Electronic Supplementary Information for Dual electrochemical and chemical control in atom transfer radical polymerization with copper electrodes

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S1. Materials and methods

Materials

n-Butyl acrylate (nBA, 99% Sigma Aldrich), methyl methacrylate (MMA, 99%, Acros Organics), methyl acrylate (MA, 99%, Acros Organics) and tert-butyl acrylate (tBA, 98% Sigma Aldrich) were passed through a column filled with basic alumina to remove the inhibitor (30-60 ppm of MEHQ). Acrylamide (AAm 98.5+%, Acros Organics, inhibitor free) was used without purification. Copper (II) triflate (Cu(OTf)₂, Alfa Aesar, 99.999% trace metal basis), copper (II) bromide (CuBr₂, Alfa Aesar, 99%), ethyl 2-bromoisobutyrate (EBiB, Sigma-Aldrich, 98%), 2-bromopropionitrile (BPN, 97%, Sigma Aldrich), tetrabutylammonium chloride (Bu₄NCl, Fisher Sci, 98%), tetraethylammonium bromide (Et₄NBr, Acros Organics, 98%), HPLC-grade dimethylformamide (DMF, VWR, >99.5%), absolute ethanol (EtOH, 99.9%, Honeywell) were used as received. and Tetraethylammonium tetrafluoroborate (Et₄NBF₄, Alfa Aesar, 97%) was recrystallized twice from ethanol and dried in a vacuum oven at 40 °C, over a weekend. Dimethyl sulfoxide (DMSO) and chloroform (CHCl₃) were distilled from CaH₂ under reduced pressure and stored under N2 in an amber bottle. Deionized water was obtained by reverse osmosis. Metallic copper (99.9% purity) and aluminium wires (99% purity) were purchased from Alfa Aesar, whereas stainless steel (SS304) wire was purchased from Leroy Merlin Portugal. All wires had 1 mm diameter.

Instrumentation

The chromatographic parameters of poly(n-butyl acrylate) (P(nBA)-Br), poly(methylacrylate) (PMA-Br) and poly(methyl methacrylate) (PMMA-Cl), were determined using an Agilent 1260 Infinity GPC running stabilized THF at a flow rate of 1.0 mL/min, with a refractive index detector and two PLgel Mixed-D columns (300 mm, 5 µm) connected in series. The detector and columns were thermostated at 30 °C. Mn determination was based on a calibration curve with 12 linear poly(methyl methacrylate) standards ($M_n = 640$ -1560000 Da). Alternatively, a GPC equipped with Polymer Standards Services (PSS) columns (guard, 10⁵, 10³, and 10² Å) and a differential refractive index detector (Waters, 2410), with THF as eluent at a flow rate of 1.00 mL/min (T = 35 °C) was used. GPC traces were processed by WinGPC 8.0 software (PSS) using a calibration based on linear polystyrene. High performance size exclusion chromatography HPSEC was used to determine the properties of PBA-b-P(n-BA-stat-BA)-Br copolymer and of high molecular weight P(n-BA)-Br with a Viscotek SEC (Viscotek TDAmax) composed of a differential viscometer (DV), a right-angle laser-light scattering (RALLS, Viscotek), a low-angle laserlight scattering (LALLS, Viscotek) and refractive index (RI) detectors. The column set consisted of a PL 10 mm guard column (50×7.5 mm) followed by one Viscotek Tguard column (8 µm), one Viscotek T2000 column (6 µm), one Viscotek T3000 column (6 µm) and one Viscotek LT4000L column (7 µm). HPLC dual piston pump was set with a flow rate of 1 mL/min. The eluent (THF) was previously filtered through a 0.1 µm filter. The system was also equipped with an on-line degasser. The columns were thermostated at 30 °C using an Elder CH-150 heater. Before the injection (100 µL), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 200 nm pore. The system was calibrated with 9 narrow PMMA standards (1820-96000 Da). The dn/dc was determined as 0.067 for PBA, 0.064 for P(t-BA) and 0.085 for PMMA standards. Molecular weight and dispersity were determined by multi-detectors calibration.

For polyacrylamide PAAm-Br, the number average molecular weight (M_n^{GPC}) and $D = M_w/M_n$ values were determined by gel permeation chromatography (GPC), by using a Malvern OmniSEC Resolve/Reveal GPC, equipped with a refractive index detector and Agilent Aquagel-OH 30 and 50 columns (300 mm × 8 µm) connected in series, protected by an Agilent Aquagel-OH guard column (8 µm). The column compartment and the detector were thermostated at 35 °C. The eluent was a 0.02 M phosphate buffer + 0.02 wt% NaN₃ (pH = 7.4) at a flow rate of 1 mL/min. The equipment was calibrated with 12 monodisperse PEO standards (610-1510000 Da).

¹H-NMR spectra of reaction mixture samples were recorded on a Bruker Avance III 400 MHz spectrometer, with a 5-mm TIX triple resonance detection probe or with a Bruker Avance 200 MHz spectrometer, or on a Bruker Avance 500 MHz spectrometer, in CDCl₃ with tetramethylsilane (TMS) as internal standard or deuterium oxide with 2 vol% DMF as internal standard. The VIS-NIR spectra were recorded on a Jasco V-530 spectrophotometer from 385 to 850 nm. Scanning electron microscopy (SEM) images were acquired with a Zeiss Sigma HD FE-SEM equipped with an INCAx-act PentaFET Precision spectrometer (Oxford Instruments) using primary beam acceleration voltages between 10 and 20 kV.

Electrochemical experiments were carried out with a **Bio-Logic** potentiostat/galvanostat/EIS (Bio-Logic Science, France) run by a computer with EC-Lab software (Bio-Logic), an Autolab PGSTAT30 potentiostat/galvanostat (Metrohm) or an Autolab PGSTAT302N (Metrohm). Electrolysis experiments were performed in an electrochemical cell (Pine Research) equipped with various electrode pairs (Pt/Pt, Pt/Al, SS304/Al, Cu/Pt, Cu/Cu and Cu/Al). Mixing (at least 700 rpm during electrolysis) was ensured by a PTFE cylindrical magnet. During cyclic voltammetry, a glassy carbon electrode (GC, Pine Research) was used as working electrode. The reference electrode (RE) was an Ag|AgI|TBAI (0.1 M) electrode for non-aqueous mixtures, which was calibrated against Fc/Fc⁺ (ferrocene/ferrocenium) or a saturated calomel electrode (SCE) for aqueous mixtures. All reference electrodes were from Pine Research.

