Supplementary Information

Double-hydrophilic block copolymers based on functional poly(ε-caprolactone)s for pH-dependent controlled drug delivery

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List of supplementary material

Table S1: Characterization of PEG-*b*-PCL diblock copolymers.

Copolymer	Targeted Mn for PCL block (g/mol)	Mn_{NMR} PEG[a] (g/mol)	Mn_{NMR} PCL[b] (g/mol)	Mn_{NMR} PEG-*b*-PCL (g/mol)	Mn_{SEC} (g/mol)	Đ	EG/CL[c]
$PEG_{4.9K}$-*b*-$PCL_{4.7K}$	5000	4900	4700	9600	9000	1.4	2.8
$PEG_{1.9K}$-*b*-$PCL_{1.9K}$	2000	1900	1900	3800	4500	1.4	2.5

[a] Calculated from the ^{1}H NMR spectra by comparison of the peak at 3.6 ppm of the methylene groups with the peak at 3.3 ppm of the terminal methyl group of PEG.

[b] Calculated from the ^{1}H NMR spectra by comparison of the peak at 3.6 ppm of the methylene groups of PEG with the peak at 4.0 ppm of the methylene group of PCL.

[c] Ratio of ethylene glycol / ε-caprolactone units as determined by ^{1}H NMR spectroscopy.

Table S2: Parameters study for the propargylation of PEG-*b*-PCL diblock copolymers

Entry	Starting copolymer	LDA (eq. / CL units)	PgBr (eq. / CL units)	SD[a] (%)	Mn_{NMR}[b] PCL (g/mol)	Đ	Yield (wt%)
1	$PEG_{1.9k}$-*b*-$PCL_{1.7K}$	1	2	26	1200	1.6	50%
2	$PEG_{1.9k}$-*b*-$PCL_{1.7K}$	1	2	28	1100	1.9	45%
3	$PEG_{1.9k}$-*b*-$PCL_{1.7K}$	0.5	2	15	1300	1.7	80%
4	$PEG_{1.9K}$-*b*-$PCL_{1.7K}$	0.5	2	16	1400	1.7	80%
5	$PEG_{1.9K}$-*b*-$PCL_{1.7K}$	1	2	25	1100	1.7	55%
6	$PEG_{1.9K}$-*b*-$PCL_{1.7K}$	0.5	2	17	1400	1.7	70%
7	$PEG_{1.9K}$-*b*-$PCL_{1.9K}$	0.5	2	18	1300	1.7	70%
8	$PEG_{1.9K}$-*b*-$PCL_{1.9K}$	0.5	2	15	1300	1.8	75%
9	$PEG_{4.9k}$-*b*-$PCL_{4.7K}$	1	2	17	2900	1.6	50%
10	$PEG_{4.9K}$-*b*-$PCL_{4.7k}$	0.5	2	8	3700	1.7	70%

[a] Substitution degree defined as the percentage of CL units substituted by alkyne groups, calculated from the ^{1}H NMR spectra by comparison of the peaks at 2.0 ppm and 2.4-2.6 ppm of the propargyl group with the peak at 4.1 ppm of the methylene group of PCL.

[b] Calculated from the ^{1}H NMR spectra by comparison of the peak at 3.6 ppm of the methylene groups of PEG with the peak at 4.1 ppm of the methylene group of PCL.

