

Supporting Information

Aqueous Electrochemically-Triggered Atom Transfer Radical Polymerization

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Experimental

1. Materials

Copper(II) bromide ($\text{Cu}^{\text{II}}\text{Br}_2$, Sigma-Aldrich, 99%), copper(I) bromide ($\text{Cu}^{\text{I}}\text{Br}$, Sigma-Aldrich, 99%), potassium chloride (KCl, Sigma-Aldrich, 99%), 2-pyridine carboxaldehyde (Aldrich, 99%), 2-picolylamine (Aldrich, 99%) sodium triacetoxyborohydride (Acros Organics, 97%), ethylene glycol, α -bromoisobutyryl bromide (Sigma Aldrich, 98%), triethylamine (Fisher Scientific, Lab grade), poly(ethylene glycol) methyl ether methacrylate ($M_n = 300, 500, 1100 \text{ g}\cdot\text{mol}^{-1}$, Sigma-Aldrich, $\geq 99\%$, with 100 ppm MEHQ as inhibitor, 300 ppm BHT as inhibitor) and tetraethylammonium tetrafluoroborate (Et_4NBF_4 , AlfaAesar, 99%) were used as received without any further purification. All aqueous solutions were prepared using deionised water (15.6 M Ω , VEOLIA Elga Purelab). *N*-propyl(2-pyridyl)methanimine (NPPI), *tris*[2-(dimethylamino)ethyl]amine (Me_6TREN),¹ *tris*(2-pyridylmethyl)amine (TPMA)² and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB)³ were synthesised according to literature procedure and obtained with high spectroscopic purity. $\text{Cu}^{\text{I}}\text{Br}$ was purified by consecutive washes with glacial Acetic Acid (Sigma-Aldrich) and ethanol absolute (Sigma-Aldrich) to until the green colour was removed. An off white solid finally obtained after the final filtration and wash with ethanol.

2. Instruments

¹H Nuclear Magnetic Resonance. ¹H NMR spectra were recorded on Bruker HD-300 spectrometer utilising D₂O (Sigma-Aldrich) as solvent. Spectra were referenced and resulting chemical shifts are given in ppm relative to the residual solvent peak ($\delta = 4.75$ ppm).

Size Exclusion Chromatography. SEC measurements were carried out using THF as the eluent with an Agilent 390-LC MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and dual wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 μ m guard column. The eluent was THF with 2 % TEA (triethylamine) and 0.01 % BHT (butylated hydroxytoluene) additives. Samples were run at 1 mL / min at 30 °C. Poly(methyl methacrylate) standards (Agilent EasyVials) were used to create a third order calibration between 550 gmol⁻¹ and 1,568,000 gmol⁻¹. Analytical samples were filtered through a GVHP membrane with 0.22 μ m pore size before injection. Experimental molar mass ($M_{n,SEC}$) and dispersity (D_m) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software (version A.02.01).

UV-Vis spectroscopy. UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in the range of 250-1050 nm using a quartz cuvette (purchased from Starna) with 10 mm optical length. The Cu^I(NPPI)₂ calibration samples were prepared from a stock solution (10 mM) containing purified Cu^IBr (12.6 mg, 87.8 μ mol, 1 eq.) and NPPI ligand (32.5 mg, 219.5 μ mol, 2.5 eq.) in 9 mL DI water and Et₄NBF₄ (217 mg, 1 mmol) was added for consistency with reaction samples. Baseline measurements were recorded in DI water containing Et₄NBF₄ (217 mg, 1 mmol)

Cyclic Voltammetry (CV). Cyclic voltammetry was conducted on a CH-Instruments 600 E potentiostat using a 3 mm glassy carbon disc electrode which was polished with 0.05 μ m alumina powder, rinsed sequentially with acetone, ethanol and MilliQ water prior to each use. The counter electrode was a platinum wire coil. The reference electrode

was Ag/AgCl, the silver wire was polished and rinsed sequentially with acetone, ethanol and MilliQ water the wire was then placed into a glass capillary tube fitted with a vycor frit and filled 3 M KCl solution. The supporting electrolyte Et₄NBF₄ (0.217 g, 1 mmol) and DI water (10 mL) were mixed and used as background electrolyte. A background CV was recorded to confirm the absence of impurities and oxygen. All measurements were made at a concentration of 0.0088 M with respect to Cu^{II}L, using Cu^{II}Br₂ (1 eq) as the Cu^{II} salt and NPPI (2.5 eq), TPMA (1.25 eq) and Me₆-Tren (1.25 eq) as the ligands. A CV of the catalyst system only was recorded to measure its standard reduction potential (E^{θ}) in pure water. To determine the E^{θ} in presence of monomer OEGMA₃₀₀ the process was repeated in the presence of varying amounts of OEGMA₃₀₀. Finally, HEBiB was added to evaluate the redox activity and activation behaviour of each Cu^IL complex.

3. Experimental procedures

3.1 IKA Electrasyn reaction set-up for seATRP

The IKA electrochemical cell is composed of an undivided reaction vial and an electrode head to which working, counter and reference electrodes can be attached. For seATRP reactions an IKA manufactured Pt-coated electrode was used as the working electrode (cathode) and an IKA manufacture Ag/AgCl (using 3 M KCl) electrode was used as reference electrode. For the counter electrode, a sacrificial anode in the case of seATRP, aluminium wire (Alfa-Aesar, length = 15 cm, diameter = 1.0 mm, annealed) was manipulated to a size comparable to the IKA Pt-coated electrode and affixed into the head of the IKA electrochemical cell to serve as the counter electrode for electrolysis as reported in our previous work.⁴

3.2 General procedure for seATRP under potentiostatic conditions

In an IKA reaction vial, triethylammonium tetrafluoroborate (Et₄NBF₄, 0.217 g, 1 mmol) was dissolved in H₂O (9 mL). CuBr₂ (19.6 mg, 0.088 mmol), NPPI (35 μL, 0.22 mmol) were added to the solution of electrolyte and allowed to dissolve before addition of OEGMA₃₀₀ (1 mL, 3.5 mmol, 10 % v/v). HEBiB (0.175 mmol, for [M] : [I] =

[20] : [1]). The vial was then fitted with the IKA electrode head, equipped with the Pt-coated working electrode (cathode), the Ag/AgCl (using 3 M KCl) reference electrode and the aluminium counter electrode (sacrifice anode). The Electrosyn was programmed to perform electrolysis in potentiostatic mode with $E_{app} = -0.16$ V (this was varied depending on desired E_{app}) for a given period of time ($t = 2$ hr) with a stirring rate of 450 rpm (Fig. S1) at room temperature. Current vs time plots were automatically collected and stored on the IKA mobile app. Reactions were sampled periodically for reaction monitoring by ^1H NMR (D_2O) and SEC (THF).

3.3 Procedure for triggered seATRP under potentiostatic conditions

In an IKA reaction vial, triethylammonium tetrafluoroborate (Et_4NBF_4 , 0.217 g, 1 mmol) was dissolved in H_2O (9 mL). CuBr_2 (19.6 mg, 0.088 mmol), NPPI (35 μL , 0.22 mmol) were added to the solution of electrolyte and allowed to dissolve before addition of OEGMA₃₀₀ (1 mL, 3.5 mmol, 10 % v/v). HEBiB (0.175 mmol, for [M] : [I] = [20] : [1]). The vial was then fitted with the IKA electrode head, equipped with the Pt-coated working electrode (cathode), the Ag/AgCl (using 3 M KCl) reference electrode and the aluminium counter electrode (sacrifice anode). The Electrosyn was programmed to perform electrolysis in potentiostatic mode with $E_{app} = -0.08$ V for a given period of time; $t_{Eapp} = 5, 10, 20, 30$ min, with a stirring rate of 450 rpm. After t_{Eapp} had elapsed the applied potential was removed ($E_{app} = 0$ V), a sample was taken immediately for ^1H NMR and UV-vis analysis, then stirring was continued at 450 rpm at room temperature. Reactions were sampled periodically for reaction monitoring by ^1H NMR (D_2O) and UV-vis analysis.