S2. Procedures for ligand synthesis and for polymerizations

Ligand synthesis

Tris(2-dimethylaminoethyl)amine (Me₆TREN). Tris(2-dimethylaminoethyl)amine was prepared by reductive methylation of tris(2-aminoethyl)amine (TREN) according to a published procedure.¹

Tris(2-pyridylmethyl)amine (TPMA). Under N₂ atmosphere, 2-pycolyl amine (3 g, 27.74 mmol) was added to 25 mL of anhydrous chloroform under stirring at room temperature in a 50 mL round bottom flask. Anhydrous sodium sulfate was also grounded into the flask. 2-pycolyl aldehyde (6.24 g, 58.26 mmol) was added dropwise with a syringe under stirring, and the mixture was stirred for 2 hours before adding slowly sodium triacetoxyborohydride (12.94 g, 61.03 mmol). The reduction was let to occur overnight with stirring. After workup (washing 2× with saturated NaHCO₃ and 3× with water) the solvent was removed under reduced pressure. The brown oily liquid was recrystallized from acetonitrile/diethyl ether at -20 °C to obtain tris(2-pyridylmethyl)amine as off-white crystals, which were then dried

at 40 °C in a vacuum over for 3 days. Another crop of crystals was obtained by evaporation of the supernatant and a second identical recrystallization. Combined yield = 75%. ¹H-NMR (400 MHz, CD₃OD) matched literature reports ².

TPMA-3Cl precursor. Tris(4-chloropyridylmethyl)amine (TPMA-3Cl) was synthesized according to previous reports³ using anhydrous CHCl₃ instead of dichloromethane as the reaction solvent. Yield (after column chromatography) = 61%. ¹H-NMR (400 MHz, CDCl₃) matched literature reports. ³

TPMA-PYR. The ligand was obtained by following a literature procedure with minor changes. TPMA-3Cl (1.00 g, 2.54 mmol) was dissolved in excess pyrrolidine (12.7 mL) and water (12.9 mL) into an AceGlass pressure tube. NaOH pellets (314.8 mg, 7.87 mmol) were added, and the mixture was stirred at room temperature for 5 minutes before sealing and heating the tube at 125 °C for 18 hours. During cooling, small crystals appeared on the bottom of the tube. The mixture, once completely cooled, was diluted with water and an almost white solid (the ligand) precipitated out. The ligand was collected by filtration, washed with abundant water to leave an almost white crystalline material. The crystals were dried overnight under a stream of air in the dark. Yield = 99%. ¹H-NMR (400 MHz, CDCl₃) matched literature reports. ³

Polymerizations

Activation of working electrodes. Before each polymerization, the metal wires were washed with chloroform to remove any residual polymer traces. No specific polishing or activation of SS304 and Al wires was adopted. Copper wires were activated with HCl/MeOH 1/3 (v/v) before use to make the surface bright and shiny. Pt gauze electrode was activated by sonication in 65 vol% HNO₃ for 10 minutes, followed by rinsing with abundant water and acetone; it was then dried in air. Alternatively, the electrode was activated by cycling the potential between -0.7 and 1 V vs. Hg/Hg₂SO₄ at v = 0.2 V/s in a 0.5 M H₂SO₄ solution for 60 times.

Typical SARA ATRP procedure for nBA polymerization. A Schlenk reactor equipped with a PTFE magnet and a Cu wire was purged with N₂. A solution of DMF (7.5 mL) containing Cu(OTf)₂ (5.43 mg, 0.015 mmol), Me₆TREN (10.37 mg, 0.045 mmol), ethyl 2-bromoisobutyrate (29.25 mg, 0.15 mmol), Et₄NBr (3.16 mg, 0.015 mmol) and *n*BA (7.5 mL, 52.03 mmol), was added to the reactor after being purged with N₂ for 30 min at room temperature. The Schlenk was thermostated at 45 °C with a water bath. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

Typical eATRP procedure for nBA polymerization with a Cu cathode. The electrochemical cell was equipped with 14 cm wires of Al anode and Cu cathode, an Ag/AgI reference electrode, a glassy carbon (GC) electrode, and a PTFE stir bar and purged with N₂. DMF (7.5 mL), Cu(OTf)₂ (5.43 mg, 0.015 mmol), Me₆TREN (10.37 mg, 0.045 mmol), Et₄NBr (3.16 mg, 0.015 mmol), and Et₄NBF₄ (0.325 g, 1 mmol), *n*-BA (7.5 mL) were added and purged with N₂ for 30 min at room temperature. After the degassing time, the cell was thermostated at 45 °C with a circulating water bath; the solution was let to reach thermal equilibrium, under gentle stirring (200 rpm). Then ethyl 2-bromoisobutyrate (29.25 mg, 0.15 mmol) was added and further purged with N₂ for 15 min. CVs were recorded on the GC electrode before and after EBiB addition to obtain the standard redox potential of the catalyst and evaluate the initiator effect. Electrolysis was initiated by applying the appropriate current or potential (E_{app} or I_{app}) at a stirring rate of 700 rpm. Electrolysis was automatically followed by the electrochemical software. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

Chain extension of PBA-Br with tBA by eATRP. A P(*n*BA)-Br macroinitiator was obtained after 1 h of electrolysis (M_n^{GPC} = 27.0 kDa, D = 1.11; for the reaction conditions see Table 2, entry 9 of the main text). P(*n*BA)-Br was not isolated; rather the chain extension was carried out by first oxidizing electrochemically all [Cu^IL]⁺ at a Cu electrode by applying $E_{app} = E_{1/2} + 0.3$ V for 10 min and then removing the electrode from the mixture. Then 7.5 mL of *t*BA were injected into the mixture, which was then degassed for additional 30 min. After re-immersing the Cu cathode, the electrolysis was restarted in the same manner of the first block. Samples for GPC and NMR analysis were withdrawn with degassed syringes.

