

Supplementary Information for

**Under Pressure: Electrochemically-mediated Atom Transfer Radical
Polymerization of Vinyl Chloride**

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S1. Comparison of different ATRP techniques and blank tests

To compare SARA and *e*ATRP, a SARA ATRP of VC was performed with identically experimental conditions (VC/DMSO = 1:1 v/v), $C_{VC}:C_{Cu}:C_{TREN}:C_{CHBr_3} = 728:0.1:0.2:1.5$, and initial $C_{Cu} = 10^{-3}$ M). The results are listed in Table S1.

Table S1. *e*ATRP vs SARA ATRP of 50 vol% VC at $T = 40$ °C in DMSO, catalyzed by $[Cu^{II}TREN]^{2+}$.^a

Entry	t (h)	M_n^{th}	M_n^{app}	$\bar{D}$	Conv. (%)	I_{eff}	$ Q $ (C)
SARA	6	7300	7700	1.90	24	0.93	-
<i>e</i> ATRP	6	9400	10900	1.35	31	0.86	2.95

^aOther experimental conditions: $C_{VC}:C_{TREN}:C_{Cu}:C_{CHBr_3} = 728:0.2:0.1:1.5$; Cu^0 wire $l = 5$ cm, $d = 1$ mm. 0.1 M Et_4NBF_4 was used as a supporting electrolyte in DMSO during *e*ATRP; estimated surface area of the Pt working electrode = 6 cm².

Polymerization of VC by SARA ATRP was less controlled than *e*ATRP in DMSO with the same conditions and provided lower conversion than *e*ATRP. These findings are consistent with the superior control provided by electrochemistry.¹⁻³ The choice of an appropriate current/time program in conjunction with the electrochemical control forced the polymerization to obey to the applied stimulus and promoting a more controlled PVC.⁴

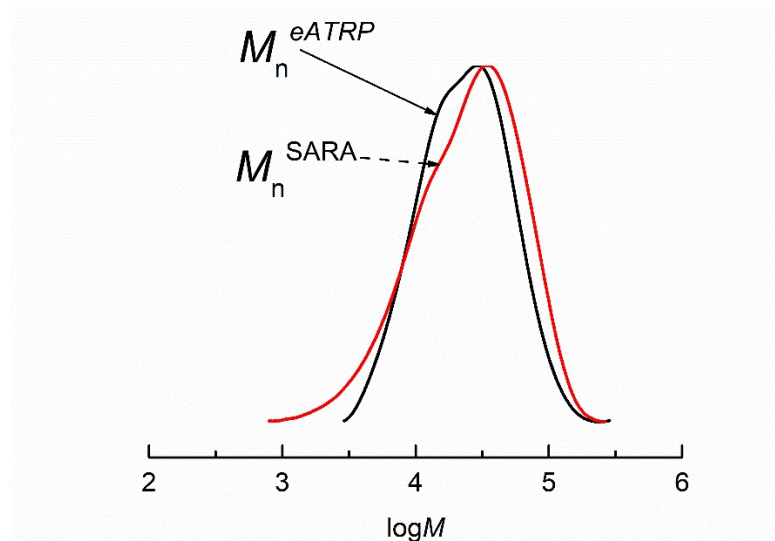


Fig. S1. Molecular weight distributions of PVC-Br obtained during *e*ATRP (—) or SARA ATRP (—) at $T = 40\text{ }^{\circ}\text{C}$ after 6 hours of reaction in DMSO catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$.

It is known that zerovalent metals, including iron (the main component of SS304 alloy), may promote SARA ATRP.⁵ However, as shown in the literature, no SARA ATRP takes place if a very small excess amount of ligand is present.^{4, 6, 7} To further exclude that SS304 surface may trigger supplemental activation of bromoform and concurrently start the polymerization, blank tests were performed (Table S2).

Table S2. Blank tests of SARA ATRP of VC at $T = 40\text{ }^{\circ}\text{C}$ in DMSO using SS304 catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$.^a

Entry	t (h)	$C_{\text{Cu}}:C_{\text{TREN}}$	M_n^{th}	M_n^{app}	D	Conv. (%)	I_{eff}
1	6	1:1	200	-	-	<1	-
2	6	1:2	400	-	-	<1	-
3	6	1:5	400	-	-	<1	-

^aOther experimental conditions: $C_{\text{VC}}:C_{\text{CHBr}_3}:C_{\text{TREN}}:C_{\text{Cu}} = 728:1.5:x:0.1$; $x = 0.1, 0.2$ and 0.5 . $V = 10\text{ mL}$, $T = 40\text{ }^{\circ}\text{C}$. Initial $\text{CCu} = 1 \times 10^{-3}\text{ M}$.