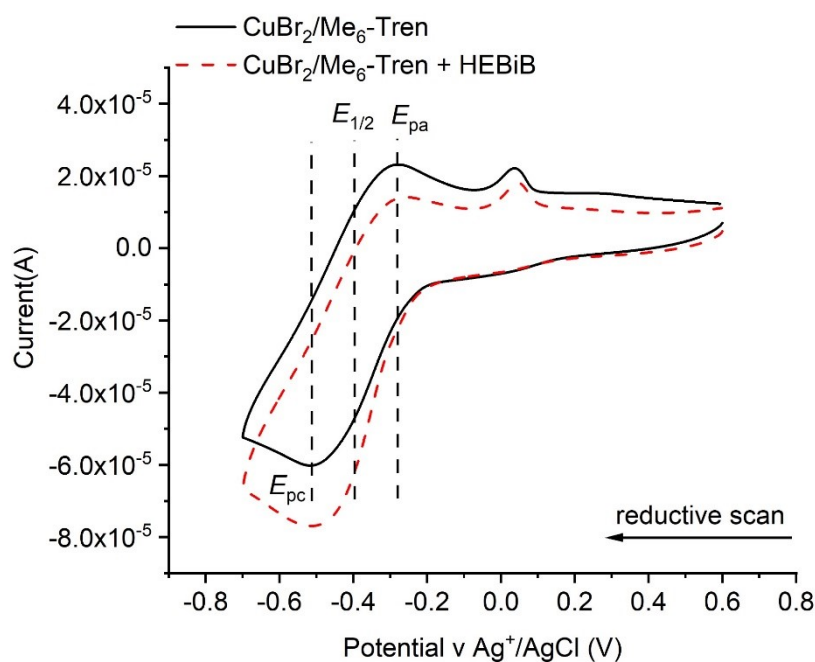


Fig S1. Cyclic voltammetry for $\text{Cu}^{\text{II}}\text{Me}_6\text{Tren}$ (8.8 mM) in $\text{H}_2\text{O}/\text{OEGMA}_{300}$ (9 : 1 v/v) + 0.1 M Et_4NBF_4 in the absence (black line) and presence (dashed red line) of 2-hydroxyethyl 2-bromoisobutyrate (HEBiB). $E_{1/2} = -0.40$ V; $E_{p,c} = -0.51$ V; $E_{p,a} = -0.28$ V. Recorded on a GC electrode at $\nu = 0.1$ $\text{V}\cdot\text{s}^{-1}$, room temperature.

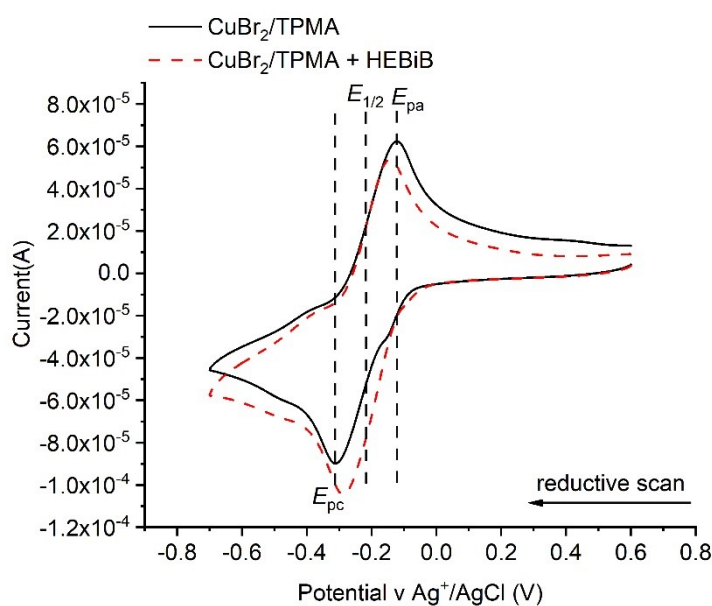


Fig S2. Cyclic voltammetry for $\text{Cu}^{\text{II}}\text{TPMA}$ (8.8 mM) in $\text{H}_2\text{O}/\text{OEGMA}_{300}$ (9 : 1 v/v) + 0.1 M Et_4NBF_4 in the absence (black line) and presence (dashed red line) of 2-hydroxyethyl 2-bromoisobutyrate (HEBiB). $E_{1/2} = -0.21$ V; $E_{p,c} = -0.31$ V; $E_{p,a} = -0.12$ V. Recorded on a GC electrode at $\nu = 0.1$ $\text{V}\cdot\text{s}^{-1}$, room temperature.

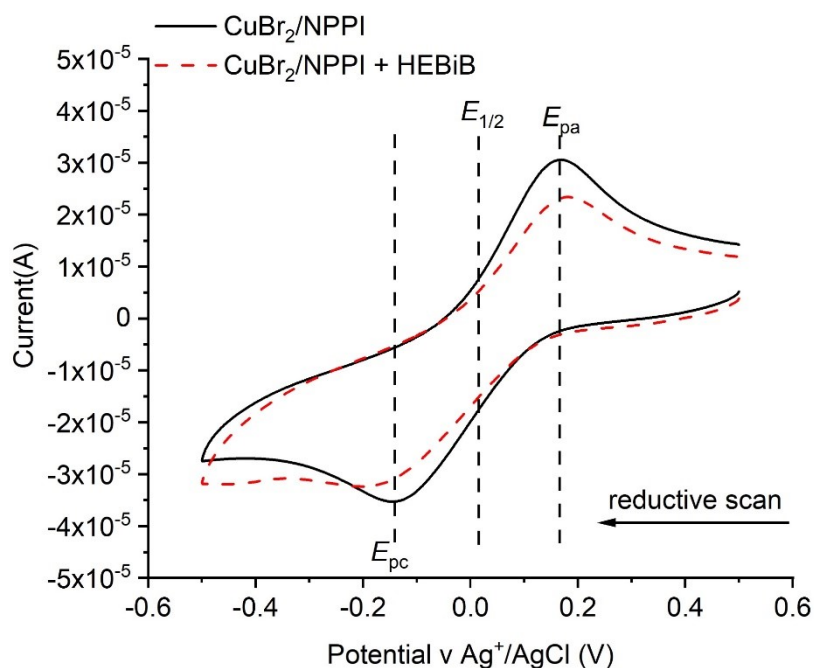


Fig S3. Cyclic voltammetry for $\text{Cu}^{\text{II}}(\text{NPPI})_2$ (8.8 mM) in $\text{H}_2\text{O}/\text{OEGMA}_{300}$ (9 : 1 v/v) + 0.1 M Et_4NBF_4 in the absence (black line) and presence (dashed red line) of 2-hydroxyethyl 2-bromoisobutyrate (HEBiB). $E_{1/2} = 0.02$ V; $E_{p,c} = -0.14$ V; $E_{p,a} = 0.17$ V. Recorded on a GC electrode at $\nu = 0.1$ $\text{V}\cdot\text{s}^{-1}$, room temperature.

Table S1. seATRP of OEGMA_{300} (10% v/v, unless stated otherwise) in H_2O . [OEGMA_{300}] : [HEBiB] = [20] : [1]

Entry	Ligand	[$\text{Cu}^{\text{II}}\text{Br}_2$] : [L]	E_{app} / V	Time / h	Conv ^[a]	$M_{n,th}$ ^[b] / $\text{g}\cdot\text{mol}^{-1}$	$M_{n,SEC}$ ^[c] / $\text{g}\cdot\text{mol}^{-1}$	D_m ^[c]
1	NPPI	[0.5] : [1.25]	-0.04	2	100%	6211	9200	1.31
2	Me_6Tren	[0.5] : [0.6]	-0.4	4	70%	4348	21200	5.05
3	TPMA	[0.5] : [0.6]	-0.2	4	80%	4969	5400	4.24

[a] Determined via ^1H NMR of reaction samples performed in D_2O . [b] $M_{n,th} = [(\text{conv.}/100 \times \text{DP}_{n,th}) \times 300] + 211$ [c] From THF SEC of purified polymers.

