Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Blue LED-light activated RAFT polymerization of PEG acrylate with high chain end fidelity for efficient PEGylation

Alicia Rasines Mazo, [a] Thi Nga Tran, [b] Wenhao Zhang, [b] Yuwen Meng, [b] Amin Reyhani, [a] Sagrario Pascual, [b] Laurent Fontaine, [b] Greg Qiao, [a]* and Sandie Piogé [b]*

[a]*Polymer Science Group, The University of Melbourne, Department of Chemical and Biomolecular Engineering Melbourne, 3010 (Australia)*

[b]*Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS - Le Mans Université, Av O. Messiaen, 72085 Le Mans Cedex 9 (France)*

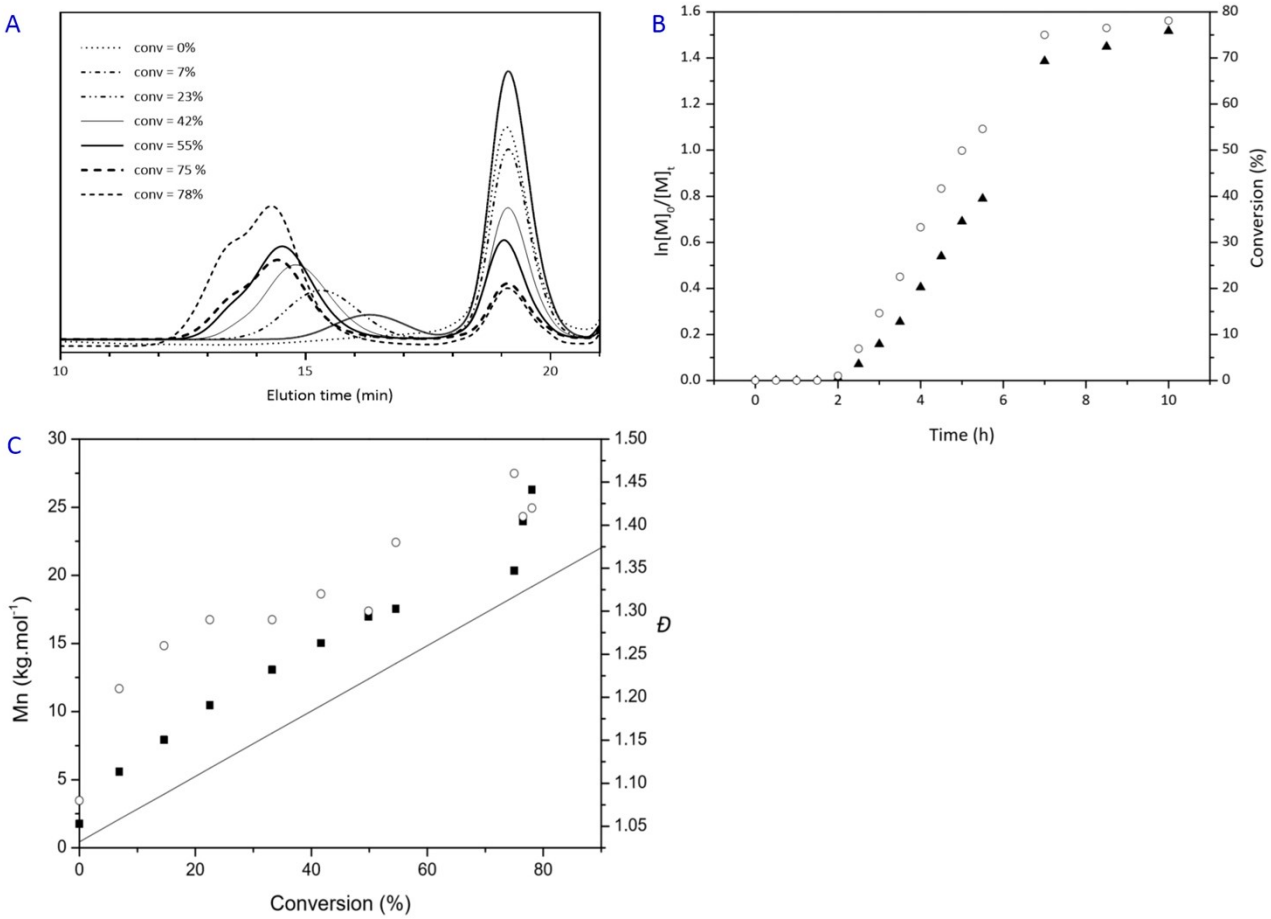


Fig. S 1. Overlaid SEC (THF) traces of PPEGA using RI detection obtained by UV-light-initiated RAFT polymerization of PEGA mediated through COPYDC ($[PEGA]_0/[COPYDC]_0$ = 50/1), without initiator, in DMF ([PEGA]0 = 42 wt %) at room temperature and at different conversions (A). Evolution of ln([M]0/[M]t) (▲) and conversion (○) versus time, (B) Evolution of $M_{n,\,SEC}^{-}$ (■) and $M_{n,\,theo}^{-}$ (line) (A) and Đ (○) obtained by SEC (THF) versus PEGA conversion during the RAFT polymerization of PEGA (C).

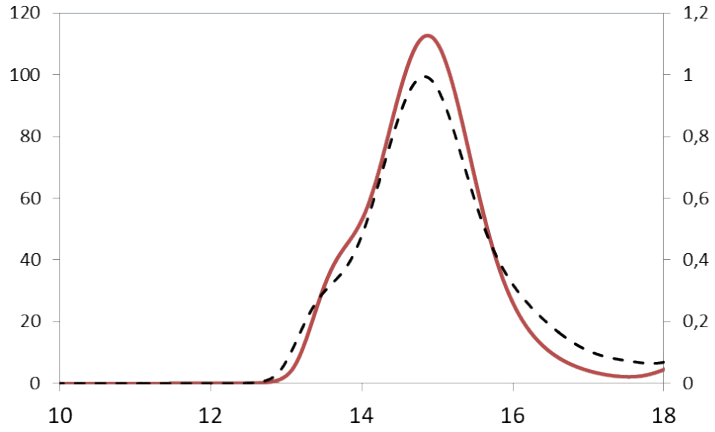


Fig. S 2. Overlaid SEC (THF) traces of PPEGA using RI detection (—) and UV detection at 310 nm (---) obtained by UV-light-initiated RAFT polymerization of PEGA mediated through Irgacure 2959 and COPYDC at final time. ($[PEGA]_0/[COPYDC]_0/[Irgacure]_0$ = 50/1/0.1) in DMF at room temperature at $[PEGA]_0$ = 42 wt %.

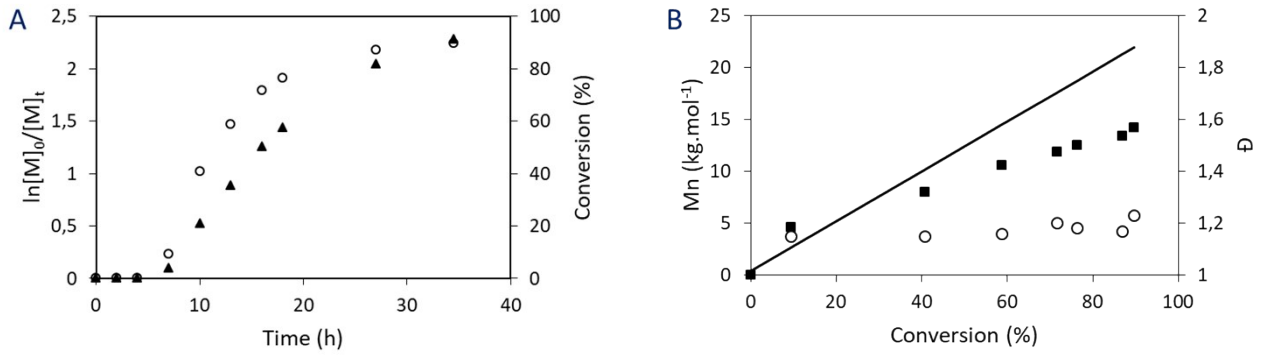


Fig. S 3. (A) Evolution of $\ln([M]_0/[M]_t)$ (▲) and conversion (○) *versus* time, (B) Evolution of $M_{n,\,SEC}^{-}$ (■) and $M_{n,\,theo}^{-}$ (line) (A) and *Đ* (○) obtained by SEC (THF) *versus* PEGA conversion during the blue LED-light initiated RAFT polymerization of PEGA mediated through COPYDC in DMF at room temperature ($[PEGA]_0/[COPYDC]_0 = 50/1$, $[PEGA]_0 = 67$ wt %).

