Supporting Information

Aqueous copper(II) photoinduced polymerization of acrylates: Low copper concentration and the importance of sodium halide salts

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Materials

All materials were purchased from Sigma Aldrich and used as received unless otherwise stated.

Tris[2-(dimethylamino)ethyl]-amine (Me_6TREN) was synthesized according to literature procedure (Ciampolini, M.; Nardi, N., *Inorg. Chem.* **1966,** *5* (1), 41-44) and stored under nitrogen and refrigerated prior to use.

The water soluble initiator 2,3-dihydroxypropyl 2-bromo-2-methyl propanoate was synthesized according to literature procedure (Perrier, S., Armes, S. P., Wang, X. S., Malet, F. and Haddleton, D. M., *J. Polym. Sci. A Polym. Chem.* **2001** *39*, 1696–1707).

Hydroxyethyl acrylate was purified according to a procedure by Matyjaszewski *et al.* (Coca, S.; Jasieczek, C. B.; Beers, K. L.; Matyjaszewski, K., *J. Polym. Sci., Part A: Polym. Chem.* **1998** *36,* 1417-1424).

HPLC grade water (H_2O, VWR international, LLC) was used as the solvent for all polymerizations.

Sodium bromide (NaBr) 99+% (dry wt.) was purchased from Alfa Aesar and used as received.

Instruments and analysis

NMR spectra were recorded on Bruker AV-300 and DPX-400 spectrometers using deuterated solvent (D_2O) purchased from Sigma-Aldrich. Monomer conversion was calculated by comparison of vinyl protons (5.8-6.5 ppm) with methyl ether protons (3.36 ppm.)

Size exclusion chromatography was conducted on a Varian 390-LC system using DMF as the Mobile phase with 5 mM NH_4BF_4 additive (50 ^oC). The system was equipped with Refractive index, viscometer and UV detectors, 2 PLgel 5 mm mixed-D columns (300 x 7.5 mm), 1 PLgel 5 mm guard column (50 x 7.5 mm) and autosampler. The system was calibrated using commercial linear poly(methyl methacrylate) standards (200 Da – 1 x 10^6 Da). Samples were filtered through a plug of neutral alumina followed by filtration through 0.45 μm PTFE filter prior to analysis.

Aqueous SEC was conducted on an Agilent Technologies Infinity 1260 MDS instrument equipped with differential refractive index (DRI) and UV detectors. The column set used were Agilent PLAquagel OH30 * 2 and a 5 μm Aquagel guard column. 0.1 M NaNO3 was used as the mobile phase and column oven and detector temperatures were regulated to 35°C, at a flow rate 1 mL/min. Poly(ethyleneoxide) standards (Agilent EasyVials) were used for

calibration (100-30,000 g mol^{-1}). Samples were filtered through a hydrophilic membrane with 0.22 µm pore size before injection.

The UV source used for all polymerizations was a UV nail gel curing lamp (λ_{max} ~ 365 nm) with four 9 Watt bulbs (figure S1).

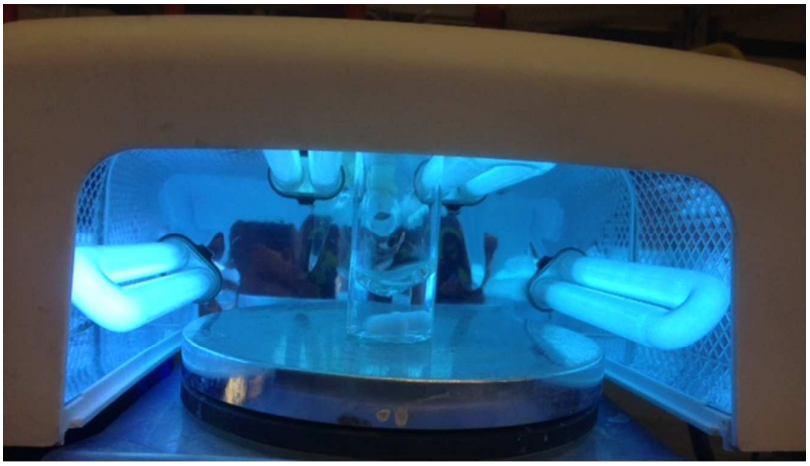


Figure S1: photo of UV lamp used for polymerizations.