With up to $C_{\text{Cu}}:C_{\text{TREN}} = 1:5$ equivalents of TREN, no polymer was detected by SEC and no monomer conversion was measured. Indeed, a significant excess of ligand is required to trigger the activation of the initiator by the metal surface, at least for metallic copper.⁸ In the case of *e*ATRP, only a two-fold excess of ligand is required: one equivalent to complex copper salt and an additional one to complex electrogenerated aluminum. In conclusion, this slight excess is not enough to start the polymerization without applying an external stimulus.

S2. Profiles of $E_{\text{WE}} - E_{\text{CE}}$ vs time recorded during galvanostatic experiments.

Applying a fixed current (i_{app}), instead of a fixed potential (E_{app}), causes the working electrode potential (E_{WE}) to drift over time. Profiles of $E_{\text{WE}} - E_{\text{CE}}$ vs time were monitored during *e*ATRP and for some galvanostatic *e*ATRP, are presented in the next Figures S2-S11.

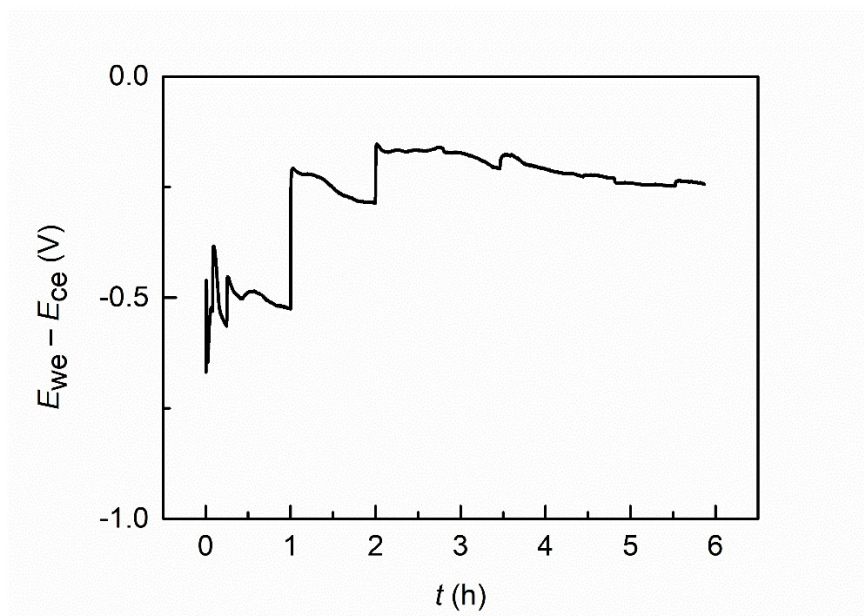


Fig. S2. Profile of $E_{\text{WE}} - E_{\text{CE}}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride using electrolysis program III, catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$ in DMSO at $T = 40\text{ }^{\circ}\text{C}$;

multistep electrolysis of 6 hours at $i_{\text{app}} = (-4, -3, -2.5, -1.5 \text{ and } -1.0) \times 10^{-4} \text{ A}$ for 300, 600, 2700, 3600 and 14400 seconds, respectively.