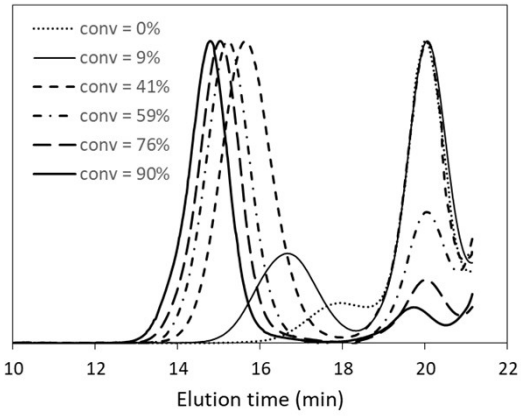


Fig. S 4. Overlaid SEC (THF) traces of PPEGA using RI detection obtained by Blue LED-light initiated RAFT polymerization of PEGA mediated through COPYDC ($[PEGA]_0/[COPYDC]_0 = 50/1$) in DMF at room temperature at $[PEGA]_0 = 67$ wt %.

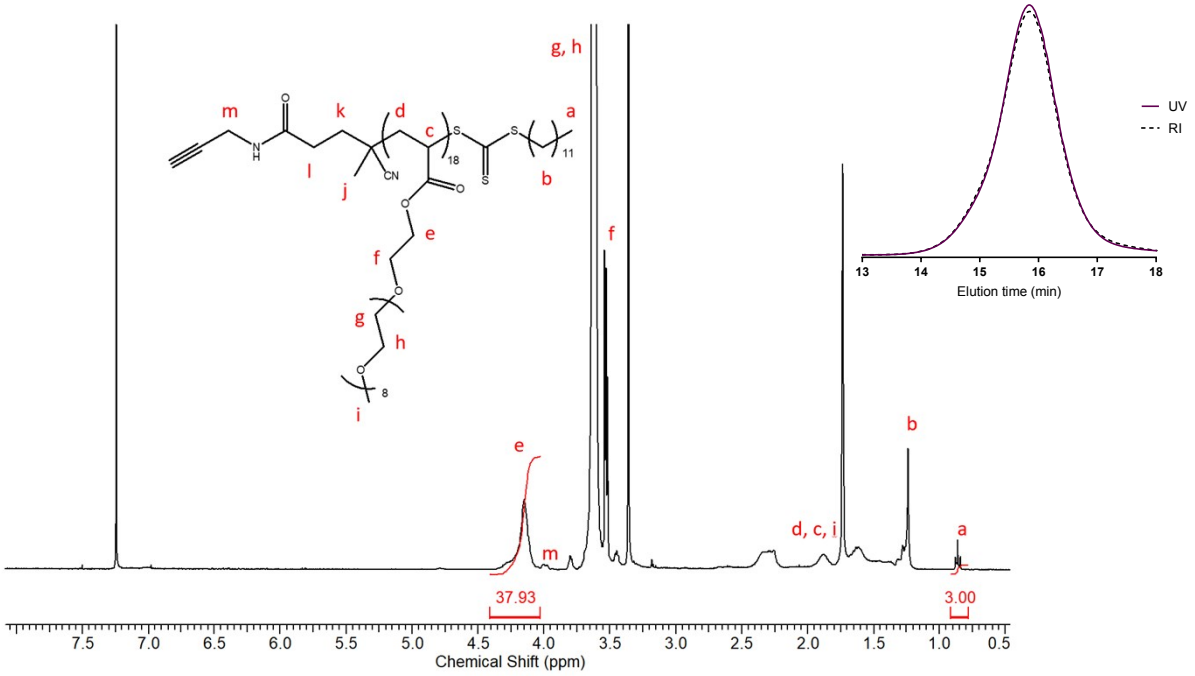
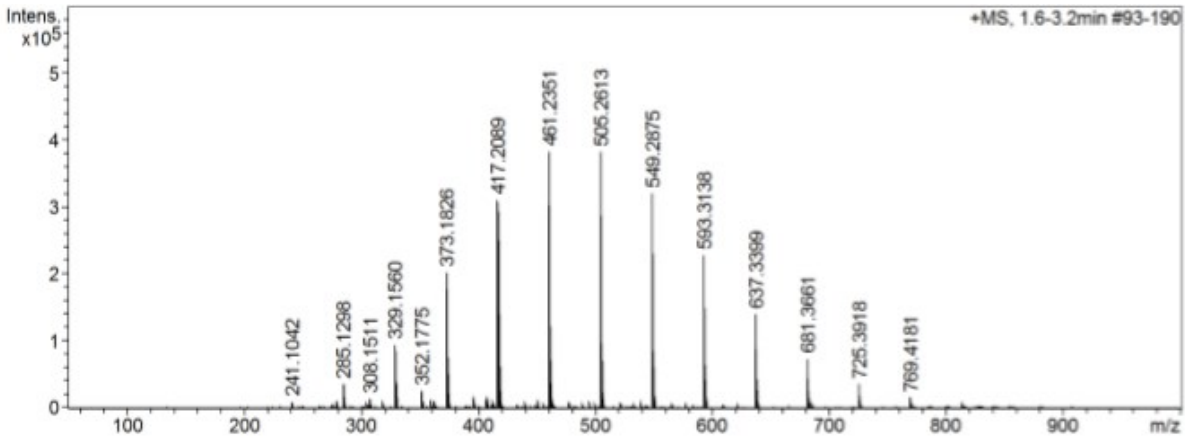