Experimental

Example photoinduced polymerization in the presence of sodium bromide (targeted DP_n = 20)

A 20ml vial containing 140 mg of NaBr was charged with a 4 ml aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (0.51 mg/mL) and a stirrer bar. 14.6 µL of Me_6Tren was added via microliter syringe prior to the addition of 4 mL of poly(ethylene glycol methyl ether) acrylate and 66.7 µL of ethyl α-bromoisobutyrate (EBiB). The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time the vial was placed in a UV nail lamp with a stirrer (see figure S1). After 8 hours the reaction was sampled and analysed by proton NMR and SEC.

Example kinetic analysis (polymerization in the presence of sodium bromide (targeted DP_n = 20)

A 20ml vial containing 140 mg of NaBr was charged with a 4 ml aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (0.51 mg/mL) and a stirrer bar. 14.6 µL of Me_6Tren was added via microliter syringe prior to the addition of 4 mL of poly(ethylene glycol methyl ether) acrylate and 66.7 µL of ethyl α-bromoisobutyrate (EBiB). The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time

the vial was placed in a UV nail lamp with a stirrer (see figure S1). Sampling was performed under a positive pressure of nitrogen at regular intervals (30, 60, 90, 120, 180, 240 and 300 minutes). All samples were diluted in cold D_2O and stored in foil wrapped vials immediately after sampling in order to stop polymerization.

Example temporal control experiment

A reaction was set up as described above, and degassed in a darkroom. The reaction mixture was placed in a UV nail lamp with stirring. After 45 minutes the reaction was removed from the UV lamp, sampled under a positive pressure of nitrogen and placed on a stirrer in a darkroom. After one hour the solution was sampled and again placed in the UV lamp. This process was repeated for a total of 285 minutes of exposure to light. All samples were diluted in cold D_2O and stored in foil wrapped vials immediately after sampling in order to stop polymerization.

Polymerization of sulfopropyl acrylate potassium salt (targeted DP_n = 20)

A vial containing 133 mg of NaBr was charged with 2 mL aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (0.96 mg/mL) and a stirrer bar. 13.8 μL of Me_6Tren was added via microliter syringe prior to the addition of 2 g of sulfopropyl acrylate potassium salt and 63.1 mg of water soluble initiator, 2,3-dihydroxypropyl 2-bromo-2-methyl propanoate. The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time the vial was placed in a UV nail lamp with a stirrer (see figure S1).

Polymerization of $PEGMA_{500}$ (targeted DP_n = 20)

A 20ml vial containing 133 mg of NaBr was charged with a 4 ml aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (0.48 mg/mL) and a stirrer bar. 17.5 mg of TPMA was added prior to the addition of 4 mL of poly(ethylene glycol methyl ether) methacrylate and 63.4 μL of ethyl α-bromoisobutyrate (EBiB). The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time the vial was placed in a UV nail lamp with a stirrer (see figure S1). After 8 hours the reaction was sampled and analysed by proton NMR and SEC.

Chain extension

A 20ml vial containing 280 mg of NaBr was charged with a 4ml aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (1.02 mg/mL) and a stirrer bar. 29.1 μL of Me_6Tren was

added via microliter syringe prior to the addition of 4 mL of poly(ethylene glycol methyl ether) acrylate and 133.3 μL of ethyl α-bromoisobutyrate (EBiB). The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time the vial was placed in a UV nail lamp with a stirrer (see figure S1). After 6 hours the reaction was sampled and analysed by proton NMR and SEC. A degassed aliquot of 4 mL of PEGA in 4 mL of water was then transferred into the reaction vessel which was subsequently placed into the UV lamp overnight.