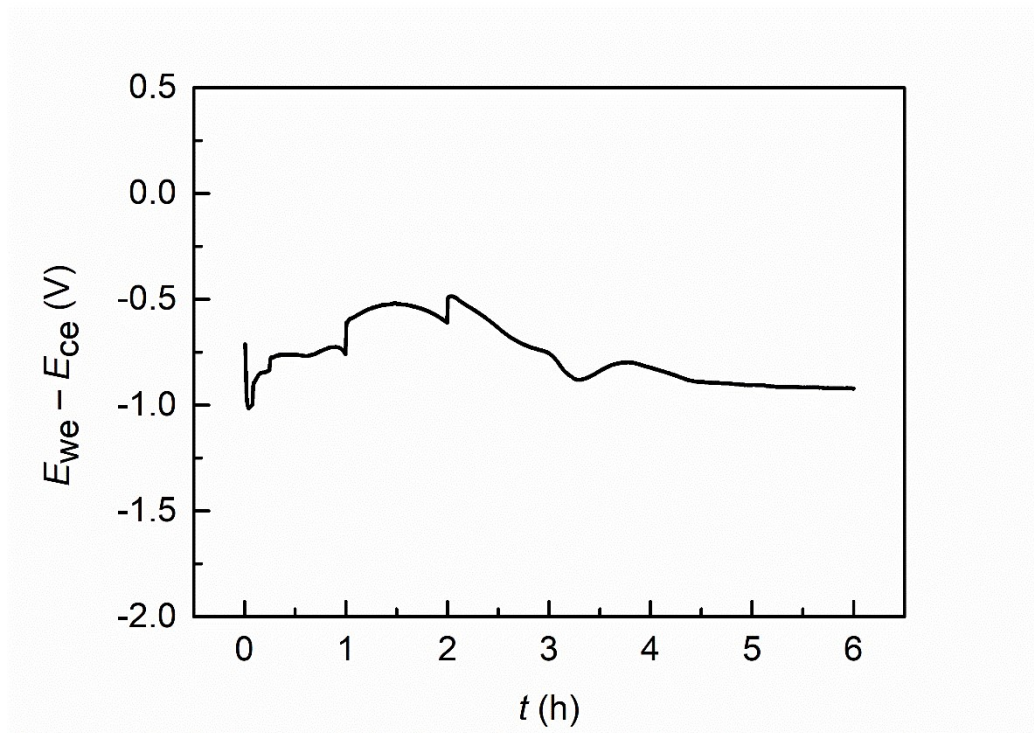


Fig. S3. Profile of $E_{\text{WE}} - E_{\text{CE}}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride using electrolysis program IV catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$ in DMSO at $T = 40 \text{ }^{\circ}\text{C}$; multistep electrolysis of 6 hours at $i_{\text{app}} = (8.0, 6.0, 5.0, \text{ and } 3.0) \times 10^{-4} \text{ A}$ for 300, 600, 2700, 3600 and 14400 seconds, respectively.

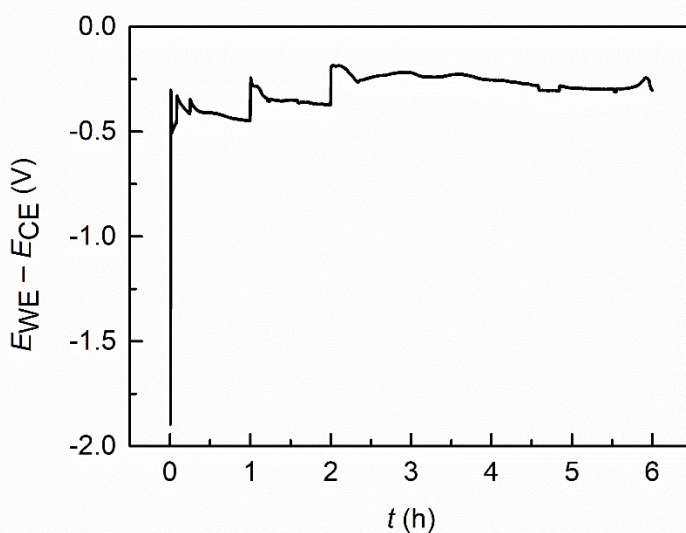


Fig. S4. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride, catalyzed by $[Cu^{II}TREN]^{2+}$ and initiated by MBP in DMSO at $T = 40\text{ }^{\circ}C$. Electrolysis program III.

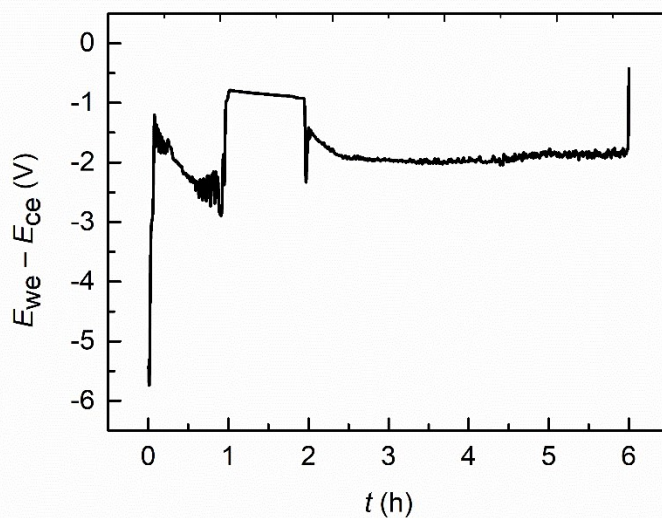


Fig. S5. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride catalyzed by $[Cu^{II}TREN]^{2+}$ and initiated by $CHBr_3$ in DMSO at $T = 40\text{ }^{\circ}C$. The SS304 scaffold is used as working electrode. Electrolysis program III.

