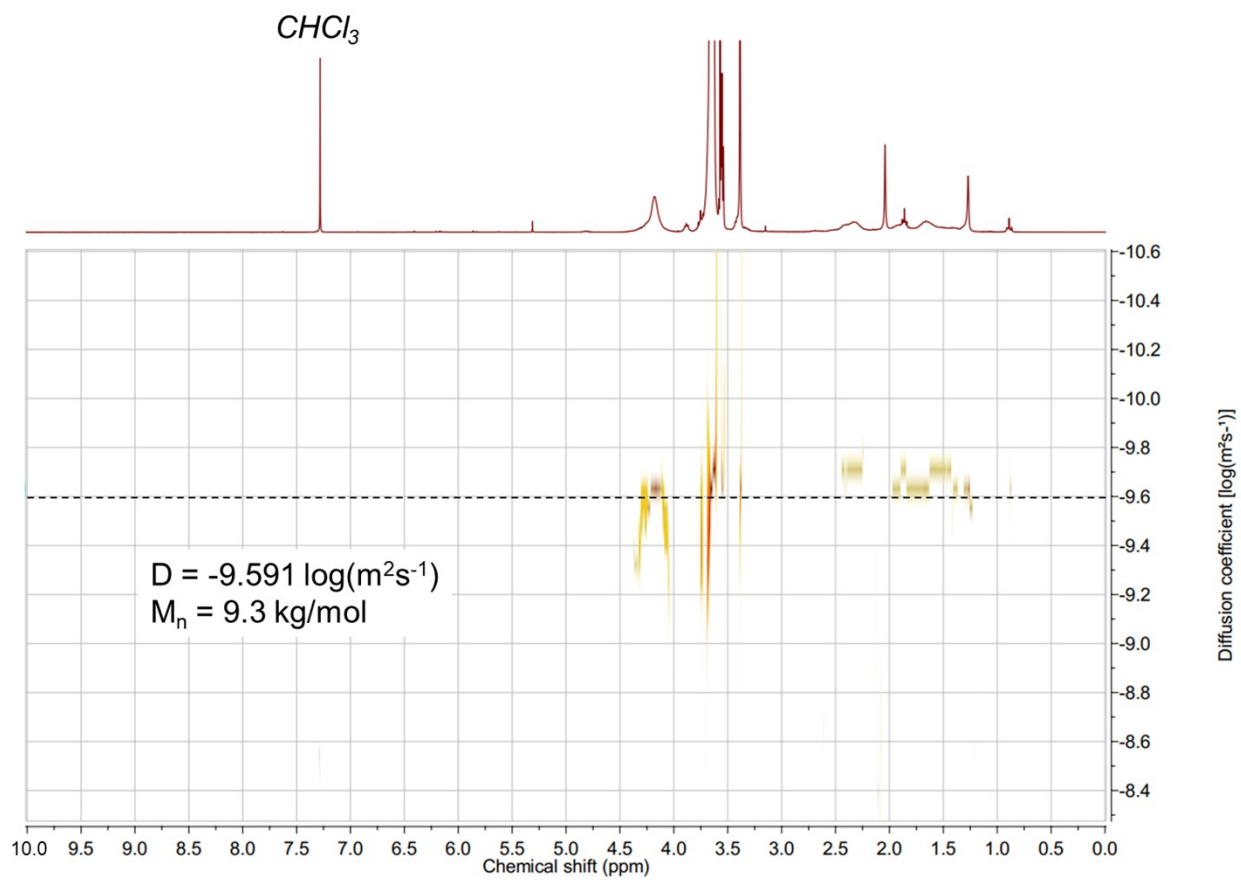


Figure S5. DOSY spectrum of POEGA₁₉.