eATRP procedure for MMA polymerization with a Cu cathode. The electrochemical cell was equipped with 14 cm wires of Al anode and Cu cathode, an Ag/AgI reference electrode, a glassy carbon (GC) electrode, and a PTFE stir bar and purged with N₂. EtOH (7.5 mL), CuCl₂ (2.00 mg, 0.015 mmol), TPMA (13.06 mg, 0.045 mmol), Bu₄NCl (208.44 mg, 0.75 mmol), and MMA (7.5 mL) were added and purged with N₂ for 30 min at room temperature. After the degassing time, the cell was thermostated at 50 °C with a circulating water bath; the solution was let to reach thermal equilibrium, under gentle stirring (200 rpm). Then 2-bromopropionitrile (13.0 μ L, 0.15 mmol) was added and the solution was further purged with N₂ for 15 min. CVs were recorded on the GC electrode before and after BPN addition to obtain the standard redox potential of the catalyst and evaluate the initiator effect. Electrolysis was initiated by applying the appropriate potential (*E*_{app}) at a stirring

rate of 700 rpm. Electrolysis was automatically followed by the electrochemical software. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

SARA ATRP procedure for MMA polymerization with a Cu wire. The Schlenk flask was equipped with a 14 cm Cu wire and PTFE stir bar and degassed 3 times with N₂/vacuum cycles. EtOH (7.5 mL), CuCl₂ (2.00 mg, 0.015 mmol), TPMA (13.06 mg, 0.045 mmol), Bu₄NCl (208.44 mg, 0.75 mmol), 2-bromopropionitrile (13.0 μ L, 0.15 mmol) and MMA (7.5 mL) were added to a round bottom flask and purged with N₂ for 30 min at room temperature. After the degassing time, the solution was withdrawn with a degassed syringe and put inside the Schlenk. The reactor was put rapidly in a water bath at 50 °C. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

Typical eATRP procedure for AAm polymerization with a Cu cathode. The electrochemical cell was equipped with 14 cm wires of Al anode and Cu cathode, SCE reference electrode, a glassy carbon (GC) electrode, and a PTFE stir bar and purged with N₂. Water (9 mL), Cu(OTf)₂ (5.43 mg, 0.015 mmol), Me₆TREN (13.80 mg, 0.06 mmol), NaBr (153.7 mg, 1.5 mmol), and AAm (1.0 g) were added and purged with N₂ for 30 min at room temperature. After the degassing time, the cell was thermostated at 0 °C with a refrigerating bath; the solution was let to reach thermal equilibrium, under gentle stirring (200 rpm). Then 2-hydroxyethyl 2-bromoisobutyrate (HEBiB, 4.34 μ L, 0.3 mmol) was added and the solution was further purged with N₂ for 15 min. CVs were recorded on the GC electrode before and after HEBiB addition to obtain the standard redox potential of the catalyst and evaluate the initiator effect. Electrolysis was initiated by applying the appropriate potential (*E*_{app}) at a stirring rate of 700 rpm. Electrolysis was automatically followed by the electrochemical software. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

SARA ATRP procedure for AAm polymerization with a Cu wire. The Schlenk flask was equipped with a 14 cm Cu wire and PTFE stir bar and degassed 3 times with N₂/vacuum cycles. Water (9 mL), Cu(OTf)₂ (5.43 mg, 0.015 mmol), Me₆TREN (13.80 mg, 0.06 mmol), NaBr (153.7 mg, 1.5 mmol), 2-hydroxyethyl 2-bromoisobutyrate (HEBiB, 4.34 μ L, 0.3 mmol) and AAm (1.0 g) were added to a round bottom flask and purged with N₂ for 30 min at room temperature. After the degassing time, the solution was withdrawn with a degassed syringe and put inside the Schlenk. The reactor was put rapidly in a refrigerating bath at 0

°C. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

eATRP procedure for MA polymerization with Cu cathode. The electrochemical cell was equipped with 14 cm wires of Al anode and Cu cathode, an Ag/AgI reference electrode, a glassy carbon (GC) electrode, and a PTFE stir bar and purged with N₂. DMSO (7.5 mL), CuBr₂ (1.0 mg, 0.0045 mmol), TPMA-PYR (6.71 mg, 0.0135 mmol), Et₄NBF₄ (0.325 g, 1 mmol), and MA (7.5 mL) were added and purged with N₂ for 30 min at room temperature. After the degassing time, the cell was thermostated at 40 °C with a circulating water bath; the solution was let to reach thermal equilibrium, under gentle stirring (200 rpm). Then ethyl 2-bromoisobutyrate (29.25 mg, 0.15 mmol) was added and the solution was further purged with N₂ for 15 min. CVs were recorded on the GC electrode before and after EBiB addition to obtain the standard redox potential of the catalyst and evaluate the initiator effect. Electrolysis was initiated by applying the appropriate potential (*E*_{app}) at a stirring rate of 700 rpm. Electrolysis was automatically followed by the electrochemical software. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

SARA ATRP procedure for MA polymerization with a Cu wire. The Schlenk flask was equipped with a 14 cm Cu wire and PTFE stir bar and degassed 3 times with N₂/vacuum cycles. DMSO (7.5 mL), CuBr₂ (1.0 mg, 0.0045 mmol), TPMA-PYR (6.71 mg, 0.0135 mmol), Et₄NBF₄ (0.325 g, 1 mmol), ethyl 2-bromoisobutyrate (29.25 mg, 0.15 mmol) and MA (7.5 mL) were added to a round bottom flask and purged with N₂ for 30 min at room temperature. After the degassing time, the solution was withdrawn with a degassed syringe and put inside the Schlenk. The reactor was put rapidly in a circulating water bath at 40 °C. Samples for GPC and NMR analysis were periodically withdrawn with degassed syringes.

S3. Electrochemical and spectrochemical characterization of the polymerization systems before and after polymerization

Before the onset of polymerization, cyclic voltammetry of the system was always performed on a GC disk, to measure $E_{1/2}$ of the copper complex and evaluate the effect of the initiator (Fig. S1). A reversible peak couple attributed to the reversible reduction of [BrCu^{II}Me₆TREN]⁺ to [BrCu^IMe₆TREN] was observed in the absence of initiator. Addition of 10 mM EBiB changed the voltammetric response: the cathodic peak increased. On the electrode surface, [BrCu^{II}Me₆TREN]⁺ was reduced to [BrCu^IMe₆TREN]⁺, which partially dissociated generating the active form of the catalyst, [Cu^IMe₆TREN]⁺. The latter reacted with EBiB, forming an alkyl radical and the oxidized catalyst species [BrCu^{II}Me₆TREN]⁺, which diffuses again to the electrode to be reduced again. Therefore, the cathodic peak became catalytic.



