High Frequency sonoATRP of 2-Hydroxyethyl Acrylate in an Aqueous Medium

Joe Collins, Thomas G. McKenzie, Mitchell D. Nothling, Muthupandian Ashokkumar*, and Greg G. Qiao*

Materials

Sodium bromide (NaBr, Chem Supply, 99%) and copper(II) bromide ($CuBr_2$, Lab Chem, >98%) were used as received. 2-Hydroxyethyl acrylate (HEA, Sigma-Aldrich, 96%) was purified following a previously reported procedure.[1] Briefly, HEA was washed with hexane 10 times to remove divinyl impurities and passed through a short column of alumina to remove inhibitors. 2-Hydroxyethyl bromoisobutyrate (HEBriB) was prepared via the esterification of 1,2-ethanediol with α-bromoisobutyryl bromide (98%, Aldrich), purified by flash column chromatography, and analysed via ^{1}H- and ^{13}C-NMR. Tris[2-(diethylamino)ethyl]amine (Me_6TREN) was prepared according to a previously reported procedure.[2]

Instruments and Characterization

Samples were extracted via degassed syringe for testing by aqueous gel permeation chromatography (GPC) with inline differential refractive index (DRI) and multi-angle light scattering (MALS) detectors, and nuclear magnetic resonance (NMR) spectroscopy. The GPC system consisted of three Waters Ultrahydrogel columns in series ((i) 250 Å porosity, 6 µm bead size; (ii) and (iii) linear, 10 µm bead size). A Shimadzu RID-10 refractometer and Wyatt 3-angle MiniDawn light scattering detector were connected in series. Milli-Q water with 0.1 vol% TFA was used as eluent at a flow rate of 1 mL min-1 and the system operated at ambient temperature. For all polymers, dn/dc values were determined via a method of 100% mass recovery. Molecular weight and dispersity values were calculated using the Wyatt ASTRA software package from MALS data using a Debye model. For ^{1}H-NMR spectra, D_2O was used as a reference and the spectra were obtained using a Varian Unity 400 MHz spectrometer operating at 400 MHz at ambient temperature. An RF generator (AG series amplifier LVG 60-10 produced by T&C Power Conversion Inc.) in combination with a 400 kHz plate transducer (Model 6G12 by Honda Electronics Co. Ltd.) operating at powers of 20 or 40 W was used for high frequency (490 kHz) experiments. A 45 kHz, 230 W Branson ultrasonic bath (20 L, model 8510-DTH) was used for low frequency experiments. UV-vis absorbance spectra were obtained using a Shimadzu UV-1800 Spectrophotometer and UVProbe software package. Matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectroscopy was performed on a Bruker Autoflex III Mass Spectrometer operating in positive linear mode; the analyte, matrix (trans-3-indole acrylic acid) and cationisation agent (KTFA) were dissolved in MeOH at a concentration of 10 mg mL−1, and then mixed in a volume ratio of 1 : 10 : 1. Then 0.3 µL of this solution was spotted onto a ground steel target plate and the solvent was allowed to evaporate prior to analysis. FlexAnalysis (Bruker) was used to analyse the data.

Methods

UV-Vis analysis of Cu(II) reduction: An aqueous $CuBr_2$/Me_6TREN solution (4 mL, 10 mM $CuBr_2$, 1:6 [Cu]:[Me_6TREN]) was degassed by argon bubbling for 30 min, placed in the ultrasonic bath, and subjected to ultrasonic treatment (490 kHz, 40 W) for 60 min. Samples (0.5 mL) were taken periodically, diluted to 3 mL with DI water, and quickly analysed via UV-Vis spectroscopy.

Typical sonoATRP procedure: To a 14 mL glass vial was added HEA (242 µL, 2.23 mmol) and an appropriate mass of $CuBr_2$, Me_6TREN ([$CuBr_2$]:[Me_6TREN] = 1:6), and 2-hydroxyethyl bromoisobutryate to create a reaction series with different amounts of Cu (50 – 1000 ppm) and a variety of DPs (100 – 800) (See Table S1 for mass calculations). The samples were then made up to 3.0 mL with an aqueous NaBr solution (10 mM) to give a [HEA] of 0.75 M. The sample was degassed via argon bubbling for 30 min before being submerged in the ultrasonic water bath (fitted with

circulating water to keep the temperature of the sample at 25° C). The ultrasonic plate was then turned ON (490 kHz, 40 W) and samples were taken periodically to monitor the reaction.