Chain extension of PPEGA with HEA

A 20ml vial containing 280 mg of NaBr was charged with a 4ml aliquot of stock solution of Cu(II)Br_2 in HPLC grade water (1.02 mg/mL) and a stirrer bar. 29.1 μL of Me_6Tren was added via microliter syringe prior to the addition of 4 mL of poly(ethylene glycol methyl ether) acrylate and 133.3 μL of ethyl α-bromoisobutyrate (EBiB). The vial was fitted with a rubber septum and deoxygenated by bubbling with nitrogen for 15 minutes. After this time the vial was placed in a UV nail lamp with a stirrer (see figure S1). After 6 hours the reaction was sampled and analysed by proton NMR and SEC. 4.16 mL of a degassed 50% (v/v) aqueous solution of HEA (20 eq. rel. to PPEGA) with 4.08 mg of Cu(II)Br_2 and 14.6 μL of Me_6Tren was then added to the reaction mixture via degassed syringe and placed into the UV lamp and left to react overnight.

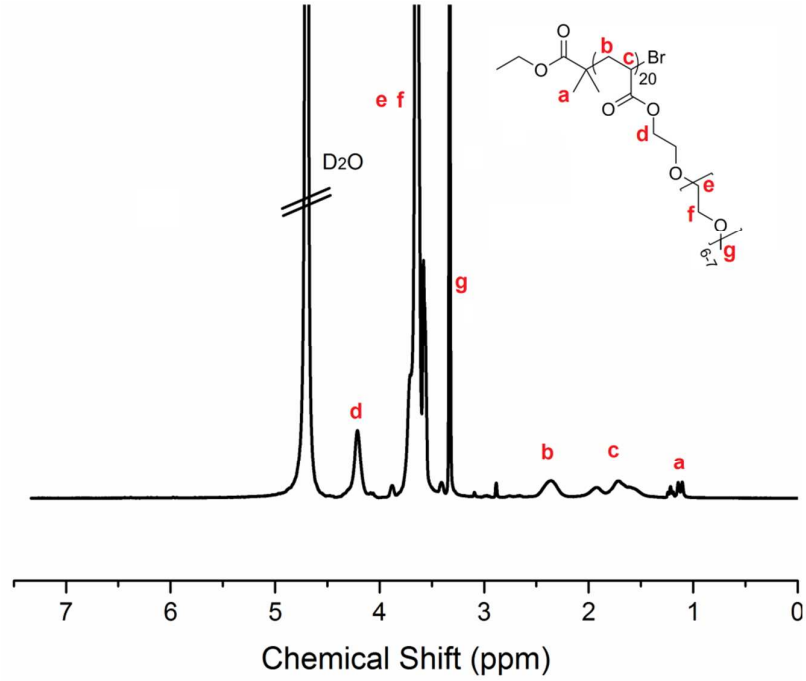
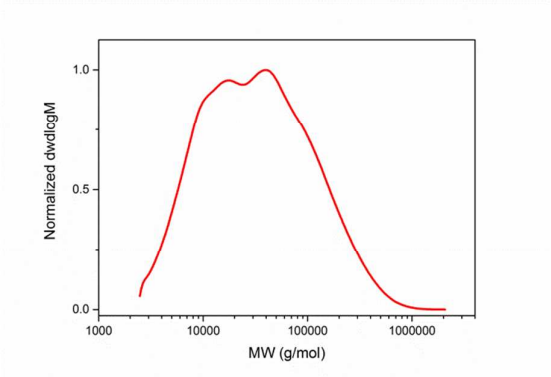
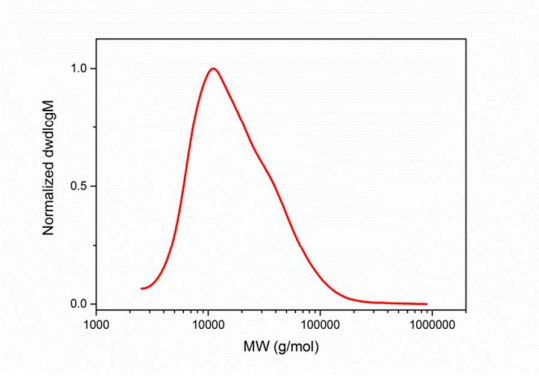


