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Supplementary Information

Electrochemically mediated atom transfer radical polymerization of *n*-butyl acrylate on non-platinum cathodes

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S1. Experimental section

Cleaning/activation of working electrodes. Platinum gauze electrode was electrochemically activated in 0.5 M H_2SO_4 by first applying a series of anodic/cathodic steps of 6 s each, with a current density of *ca* 0.4 mA cm^{-2}, for a total time of 15 min, and then 50 voltammetric cycles at 0.1 V s^{-1} in a potential range between -0.7 and 1.0 V vs. Hg/Hg_2SO_4 reference electrode.

Glassy carbon foil was polished with 1000, 2500 and 4000 grit silicon carbide papers, and 3-, 1-, 0.25-µm diamond pastes. Each polishing step was followed by ultrasonic rinsing in ethanol for 5 min.

Gold foil was cleaned with aqua regia ($HCl:HNO_3$ = 3:1, v/v) and then washed with abundant deionized water. Before use, the electrode was electrochemically activated in 0.5 M H_2SO_4 with cyclic anodic/cathodic steps of 6 s each, with a current density of ca 0.4 mA cm^{-2}, for a total time of 15 min, followed by 50 CV cycles at 0.2 V s^{-1} in a potential range between -0.7 and 1.2 V vs. Hg/Hg_2SO_4 reference electrode.

Nickel-chromium wire, iron wire, and 304 stainless steel foil were polished with 1000, 2500 and 4000 grit silicon carbide papers, and 3-, 1-, 0.25-µm diamond pastes, with ultrasonic rinsing in ethanol for 5 min after each polishing step. They were then chemically activated by soaking in a dilute solution of HCl for 10 min. In the case of NiCr, the wire was immersed also in dilute HNO_3 after polishing. Finally the electrodes were rinsed with plenty of distilled water.

General procedure of polymerization. All electrochemical experiments were carried out in a six-neck electrochemical cell maintained at 45 °C with a thermostat and purged with Ar. A 3 mm diameter GC disk used for voltammetric analysis, a bulk working electrode (of different materials) for electrolysis and a counter electrode made of Pt in a separated compartment were inserted. Et_4NBF_4 (0.3256 g, 1.5×10^{-3} mol) was put in the cell as supporting electrolyte together with DMF (6.35 mL) and *n*-butyl acrylate (7.5 mL, 5.2×10^{-2} mol). Then 1 mL of an Ar purged 0.015 M stock solution of $Cu(OTf)_2$ (1.5×10^{-5} mol) in DMF, 0.15 mL of an Ar purged 0.1 M stock DMF solution of Et_4NBr (1.5×10^{-5} mol) and 4 µL of Me_6TREN (1.5×10^{-5} mol) were added into the cell. A CV of the catalyst was recorded with this setup on the GC disk electrode. Then 19.3 µL of methyl bromoisobutyrate (MBiB, 1.5×10^{-4} mol) were added to the solution and another CV was recorded to verify the catalytic effect. At this point, the bulk working electrode, which was previously activated and already in the cell, at rest above the solution, was immersed into the polymerization mixture and a fixed potential (or a current program) was applied to the system. Samples were withdrawn periodically to determine the molecular weight distribution ($Đ$), the number average molecular weight (M_n) and the monomer conversion.

Polymerization procedure with Al as sacrificial anode. The procedure was the same as described in the last paragraph, but the Pt counter electrode was replaced by an Al wire. Before use, Al was washed with THF and acetone and directly immersed into the reaction mixture.