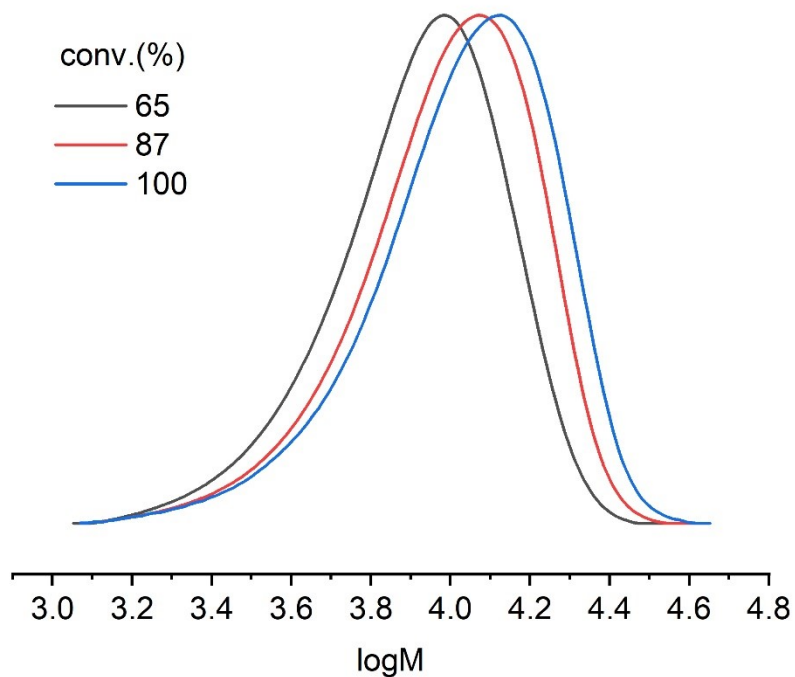


Fig S4. SEC in THF of reaction samples taken during the potentiostatic ($E_{app} = -0.04$ V) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,SEC} = 9200$ g.mol⁻¹ and $D_m = 1.31$ (blue trace).

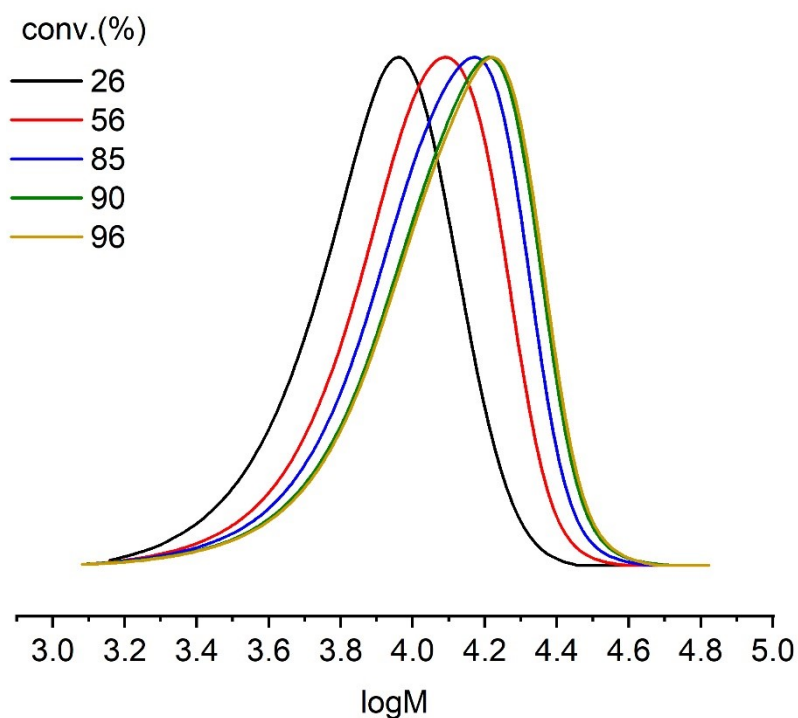


Fig S5. SEC in THF of reaction samples taken during the potentiostatic ($E_{app} = -0.08$ V) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,SEC} = 11000$ g.mol⁻¹ and $D_m = 1.30$ (gold trace).

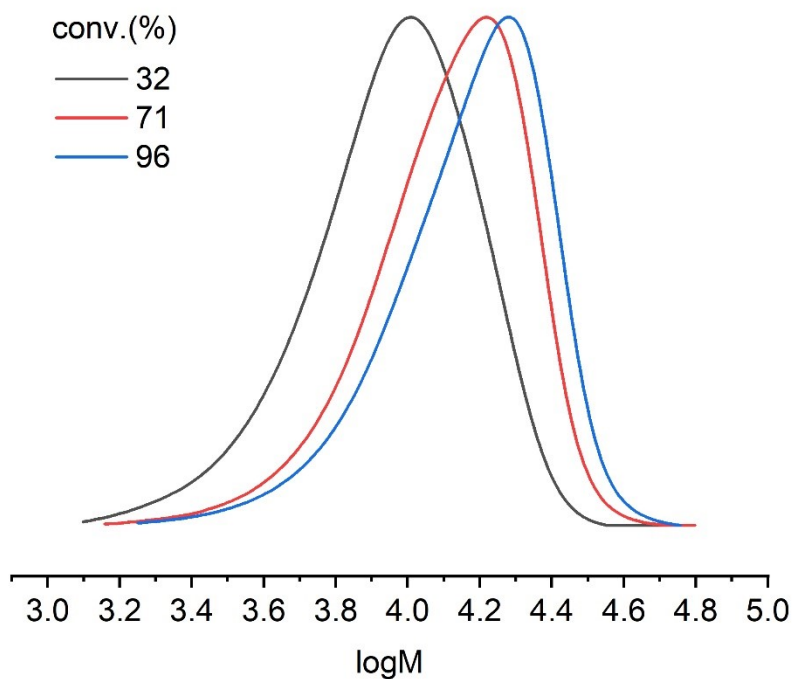


Fig S6. SEC in THF of reaction samples taken during the potentiostatic ($E_{\text{app}} = -0.12 \text{ V}$) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,\text{SEC}} = 12800 \text{ g}\cdot\text{mol}^{-1}$ and $\mathcal{D}_m = 1.29$ (blue trace).

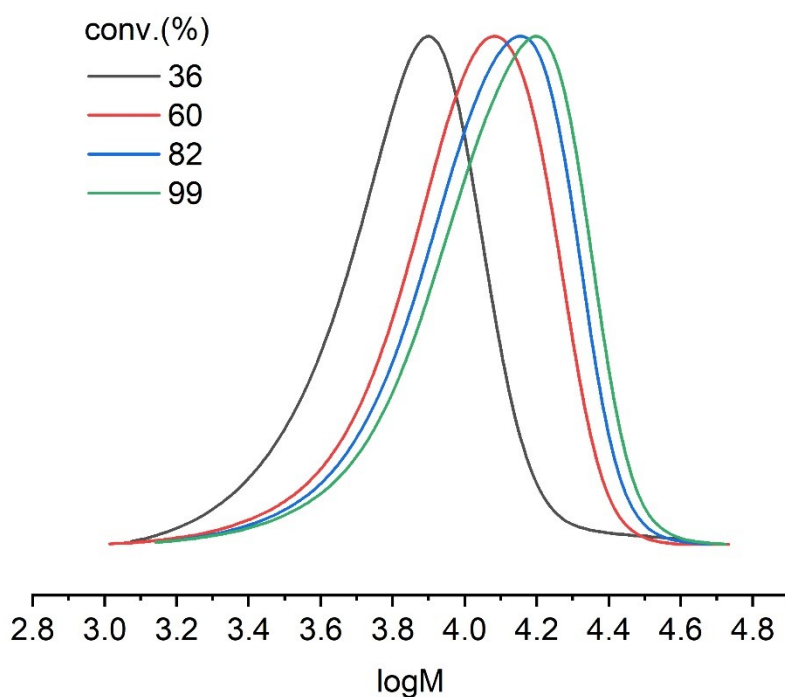


Fig S7. SEC in THF of reaction samples taken during the potentiostatic ($E_{\text{app}} = -0.16 \text{ V}$) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,\text{SEC}} = 10200 \text{ g}\cdot\text{mol}^{-1}$ and $\mathcal{D}_m = 1.32$ (green trace).