ON/OFF Experiment: A reaction mixture prepared according to conditions outlined in Table S1, entry 2 (DP200, 250 ppm Cu) was degassed via argon bubbling for 30 min, placed in the ultrasonic bath, and subjected to ultrasonic treatment (490 kHz, 40 W) for 2 min (ON). A sample was then taken for analysis and the reaction was left standing with the ultrasound off for a further 2 min (OFF). The ultrasound was the turned on and the procedure repeated (i.e. 2 minute intervals).

Chain Extension: A reaction mixture prepared according to conditions outlined in Table S1, entry 2 (DP200, 250 ppm Cu) was degassed via argon bubbling for 30 min before being placed in the ultrasonic bath and subjected to ultrasonic treatment (490 kHz, 40 W) for 30 min. The addition of ice to the circulating water tank maintained the temperature below 5°C. After 30 min irradiation time a sample was taken for GPC and ^{1}H-NMR analysis. Following this, a degassed HEA solution (3 mL, 0.75 M) was added and ultrasonic irradiation continued for a further 60 min. After this time samples were taken for ^{1}H-NMR and GPC analysis.

Low Intensity (20W) sonoATRP: A reaction mixture prepared according to conditions outlined in Table S1, entry 2 (DP200, 250 ppm Cu) was degassed via argon bubbling for 30 min before being placed in the ultrasonic bath and subjected to ultrasonic treatment (490 kHz, 20 W) for 60 min. Samples were taken periodically for ^{1}H-NMR and GPC analysis to monitor the reaction progress.

Low Frequency (40 kHz) sonoATRP: A reaction mixture prepared according to conditions outlined in Table S1, entry 2 (DP200, 250 ppm Cu) was degassed via argon bubbling for 30 min before being placed in the ultrasonic bath and subjected to ultrasonic treatment (40 kHz, 230 W) for 60 min. After this time a sample was taken for ^{1}H-NMR and GPC analysis.

Table S1 Experimental conditions for sonoATRP

Entry	[M]:[I]:[Me_6TREN]:[$CuBr_2$]	Cu (ppm)	$CuBr_2$ (mg, µmol)	Me_6TREN (µL, µmol)	HEBriB (µL, µmol)
1	200:1:0.06:0.01	50	0.025 mg, 0.112 µmol	0.18 µL, 0.674 µmol	1.63 µL , 11.2 µmol
2	200:1:0.3:0.05	250	0.125 mg, 0.56 µmol	0.9 µL, 3.37 µmol	1.63 µL , 11.2 µmol
3	200:1:0.6:0.1	500	0.25 mg, 1.12 µmol	1.8 µL, 6.74 µmol	1.63 µL , 11.2 µmol
4	200:1:1.2:0.2	1000	0.5 mg, 2.24 µmol	3.6 µL, 13.48 µmol	1.63 µL , 11.2 µmol
5	100:1:0.3:0.05	250	0.125 mg, 0.56 µmol	0.9 µL, 3.37 µmol	0.815 µL, 5.6 µmol
6	400:1:0.3:0.05	250	0.125 mg, 0.56 µmol	0.9 µL, 3.37 µmol	3.26 µL, 22.4 µmol
7	800:1:0.3:0.05	250	0.125 mg, 0.56 µmol	0.9 µL, 3.37 µmol	6.52 µL, 44.8 µmol

$$H_2O \longrightarrow OH^{\cdot} + H^{\cdot} \quad (1)$$

$$RH + OH^{\cdot}(H^{\cdot}) \longrightarrow R^{\cdot} + H_2O\,(H_2) \quad (2)$$

$$RH \longrightarrow \text{pyrolysis radicals and unstable products} \quad (3)$$

$$Cu(II) + \text{reducing species } (R^{\cdot}, H^{\cdot}, \text{etc}) \longrightarrow Cu(I) \quad (4)$$

Figure S1 Proposed pathway for the reduction of metal ions (in this case, Cu(II) to Cu(I)) via US treatment.[3] Ultrasound produces hydroxyl and hydrogen radicals from solvent water molecules (1). The hydroxyl/hydrogen radical species can then react with organic molecules (R), e.g. monomers, to form carbon centred radicals (2). Organic molecules can also degrade via pyrolysis to form a variety of radical species (3). The reducing radicals (e.g. carbon-centred radicals, hydrogen radicals) can go on to reduce Cu(II) to Cu(I) (4).