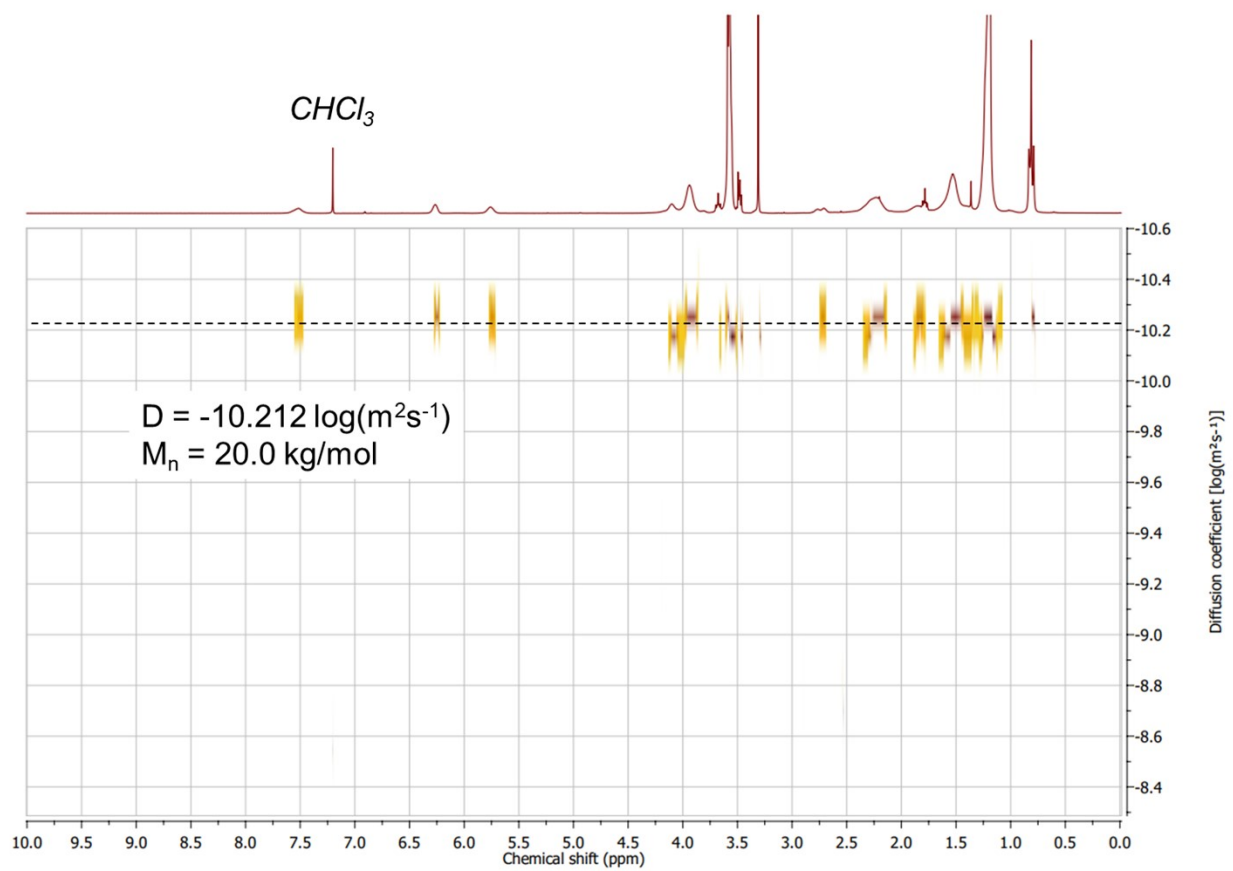


Figure S6. DOSY spectrum of POEGA₁₉-HB₅₀.