Figure S1. (a) CVs of 10^{-3} M [BrCu^{II}Me₆TREN]⁺ in DMF + 50 vol% BA, from 20 to 500 mV/s; (b) CVs of 10^{-3} M [BrCu^{II}Me₆TREN]⁺ in DMF + 50 vol% BA without (—) or with (—) 10^{-2} M EBiB at 200 mV/s. CVs were recorded on a glassy carbon electrode at T = 45 °C in the presence of 0.1 M Et₄NBF₄ as a background electrolyte.

Relevant VIS-NIR spectra recorded before and after the polymerizations by *e*ATRP with a Cu cathode or by SARA ATRP are shown in Figure S2. When no excess L was present, the concentration of Cu^{II} remained constant. This clearly demonstrates that in this circumstance Cu merely acts as a cathode and the process proceeds by *e*ATRP without any significant contribution from SARA ATRP. Conversely, in experiments with starting excess ligand, the final concentration of Cu^{II} was higher than the starting value. This result was also confirmed by CV analysis of the reaction mixture before and after polymerization (Fig. S3) if one takes into account that CV signals are affected by viscosity, which increases after polymerization.



Figure S2. VIS-NIR spectra recorded at the beginning and at the end of relevant polymerizations of 3.49 M *n*BA in DMF: (a) potentiostatic electrolysis with a Cu/Pt setup: $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.1/0.1; E_{app} = E_{1/2} - 0.06 V$ (no free L, Table 1, entry 2); (b) PGE *e*ATRP with a Cu/Al setup: $|I_{app}| = 0.227$ mA; $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 4, entry 2); (c) PGE *e*ATRP with a Cu/Al setup: $|I_{app}| = 0.227$ mA; $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 4, entry 2); (c) PGE eATRP with a Cu/Al setup: $|I_{app}| = 0.227$ mA, $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 4, entry 2); (c) PGE $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 51, entry 1).



Figure S3. CVs recorded at the beginning and at the end of relevant polymerizations of 3.49 M *n*BA in DMF: (a) potentiostatic electrolysis with a Cu/Pt setup:

 $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.1/0.1; E_{app} = E_{1/2} - 0.06 V$ (no free L, Table 1, entry 2); (b) PGE *e*ATRP with a Cu/Al setup: $|I_{app}| = 0.227$ mA; $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 4, entry 2); (c) PGE *e*ATRP with a Cu/Al setup: $|I_{app}| = 0.227$ mA, $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (no initial Cu^{II}, Table 4, entry 4) and (d) conventional SARA ATRP: $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$ (Table 51, entry 1).

S4. Additional data for continuous potentiostatic and galvanostatic *e*ATRPs with various electrode materials



Figure S4. Semi-logarithmic kinetic plots of *e*ATRP at different E_{app} values using a Cu/Pt setup (divided cell) and no Cu^{II} salt initially present in solution, and comparison with a similar systems without any applied potential (*i.e.* SARA ATRP). The graph on the right is a zoom in of the graph on the left. Conditions: *n*BA/EBiB/Me₆TREN/Et₄NBr = 349/1/0.1/0.1; $C_{nBA} = 3.49$ M in DMF + 0.1 M Et₄NBF₄, T = 45 °C; activated Cu wire with l = 14 cm (see Table 1, entries 3-8).



Figure S5. Evolution of molecular weight and dispersity for the polymerizations of **Figure S4**. Conditions: $nBA/EBiB/Me_6TREN/Et_4NBr = 349/1/0.1/0.1$; $C_{nBA} = 3.49$ M in DMF + 0.1 M Et_4NBF_4, T = 45 °C; activated Cu wire with l = 14 cm (see Table 1, entries 3-8).



Figure S6. GPC traces of *e*ATRP at different E_{app} values using a Cu/Pt setup (divided cell) and no Cu^{II} salt initially present in solution: (a) $E_{1/2}$ - 180 mV, (b) $E_{1/2}$ - 60 mV, (c) $E_{1/2}$ + 60 mV, (d) $E_{1/2}$ + 180 mV, (e) $E_{1/2}$ + 300 mV; and of (f) SARA ATRP. Conditions: *n*BA/EBiB/Me₆TREN/Et₄NBr = 349/1/0.1/0.1; C_{nBA} = 3.49 M in DMF + 0.1 M Et₄NBF₄, T = 45 °C; activated Cu wire = 14 cm (see Table 1, entries 3-8).



Figure S7. Profile of *I vs t* recorded during a potentiostatic *e*ATRP of *n*BA on a Pt cathode coupled with an Al anode in DMF + 0.1 M Et₄NBF₄ (Table 2, entry 1). Other conditions: $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1$; $C_{nBA} = 3.49$ M; $E_{app} = E_{1/2} - 0.06$ V; T = 45 °C.



Figure S8. Profile of *I vs t* recorded during a potentiostatic *e*ATRP of *n*BA on a Pt cathode coupled with a Cu anode in DMF + 0.1 M Et₄NBF₄ (Table 2, entry 3). Other conditions: $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.1/0.1; C_{nBA} = 3.49 \text{ M}; E_{app} = E_{1/2} - 0.06 \text{ V}; T = 45 \text{ °C}.$



Figure S9. Profile of *I vs t* recorded during a potentiostatic *e*ATRP of *n*BA on a Cu/Cu electrode pair in DMF + 0.1 M Et₄NBF₄ (Table 2, entry 4). Other conditions: $nBA/EBiB/Cu^{II}(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.1/0.1; C_{nBA} = 3.49 \text{ M}; E_{app} = E_{1/2} - 0.06 \text{ V}; T = 45 \text{ °C}.$



Figure S10. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by potentiostatic *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C; cathode/anode pair: Cu/Al (Table 2, entry 5). Other conditions: *n*BA/EBiB/Cu^{II}(OTf)₂/ Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1; $C_{nBA} = 3.49$ M; $E_{app} = E_{1/2}$ -0.06 V.

Three control ATRPs were performed to have an additional comparison for our results: a SARA ATRP of *n*BA and two continuous galvanostatic *e*ATRPs on a Pt cathode coupled with an Al anode, with Q = 0.83 C and Q = 1.632 C. (Table S1). A SARA ATRP in the same conditions of Table 1, entry 12, afforded high monomer conversion and P(*n*BA)-Br of excellent dispersity. The CGE *e*ATRP with Q = 0.83 C gave P(*n*BA)-Br of the same

dispersity but conversion was lower (56%). When the experiment was repeated with Q = 1.66 C, conversion reached 85% while the dispersity remained practically unchanged.