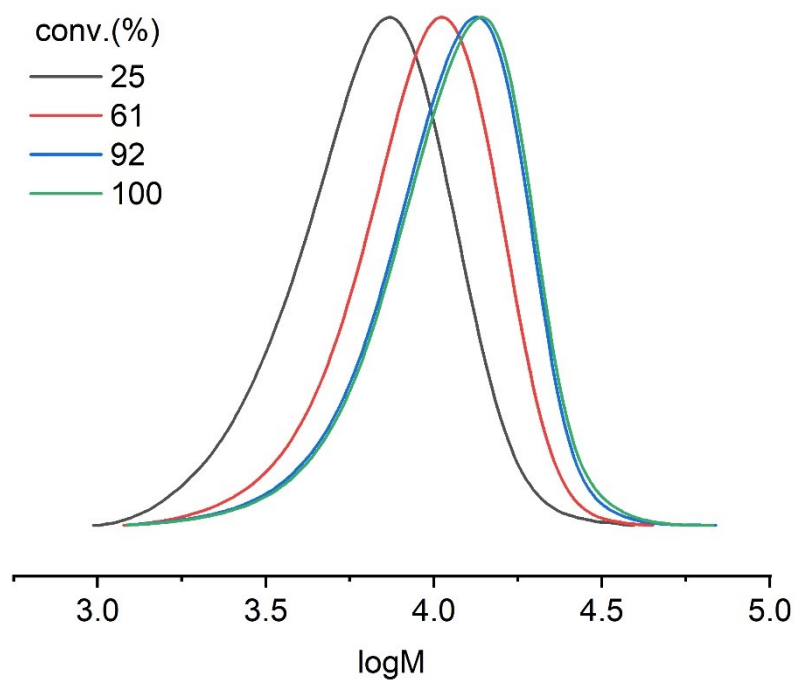


Fig S8. SEC in THF of reaction samples taken during the potentiostatic ($E_{\text{app}} = -0.16$ V) seATRP of OEGMA₃₀₀ (20% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,\text{SEC}} = 10000$ g.mol⁻¹ and $\bar{D}_m = 1.28$ (green trace).

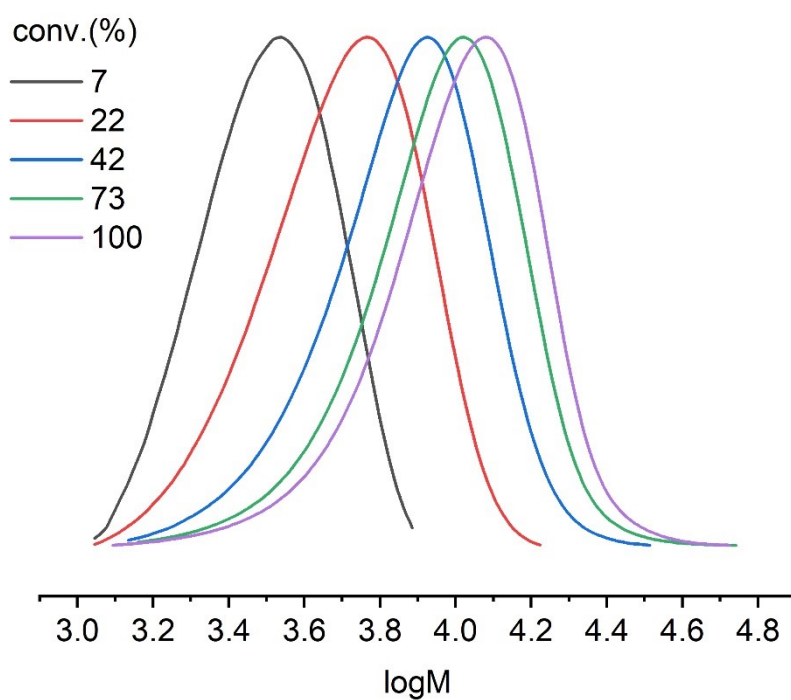


Fig S9. SEC in THF of reaction samples taken during the potentiostatic ($E_{\text{app}} = -0.16$ V) seATRP of OEGMA₃₀₀ (30% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]); $M_{n,\text{SEC}} = 9000$ g.mol⁻¹ and $\bar{D}_m = 1.26$ (green trace).

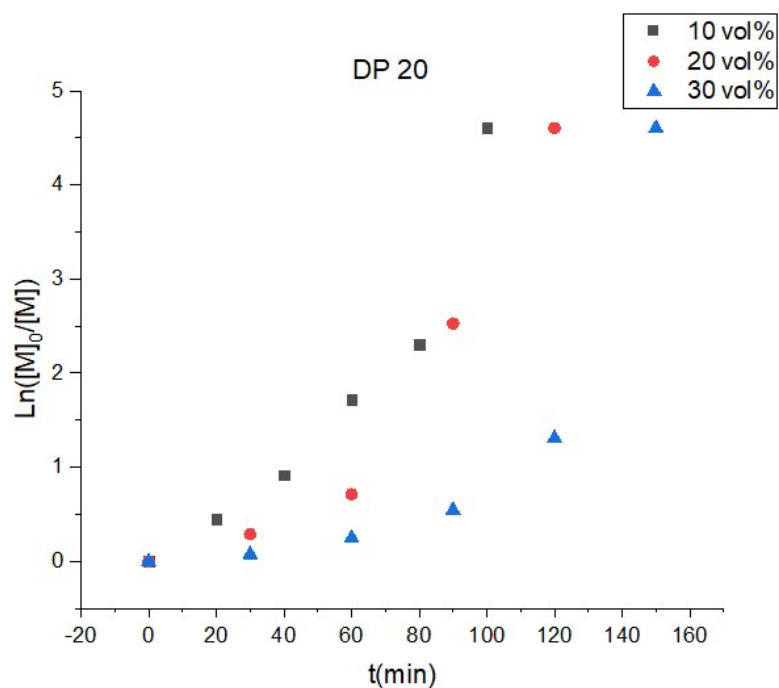


Fig S10. Kinetic analysis for [OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25] at 10 % (black), 20 % (red) and 30 % (blue) v/v OEGMA₃₀₀. ($E_{app} = -0.16$ V)

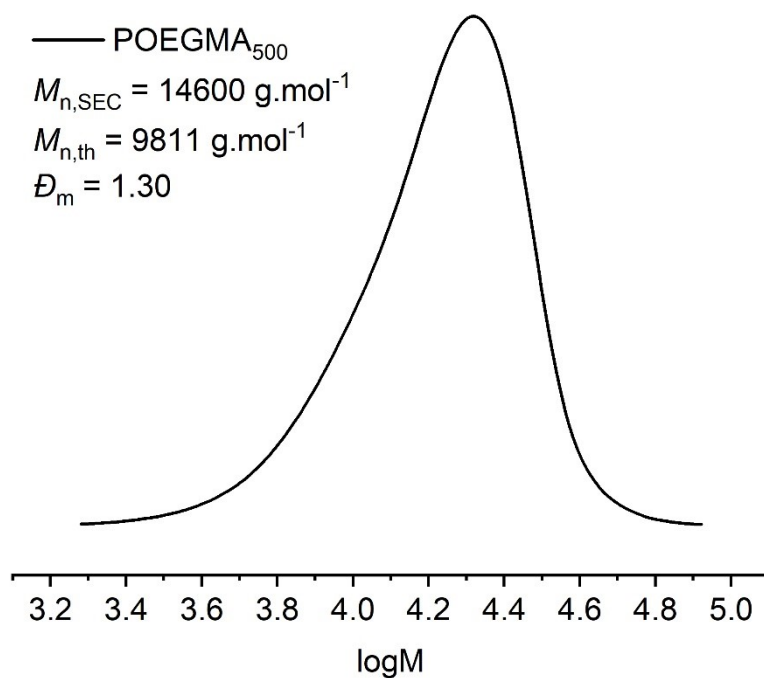


Fig S11. SEC in THF of reaction samples taken during the potentiostatic ($E_{app} = -0.16$ V) seATRP of OEGMA₅₀₀ (10% v/v) in H₂O ([OEGMA₅₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]).