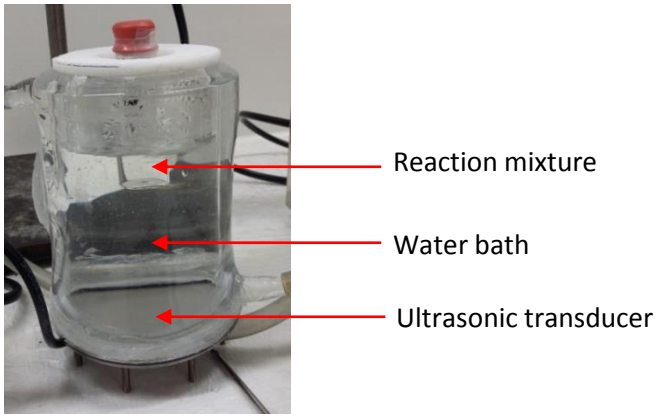
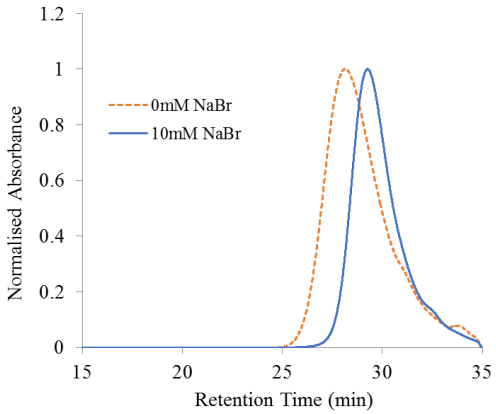
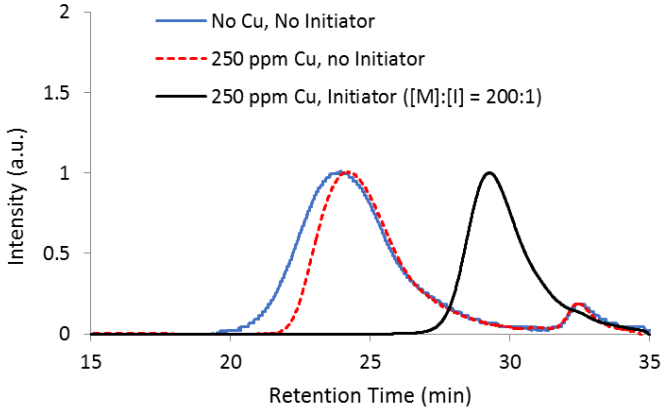


Figure S2 Experimental setup for sonoATRP experiments. Power supply and water circulation pump not shown.



Entry	[M]:[I]:[Me_6TREN]:[$CuBr_2$]	Cu (ppm)	[NaBr] (mM)	DP	T (min)	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	200:1:0.24:0.04	200	0	200	120	73	16,944	48,000	1.25
2	200:1:0.3:0.05	250	10	200	60	90.1	20,937	27,430	1.08

Figure S3 GPC trace and table of results for the sonoATRP of 0.75 M HEA samples in H_2O (3mL) with blue trace, entry 2)and without (orange dashed trace, entry 1) the addition of sodium bromide (10 mM). Sonication was performed at 490 kHz with a power of 40W.



Entry	[M]:[I]:[Me_6TREN]:[$CuBr_2$]	Cu (ppm)	[NaBr] (mM)	DP	T (min)	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	200:0:0:0	0	10	-	60	50.5	-	1,215,000	1.60
2	200:0:0.3:0.05	250	10	-	60	75	-	2,073,000	1.32
3	200:1:0.3:0.05	250	10	200	60	90.1	20,937	27,430	1.08

Figure S4 GPC trace and table of results for the sonoATRP of 0.75 M HEA samples without the addition of either Cu or initiator (blue trace, entry 1), with the addition of Cu (250 ppm) but with no initiator (red dashed trace, entry 2), or with the addition of both Cu (250 ppm) and initiator ([M]:[I] = 200:1) (black trace, entry 3).