Fig. S 5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Blue-LED-PPEGA$_{18}$ synthesized by Blue LED-light-initiated RAFT polymerization of PEGA with COPYDC ($[PEGA]_0/[COPYDC]_0 = 20/1$, $[PEGA]_0 = 67$ wt %) in DMF at room temperature. Overlaid SEC traces (DMF) traces of purified Blue-LED-PPEGA$_{18}$ (Table S1, entry 3) using RI detection (line) and UV-vis detection (dash line) at 309 nm obtained by Blue LED-light initiated RAFT polymerization of PEGA and COPYDC ($[PEGA]_0/[COPYDC]_0 = 20/1$, $[PEGA]_0 = 67$ wt %)).



Meas. m/z	m/z	Adduct	Ion Formula	err [ppm]	err [mDa]	mSigma
417.2089	417.2095	M+Na	C18H34NaO9	1.4	0.6	19.0
461.2351	461.2357	M+Na	C20H38NaO10	-1.4	-0.6	3.0
477.2087	477.2097	M+K	C20H38KO10	2.0	1.0	111.5
505.2613	505.2619	M+Na	C22H42NaO11	-1.3	-0.6	0.6
521.2346	521.2359	M+K	C22H42KO11	-2.5	-1.3	116.2
549.2875	549.2881	M+Na	C24H46NaO12	-1.2	-0.7	1.1
565.2609	565.2621	M+K	C24H46KO12	2.2	1.2	160.5

Fig. S 6. Q-TOF Analysis of commercial oligo(ethylene glycol) acrylate PEGA monomer.