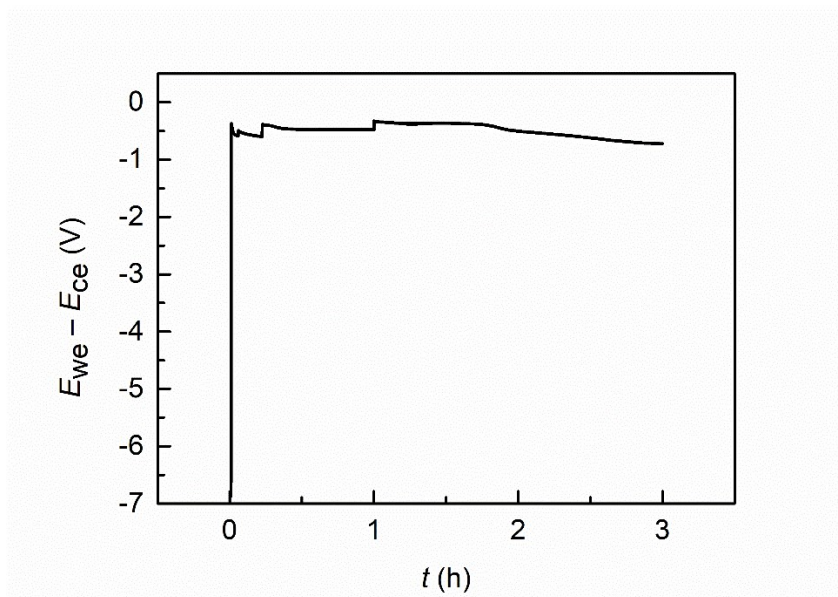


Fig. S6. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride catalyzed by $[Cu^{II}TREN]^{2+}$ and initiated by EBiB-4*f* in DMSO at $T = 40\text{ }^{\circ}\text{C}$. Electrolysis program V.

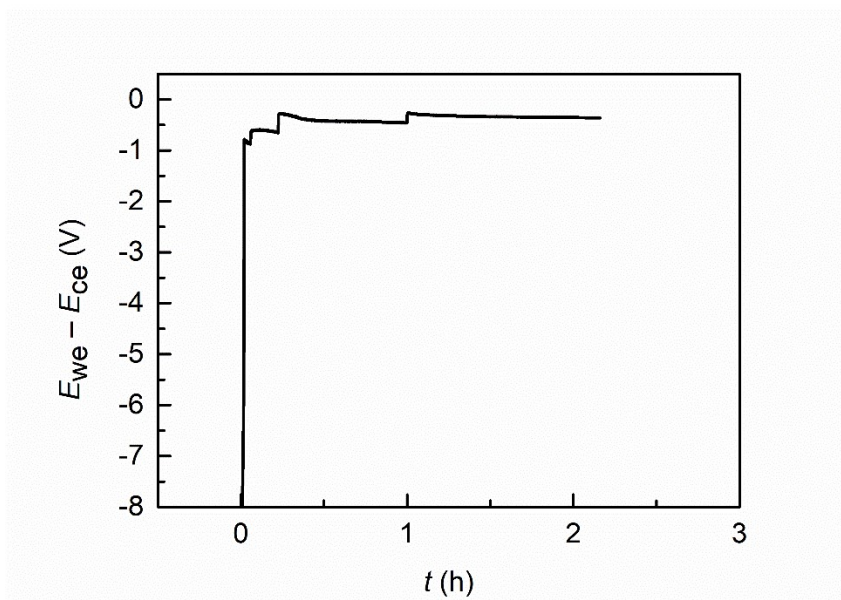


Fig. S7. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP chain extension of a PVC-Br macroinitiator with MA, catalyzed by $[Cu^{II}TREN]^{2+}$ in DMSO at $T = 40\text{ }^{\circ}\text{C}$. Electrolysis program V.