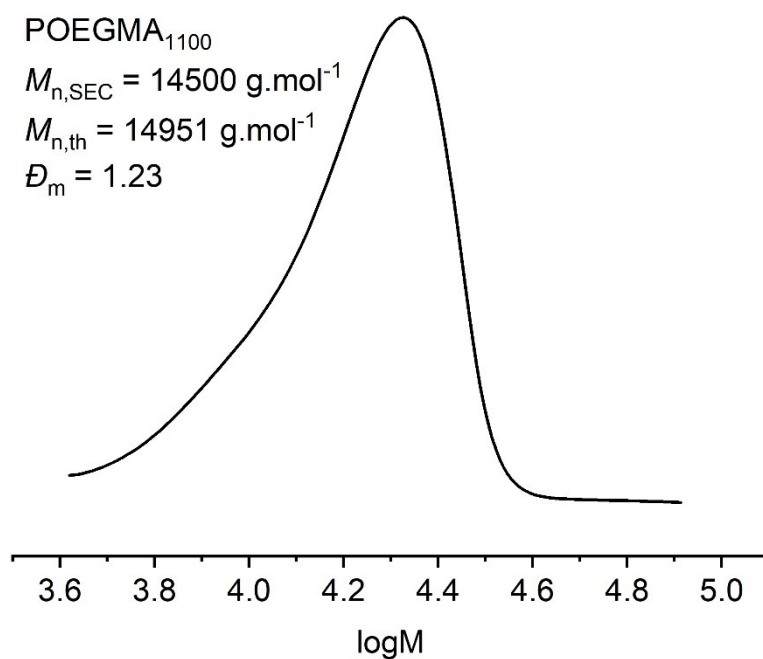


Fig S12. SEC in THF of reaction samples taken during the potentiostatic ($E_{app} = -0.16 \text{ V}$) seATRP of OEGMA₁₁₀₀ (10% v/v) in H₂O ([OEGMA₁₁₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]).



Fig S14. Example of the ElectroSyn interface used to set the reaction parameters. Here a potentiostatic reaction at $E_{app} = -0.16 \text{ V}$ is demonstrated. The observed colour change from green to brown is attributed to electrochemical reduction of Cu^{II}(NPPI)₂ (green) to Cu^I(NPPI)₂ (brown).

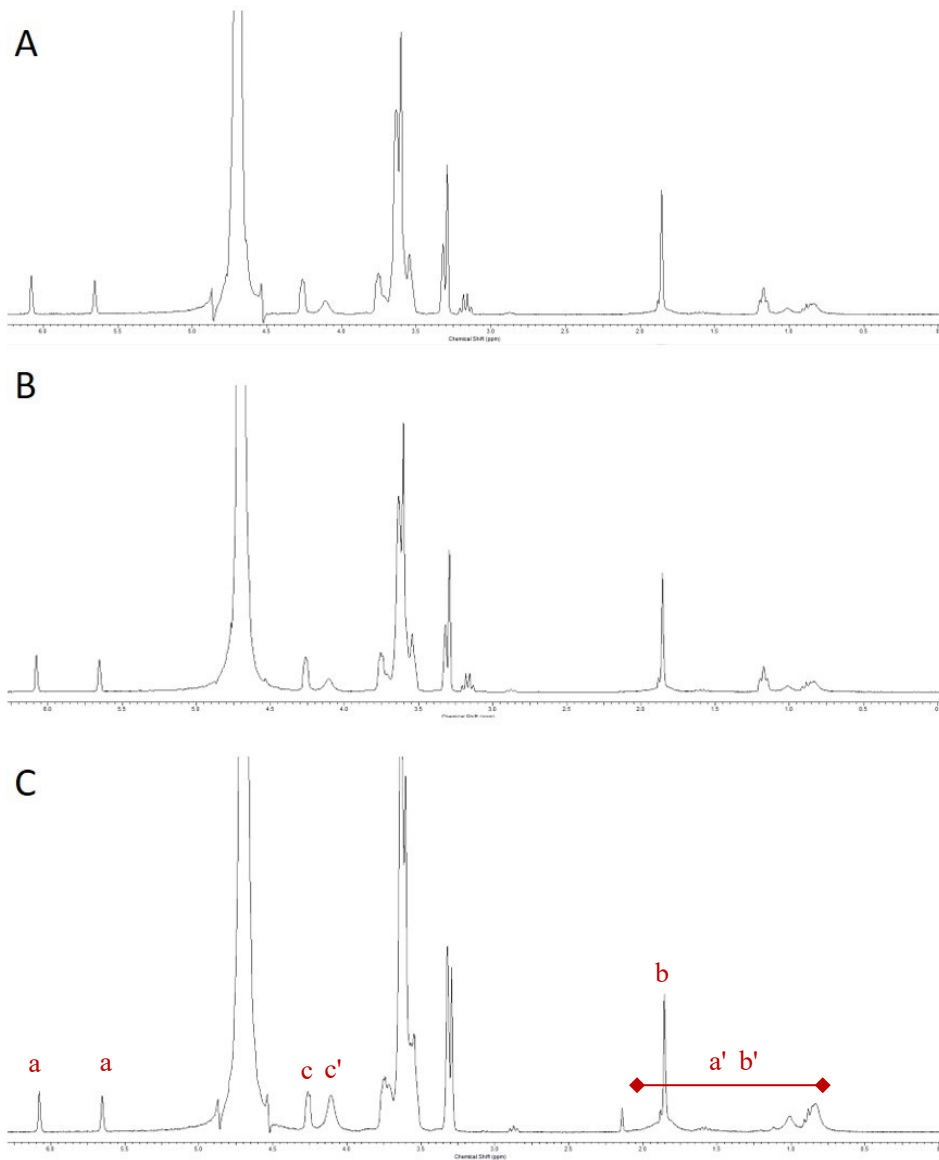
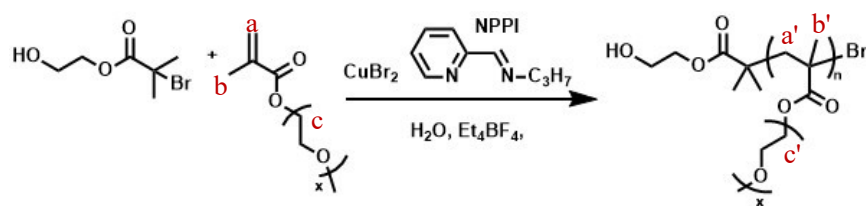


Fig S15. ^1H NMR for the potentiostatic ($E_{\text{app}} = -0.08$ V) seATRP of OEGMA₃₀₀ (10% v/v) in H_2O ($[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$). (A) $E_{\text{app}} = -0.08$ V, $t = 30$ min, conversion = 33%. (B) $E_{\text{app}} = 0$ V with sparging with compressed air, $t = 30$ min, conversion = 33%. (C) N_2 sparging (15 min) then $E_{\text{app}} = -0.08$ V, $t = 30$ min, conversion = 64% (Conversions calculated from the relative integrals of H_c and $\text{H}_{c'}$).

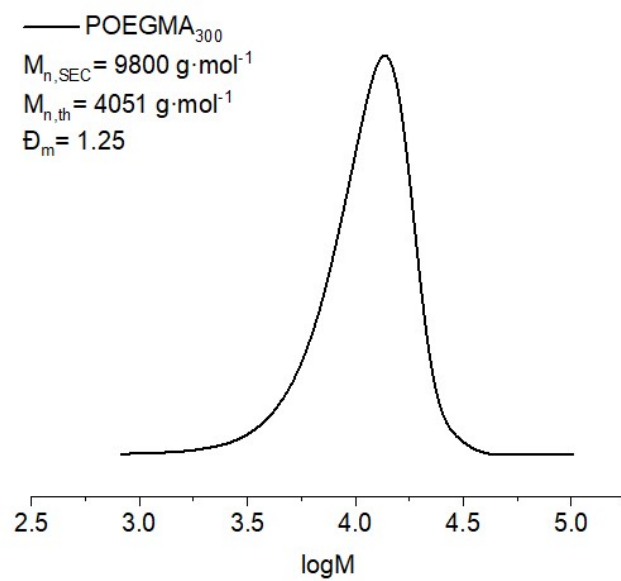


Fig S16. SEC in THF of POEGMA₃₀₀ obtained from Fig S15C.