S2. Voltammetric analysis of catalyst behavior

Before starting the polymerization process, cyclic voltammetry of the system was always performed on a GC disk, to measure the formal reduction potential of the copper complex and to evaluate the effect of the initiator (Fig. S1). A reversible peak couple attributed to the reversible reduction of $[BrCu^{II}L]^+$ to $[BrCu^{I}L]$ (L = Me_6TREN) was observed in the absence of initiator. Addition of MBiB in a 10-fold excess with respect to the catalyst drastically changed the voltammetric response: the cathodic peak increased, while the anodic one decreased and nearly disappeared. On the electrode surface, $[BrCu^{II}L]^+$ was reduced to $[BrCu^{I}L]$, which partially dissociated generating the active form of the catalyst, $[Cu^{I}L]^+$.[1,2] The latter reacted with the polymerization initiator, forming an alkyl radical and the oxidized catalyst species $[BrCu^{II}L]^+$, which diffuses back to the electrode to be reduced again to $[BrCu^{I}L]$. Consequently, the cathodic peak became catalytic while the anodic one decreased because of the disappearance of $[BrCu^{I}L]$ via reaction with RX.

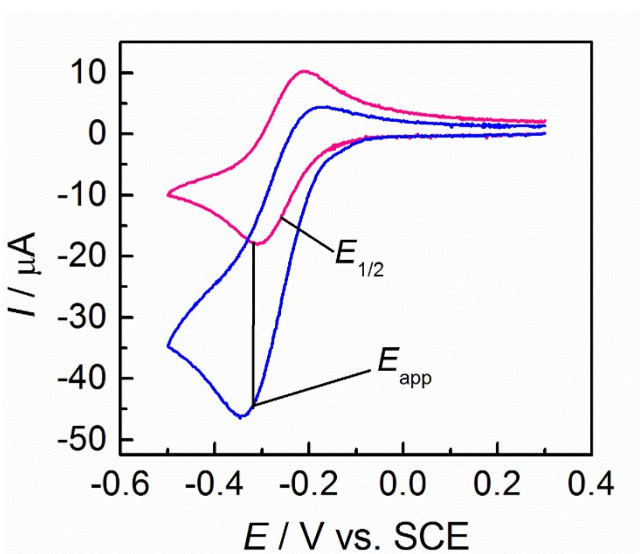

Fig. S1 Cyclic voltammetry of 1 mM $[BrCu^{II}Me_6TREN]^+$ in 50% (v/v) n-BuA in DMF, with $C_{Et_4NBF_4}$ = 0.1 M, recorded in the absence (pink) and presence (blue) of 10 mM MBiB; v = 0.2 Vs^{-1}, T = 45 °C.

S3. Effect of C_{Br^-} on potentiostatic *e*ATRP of 50% (v/v) *n*-BuA in DMF on a Pt electrode

Potentiostatic *e*ATRPs were carried out with $Cu(OTf)_2/Me_6TREN$ = 1/1 and different initial Br^- concentrations, at a fixed $E_{app} = E_{1/2} - 60$ mV. Polymerization in the absence of Br^- was slower and less controlled than in the presence of 1 or 2 mM Br^- (Table S1, Fig. S2). The expected effect of bromide ions was to convert Cu^{II} species to $[BrCu^{II}L]^+$ at the beginning of the polymerization, thereby increasing the rate of deactivation and control over molecular weight distribution. Addition of one equivalent of Br^- to the Cu^{II} solution improved both conversion and dispersity (compare entries 1 and 2 of Table S1). Polymerizations with 1 to 10 mM Br^- were equally controlled ($Đ$ = 1.15–1.16), but showed decreasing reaction rate with increasing C_{Br^-}, because of decreased activation rate.[1,2] Therefore, a $C_{[Cu^{II}L]^{2+}}/C_{Br^-}$ ratio of 1/1, which gave the highest reaction rate, was used for the polymerization with all tested working electrode materials.

Table S1 Effect of C_{Br^-} on potentiostatic *e*ATRP of 50% (v/v) *n*-BuA in DMF on a Pt electrode[a]

Entry	C_{Et_4NBr} (mM)	t (h)	Q (C)	Conv.[b] (%)	$M_{n,th}\times10^{-3}$ [c]	$M_n\times10^{-3}$ [d]	$k_p^{app}\times10^4$ [e] (s^{-1})	$Đ$ [d]
1	-	2.0	4.9	86	39.7	38.2	3.5	1.22
2	1	1.5	2.4	91	40.9	35.5	5.1	1.16
3	2	2.0	2.2	92	41.3	35.7	3.8	1.15
4	10	4.0	2.2	92	41.3	35.7	1.8	1.16