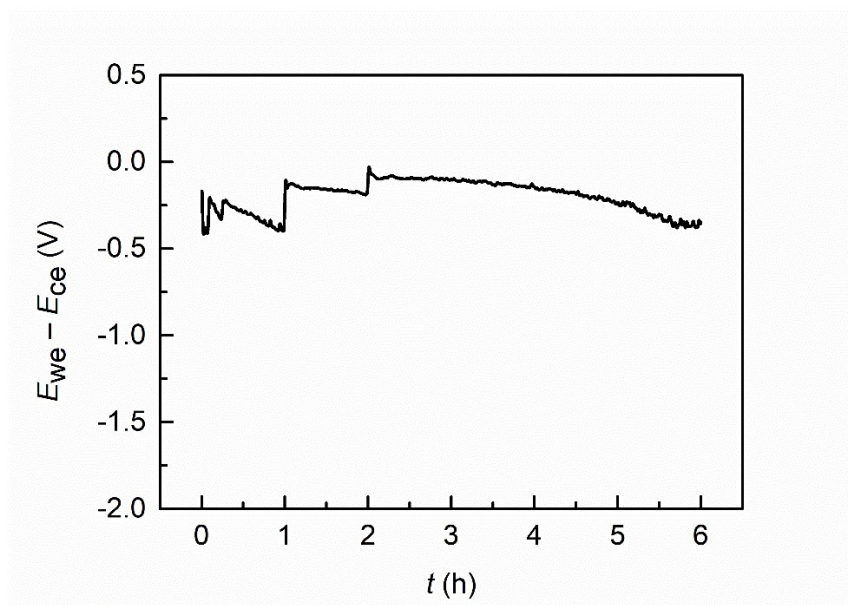


Fig. S8. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride, catalyzed by $[Cu^{II}Me_6TREN]^{2+}$ in DMSO at $T = 40$ °C. No polymerization occurred due to trapping of radicals by organometallic formation. Electrolysis program III.

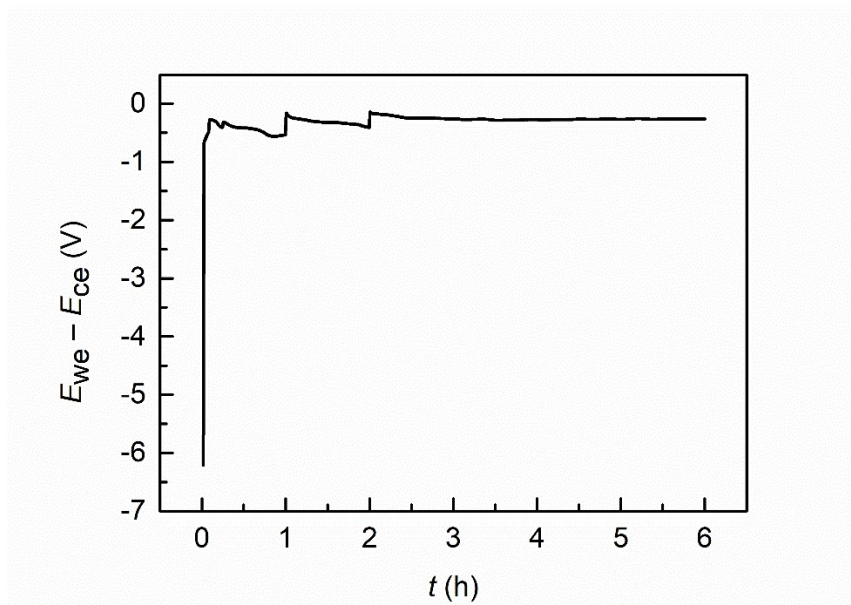


Fig. S9. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP copolymerization of VC + MA ($C_{VC} = C_{MA}$), catalyzed by $[Cu^{II}TREN]^{2+}$ in DMSO at $T = 40$ °C. Electrolysis program III.