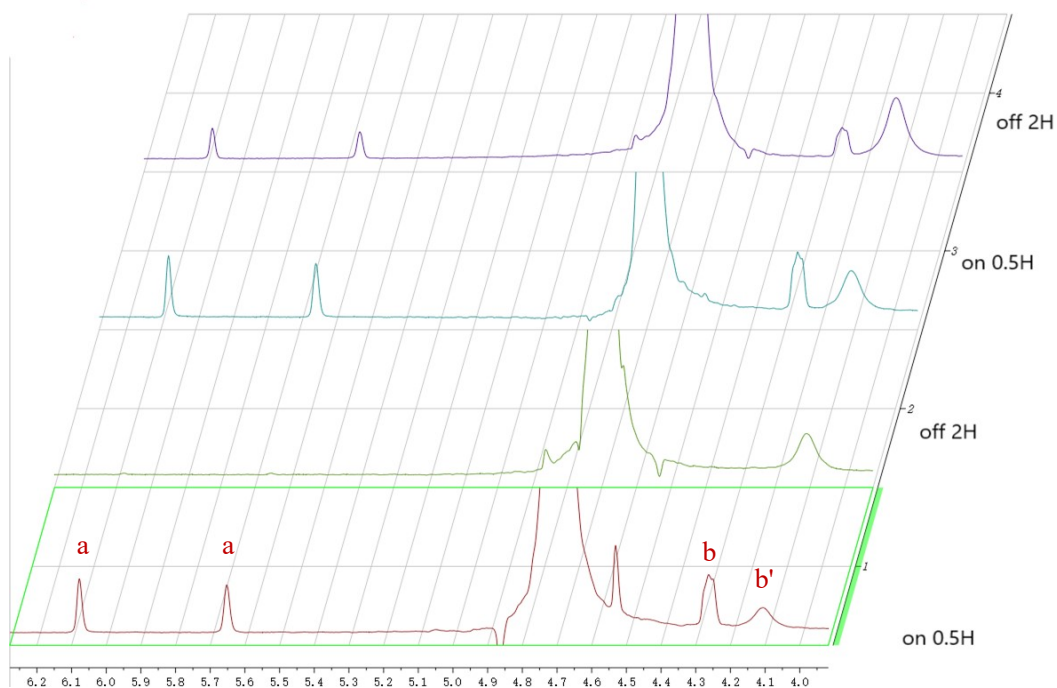


Fig S17. ^1H NMR for electrochemically triggered eATRP of OEGMA₃₀₀ ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]; $E_{\text{app}} = -0.08$ V; $t_{E\text{app}} = 30$ min) and chain extension ([OEGMA₃₀₀] : [POEGMA₃₀₀-Br] = [20] : [1]; $E_{\text{app}} = -0.08$ V; $t_{E\text{app}} = 30$ min) (Conversions reported in Table 2 were calculated from the relative integrals of H_b and H_{b'}).

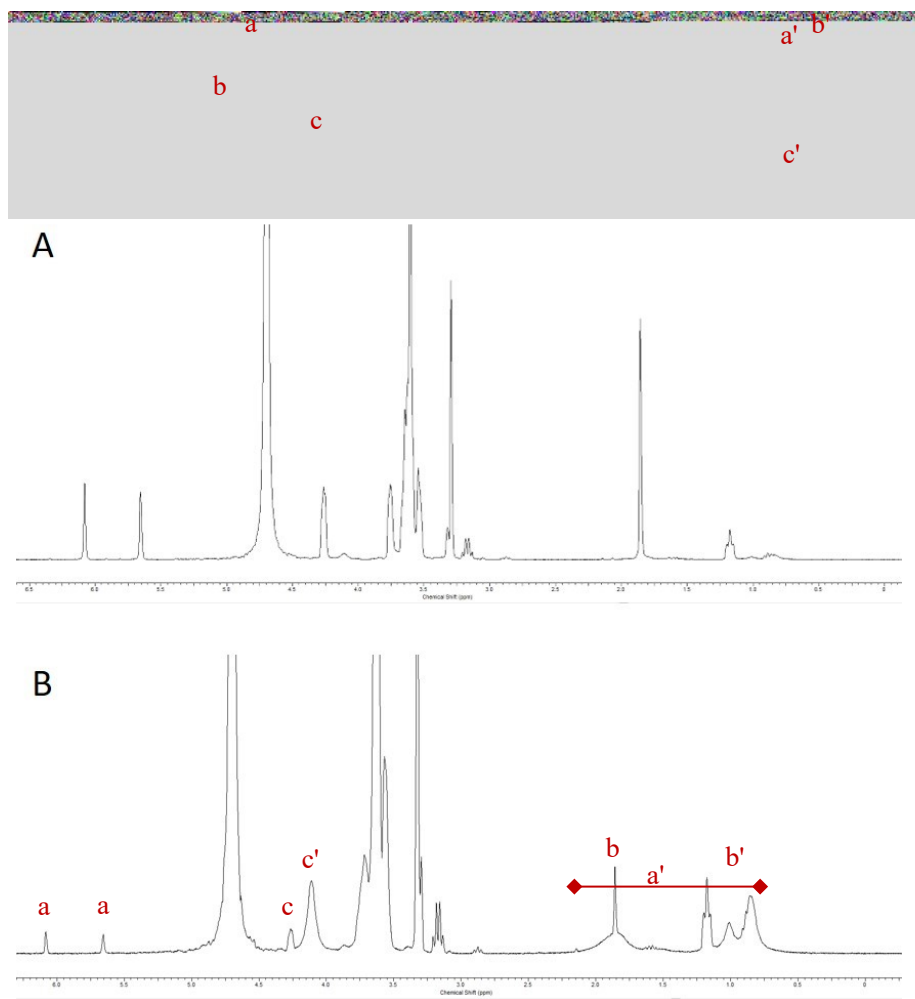


Fig S18. ¹H NMR for the potentiostatic ($E_{\text{app}} = -0.08 \text{ V}$) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [200] : [1] : [0.5] : [1.25]). (A) $E_{\text{app}} = -0.08 \text{ V}$, $t = 30 \text{ min}$, conversion = 13%. (B) $E_{\text{app}} = 0 \text{ V}$, $t = 90 \text{ min}$, conversion = 89% (Conversions calculated from the relative integrals of H_c and H_{c'}).

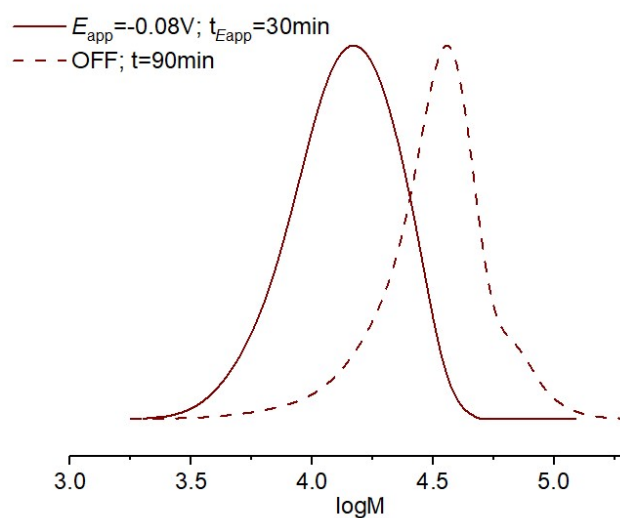


Fig S19. SEC in THF for the potentiostatic ($E_{app} = -0.08$ V) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [200] : [1] : [0.5] : [1.25]) showing the evolution of the molecular weight distribution after electrolysis ($E_{app} = -0.08$ V, $t_{Eapp} = 30$ min, solid line) and after the potential was removed ($E_{app} = 0$ V, dashed lines, $t = 90$ min) final $M_{n,SEC} = 27200$ g.mol⁻¹, $D_m = 1.32$).