[a] Polymerization conditions: *n*-BuA/MBiB/$Cu(OTf)_2/Me_6TREN$ = 349/1/0.1/0.1 with initial $C_{Cu^{II}} = 10^{-3}$ M; $C_{Et_4NBF_4}$ = 0.1 M; V_{tot} = 15 mL; $E_{app} = E_{1/2} - 60$ mV; T = 45 °C. [b] Conversion determined by ^{1}H NMR. [c] Calculated on the basis of conversion obtained by ^{1}H NMR (*i.e.* $M_{n,th} = M_{MBiB} + 349 \times$ conversion $\times M_{n\text{-BuA}}$) [d] Determined by GPC. [e] Slope of the linear plot of $\ln(C_M^0/C_M)$ vs. time.

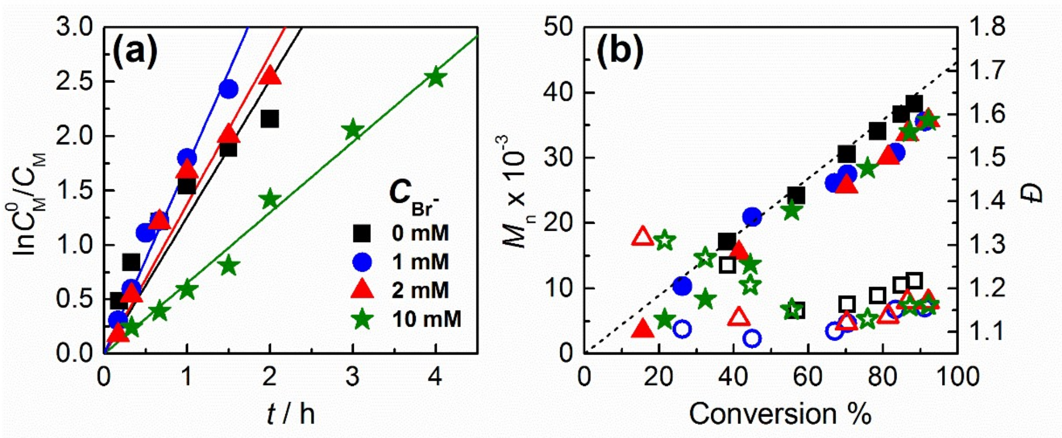

Fig. S2 Potentiostatic *e*ATRP of 50% (v/v) *n*-BuA in DMF performed on $E_{app} - E_{1/2}$ = 60 mV on a Pt electrode. (a) First-order kinetic plot and (b) M_n and dispersity vs. conversion. The dashed line indicates the theoretical M_n. Polymerization conditions: *n*-BuA/MBiB/$[Cu^{II}Me_6TREN]^{2+}$ =349/1/0.1 with initial $C_{Cu^{II}} = 10^{-3}$ M, $C_{Et_4NBF_4}$ = 0.1 M, T = 45 °C; C_{Br^-} (mM): 0 (squares), 1 (circles), 2 (triangles), 10 (stars).

S4. Potentiostatic *e*ATRP: choice of E_{app} on non-noble metal cathodes

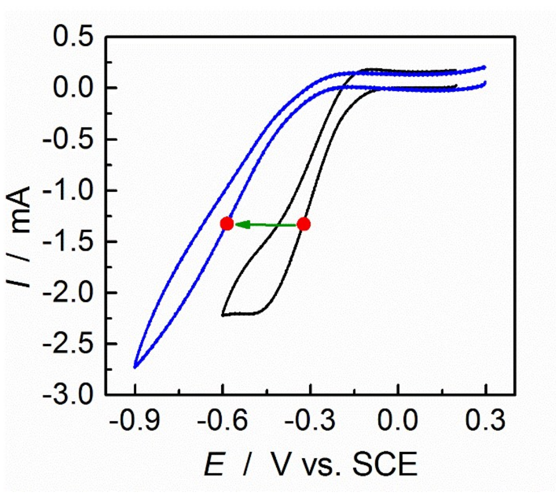

Fig. S3 Cyclic voltammetry of 1 mM $[BrCu^{II}Me_6TREN]^+$ + 10 mM MBiB in 50% (v/v) *n*-BuA in DMF, with $C_{Et_4NBF_4}$ = 0.1 M, registered on Pt (black line) and NiCr (blue line) bulky electrodes; v = 0.2 V s^{-1}, T = 45 °C. The red dots represent E_{app} used in the respective potentiostatic *e*ATRPs.