Figure S2: Proton NMR of poly(PEGA), (entry 11, table 1)

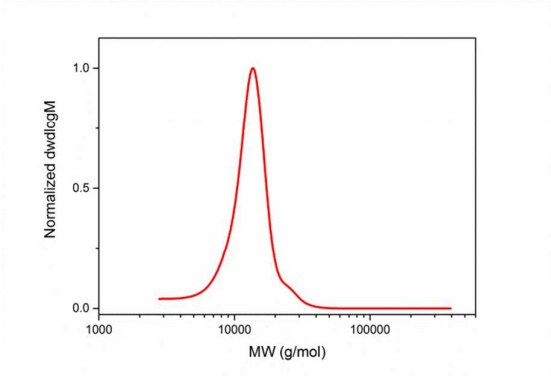
Supplementary SEC traces from table 1



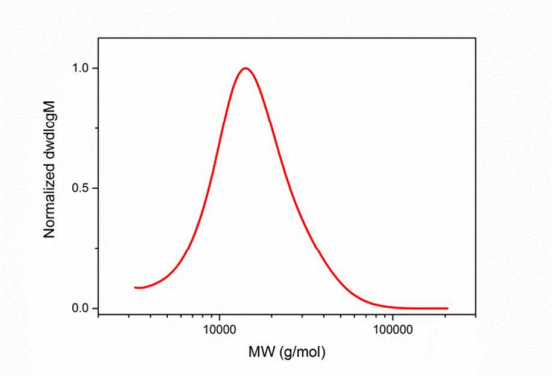
(a) entry 1, table 1



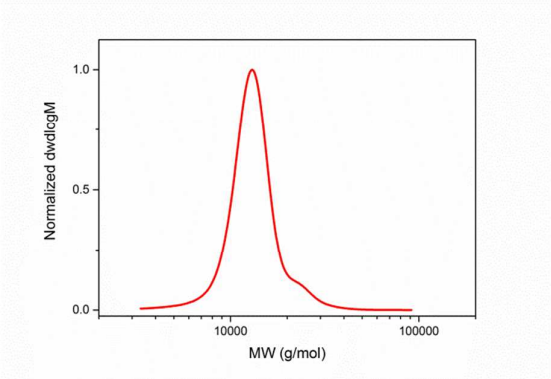
(b) entry 2, table 1



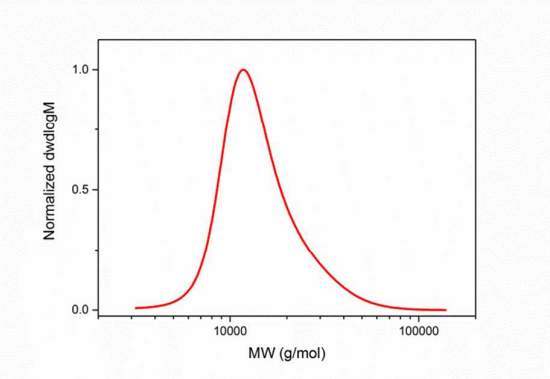
(c) entry 3, table 1