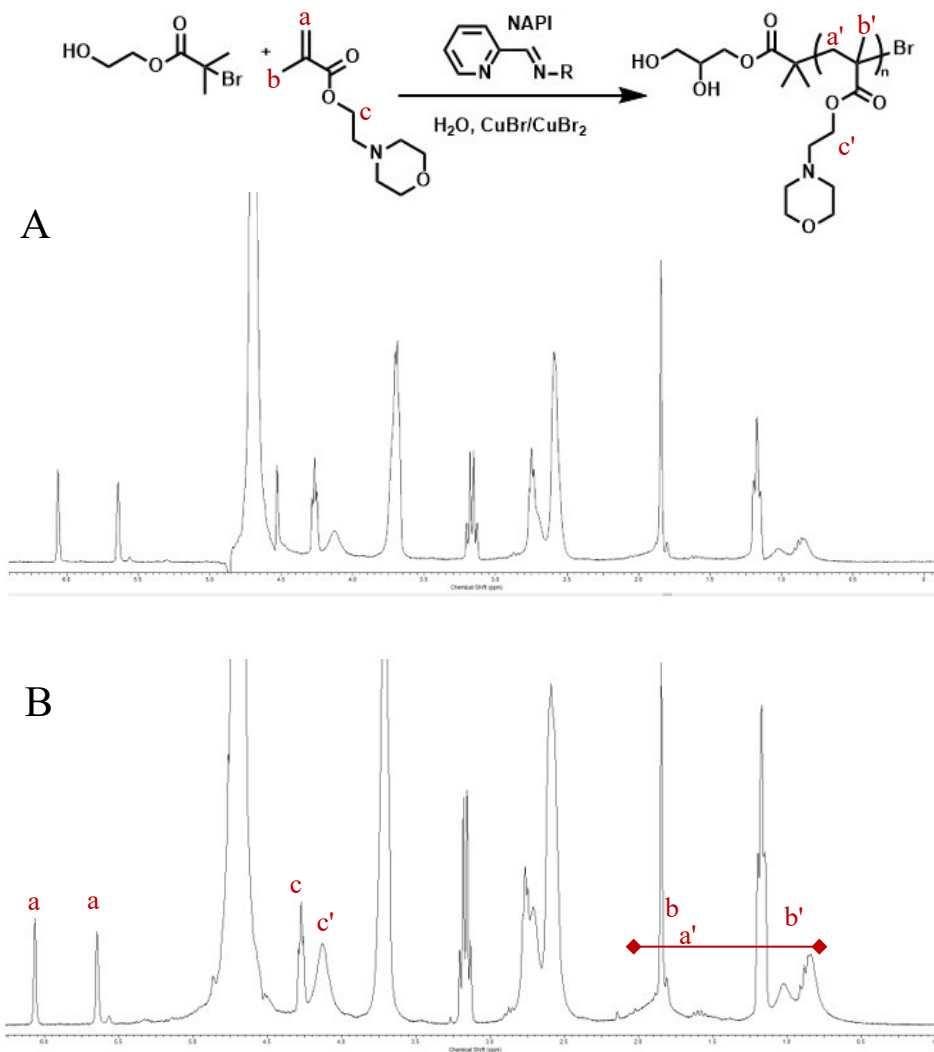


Fig S20. ^1H NMR for the potentiostatic ($E_{\text{app}} = -0.08$ V) seATRP of 2-*N*-morpholinoethyl methacrylate (10% v/v) in H_2O ($[\text{M}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [200] : [1] : [0.5] : [1.25]$). (A) $E_{\text{app}} = -0.08$ V, $t = 30$ min, conversion = 40%. (B) $E_{\text{app}} = 0$ V, $t = 90$ min, conversion = 65% (Conversions calculated from the relative integrals of H_c and $\text{H}_{c'}$).

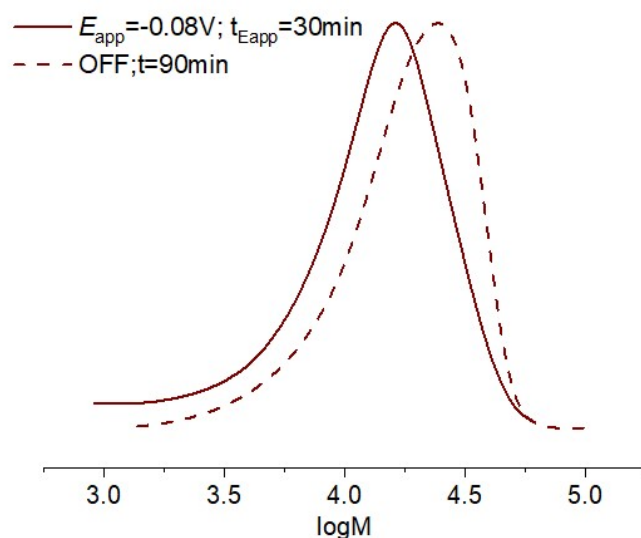


Fig S21. SEC in THF for the potentiostatic ($E_{app} = -0.08$ V) seATRP of 2-*N*-morpholinoethyl methacrylate (10% v/v) in H₂O ([M] : [HEBiB] : [CuBr₂] : [NPPI] = [200] : [1] : [0.5] : [1.25]) showing the evolution of the molecular weight distribution after electrolysis ($E_{app} = -0.08$ V, $t_{Eapp} = 30$ min, solid line) and after the potential was removed ($E_{app} = 0$ V, dashed lines, $t = 90$ min) final $M_{n,SEC} = 14000$ g.mol⁻¹, $D_m = 1.47$).

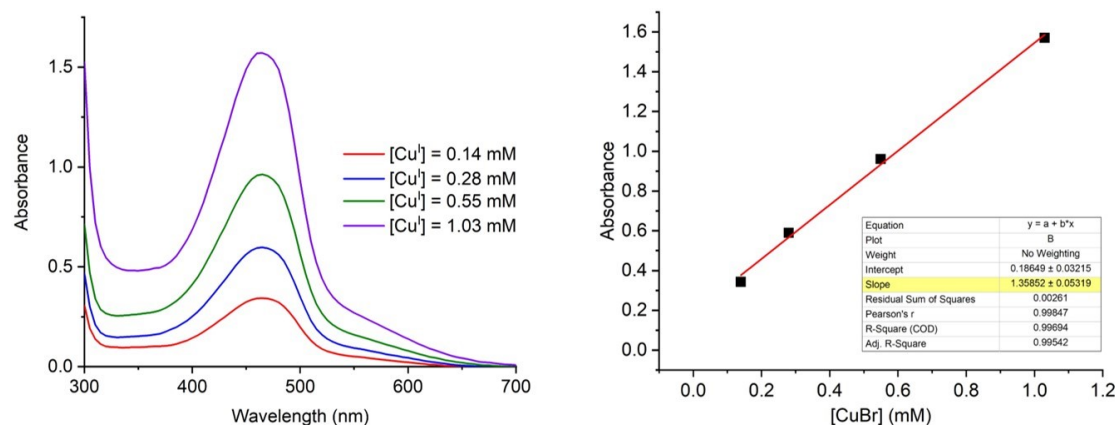


Fig S22. UV-vis calibration data to determine the molar extinction coefficient (ϵ) for Cu^I(NPPI)₂. Samples were prepared from a stock solution of Cu^I(NPPI)₂ (10 mM) which was diluted in order to obtain a maximum absorbance close to 1 (left). Serial dilution allowed a calibration plot to be constructed (right) from which $\epsilon = 1359$ M⁻¹.cm⁻¹. For the following reactions this was used to quantify [Cu^I(NPPI)₂] using the Beer-Lambert Law $A = \epsilon.c.l$.

Determination of [Cu^I(NPPI)₂] in triggered seATRP reactions

Triggered seATRP reactions were performed using [OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25], $E_{app} = -0.08$ V and $t_{Eapp} = 30$ mins. Undiluted reaction samples gave absorbance values at $\lambda = 464$ nm > 5 A.U. Consequently, 0.5 mL of the reaction solution was taken and diluted with 2.5 mL DI water i.e. 6x dilution. This gave a maximum absorbance close to 1 A.U. [Cu^I(NPPI)₂] in mM was determined using the Beer-Lambert Law $c = (A / \epsilon \cdot l) \times 6$. Where $c = [\text{Cu}^{\text{I}}(\text{NPPI})_2]$, A = measure absorbance (at 6x dilution), ϵ = molar extinction coefficient of Cu^I(NPPI)₂ ($1359 \text{ M}^{-1} \cdot \text{cm}^{-1} = 1.36 \text{ mM}^{-1} \cdot \text{cm}^{-1}$), l = pathlength (1 cm) and X 6 accounts for the dilution factor applied.