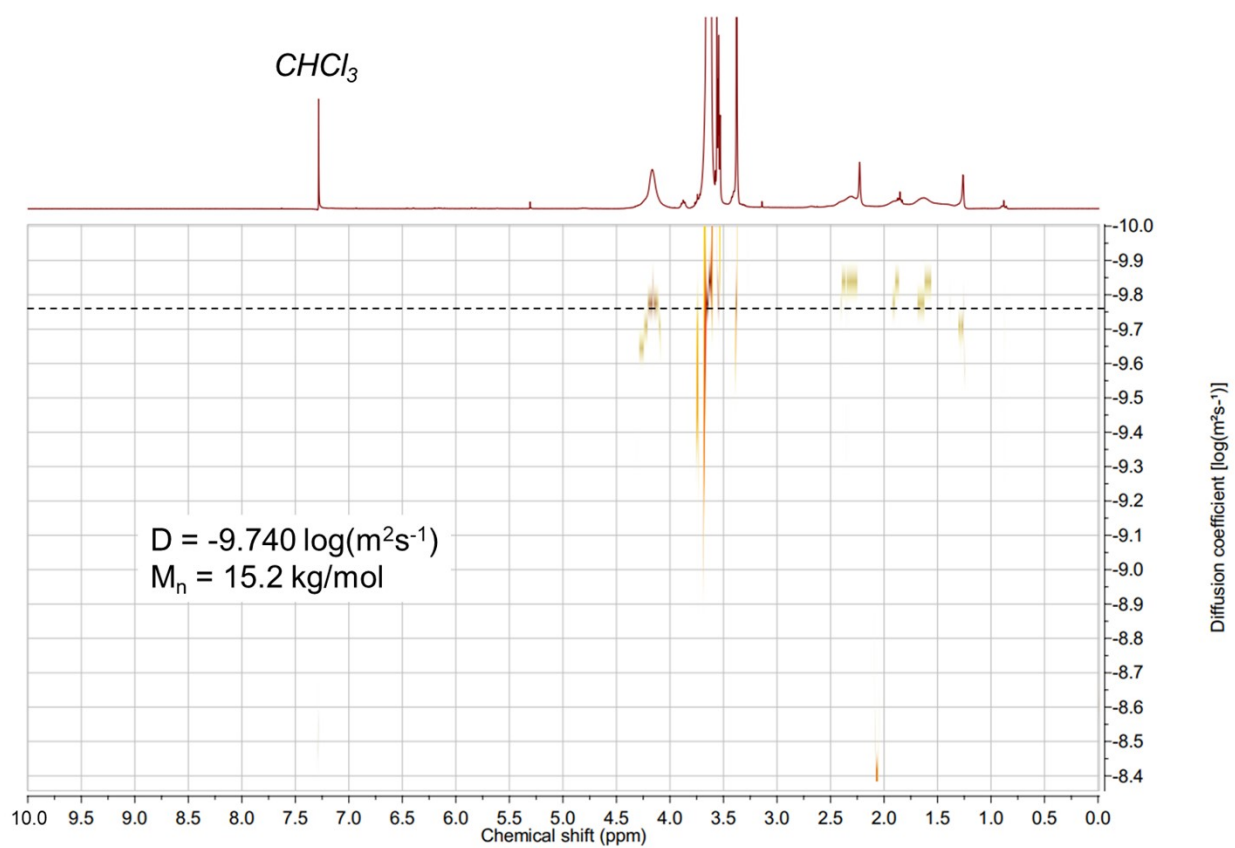


Figure S7. DOSY spectrum of POEGA₃₁.

Table S2. Results of the surface tension measurements of POEGA macro-RAFT agents and block copolymers.

Entry	$M_{n,th}$ (kg/mol)	CAC (mM)	CAC (mg/L)
POEGA ₁₉	9.3	0.0050	47
POEGA ₃₁	15.2	0.0028	43
POEGA ₅₁	24.3	0.0017	41
POEGA ₁₉ -HB ₁₆	12.8	0.0122	156
POEGA ₁₉ -HB ₃₇	17.1	0.0120	205
POEGA ₁₉ -HB ₅₀	20.0	0.0393	786
POEGA ₃₁ -HB ₁₇	18.9	0.0085	161
POEGA ₃₁ -HB ₃₈	23.3	0.0076	177
POEGA ₃₁ -HB ₄₉	25.7	0.0082	211
POEGA ₅₁ -HB ₁₅	27.6	0.0040	110
POEGA ₅₁ -HB ₃₂	31.2	0.0036	112
POEGA ₅₁ -HB ₄₇	34.5	0.0039	135

Table S3. DLS results for the prepared block-copolymers directly dissolved in water, and prepared via the solvent-switch method before dialysis (90/10 v/v% H₂O/THF) and after dialysis (100% H₂O).

