Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Plug-and-Play Aqueous Electrochemical Atom Transfer Radical Polymerization

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Experimental

1. Materials

Copper(II) trifluoromethanesulfonate (Cu^{II}(OTf)$_,$ Acros Organics, 98%), sodium bromide (NaBr, Alfa Aesar, >99.9%) potassium chloride (KCl, Sigma-Aldrich, 99%), 2-pyridine carboxaldehyde (Aldrich, 99%), 2-picolylamine (Aldrich, 99%) sodium triacetoxyborohydride (Acros Organics, 97%), ethylene glycol, α-bromoisobutyryl brominde (Sigma Aldrich, 98%) and trimethylamine (Fisher Scientific, Lab grade) were used as received without any further purification. All aqueous solutions were prepared using deionised water (15.6 MΩ, VEOLIA Elga Purelab). Tris(2-pyridylmethyl)amine (TPMA) and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) were synthesised according to literature procedure and obtained with high spectroscopic purity The monomer, poly(ethylene glycol) methyl ether acrylate (M_n = 480 g.mol^{-1}, Sigma-Aldrich, ≥99%, with 100 ppm BHT and 100 ppm MEHQ as inhibitors) was passed through a column filled with basic alumina (Al_2O_3, VWR), to remove the inhibitors. Tetraethylammonium tetrafluoroborate (Et_4NBF_4, AlfaAesar, 99%) was used as background electrolyte.

2. Instruments

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 µm 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 Et_4NBF_4 (0.325 g, 1.5 mmol) and water (15 mL) were mixed as background electrolyte. Before CVs, the reaction cell was purged with N_2 for 15 mins. A background CV was recorded to confirm the absence of impurities and oxygen. $Cu^{II}(OTf)_2$ (5.4 mg, 0.015 mmol) and TPMA (13.1 mg, 0.045 mmol) were added to the solution. After stirring and purging with N_2 for a further 15 minutes, a CV of the catalyst was recorded to measure its standard reduction potential (E^{θ}) in pure water. To determine the E^{θ} in presence of $PEGA_{480}$ the process was repeated in the presence of varying amounts of $PEGA_{480}$. Finally, HEBiB was added to evaluate the redox activity and activation behaviour of $Cu^{II}(OTf)_2$/TPMA and HEBiB respectively (Fig. S1).

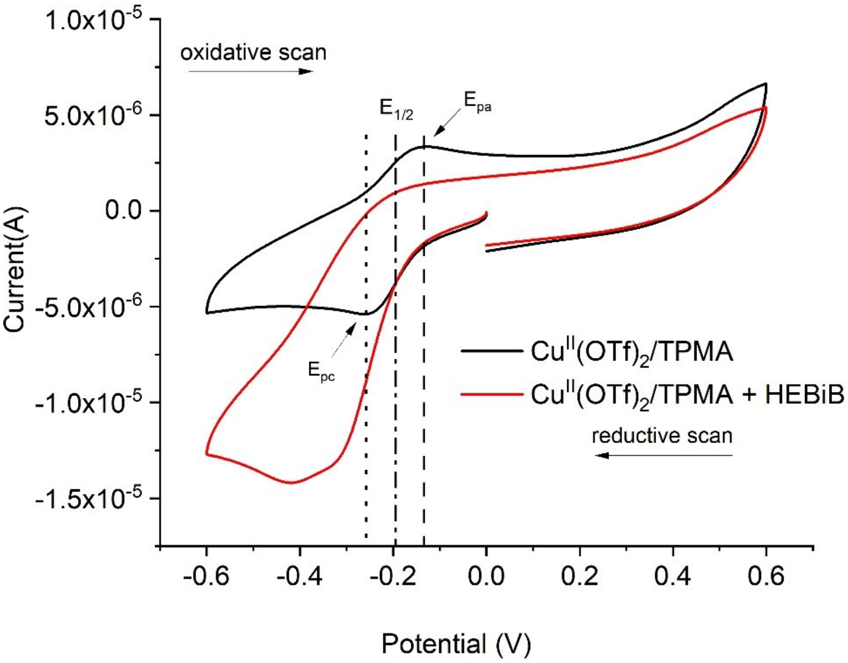

Fig S1. Cyclic voltammetry for Cu^{II}/TPMA (1 mM) in H_2O/PEGA (9 : 1 v/v) + 0.1M Et_4NBF_4 + 1mM NaBr in the absence (black line) and presence (red line) of 2-hydroxyethyl 2-bromoisobutyrate (HEBiB). $E_{1/2}$ = -0.197 V; $E_{p,c}$ = -0.26 V; $E_{p,a}$ = -0.13 V. Recorded on a GC electrode at v = 0.1 V.s^{-1}, room temperature.