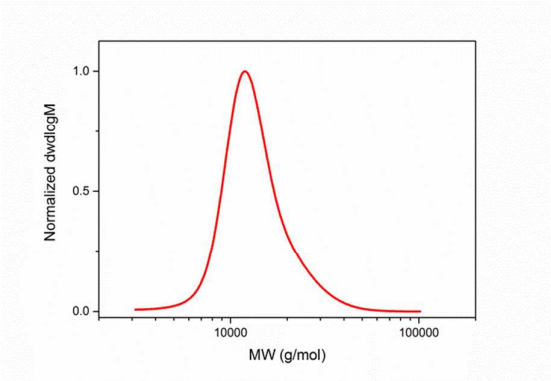
(d) entry 6, table 1



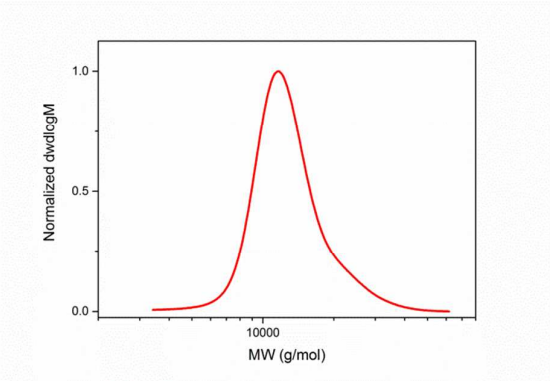
(e) entry 7, table 1



(f) entry 8, table 1



(g) entry 9, table 1



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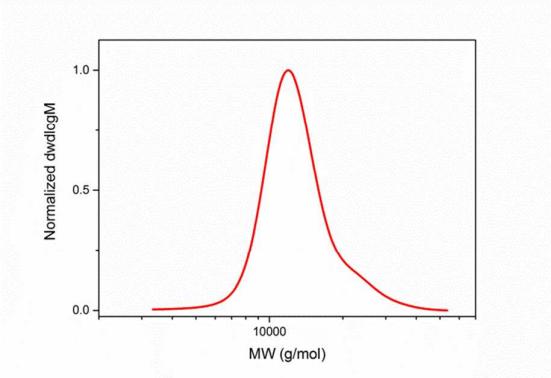
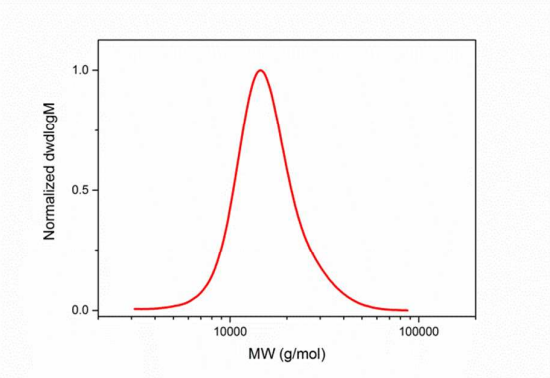
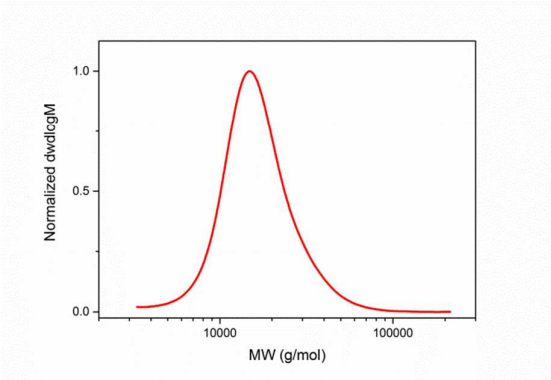