Entry	Directly dissolved in H ₂ O			Prepared by solvent-exchange method					
	Peak 1 size (nm)	Peak 2 size (nm)	Đ	Before dialysis			After dialysis		
				Peak 1 size (nm)	Peak 2 size (nm)	PDI	Peak 1 size (nm)	Peak 2 size (nm)	Đ
POEGA ₁₉ -HB ₁₆	99	-	0.368	310	-	0.215	161	-	0.274
POEGA ₁₉ -HB ₃₇	29	167	0.470	45	-	0.554	27	-	0.181
POEGA ₁₉ -HB ₅₀	257	-	0.396	63	-	0.193	43	-	0.250
POEGA ₃₁ -HB ₁₇	104	-	0.294	219	-	0.210	88	-	0.455
POEGA ₃₁ -HB ₃₈	89	378	0.745	63	-	0.258	40	192	0.341
POEGA ₃₁ -HB ₄₉	67	813	0.703	47	-	0.189	36	-	0.220
POEGA ₅₁ -HB ₁₅	61	-	0.226	297	-	0.236	149	-	0.278
POEGA ₅₁ -HB ₃₂	69	264	0.429	42	260	0.634	29	198	0.506
POEGA ₅₁ -HB ₄₇	202	-	0.375	66	600	0.309	50	286	0.355

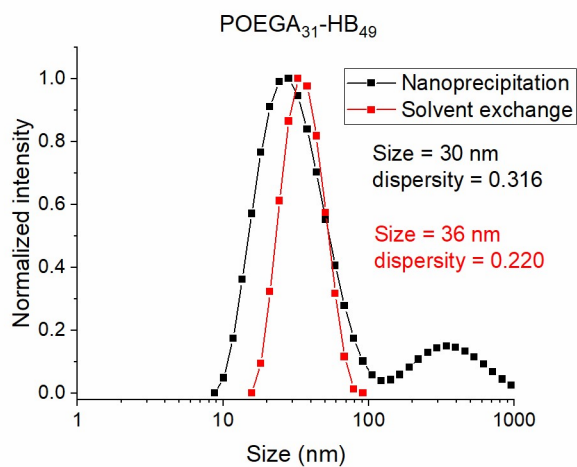


Figure S8. DLS results of POEGA₃₁-HB₄₉ micelles obtained via solvent exchange and nanoprecipitation.

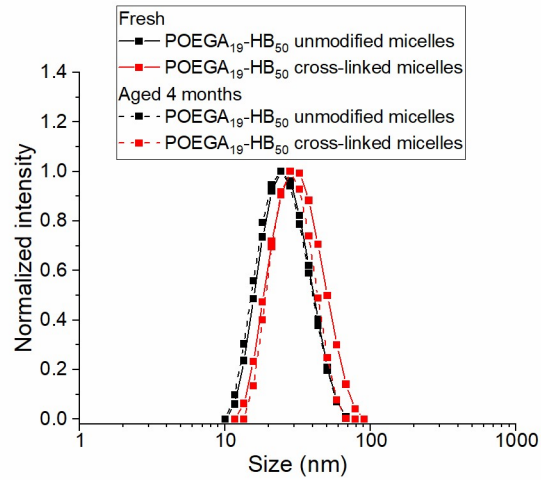


Figure S9. DLS results of unmodified micelles and cross-linked micelles obtained from block copolymer POEGA₁₉-HB₅₀ directly after preparation and after 4 months storage.

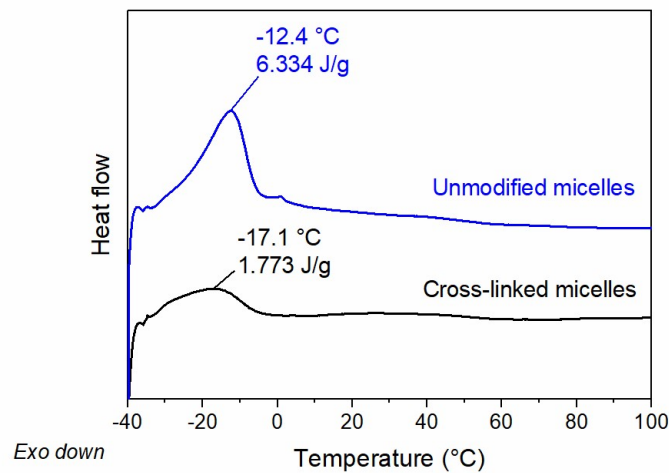


Figure S10. Overlay of the DSC traces of unmodified micelles (blue) and UV cross-linked micelles (black) of POEGA₁₉-HB₅₀.