^1H NMR spectroscopy was performed using Bruker HD-300 spectrometer utilising D_2O (Sigma-Aldrich) as solvent. Spectra were referenced and resulting chemical shifts are given in ppm relative to the residual solvent peak (δ = 4.75 ppm).

Size exclusion chromatography was performed using Agilent Infinity II MDS instruments equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) and multiple wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 µm guard column. The eluent is 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) and polystyrene standards (Agilent EasiVials) were used for calibration, and the calibration range was 500 – 1,500,000 g.mol^{-1}. Analyte samples were filtered through a GVHP membrane with 0.22 µm pore size before injection. Respectively, experimental number average molecular weights ($M_{\mathrm{n,SEC}}$) and dispersity ($Đ_{\mathrm{m}}$) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

3. Experimental procedures

3.1 IKA Electrasyn reaction set-up for 'plug-and-play' 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 manufacture 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 sacrifice 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 (Fig. S2).

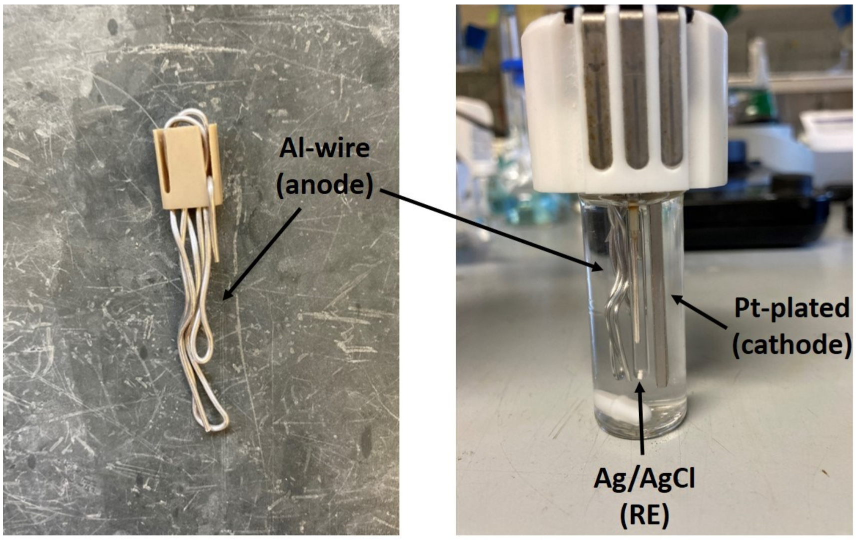

Fig S2. Potentiostatic reaction set-up and electrode configuration using the bespoke IKA manufactured vial, electrode head, Pt-working electrode and Ag/AgCl reference. Homemade, Al-wire counter electrode using an IKA electrode fitting also shown.

3.2 General procedure for 'plug-and-play' seATRP under potentiostatic conditions

In an IKA reaction vial, triethylammonium tetrafluoroborate (Et_4NBF_4, 0.325 g, 1.5 mmol) was dissolved in H_2O (13.5 mL). $Cu(OTf)_2$ (5.4 mg, 0.015 mmol), TPMA (13.1 mg, 0.045 mmol) and NaBr (1.5 mg, 0.015 mmol) were added to the solution of electrolyte as allowed to dissolve before addition of $PEGA_{480}$ (1.5 mL, 3.41 mmol, 10 % v/v). After stirring and purging with N_2 for 15 minutes, a CV of the catalyst was recorded to measure its standard reduction potential (E^{θ}) in the reaction solution (10 % v/v $PEGA_{480}$ in H_2O). HEBiB (90 µmol, for [M] : [I] = [38] : [1]) was then added and CV was repeated in order to see the effect initiator on the Cu^I/Cu^{II} redox couple. 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} = -0.15 V (this was varied depending on desired E_{app}) for a given period of time (t = 2.5 – 8 h) with a stirring rate of 400 rpm (Fig. S3). 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). Final molecular weight data reported (Table 1 – 2) for all polymers is given after purification by dialysis (nMWCO = 3.5 kDa) against MilliQ water.