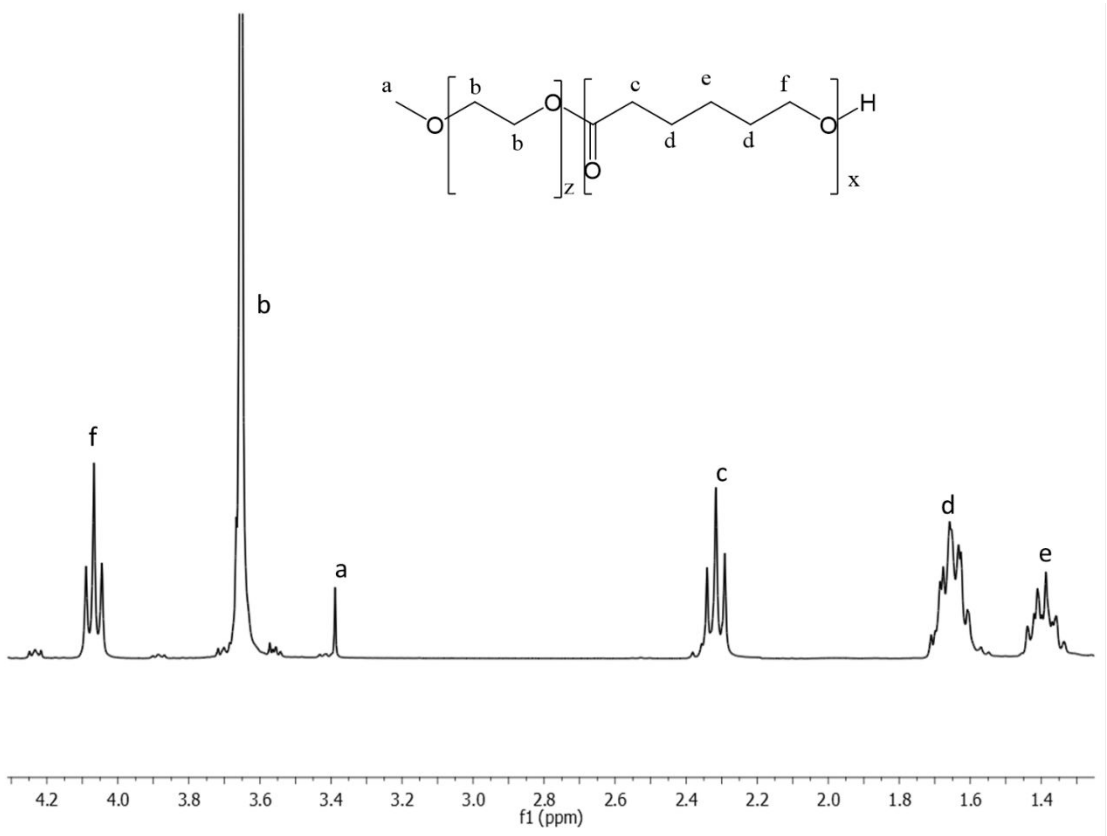

Figure S1: ^{1}H NMR (CDCl3) of $PEG_{1.9k}$-b-$PCL_{1.9k}$

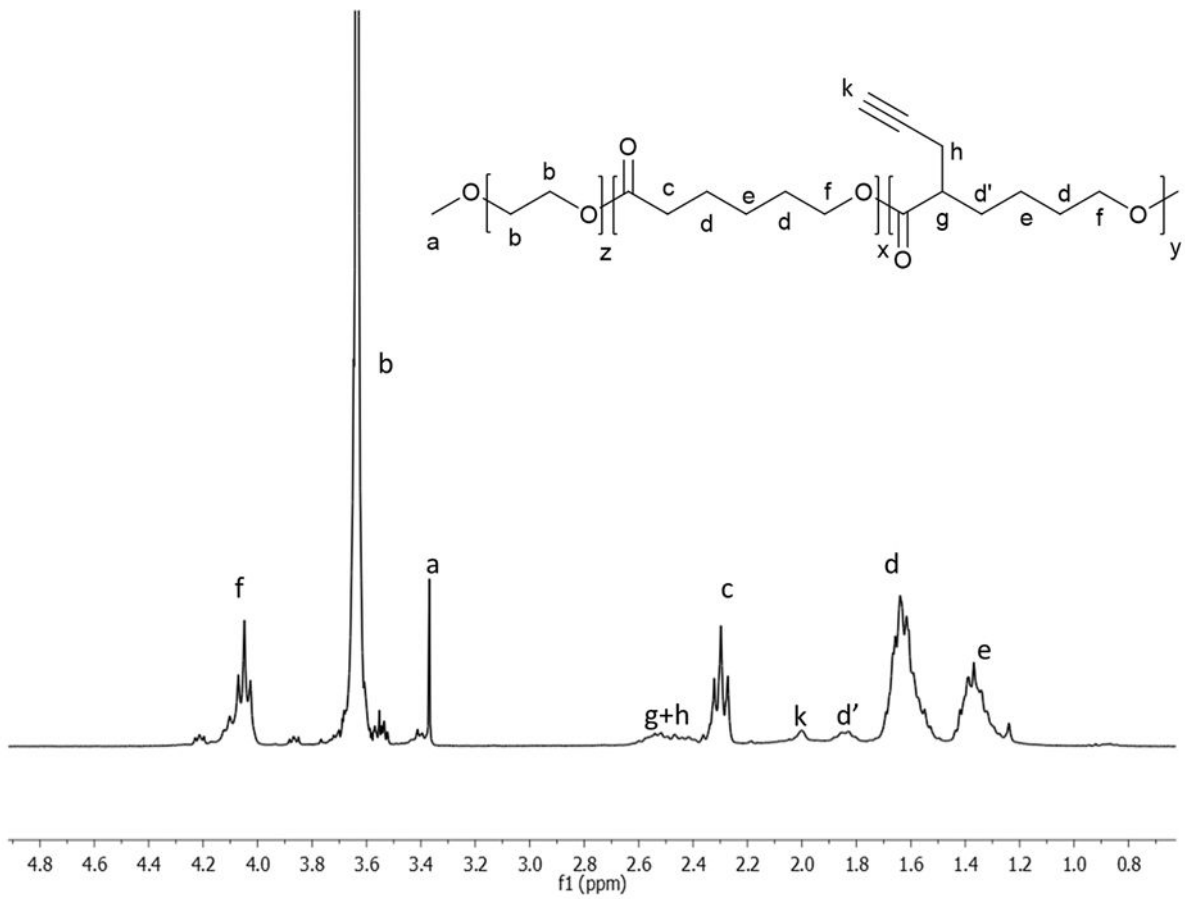