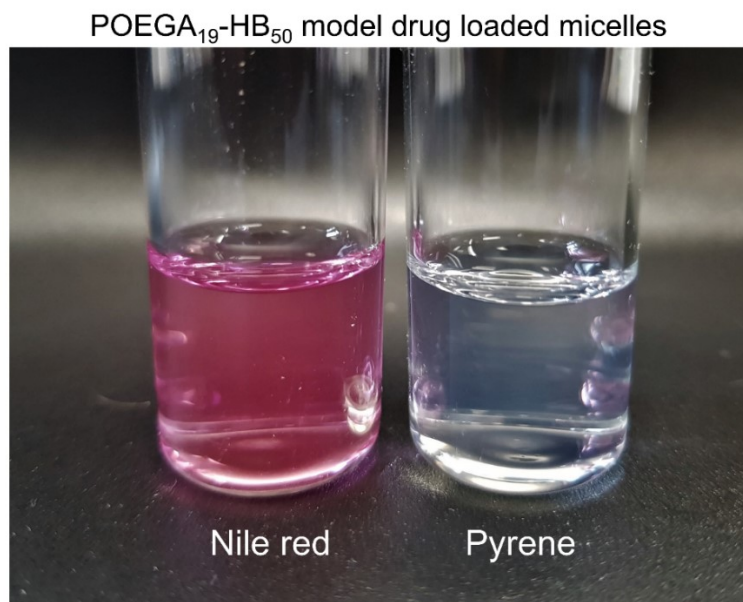


Figure S11. Photograph of Nile red and pyrene loaded micelles from block copolymer POEGA₁₉-HB₅₀.

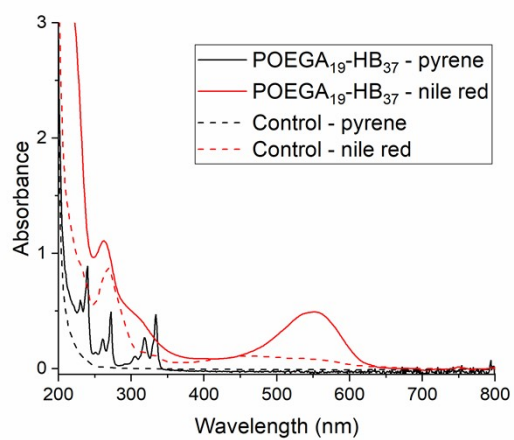


Figure S12. UV-Vis spectrum in methanol of pyrene and Nile red loaded micelles from POEGA₁₉-HB₃₇, and the control samples without block copolymer.

Table S4. Encapsulation efficiency for pyrene and Nile red.

Block copolymer	EE (pyrene) (%)	EE (Nile red) (%)
POEGA ₁₉ -HB ₁₆	2.2	2.4
POEGA ₁₉ -HB ₃₇	3.6	2.2
POEGA ₁₉ -HB ₅₀	3.7	1.8
POEGA ₃₁ -HB ₁₇	1.4	1.8
POEGA ₃₁ -HB ₃₈	2.1	1.1
POEGA ₃₁ -HB ₄₉	2.5	1.1
POEGA ₅₁ -HB ₁₅	0.5	1.4
POEGA ₅₁ -HB ₃₂	0.9	2.1
POEGA ₅₁ -HB ₄₇	1.5	1.5

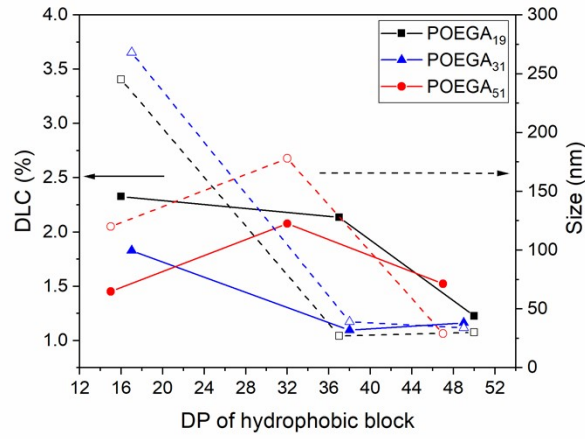


Figure S13. Investigation of the DLC and particle size in DLS of the Nile red loaded block copolymers as a function of the DP of hydrophobic block.