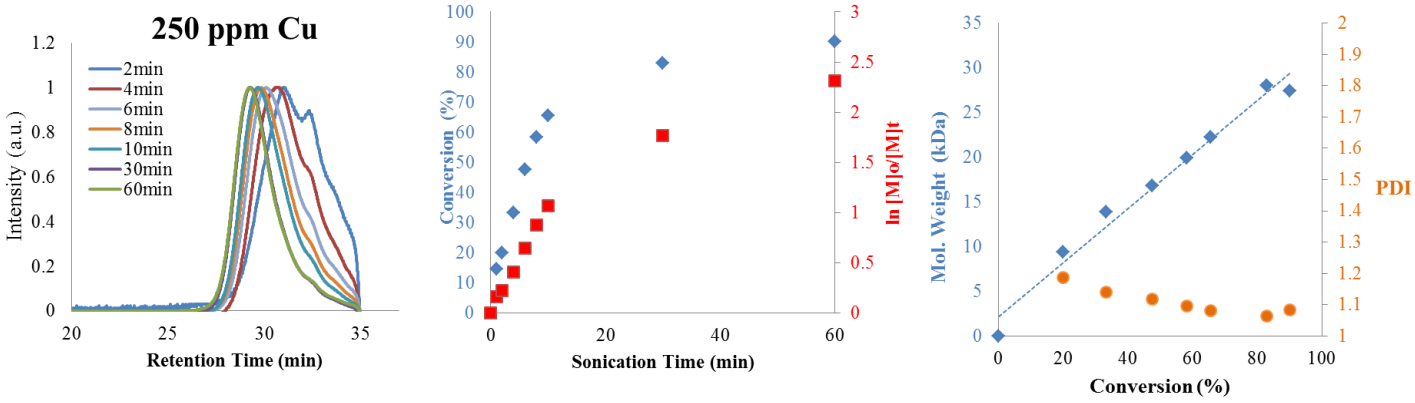


Figure S5 GPC trace evolution and kinetics of 0.75 M HEA sonoATRP (490 kHz, 40W) performed with 250 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:0.3:0.05.

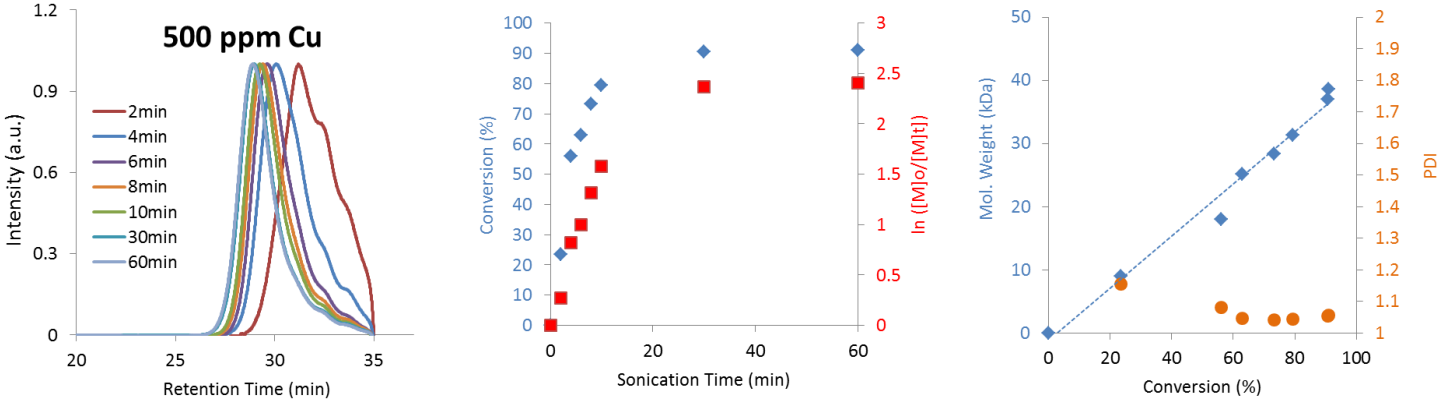


Figure S6 GPC trace evolution and kinetics of 0.75 M HEA sonoATRP (490 kHz, 40W) performed with 500 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:0.6:0.1.