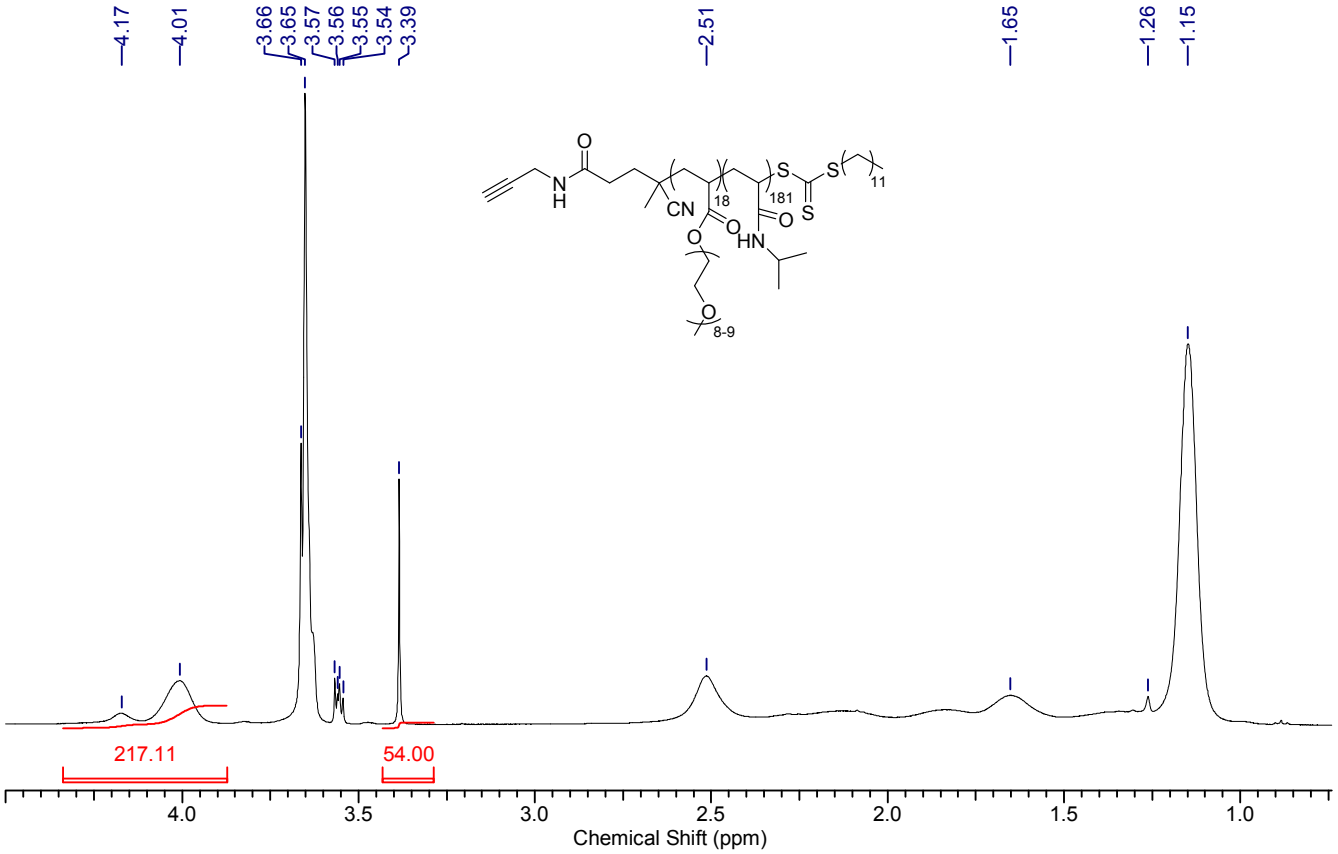


Fig. S 7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified Blue-LED-PPEGA$_{18}$-*b*-PNIPAM$_{181}$ (Table S1, entry 6) synthesized by chain extension of Blue-LED-PPEGA$_{18}$ with NIPAM. The polymerization was mediated by Blue-LED-PPEGA$_{18}$ and initiated by LAP such that $[NIPAM]_0/[PPEGA_{18}]_0/[LAP]_0$ = 204/1/0.3 in water at 25 wt%.

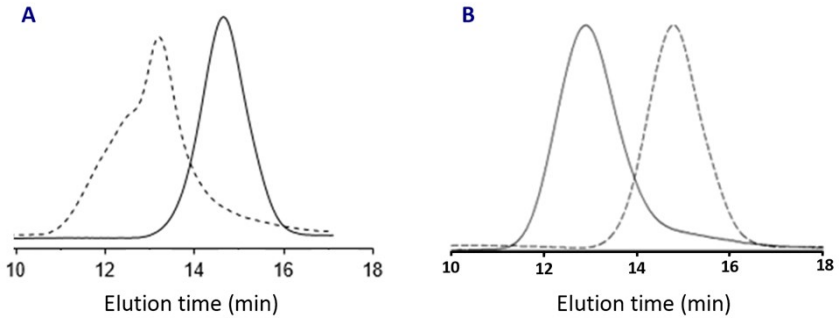


Fig. S 8. RI SEC trace evolution (DMF+LiBr) of chain extension experiments with $[NIPAM]_0/[PPEGA_{18}]_0/[I]_0 = 204/1/0.1$ activated using a thermal RAFT polymerization and ACVA as initiator (70°C) process at 2.4% wt % (A); and irradiated by UV-light using Irgacure 2959 as initiator at room temperature (B).