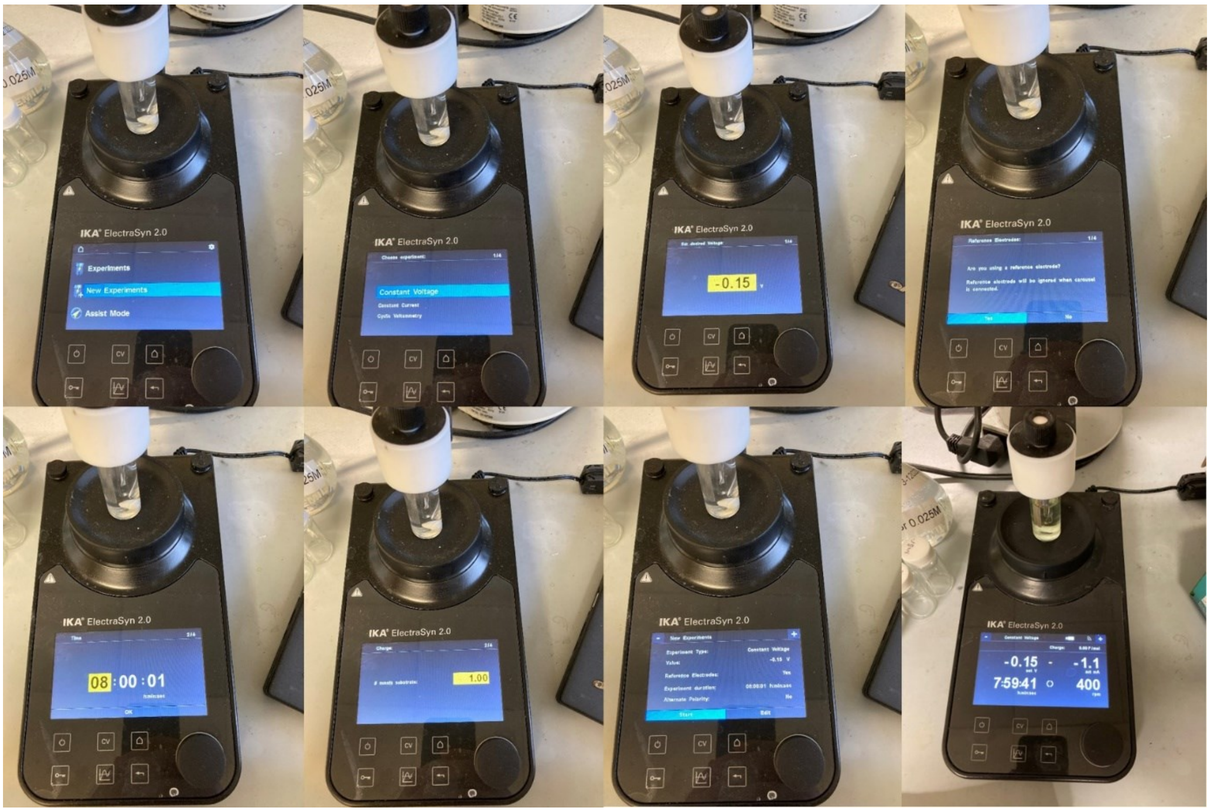

Fig S3. Example of the Electrasyn interface used to set the reaction parameters. Here a potentiostatic reaction at E_{app} = -0.15 V is demonstrated.

3.3 General procedure for 'plug-and-play' seATRP under galvanostatic conditions

In an IKA reaction vial, triethylammonium tetrafluoroborate (Et_4NBF_4, 0.325 g, 1.5 mmol) was dissolved in H_2O (13.5 mL). $Cu(OTf)_2$ (5.4 mg, 0.015 mmol), TPMA (13.1 mg, 0.045 mmol) and NaBr (1.5 mg, 0.015 mmol) were added to the solution of electrolyte as allowed to dissolve before addition of $PEGA_{480}$ (1.5 mL, 3.41 mmol, 10 % v/v). After stirring and purging with N_2 for 15 minutes, HEBiB (90 µmol, for [M] : [I] = [38] : [1]) was added. The vial was then fitted with the IKA electrode head, equipped with the Pt-coated working electrode (cathode) and the aluminium counter electrode (sacrifice anode). Based on the current vs time plots collected for analogous potentiostatic reactions (Fig. 3, manuscript), the Electrosyn was programmed to perform electrolysis in galvanostatic mode. A six step profile was designed using $I_{\mathrm{app},1} – I_{\mathrm{app},6}$ = -3.3 - -1.0 mA (see Table S2 below) over the course of 2 h, with a stirring rate of 400 rpm. After 2 h the reaction was sampled for analysis by ^{1}H NMR (D_2O) and SEC (THF).