Entry	Polymerization	$C_{[C_{\mu}]_{II}^{0}}^{0}$	$C_{L,free}^{0}$	t	O(C)	Conv.	k _{p,app}	$M_{ m n}^{ m GPC}$	$M_{ m n}^{ m th}$	De
	Mode	(mM)	(mM)	(h)	Q (C)	(%) ^b	(h ⁻¹)	(kDa) ^c	(kDa) ^d	D
1	SARA	1	2	2	-	87	1.14	40.8	39.0	1.08
2	CGE eATRP	1	2	2	0.83	56	0.41	28.0	25.1	1.08
3	CGE eATRP	1	2	2	1.66	85	1.19	40.6	37.9	1.10

Table S1. Control ATRP experiments of *n*BA 50 vol% catalyzed by $[BrCu^{II}Me_6TREN]^+$ in DMF + 0.1 M Et₄NBF₄ at T = 45 °C.^{*a*}

^{*a*}Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1. C_{nBA} = 3.49 M in DMF, T = 45°C; *e*ATRPs: supporting electrolyte = 0.1 M Et₄NBF₄; WE/CE = Pt/Al in an undivided cell; stirring = 700 rpm. ^{*b*}Calculated from ¹H-NMR in CDCl₃ using DMF as internal standard. ^{*c*}Calculated from THF GPC with narrow PMMA standards at T = 30 °C. ^{*d*}Calculated from ¹H-NMR: $M_n^{th} = \text{Conv.} \times \text{DP} \times M_{nBA} + M_{\text{EBiB}}$. ^{*e*} $D = M_w/M_n$.



Figure S11. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by SARA ATRP of *n*BA at T = 45 °C (Table S1, entry 1). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1. $C_{nBA} = 3.49$ M in DMF.



Figure S12. Monomer conversion vs time in continuous galvanostatic eATRP on a Cu/Cu pair and SARA ATRP of *n*BA at T = 45 °C in DMF + 0.1 M Et₄NBF₄ using a small loading of catalyst/ligand. Conditions: (blue squares) $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr =$ 349/1/0.01/0.01/0.01, $|I_{app}|$ = 2 mA (Table 3, entry 4); (red circles): $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0/0.01/0.01, |I_{app}| = 2 mA$ (Table 3, entry 5); (black triangles) SARA ATRP, *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0/0.01/0.01 (Table 3, entry 6).



Figure S13. Scanning electron microscopy (SEM) images of a Cu wire before and after it has been used as a cathode in *e*ATRP of *n*BA with a Cu/Cu setup and $|I_{app}| = 1$ mA (Table 3, entry 1). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.1/0.1, $C_{nBA} = 3.49$ M in DMF + 0.1 M Et₄NBF₄, T = 45 °C.



Figure S14. Scanning electron microscopy (SEM) images of a Cu wire after it has been used as an anode in *e*ATRP of *n*BA with a Cu/Cu setup and $|I_{app}| = 1$ mA (Table 3, entry 1). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.1/0.1, $C_{nBA} = 3.49$ M in DMF + 0.1 M Et₄NBF₄, T = 45 °C. For SEM images of the wire before *e*ATRP see Figure S13.



Figure S15. (a) Kinetic plots and (b) evolution of M_n and D vs conversion for eATRP of nBA using a Cu/Al setup under potentiostatic electrolysis (**•** Table 2, entry 5, conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $E_{app} = E_{1/2} - 0.06$ V), and under continuous galvanostatic electrolysis (**•** Table 3, entry 7, conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $|I_{app}| = 0.227$ mA), and comparison with a conventional SARA ATRP using a similar setup (**▲** Table S1, entry 1, conditions $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.3/0.1)$. Other conditions: $C_{nBA} = 3.49$ M in DMF + 0.1 M Et₄NBF₄, T = 45 °C. Full and empty symbols refer to the left and right ordinates, respectively. The black straight line represents M_n th.



Figure S16 Profiles of the potential recorded at the working electrode (E_{WE}) relative to the reference electrode (RE) and I_{app} vs t recorded during CGE eATRP of nBA on a Cu cathode coupled with an Al anode in DMF + 0.1 M Et₄NBF₄; Q = 1.66 C (Table 3, entry 7). The dashed line represents $E_{1/2}$ of the catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $|I_{app}| = 0.227$ mA, $C_{nBA} = 3.49$ M, T = 45 °C

S5. Estimated consumption of sacrificial anode materials

Cu anode

During eATRP with a Cu anode CuII ions are released into solution. In absence a free ligand, these ions are much easily reduced than [Cu^{II}L]²⁺ or [BrCu^{II}L]⁺. They are therefore reduced to Cu⁰ as soon as they reach the cathode. The amount of Cu^{II} that is formed at the anode and then reduced to Cu⁰ that deposits at the surface of the Cu (or Pt) cathode can be estimated from the total charge (Q) passed in the system. In fact, Q is a combination of: (i) the charge $Q_{\rm red}$ needed to reduce the starting Cu^{II} to Cu^I (the extent of this reduction depends on the applied potential or the potential at the WE); (ii) the charge Q_t needed to re-generate Cu^{I} from the Cu^{II} that is accumulated due to termination reactions; (iii) the charge Q_{Cu} due to the bielectronic reduction of Cu^{II} formed at the anode and deposited as Cu⁰ at the cathodic surface. Thus, $Q = Q_{red} + Q_t + Q_{Cu}$. Consider the representative case of an *e*ATRP with 1 mM [Cu^{II}L]²⁺, no excess L, a reaction volume of 15 mL and $E_{app} = E_{1/2}$ - 0.06 V. According to the Nernst equation ~1.36 \times 10⁻⁵ mol of Cu^{II} is reduced at the electrode surface, corresponding to $Q_{\rm red}$ = 1.32 C, according to the Faraday's law. Notice that if no Cu^{II} is present in solution at the beginning of the polymerization $Q_{red} = 0$ C. The extent of radical termination is more difficult to evaluate, however in a controlled radical polymerization the fraction of dead chains is typically < 10%. Thus, if we assume that 10% chains are dead, starting with 10 mM alkyl halide initiator, the quantity of Cu^I regenerated during polymerization is 1.5×10^{-5} mol, which corresponds to $Q_t = 1.45$ C. Therefore, Q_{Cu} can be calculated as $Q - (Q_{red} + Q_t)$. Once Q_{Cu} has been estimated, the Faraday's law is applied again to calculate the mass of Cu⁰ deposited on the WE: $m_{\rm Cu} = Q_{\rm Cu}/2F \times M_{\rm Cu}$ (where F is the Faraday's constant and M_{Cu} is the molar mass of Cu). In our systems the amount of deposited Cu⁰ ranges between ca. 3 and 7 mg at the end of the polymerization, mostly depending on the total charge passed. It should be noted that this approach likely overestimates the fraction of terminated chains. Moreover, any side reactions or eventual reduction of impurities in solution is not considered.