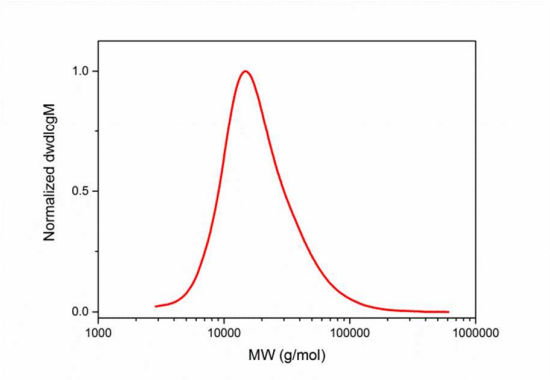
(i) entry 11, table 1



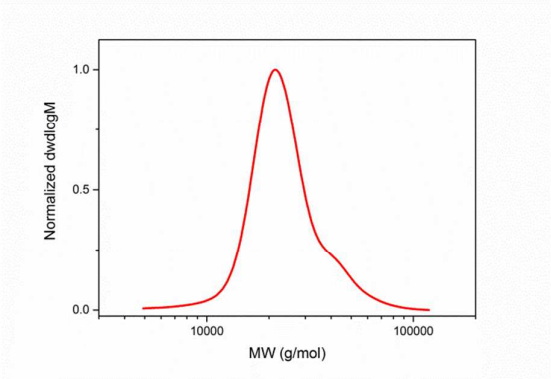
(j) entry 12, table 1



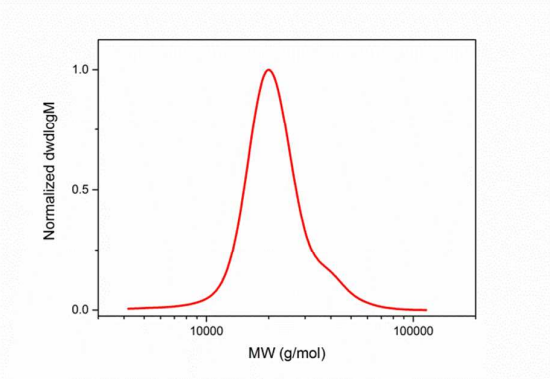
(k) entry 13, table 1



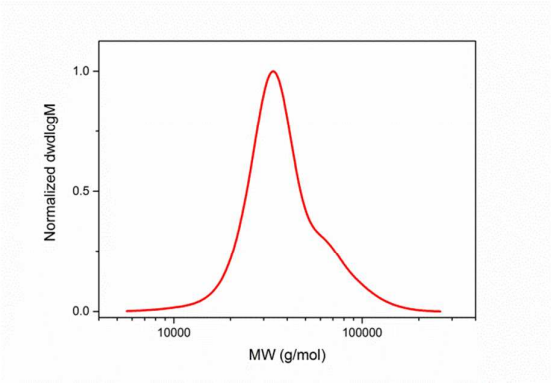
(l) entry 14, table 1



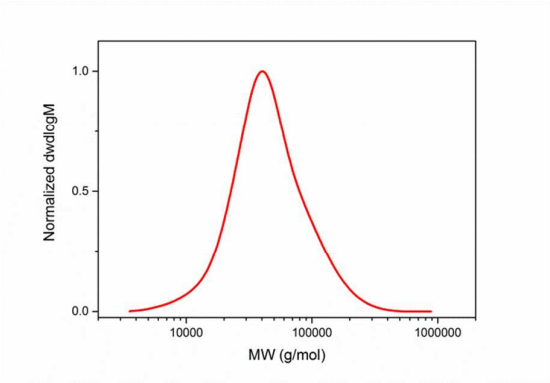
(m) entry 15, table 1



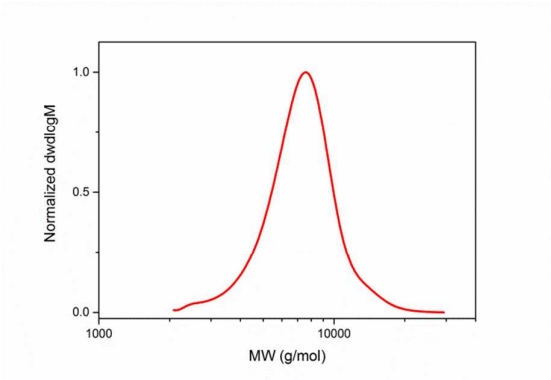
(n) entry 16, table 1



(o) entry 17, table 1



(p) entry 18, table 1



(q) entry 21, table 1

Figure S3: SEC traces from table 1.