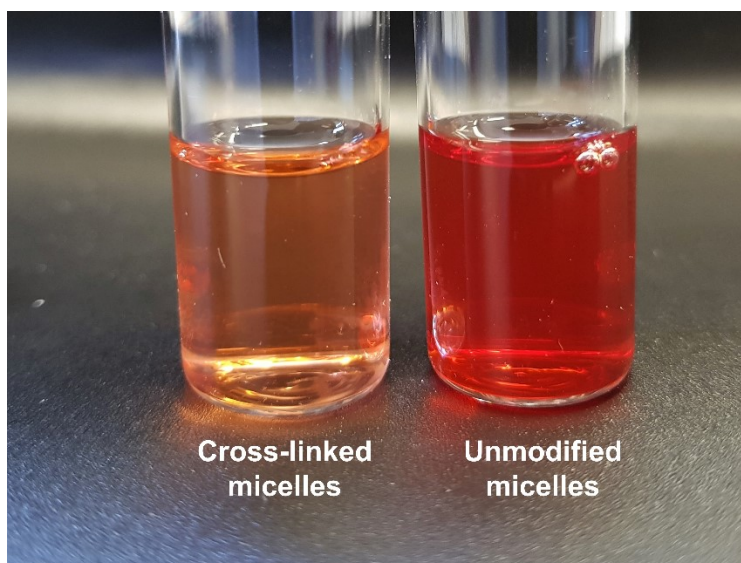


Figure S14. Photograph of the cross-linked and unmodified DOX loaded micelles from block copolymer POEGA₁₉-HB₅₀.