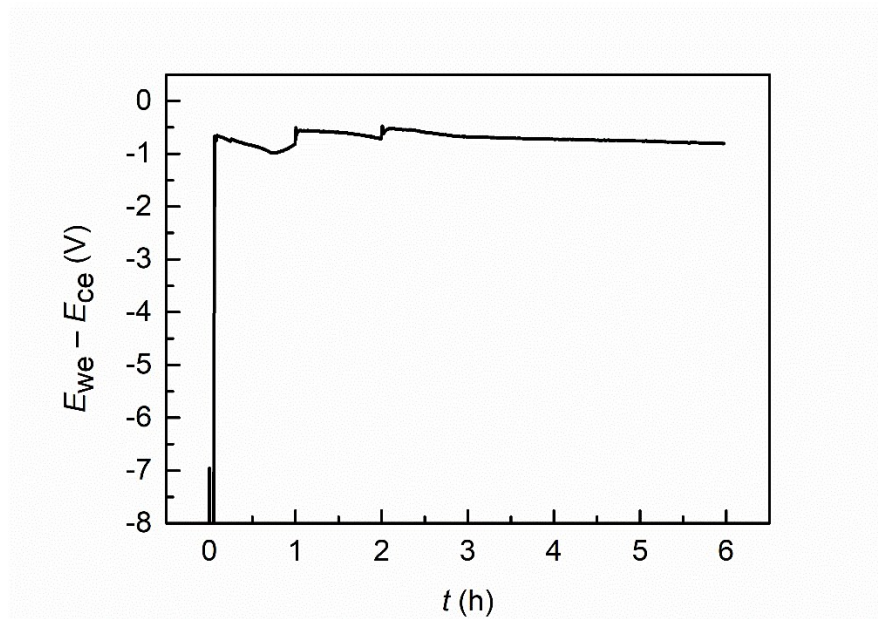


Fig. S10. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride, catalyzed by $[Cu^{II}TREN]^{2+}$ in DMSO at $T = 40\text{ }^{\circ}\text{C}$, targeting DP 970. Electrolysis program III.

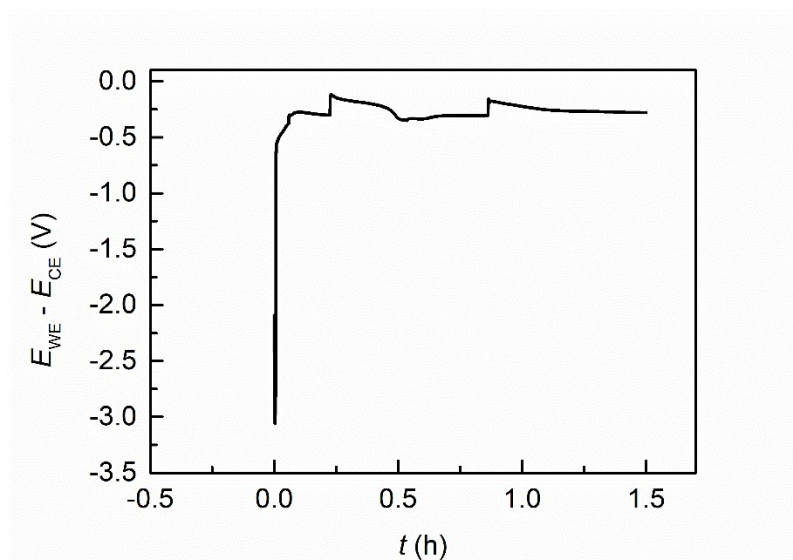


Fig. S11. Profile of $E_{WE} - E_{CE}$ (V) vs time recorded during galvanostatic *e*ATRP of vinyl chloride to obtain a PVC-Br macroinitiator, catalyzed by $[Cu^{II}TREN]^{2+}$ in DMSO at $T = 40\text{ }^{\circ}\text{C}$. Reaction time: 1.5 h. Electrolysis program V.