The procedure shown in Fig. S3 was applied to NiCr, Fe and SS304 working electrodes. Polymerization results of *e*ATRPs performed on these electrodes are reported in Table 2 in the main text.

S5. *e*ATRP of 20% (v/v) *n*-BuA in DMF

*e*ATRPs with lower *n*-BuA concentration were carried out to obtain samples suitable for inductively coupled plasma-mass spectrometry (ICP-MS) measurements. Results of potentiostatic *e*ATRPs performed on NiCr and SS304 working electrodes are reported in Table S2.

Table S2 Potentiostatic *e*ATRP of 20% (v/v) *n*-BuA in DMF on NiCr or SS304 cathode[a]

Entry	WE	A[b] (cm^2)	E_{app}-$E_{1/2}$ (mV)	t (h)	Q (C)	Conv.[c] (%)	$M_{n,th}\times10^{-3}$ [d]	$M_n\times10^{-3}$ [e]	$k_p^{app}\times10^4$ [f] (s^{-1})	$Đ$ [e]
1	NiCr	5	-300	2.5	9.8	93	16.8	13.6	3.32	1.24
2	SS304	4	-160	3	8.5	93	16.8	13.2	2.84	1.24

[a] Polymerization conditions: *n*-BuA/MBiB/$Cu(OTf)_2$/Me_6TREN/Et_4NBr = 140/1/0.1/0.1/0.1 with initial $C_{Cu^{II}}$ = 10^{-3} M, $C_{Et_4NBF_4}$ = 0.1 M, V_{tot} = 15 mL, T = 45 °C. [b] Estimated geometrical surface area of the working electrode. [c] Determined by ^{1}H NMR. [d] Calculated on the basis of conversion obtained by ^{1}H NMR (*i.e.* $M_{n,th}$ = M_{MBiB} + 140 × conversion × $M_{n\text{-BuA}}$). [e] Determined by GPC. [f] Slope of the linear plot of $\ln(C_M^0/C_M)$ vs. time.

S6. In situ preparation of aluminum ions

Et_4NBF_4 (0.3256 g, 1.5 × 10^{-3} mol), used as supporting electrolyte, and a mixture of DMF (6.35 mL) and *n*-butyl acrylate (7.5 mL, 5.2 × 10^{-2} mol) were put in a six-neck electrochemical cell, maintained at 45 °C with a thermostat and purged with Ar. Then 1 mL of an Ar purged stock solution of $Cu(OTf)_2$ (1.5 × 10^{-5} mol) in DMF, 0.15 mL of an Ar purged stock DMF solution of Et_4NBr (1.5 × 10^{-5} mol) and 4 μL of Me_6TREN (1.5 × 10^{-5} mol) were added into the cell. A CV of the catalyst was recorded with this setup on the GC disk electrode. The following three electrodes were then introduced into the cell: an Al wire used as working electrode, a Pt foil counter electrode separated from the solution by a glass frit and a salt bridge made of methylcellulose gel saturated with Et_4NBF_4, and an Ag/AgI (with 0.1 *n*-Bu_4NI in DMF) reference electrode, separated from the solution in the same way as the counter electrode. The Al wire was previously chemically activated by immersion in a HCl/H_2O 1/1 solution and rinsed with plenty of distilled water.

Electrolytic oxidation of the Al wire was performed to produce Al^{3+} ions. An anodic current of 2.5 mA was applied for 30 min (Q = 4.5 C) at the Al working electrode to produce roughly 1 mM Al^{3+} in solution.[3]

References

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