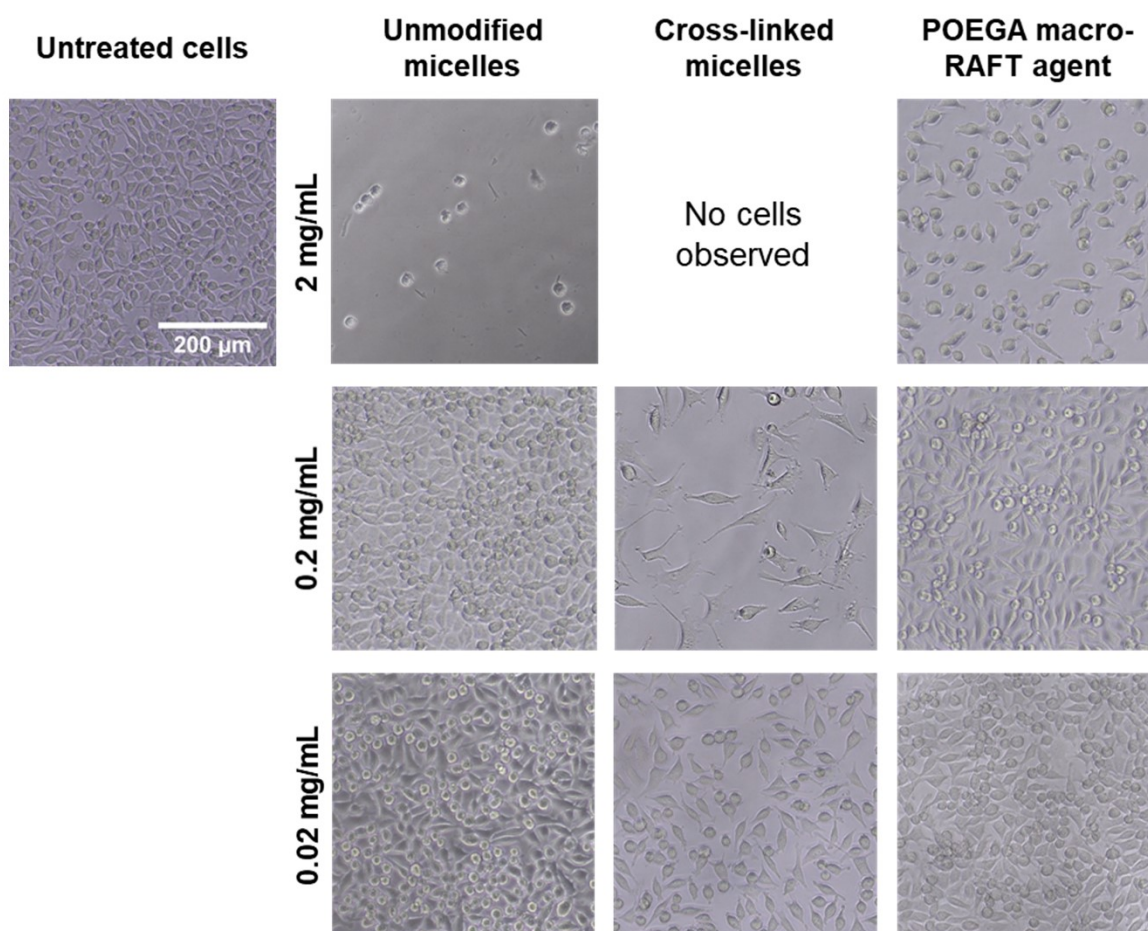


Figure S15. Microscope photographs of the L929 cell line incubated with unmodified micelles, cross-linked micelles and POEGA macro-RAFT agent at several concentrations for 72 hours.

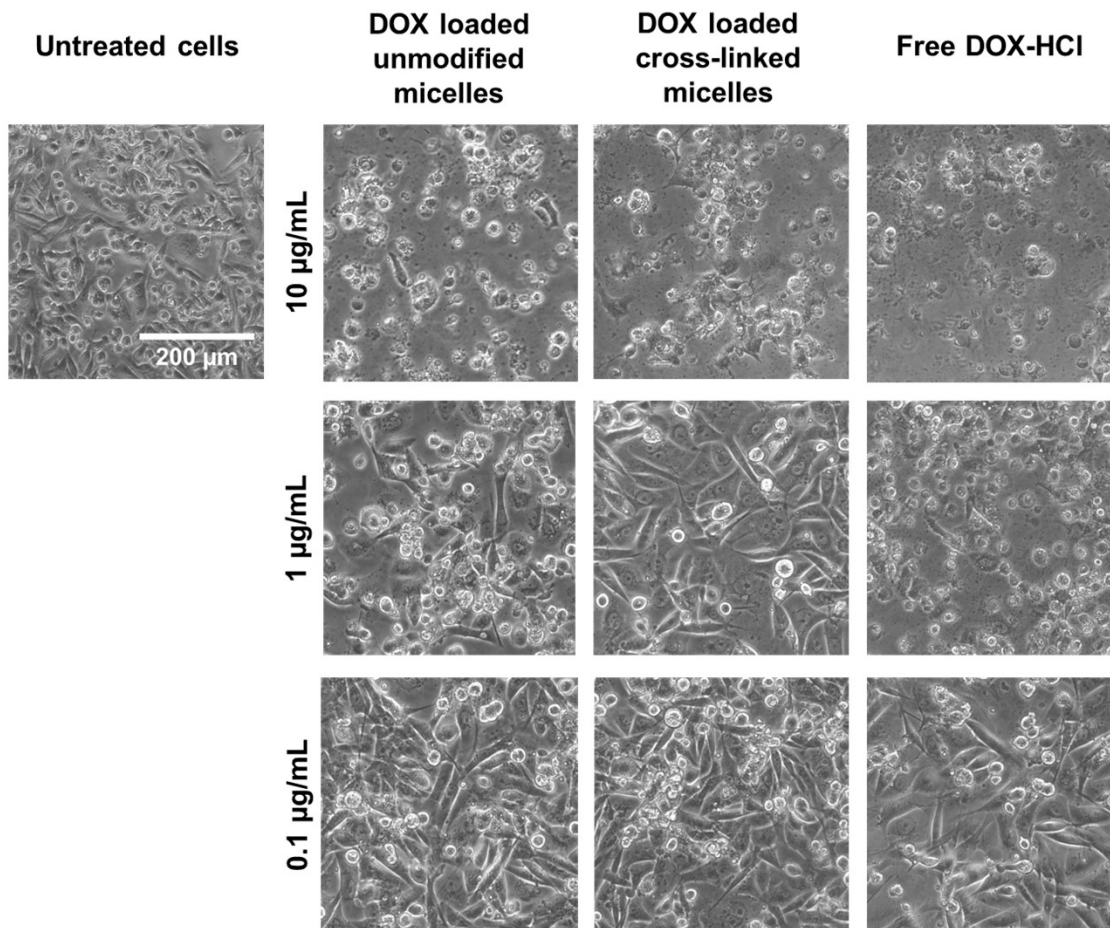


Figure S16. Microscope photographs of the MDA-MB-231 cell line incubated with DOX loaded unmodified micelles, cross-linked micelles and free DOX-HCl at several concentrations for 72 hours.