Kinetic analysis

Conversion (%)	$M_{n\ (SEC)}$	*Đ*
25	33100	1.75
67	22400	1.92
74	19800	2.09
79	19000	2.16
83	17200	2.37

87	16100	2.42
90	13320	2.77

Table S1: Supplementary data for figure 1 (a) and (b).

Conversion (%)	$M_{n\ (SEC)}$	$Đ$
21	6000	1.66
38	6600	1.40
68	8900	1.12
80	9900	1.14
87	8900	1.29

Table S2: Supplementary data for figure 1 (c) and (d).

Conversion (%)	$M_{n\ (SEC)}$	$Đ$
14	5000	1.21
28	5400	1.20
46	7300	1.14
68	9600	1.12
84	10300	1.14
90	11300	1.13

Table S3: Supplementary data for figure 1 (e) and (f).

Demonstrating temporal control

Time (minutes)	Conversion (%)
45	17
105	17
165	55
225	55
285	70
345	70
405	80
465	80
525	87

Table S4: corresponding data from figure 2.

Time (minutes)	Conversion (%)
45	12
105	12
165	49
525	49
725	75

Table S5: corresponding data from figure 3.

Monomer Scope

Monomer	[PEGA480]:[I]:[Cu(II)Br2]:[Me_6TREN] : [NaBr]	Conv.	$M_{n\ (SEC)}$ (Da)	$Đ$
HEA	20 : 1 : 0.02 : 0.12 : 3	96%	10900	1.20
HEA	20 : 1 : 0.02 : 0.12 : 3	95%	18700	1.16
HEA	20 : 1 : 0.02 : 0.12 : 3	82%	26000	1.13
SPA potas. salt	20 : 1 : 0.02 : 0.12 : 3	83%	9500	1.24
PEGMA*	20 : 1 : 0.02 : 0.12 : 3	>99%	16600	1.27

Table S6: Conditions for polymerization of HEA, sulfopropyl acrylate potassium salt and PEGMA. * using TPMA as ligand instead of Me_6TREN.