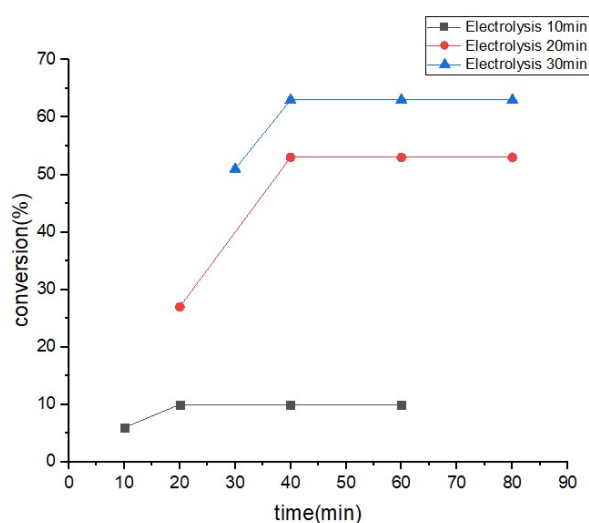


Fig S23. Conversion vs time plot for the triggered seATRP of [OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [bipy] = [20] : [1] : [0.5] : [1.25]. $E_{app} = -0.08$ V, $t_{Eapp} = 10$ min (black), 20 min (red), 30 min (blue).

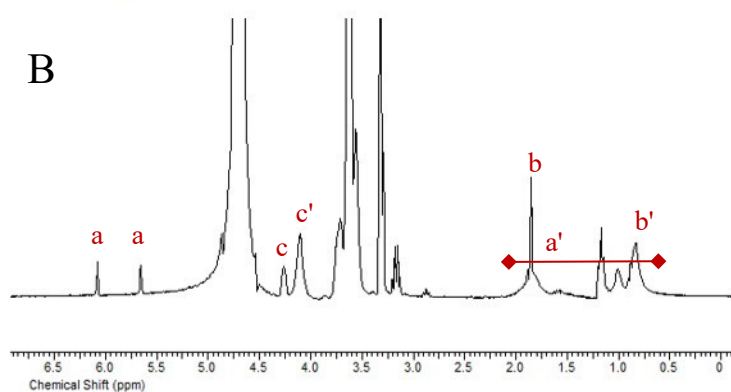
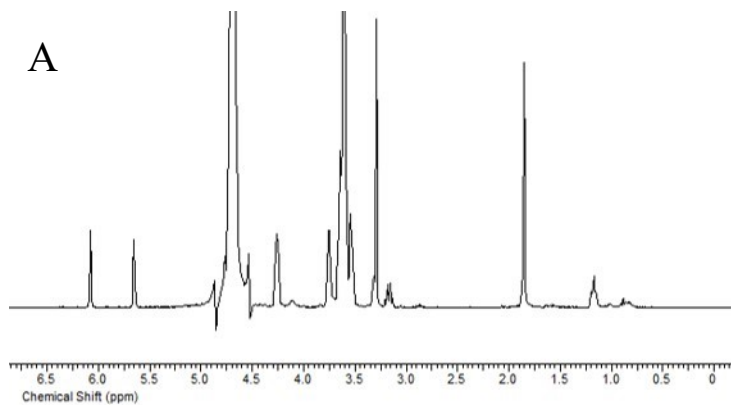
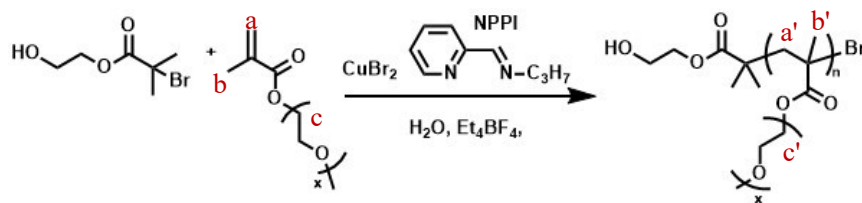


Fig S24. ¹H NMR for the seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]) using a step-wise current profile. (A) *I*_{app} = -3.5 mA, 8 min; -1.9 mA, 7 min; -0.5 mA, 15 min, conversion = 12% (*Q* = 2.93 C). (B) *I*_{app} = 0 mA, *t* = 120 min, conversion = 80%. (Conversions calculated from the relative integrals of H_c and H_{c'}).

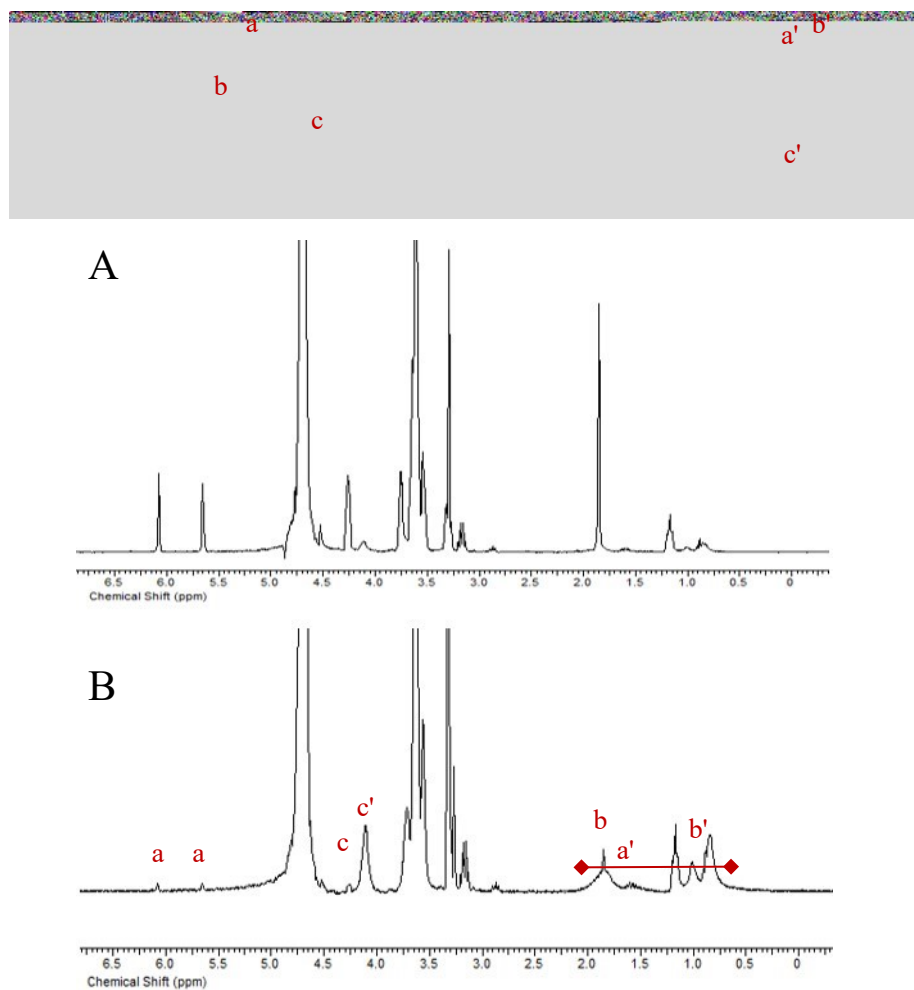


Fig S25. ^1H NMR for the seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]) using a step-wise current profile. (A) $I_{\text{app}} = -2.0$ mA, $t = 30$ min, conversion = 16% ($Q = 3.6$ C). (B) $I_{\text{app}} = 0$ mA, $t = 120$ min, conversion = 95%. (Conversions calculated from the relative integrals of H_c and H_{c'}).

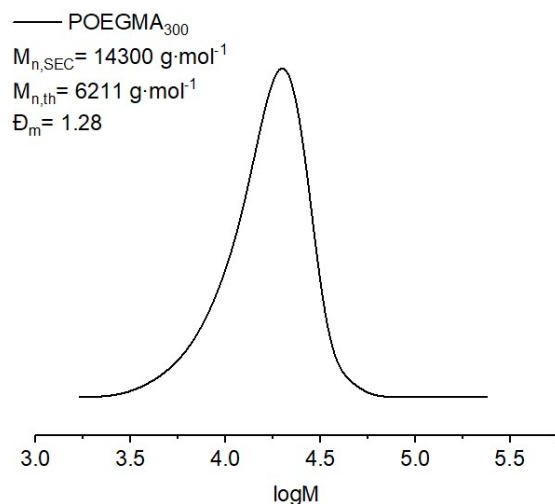


Fig S26. SEC in THF for the galvanostatic ($i_{app} = -2.0 \text{ mA}$, Fig S25B) seATRP of OEGMA₃₀₀ (10% v/v) in H₂O ([OEGMA₃₀₀] : [HEBiB] : [CuBr₂] : [NPPI] = [20] : [1] : [0.5] : [1.25]).

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