S3. NMR spectra and SEC chromatograms of PVC and copolymers

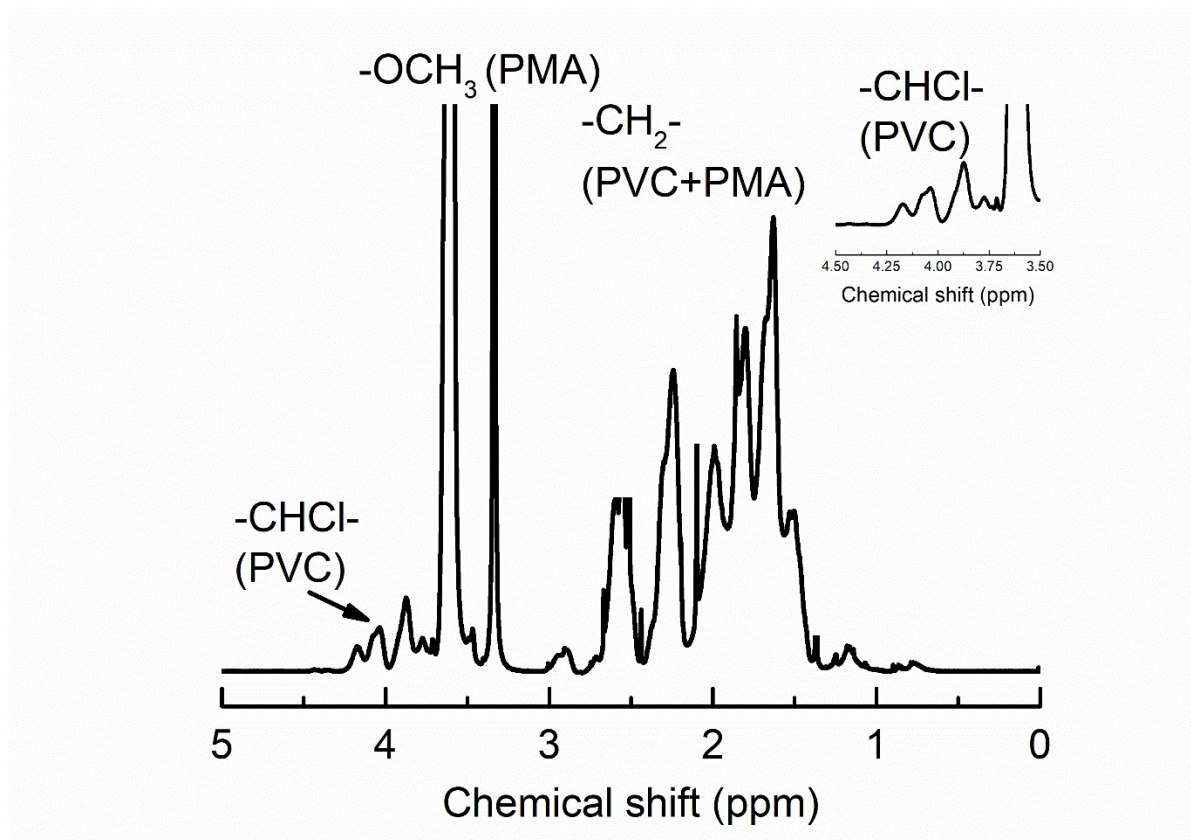


Fig. S12. 400 MHz ^1H -NMR spectra of PVC-*stat*-PMA-Br recorded in $\text{DMSO}-d_6$ obtained during *e*ATRP of VC in presence of MA ($C_{\text{MA}} = C_{\text{VC}}$). Inset shows $-\text{CHCl}-$ signals belonging to PVC segments (3.75 - 4.25 ppm).

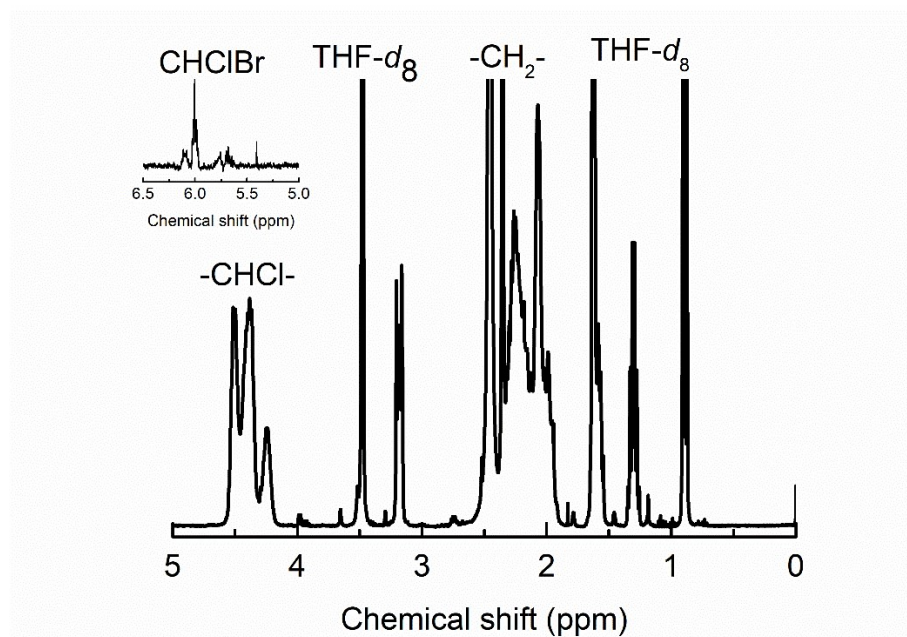


Fig. S13. 400 MHz ¹H-NMR spectrum of PVC-Br macroinitiator, recorded in THF-*d*₈. Inset shows the CHClBr chain-end functionality (6.0 – 6.15 ppm).