Supporting Figures

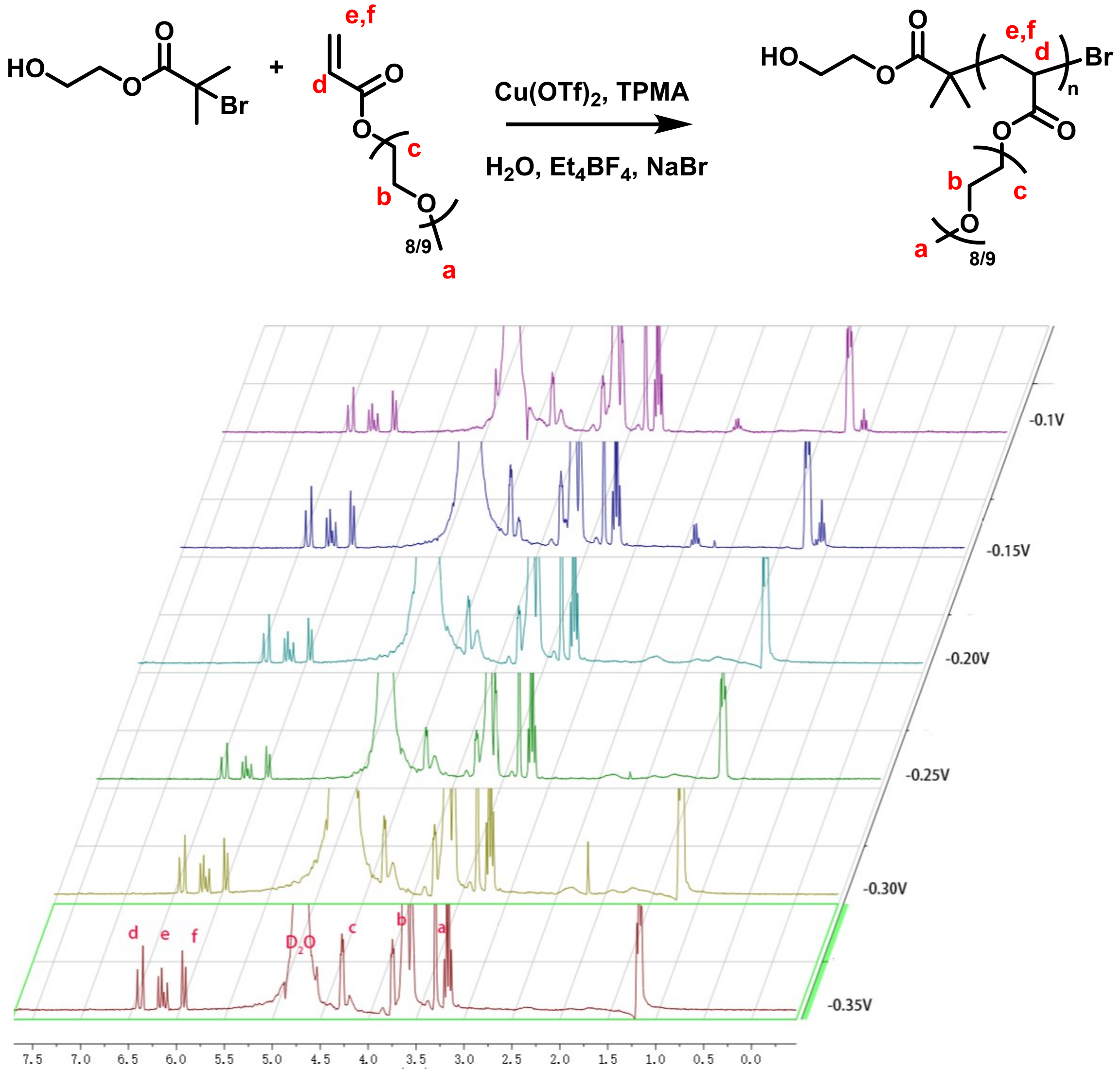

Fig S4. ^{1}H NMR in D_2O showing the effect of E_{app} on the seATRP of PEGA (10% v/v) in H_2O ($[PEGA_{480}] : [HEBiB] : [Cu(OTf)_2] : [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15]$). Monomer conversions were calculated by integration of one the vinyl protons (H_f) against the methylene protons (H_c) adjacent to the ester group of the $PEGA_{480}$ monomer and emerging polymer.