Figure S2: ^{1}H NMR (CDCl3) of $PEG_{1.9k}$-*b*-$PCL_{1.3k}(YNE)_{15}$

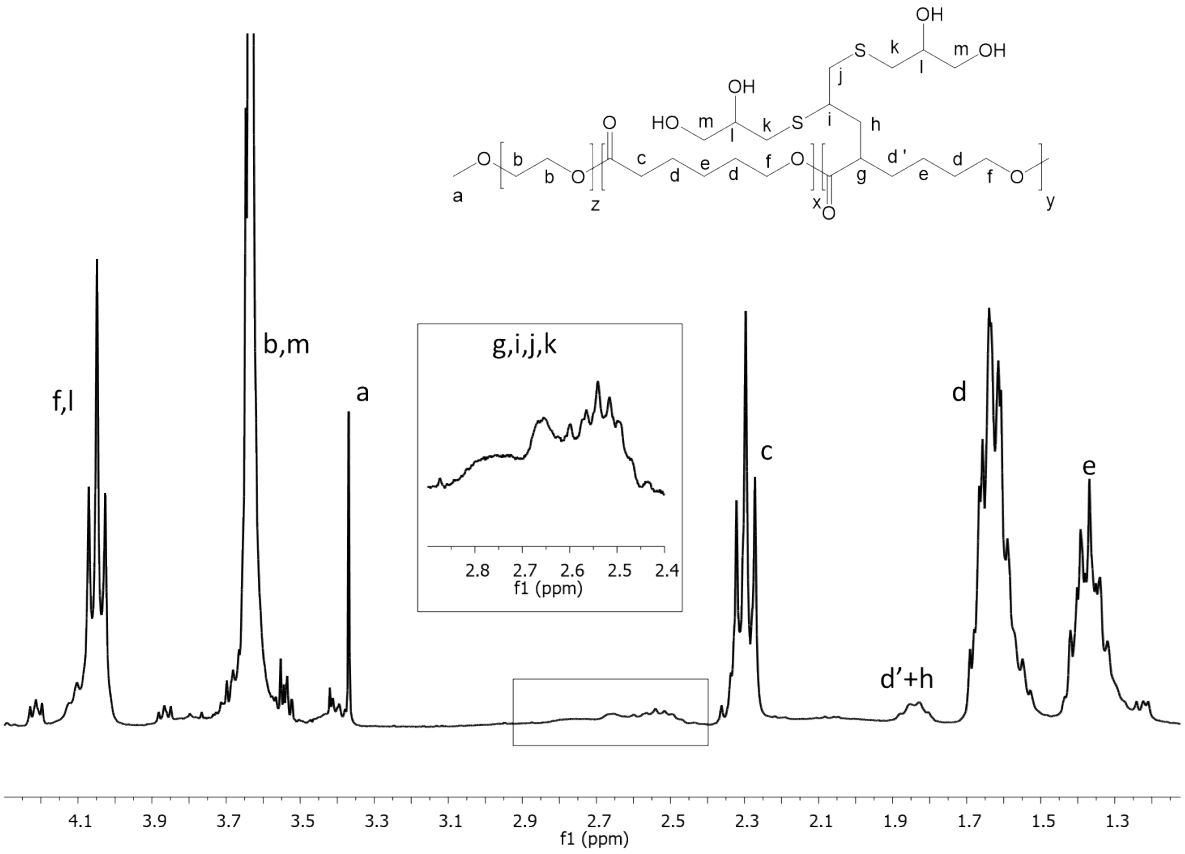

Figure S3: ^{1}H NMR ($CDCl_3$) of $PEG_{1.9k}$-*b*-$PCL_{1.1k}(OH)_{52}$

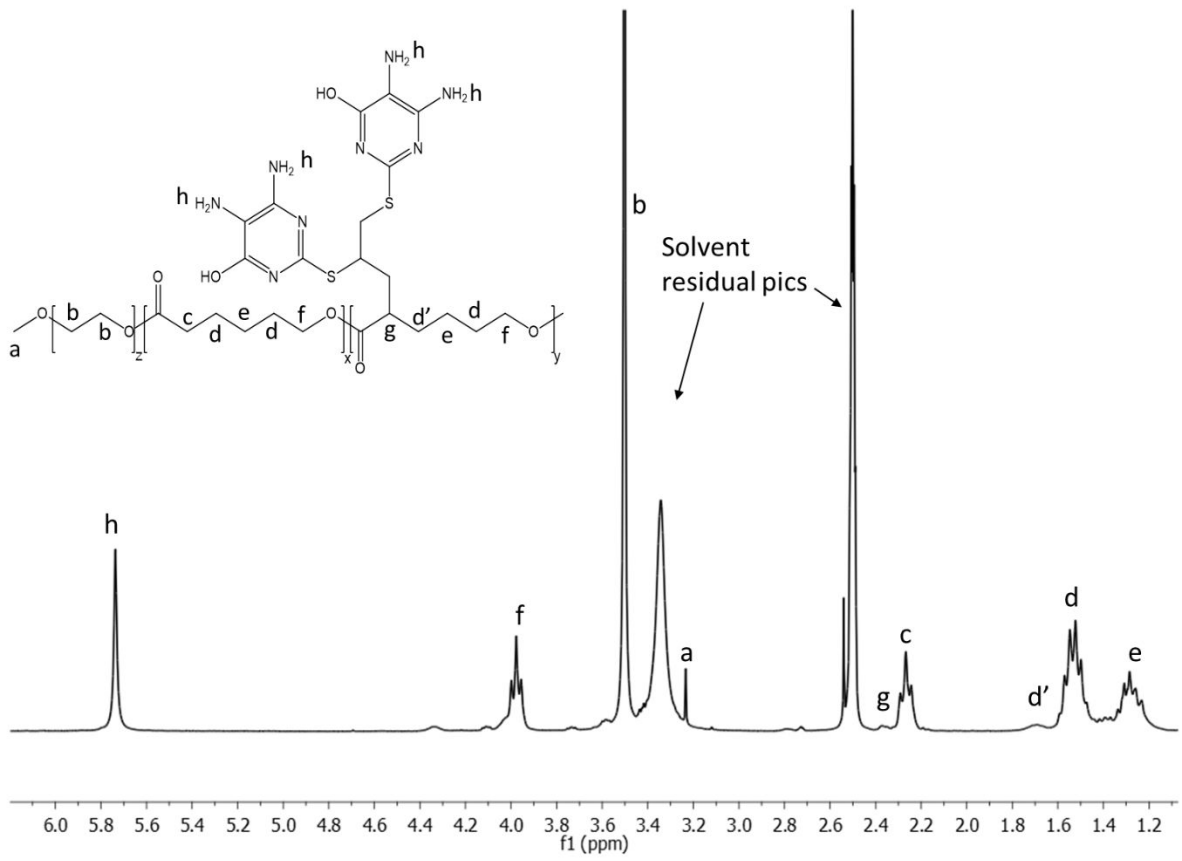

Figure S4: ^{1}H NMR ($DMSO_{d6}$) of $PEG_{1.8k}$-*b*-$PCL_{1.4k}(NH_2)_{58}$