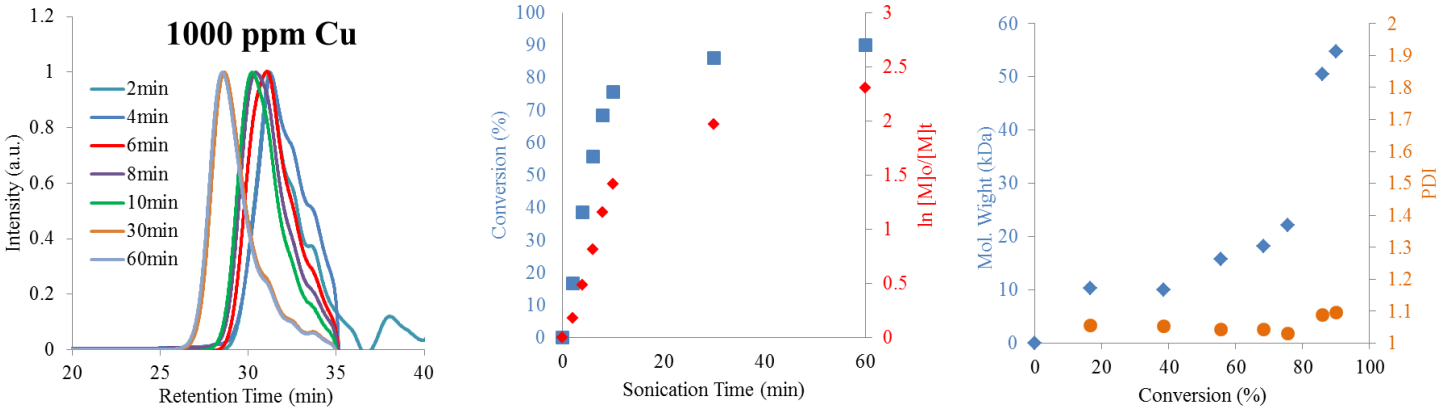


Figure S7 GPC trace evolution and kinetics of 0.75 M HEA sonoATRP (490 kHz, 40W) performed with 1000 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:1.2:0.2.

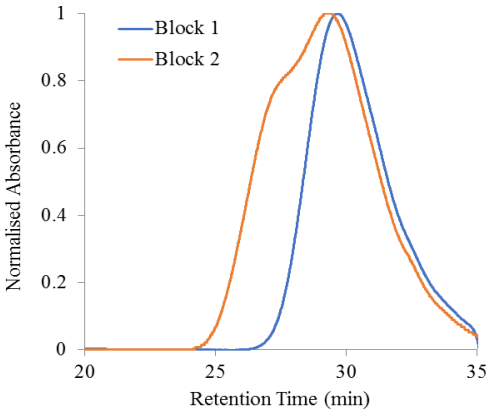


Figure S8 GPC trace for poly(HEA) block co-polymers prepared via sonoATRP at ambient temperature after 60 mins initial sonication.

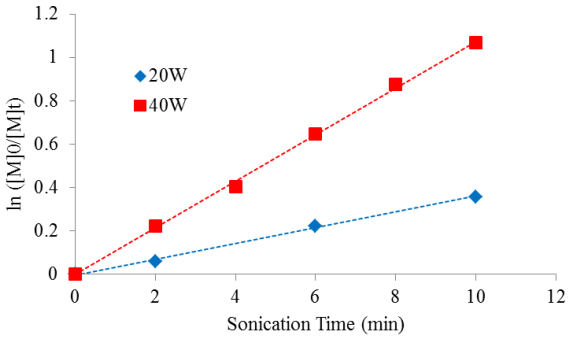


Figure S9 Kinetics of a 0.75 M HEA sonoATRP performed with 250 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:0.3:0.05. The intensity of the applied of ultrasound was either 40 W (red) or 20 W (blue).