However, if one wants to evaluate the corrosion of the CE in order to assess the need for a replacement after some time, then the calculation is simpler, as $m_{CE(Cu)}$ depends on the total Q, according to the Faraday's law, i.e. $m_{CE(Cu)} = Q/2F \times M_{Cu}$. The values of $m_{CE(Cu)}$ have been added to each Table in the main manuscript. From these, it is possible to estimate the reaction time needed to largely consume the sacrificial Cu anode, which is relevant for an eventual scale up of the process. For the estimation, we made the assumptions that the wire

is homogeneously consumed and that it needs to be replaced once its diameter is reduced from 1 mm to 0.5 mm. In the representative cases of potentiostatic *e*ATRP with a Cu/Cu system and galvanostatic *e*ATRP on Cu/Cu at $|I_{app}| = 2$ mA (Table 2, entry 4 and Table 3, entry 2, respectively), $m_{CE(Cu)} \approx 2.3$ mg/h. Considering that the Cu wire immersed in solution had a diameter of 0.1 cm and a length of 14 cm, and that the density of Cu is 8.96 g/cm³, the weight of the Cu wire in solution is 986 mg and weight loss after 50% reduction of wire diameter would be 739 mg. Therefore, it will take > 300 h of reaction to consume the anode until its diameter is decreased to 0.05 cm. In the considered polymerization cases, the amount of P(*n*-BA) produced per hour of reaction was 1.8 and 2.7 g, respectively. It follows that within the proposed setup ~1 kg of polymer can be made before replacement of the Cu wire becomes necessary.

Al anode

The amount of Al³⁺ that is formed at the CE and then complexed by excess L in solution can be estimated from the total charge passed in the system. If one wants to evaluate the corrosion of the CE to assess the need for a replacement after some time, $m_{\text{CE(Al)}} = Q/3F \times$ $M_{\rm Al}$. The values of $m_{\rm CE(Al)}$ are listed in each Table in the main manuscript. From these values, it is possible to estimate the reaction time needed to largely consume the sacrificial Al anode, which is relevant for a subsequent scale up of the process. For the estimation, we made the assumptions that the wire is homogeneously consumed and that it needs to be replaced once its diameter is decreased by a half. In the representative case of an eATRP with 1 mM $[Cu^{II}L]^{2+}$, 3-fold excess L, a reaction volume of 15 mL and Q = 0.83 C of charge imposed to the system in 2 hours, (Table 4, entries 2-5), $m_{CE(AI)} \approx 0.0387$ mg/h. Considering that the Al wire immersed in solution had a diameter of 0.1 cm and a length of 14 cm, and that the density of Al is 2.70 g/cm³, the weight of the Al wire lost by corrosion is 222.66 mg. Therefore, it will take ~ 5752 h (or 240 days) of reaction to consume the anode until its diameter is decreased to 0.05 cm. In the considered polymerization cases, the amount of P(n-BA) produced per hour of reaction was 3.1 g, according to conversion. It follows that within the proposed setup 17.8 kg of polymer can be made before the Al wire must be replaced.

S6. Considerations on the relative contributions of SARA ATRP and *e*ATRP mechanisms

In ATRP with Cu^I activator regeneration, the concentration of radicals (and thus the rate of polymerization) is determined by the ratio of the rate of Cu^I regeneration to the rate of radical termination. Thus, in the case of *e*ATRP, the radical concentration can be calculated according to equation 1,⁴ where k_t is the rate constant of radical termination, while $k_{red,app}$ is the apparent rate constant of reduction, which depends among other factors on the applied potential and area of the working electrode or on the applied current. For simplicity, Cu complexes are given in the equations and in this discussion without charge.

$$[R^{\bullet}] = \sqrt{\frac{k_{red,app}[Br-Cu^{II}/L]}{k_t}}$$
(1)

The concentration of propagating radicals in ATRP can be calculated from the semilogarithm kinetic plot, whereby the slope of $\ln([M]_0/[M])$ vs time is the apparent rate constant of propagation, $k_{p,app}$, which corresponds to the product of the equilibrium radical concentration and the rate constant of propagation, i.e. $k_{p,app} = k_p[R^{\bullet}]$. The value of k_p can be found in the literature for several monomers at various temperatures.

In order to extract a value for $k_{\text{red,app}}$ from eq. 1, one needs to know the equilibrium concentration of the Cu^{II} deactivator. In *e*ATRP the ratio of Cu^I to Cu^{II} species is dictated by the applied potential. However, this reflects the ratio at the electrode surface, which is likely different from the bulk ratio. Therefore, a better estimate of [X-Cu^{II}/L] can be obtained by re-arranging the classical equation for the ATRP equilibrium (eq. 2),⁴ provided that the equilibrium constant of ATRP (K_{ATRP}) for the given system is known, and then considering that the sum of Cu^{II} and Cu^{II} species should equal the initial loading of Cu salt. However, if excess ligand is initially present this must be considered in the total amount of Cu.

$$\frac{[Br-Cu^{II}/L]}{[Cu^{I}/L]} = K_{ATRP} \frac{[RX]}{[R^{\bullet}]}$$
(2)

In the case of SARA ATRP, the equilibrium concentration of radicals is given by equation 3,⁴ where $k_{act,0}$ is the rate constant of activation of alkyl halides by Cu⁰, k_{comp} is the rate of comproportionation, and *S/V* is the ratio of the Cu wire surface to the volume of the solution.

$$[R^{\bullet}] = \sqrt{\frac{k_{act,0}(S/V)[RX] + k_{comp}(S/V)[Br-Cu^{II}/L]}{k_t}}$$
(3)