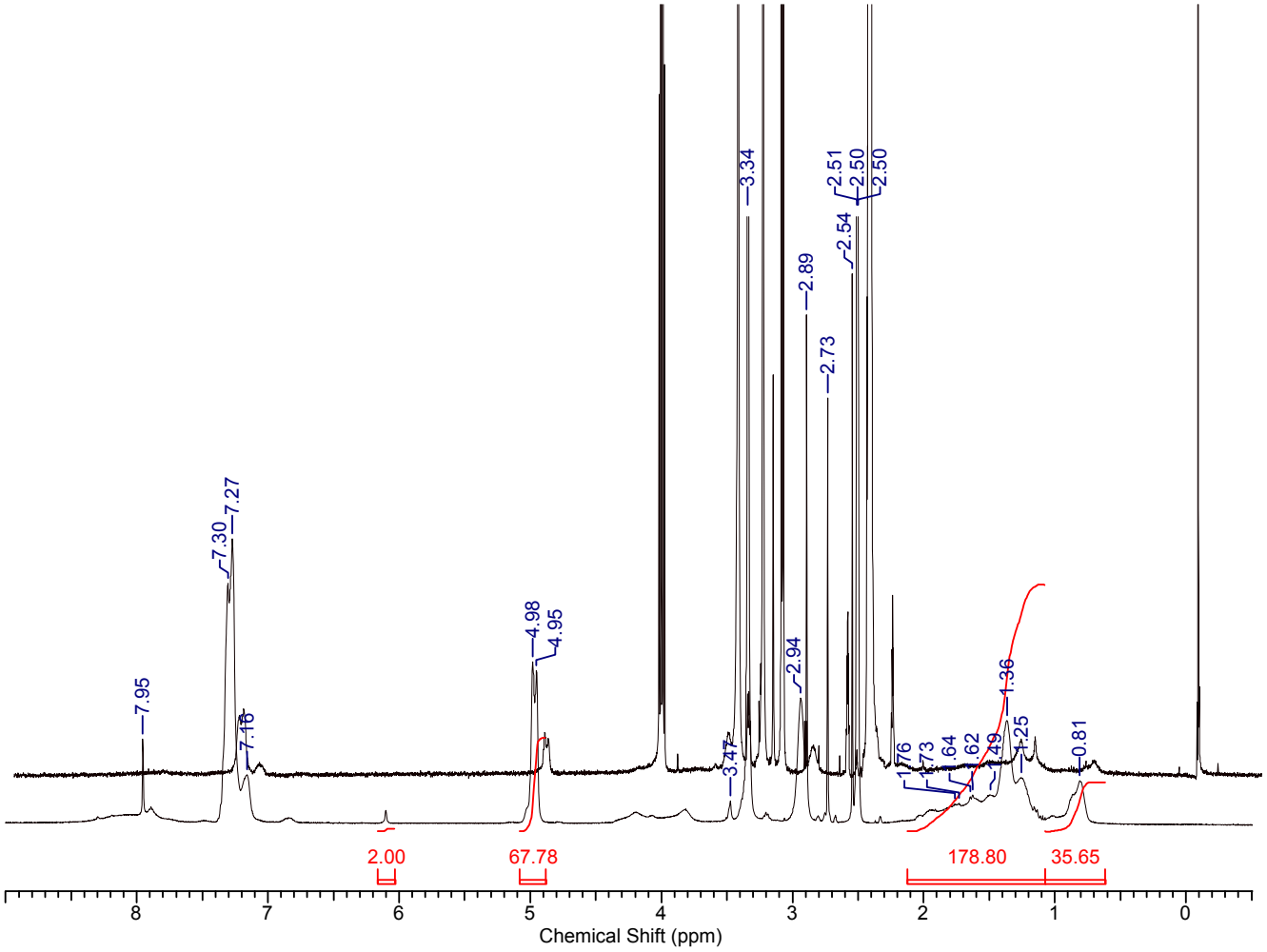


Fig. S 9. Overlaid ^{1}H NMR spectra (400 MHz, d_6-DMSO) of P(ZLL-co-DLV)-lys-N_3 (front) and P(ZLL-*co*-DLV)-*g*-PPEGA$_{26}$ (back)

TABLE S1. Macromolecular characteristics of PPEGAs and PPEGA-*b*-PNIPAMs synthesized by RAFT polymerization.