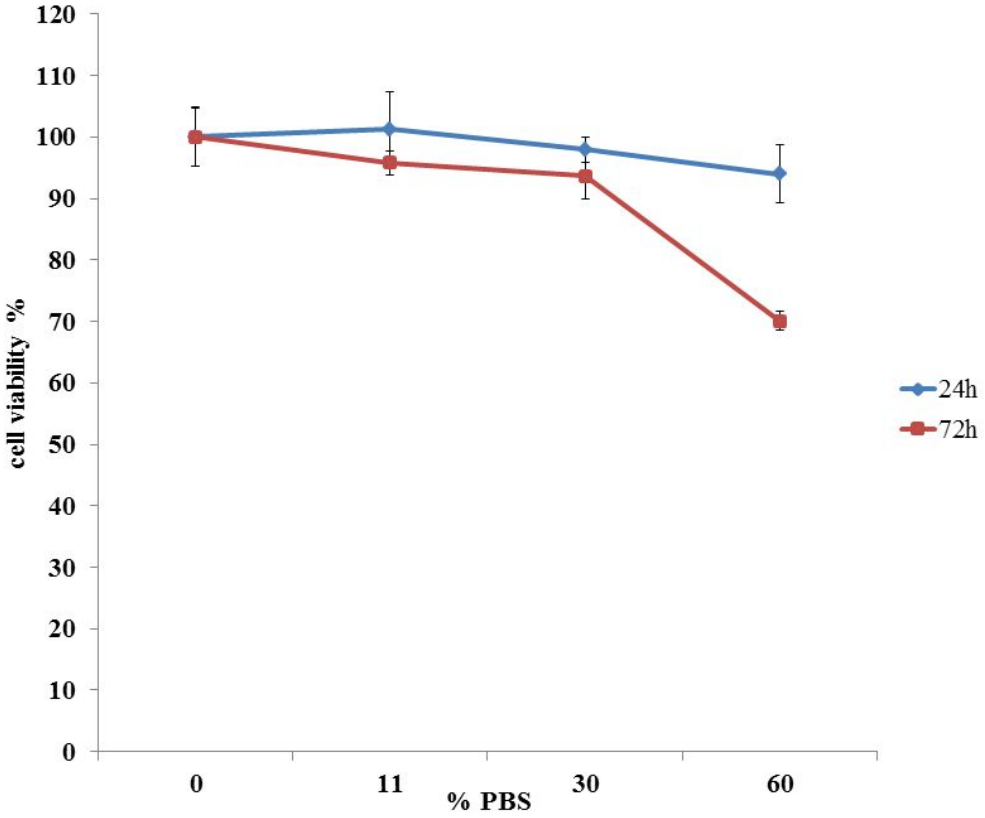

Figure S5: Dose dependent viability of MCF-7 cells in culture medium containing various PBS concentrations.