Values of $k_{act,0}$ were previously estimated in dimethyl sulfoxide (DMSO), acetonitrile (MeCN) and water, and their mixtures with acrylate monomers, in the presence of different ATRP ligands and initiators.⁵ Typical values are on the order of 10⁻⁴-10⁻⁵ cm s⁻¹, and they do not follow the known trends in k_{act} values for $[Cu^{I}L]^{+}$ complexes used in ATRP. Values of k_{comp} were previously determined for various ATRP catalysts in DMSO, MeCN and water and their mixtures with monomers.⁶ In DMSO, which is the preferred solvent for SARA ATRP, comproportionation is rather fast, with $k_{\rm comp}$ ranging from 10⁻² to 10⁻³ cm s⁻ ¹. In water, Cu^I complexes tend to rapidly disproportionate, thus k_{comp} values are typically 2 orders of magnitude lower than in DMSO. The nature of L also affects the disproportionation/comproportionation equilibrium, with for instance Cu^I/Me₆TREN undergoing faster disproportionation than CuI/TPMA. Examples of SARA ATRP in DMF are scarce. However, the disproportionation rate constant for Cu^I/TPMA in DMF was reported as $k_{\text{disp}} = 1.3 \text{ M}^{-1}\text{s}^{-1}$, while in DMSO $k_{\text{disp}} = 0.37 \text{ M}^{-1}\text{s}^{-1}$. Therefore, it is reasonable to expect lower k_{comp} values in DMF than in DMSO for conventional ATRP catalysts. For the model polymerization analyzed herein (nBA/Br-Cu^{II}Me₆TREN in DMF), the following parameters can be found in the literature (in some cases they have been rescaled to account for *T* effect):

Parameter	Value	Reference
$\overline{k_{\rm p}~({\rm M}^{-1}{\rm s}^{-1})}$	2.58×10^{4}	9
$k_{\rm t} ({ m M}^{-1}{ m s}^{-1})$	6×10^{8}	10
K _{ATRP}	3×10^{-5}	11
<i>S/V</i> (cm ⁻¹)	0.294	

These parameters and the equations above can be used to evaluate the contribution of SARA ATRP and *e*ATRP mechanisms for the case-studies in our manuscript.

(i) eATRP, WE = Cu, CE = Pt (divided cell). Conditions: $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0.1/0.1/0.1$, $C_{nBA} = 3.49$ M, $E_{app} = E_{1/2} - 0.06$ V, in DMF + 0.1 M Et_4NBF₄, T = 45 °C. (*Table 1, entry 2 in the main text, pure* eATRP). In this system, $k_{p,app} = 2.36 \times 10^{-4} \text{ s}^{-1}$, therefore $[R^{\bullet}] = 9.1 \times 10^{-9}$ M. By considering that the Cu^{II} loading is 1 mM and by using eq. 2, the equilibrium concentration of Br-Cu^{II}/L is 9.7×10^{-4} M. Thus, $k_{\text{red,app}} = 5.2 \times 10^{-5} \text{ s}^{-1}$.

(ii) **SARA ATRP**, Conditions: $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr = 349/1/0/0.1/0.1, C_{nBA} = 3.49 M, in DMF + 0.1 M Et_4NBF_4, T = 45 °C. ($ *Table 1, entry 8 in the main text* $). In this system, <math>k_{p,app} = 2.94 \times 10^{-4} \text{ s}^{-1}$, therefore $[R^{\bullet}] = 1.1 \times 10^{-8} \text{ M}$. By considering a total Cu concentration of ~0.8 mM (estimated on the basis of Figures S2 and S3) and by using eq. 2, the equilibrium concentration of Br-Cu^{II}/L is 7.7 × 10⁻⁴ M. Both $k_{act,0}$ and k_{comp} are unknown, however based on previous reports and above discussion on comproportionation/disproportionation trends and by using eq. 3, one can reasonably estimate that $k_{act,0} = 10^{-5} \text{ cm s}^{-1}$ and $k_{comp} = 2.1 \times 10^{-4} \text{ cm s}^{-1}$.

Comparing case (i) and (ii), it emerges that the rates of activator (re)generation by electrochemical reduction, Cu⁰ and comproportionation are comparable: $R_{red} = k_{red,app}[Br-Cu^{II}/L] = 5 \times 10^{-8} M s^{-1}$; $R_{act,0} = k_{act,0}(S/V)[Br-Cu^{II}/L] = 2.9 \times 10^{-8} M s^{-1}$; $R_{comp} = k_{comp}(S/V)[Br-Cu^{II}/L] = 4.8 \times 10^{-8} M s^{-1}$. Thus, all these processes contribute to a similar extent to the polymerization when *e*ATRP (with $E_{app} < E_{1/2}$) is performed with a Cu cathode in the presence of excess ligand. If no Cu^{II} is present at the beginning, a build-up of Cu^{II} (via Cu⁰, then Cu^I activation and eventual termination) is needed for comproportionation¹² and electrochemical reduction to contribute to the system. When $E_{app} > E_{1/2}$, Cu^I generated via Cu⁰ activation has two possibilities: rapid oxidation to Cu^{II} at the surface of copper electrode or activation of the dormant species. Indeed, activation by [Cu^IMe₆TREN]⁺ is fast ($k_{act} = 8 \times 10^3 M^{-1}s^{-1}$ is reported for acrylate dormant species in BA/DMSO 1/1 by Cu^I/Me₆TREN at room temperature,¹¹ so over twice this value is expected at 45 °C and over an order of magnitude higher for the activation of the initiator EBiB), which explains why polymerization still proceeds to some extent.

(iii) eATRP, WE = Pt, CE = Al. Conditions: $nBA/EBiB/Cu(OTf)_2/Me_6TREN/Et_4NBr$ = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, $E_{app} = E_{1/2} - 0.06$ V, in DMF + 0.1 M Et_4NBF₄, T = 45°C. (*Table 2, entry 1 in main text, pure eATRP*). In this system, $[R^{\bullet}] = 1.45 \times 10^{-8}$ M. By considering that the Cu loading is 1 mM and by using eq. 2, the equilibrium concentration of Br-Cu^{II}/L is 9.5×10^{-4} M. Thus, $k_{red,app} = 1.3 \times 10^{-4}$ s⁻¹.

The higher value of $k_{\text{red,app}}$ for case (iii) compared to case (i) is mainly due to the larger surface area of the Pt mesh.

The systems that employ Al as anode together with a Cu cathode are more complicated, as both Al and Cu ions can form complexes with excess L, therefore one would need to precisely measure the equilibrium concentration of Cu^{II} to make reliable estimates on the reaction parameters. However, this is outside the scope of this work.