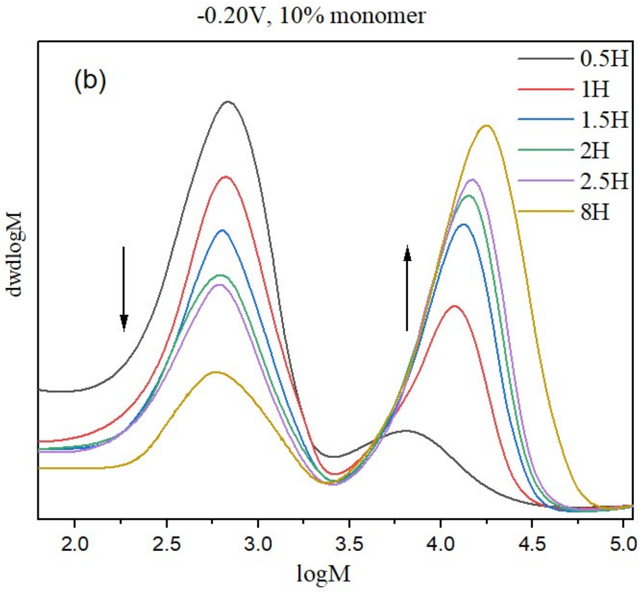

Fig S5. SEC in THF of reaction samples taken during the potentiostatic (E_{app} = -0.20 V) seATRP of PEGA (10% v/v) in H_2O ([$PEGA_{480}$] : [HEBiB] : [$Cu(OTf)_2$] : [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15]).

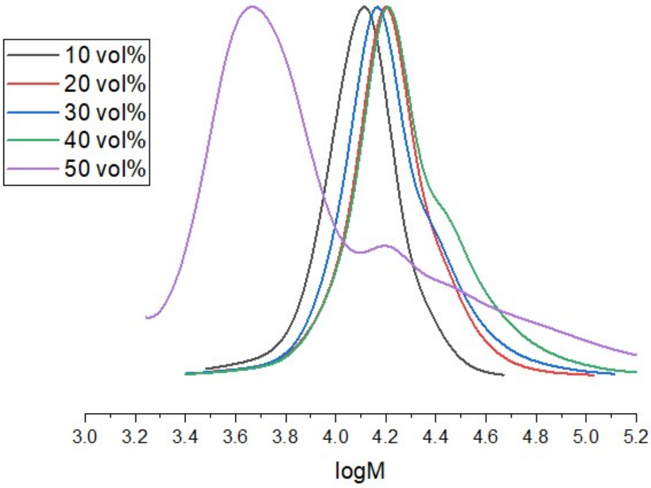

Fig S6. SEC in THF of $PPEGA_{480}$ synthesised by seATRP (E_{app} = -0.15 V) in H_2O ([$PEGA_{480}$] : [HEBiB] : [$Cu(OTf)_2$] : [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15]). Increasing [$PEGA_{480}$] > 20 % v/v leads to increased termination, manifest as the emergence of high molecular weight shoulder peaks, broader distributions and larger $Đ_m$ values (see manuscript Table 1).

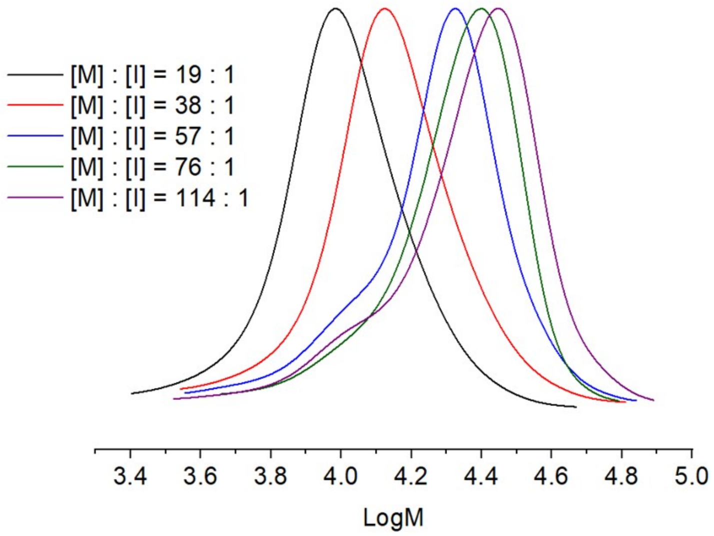

Fig S7. SEC in THF of $PPEGA_{480}$ synthesised by seATRP (E_{app} = -0.15 V) in H_2O ($[PEGA_{480}]$: [HEBiB] : $[Cu(OTf)_2]$: [TPMA] : [NaBr] = [19] - [114] : [1] : [0.15] : [0.45] : [0.15]). $[PEGA_{480}]$ = 10 % v/v (see manuscript Table 2).