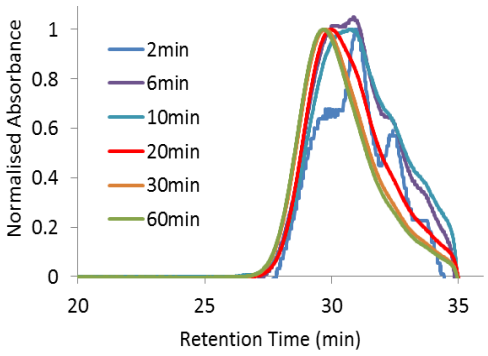


Figure S10 GPC trace evolution of a 0.75 M HEA sonoATRP (490 kHz, 20W) performed with 250 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:0.3:0.05.

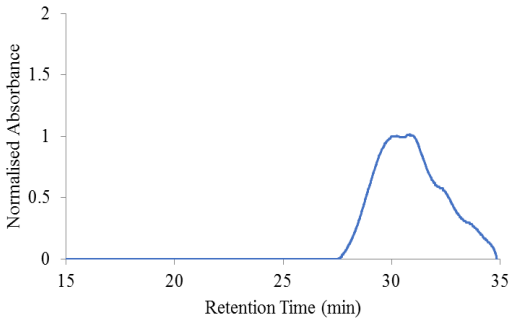


Figure S11 GPC trace of a 0.75 M HEA sonoATRP (40 kHz) performed with 250 ppm Cu in a 10 mM aqueous NaBr solution. [M]:[I]:[Me_6TREN]:[$CuBr_2$] = 200:1:0.3:0.05.

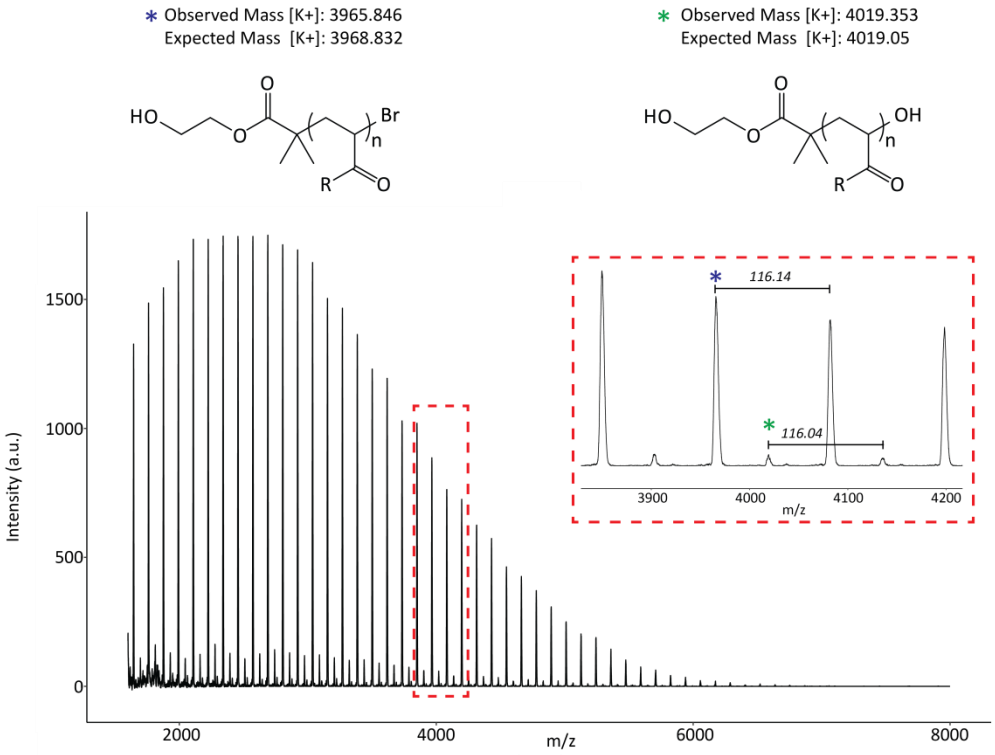


Figure S12 MALDI-TOF spectra of poly(HEA) synthesized via sonoRAFT at 45 kHz.

References

1 S. Coca, C. B. Jasieczek, K. L. Beers and K. Matyjaszewski, *J. Polym. Sci. Part A Polym. Chem.*, 1998, **36**, 1417–1424.

2 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41–44.

3 K. Okitsu, M. Ashokkumar and F. Grieser, *J. Phys. Chem. B*, 2005, **109**, 20673–20675.