Figure S17. (a) Kinetic plot and (b) evolution of M_n and D vs conversion for eATRP of nBA at T = 45 °C in DMF + 0.1 M Et₄NBF₄ used in the duty cycle determination on a Cu cathode coupled with an Al anode (Figure 3 in the main text). Full and empty symbols refer to the left and right ordinates, respectively. The black straight line represents M_n^{th} . Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, C_{nBA} = 3.49 M, $E_{app} = E_{1/2} - 0.06$ V for 30 min, then the potential was switched off.



Figure S18. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced during the duty cycle determination on a Cu cathode coupled with an Al anode (Figure 3 in main text and Figure S17) in the potentiostatic *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄. Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, $E_{app} = E_{1/2} - 0.06$ V for 30 min, then the potential was switched off.



Figure S19. Profiles of E_{WE} and I_{app} vs t recorded during galvanostatic PGE eATRP of nBA on a Cu/Al electrode pair in DMF + 0.1 M Et₄NBF₄; Q = 1.66 C; electrolysis duty cycle = 10 min (Table 4, entry 1). The dashed line represents $E_{1/2}$ of the copper catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S20. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C, electrode pair: Cu/A1. Q = 1.66 C (Table 4, entry 1 and Figure S19). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S21. Profiles of E_{WE} and I_{app} vs t recorded during galvanostatic PGE eATRP of nBA on a Cu/Al electrode pair in DMF + 0.1 M Et₄NBF₄; Q = 0.83 C; electrolysis duty cycle = 10 min (Table 4, entry 2). The dashed line represents $E_{1/2}$ of the copper catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S22. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C; cathode/anode pair: Cu/Al; Q = 0.83 C (Table 4, entry 2). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S23. (a) Kinetic plot and (b) evolution of M_n and D vs conversion for eATRP of nBA at T = 45 °C in DMF + 0.1 M Et₄NBF₄, DP_T = 1745, Q = 0.83 C (Table 4, entry 3). Full and empty symbols refer to the left and right ordinates, respectively. The black straight line represents M_n th. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/0.2/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S24. Profiles of E_{WE} and I_{app} vs t recorded during galvanostatic PGE eATRP of nBA on a Cu/Al electrode pair; Q = 0.83 C; duty cycle = 10 min; $C_{EBiB} = 2 \times 10^{-3}$ M; DP_T = 1745 (Table 4, entry 3). The dashed line represents $E_{1/2}$ of the catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/0.2/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S25. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C; cathode/anode pair: Cu/Al. DP_T = 1745; Q = 0.83 C (Table 4, entry 3). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/0.2/0.1/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S26. Profiles of E_{WE} and I_{app} vs t recorded during galvanostatic PGE eATRP of nBA on a Cu/Al electrode pair in DMF + 0.1 M Et₄NBF₄; Q = 0.83 C, electrolysis duty cycle = 10 min (Table 4, entry 4). The dashed line represents $E_{1/2}$ value of the copper catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S27. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C; cathode/anode pair: Cu/Al; Q = 0.83 C (Table 4, entry 4). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0/0.3/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S28. Profiles of E_{WE} and I_{app} vs t recorded during galvanostatic PGE eATRP of nBA on a Cu/Al electrode pair ; Q = 0.83 C, duty cycle = 10 min (Table 4, entry 5). The dashed line represents $E_{1/2}$ of the catalyst. Conditions: nBA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.01/0.29/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.



Figure S29. Normalized evolution of molecular weight distribution of P(*n*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF + 0.1 M Et₄NBF₄ at T = 45 °C; cathode/anode pair: Cu/Al; Q = 0.83 C (Table 4, entry 5). Conditions: *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.01/0.29/0.1, $C_{nBA} = 3.49$ M, T = 45 °C.

S8. Additional data for copolymerization via PGE eATRP



Figure S30. Profiles of E_{WE} and I_{app} vs t recorded during a two-step galvanostatic PGE eATRP of nBA (—) and nBA + tBA (—) on a Cu cathode coupled with an Al anode; Q = 0.416 C for each step of 1 h; electrolysis duty cycle = 10 min. The time needed for stopping the polymerization, injection and degassing of tBA is not shown in the Figure. The dashed lines represent $E_{1/2}$ of the catalyst.



Figure S31. 400 MHz ¹H-NMR of P(*n*BA)-Br produced by PGE *e*ATRP (with Cu/Al) of *n*BA in DMF + 0.1 M Et₄NBF₄, T = 45 °C, *n*BA/EBiB/Cu(OTf)₂/Me₆TREN/Et₄NBr = 349/1/0.1/0.3/0.1, $C_{nBA} = 3.49$ M (Table 4, entry 2). Assignments: 0.97 ppm CH₃ side chain, 1.43 ppm CH₂ side chain, 1.65 ppm CH₂ side chain, 1.94 ppm CH₂ backbone, 2.29 ppm CH backbone, 4.09 ppm OCH₂ side chain.



Figure S32. 400 MHz ¹H-NMR of P(*n*BA)-*b*-P(*n*BA-*stat-t*BA)-Br produced by PGE *e*ATRP of *n*BA in DMF (See *Chain extension* section of the main text for reaction conditions and polymer details). Assignments: 0.97 ppm CH₃ side chain (PBA), 1.36 ppm CH₂ side chain (PBA), 1.44 ppm C(CH₃)₃ (P*t*BA),1.65 ppm CH₂ side chain (PBA), 1.94 ppm CH₂ backbone (PBA + P*t*BA), 2.29 ppm CH backbone (PBA+ P*t*BA), 4.09 ppm OCH₂ side chain (PBA).



S9. Expanding the monomer scope of eATRP with Cu cathodes

Figure S33. (a) Kinetic plots, (b) evolution of M_n and D vs conversion during SARA ATRP (**■**) or eATRP on a Cu/Al pair (**•**) of MA in DMSO + 0.1 M Et₄NBF₄ at T = 40 °C and $E_{app} = E_{1/2}$. (c, d) Normalized evolution of molecular weight distribution of PMA-Br produced by SARA ATRP (c) or eATRP (d). Conditions: MA/EBiB/CuBr₂/TPMA-PYR =

552/1/0.03/0.09, $C_{MA} = 5.52$ M. Full and empty symbols refer to the left and right ordinates, respectively. The black straight line represents M_n^{th} in (b).

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