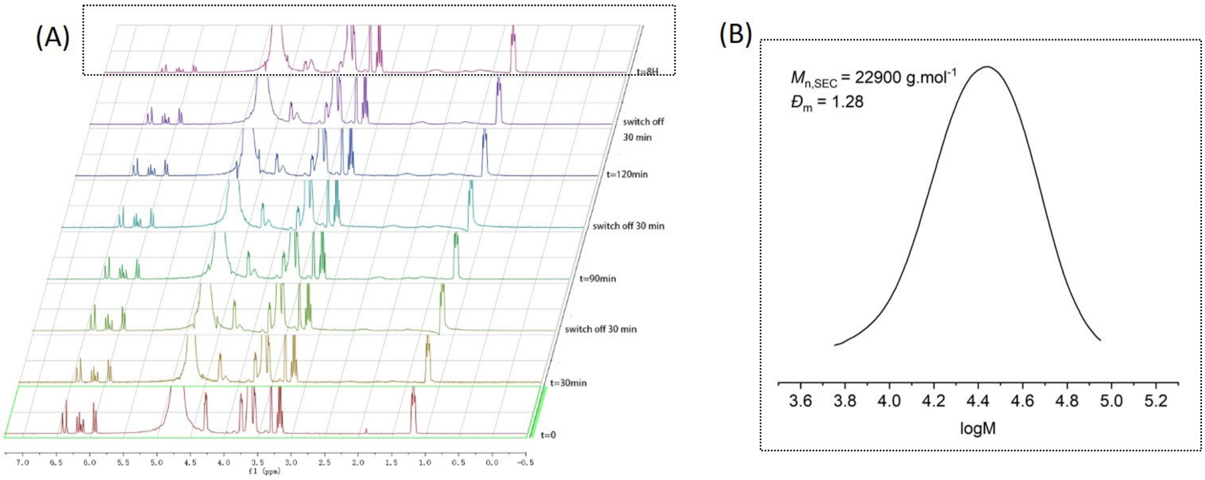

Fig S8. (A) ^1H NMR in D_2O showing the effect of switching E_{app} on and off at 30 minute intervals during the seATRP of PEGA (10% v/v) in H_2O ($[PEGA_{480}]$: [HEBiB] : $[Cu(OTf)_2]$: [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15]). As described above (Fig S4), conversions were calculated by integration of one the vinyl protons (H_f) against the methylene protons (H_c) adjacent to the ester group of the $PEGA_{480}$ monomer and emerging polymer. (B) SEC in THF of $PPEGA_{480}$ synthesised by seATRP with temporal control. $M_{n,th}$ = 13526 g.mol^{-1}, $M_{n,SEC}$ = 22900 g.mol^{-1}, $Đ_m$ = 1.28.

Table S1. Galvanostatic seATRP of PEGA (10 % v/v) in H_2O ([$PEGA_{480}$] : [HEBiB] : [$Cu(OTf)_2$] : [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15]).

Entry	**Steps**	**I_{app} / mA**	**Q[a] / C**	**Time / min**	**Conv.** [b] **(%)**	**$M_{n,th}$[c] g.mol^{-1}**	**$M_{n,SEC}$[d] / g.mol^{-1}**	**$Đ_m$[d]**
1	4	-3 to -0.3	5.7	180	60	11154	10900	1.51
2	6	-3.3 to -1	11.2	120	55	10243	11600	1.17

[a] Q was calculated using a Matlab script using the trapz function. [b] Determined via ^1H NMR of reaction samples performed in D_2O. [c] $M_{n,th}$ = [(conv./100 x $DP_{n,th}$) x 480] + 221 [d] From THF SEC of purified polymers.

Table S2. Detailed current vs time profile for the galvanostatic seATRP of PEGA (10 % v/v) in H_2O ([$PEGA_{480}$] : [HEBiB] : [$Cu(OTf)_2$] : [TPMA] : [NaBr] = [38] : [1] : [0.15] : [0.45] : [0.15], Table S2).

Time / min	**I_{app} / mA**
5	-3.3
5	-3
10	-2.5
20	-2
20	-1.5
60	-1