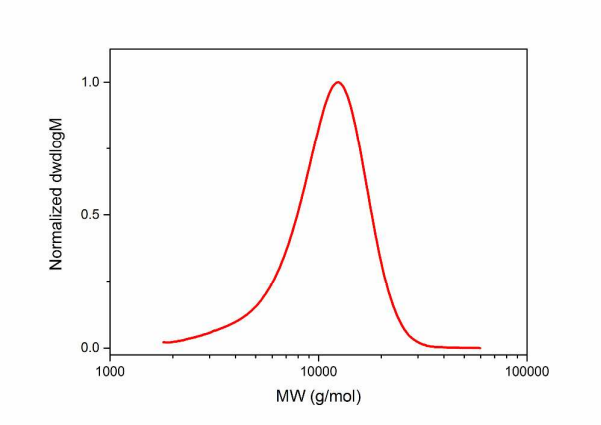


Figure S4: SEC trace of poly(sulfopropyl acrylate potassium salt)$_{20}$

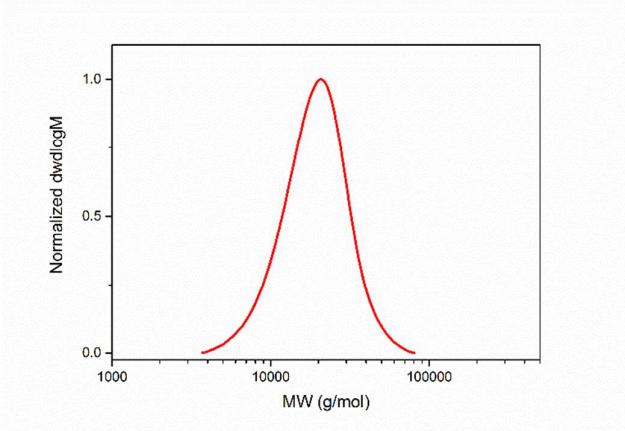


Figure S5: SEC trace of poly(PEGMA)$_{20}$

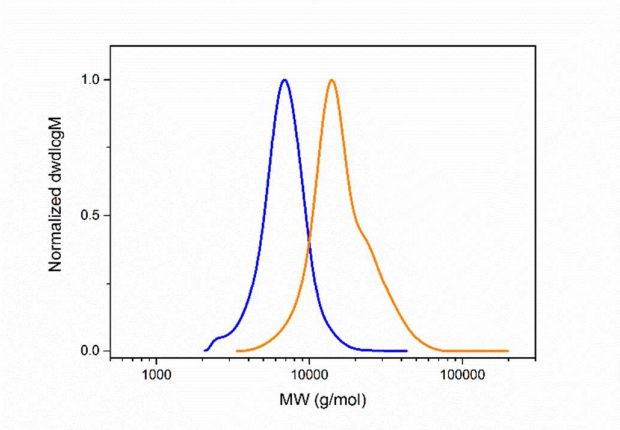


Figure S6: SEC trace of poly(PEGA)$_{10}$ (blue) and poly(PEGA)$_{10}$-(b)-poly(HEA)$_{20}$ (orange)

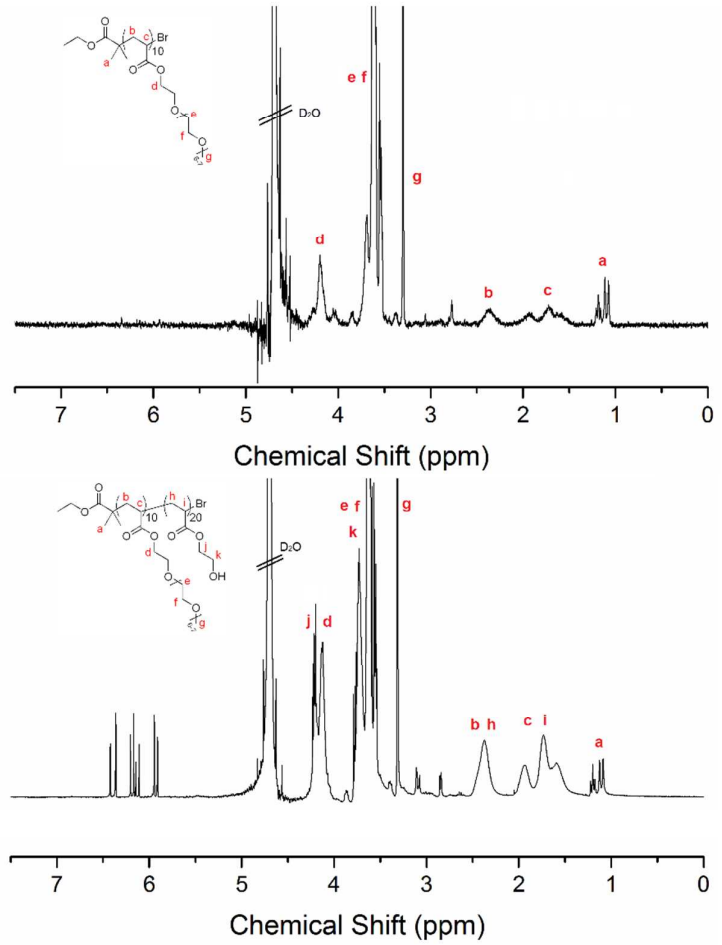


Figure S7: Top: Proton NMR of poly(PEGA)$_{10}$. **Bottom:** Proton NMR of poly(PEGA)$_{10}$-(b)-poly(HEA)$_{20}$.