PEGA polymerization carried out at 42 wt. %. The extension was carried out in water ($[NIPAM]_0/[PPEGA]_0/[I]_0$ = 204/1/0.3 at (A) 2.4 wt% or (B) 25 wt%).

Entry	Target compound	$[PEGA]_0/[COPYDC$ or $PPEGA]_0/[I]_0$	Initiator (I)	T (°C)	Time (h)	Conv. (%)[a]	$DP_{n,PEGA,NMR}$[b]	$M_{n,theo}$[c] ($g.mol^{-1}$)	$M_{n,SEC}$[d] ($g.mol^{-1}$)	$Đ$[d]
1	Thermal-$PPEGA_{20}$	50/1/0.1	ACVA	70	2	42	20	10040	8500	1.23
2	UV-$PPEGA_{20}$	50/1/0.1	Irgacure 2959	R.T.	1.45	35	18	9080	8500	1.25
3	Blue-$PPEGA_{20}$	20/1/--	--	R.T	45	89	18	9080	9700	1.16
		Initiating source				Conv. (%)[e]	$DP_{n,NIPAM,NMR}$[f]	$M_{n,theo}$[g] ($g.mol^{-1}$)	$M_{n,SEC}$[h] ($g.mol^{-1}$)	$Đ$[h]
4[A]	Thermal-$PPEGA_{20}$-*b*-$PNIPMAM_{204}$	Temperature	V50	70	6	99	200	32640	41200	1.56
5[A]	UV-$PPEGA_{18}$-*b*-$PNIPAM_{204}$	UV-light irradiation	Irgacure 2959	R.T.	1.05	98	201	31793	56400	1.34
6[B]	Blue-$PPEGA_{18}$-*b*-$PNIPAM_{204}$	Blue-LED irradiation	LAP	R.T.	22	91	181	29560	66900	1.21

[a] Determined by ^{1}HNMR spectroscopy (400 MHz, $CDCl_3$) by comparing the integration values of the formamide proton of DMF at 8.02 ppm and of the alkene protons of PEGA between 5.7 and 6.5 ppm.

[b] Determined by ^{1}HNMR spectroscopy (400 MHz, $CDCl_3$) by comparing the integration values of the methyl protons $SCH_2(CH_2)_{10}CH_3$ of the dodecyl chains (3 protons) with the methyl protons $C(=O)OCH_2CH_2O(CH_2CH_2O)_8CH_3$ (3n protons) and the methylene protons $HC{\equiv}CCH_2NH$ (2 protons).

[c] $M_{n,\,theo} = \frac{[PEGA]_0}{[COPYDC]_0} \times conv \times M_{PEGA} + M_{COPYDC}$ where conv is the conversion determined by ^{1}H NMR spectroscopy, $M_{,PEGA}$ is the number-average molar mass of PEGA ($M_{n,}$ = 480 $g.mol^{-1}$) and M_{COPYDC} = 440 $g.mol^{-1}$.

[d] Determined by SEC in THF using PS equivalents.

[e] Determined by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) by comparing the integration values of the formamide proton of DMF at 8.02 ppm and of the alkene protons of NIPAM between 5.7 and 6.5 ppm.

[f] Determined by ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$) by comparing the integration values of the methyl protons $((CH_2CH_2O)_8CH_3$ of the PEGA chains (3n protons) with the methine protons $(-NH-CH(CH_3)_2$ of PNIPAM (1) after subtraction of the methylene protons belonging to PPEGA.

[g] $M_{n,\,theo} = \frac{[NIPAM]_0}{[PPEGA]_0} \times conv \times M_{NIPAM} + M_{n,PPEGA}$ where conv is the conversion determined by ^{1}H NMR spectroscopy, M_{NIPAM} is the molar mass of NIPAM and $M_{n,\,PPEGA}$ is the number-average molar mass of PPEGA.

[g] Determined by SEC in DMF using PMMA equivalents.