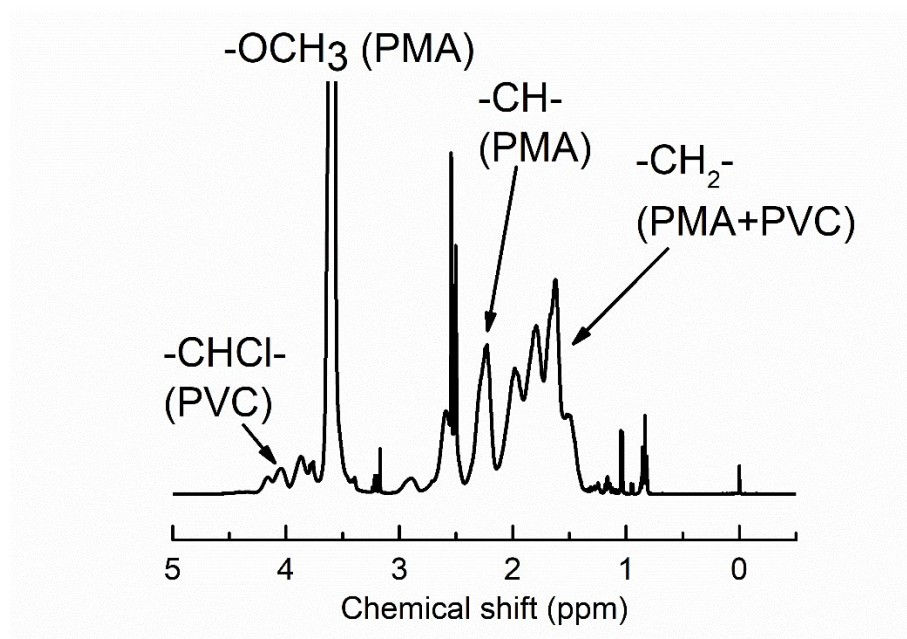


Fig. S14. 400 MHz ¹H-NMR spectrum of the PVC-*b*-PMA-Br copolymer, produced by the chain extension of a PVC-Br macroinitiator by *e*ATRP in DMSO, recorded in DMSO-*d*₆ at 25 °C.

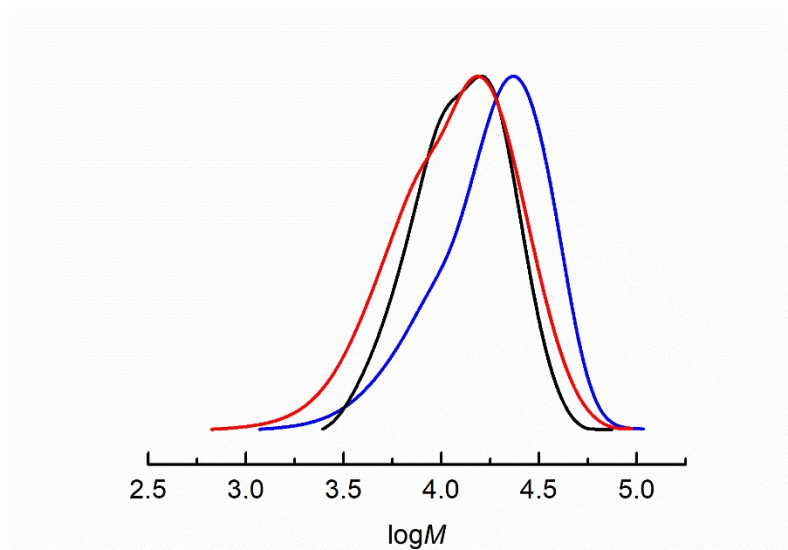


Fig. S15. Molecular weight distributions of PVC-Br obtained by *e*ATRP in DMSO at $T = 40$ °C catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$. DP = 283 (—, Entry 1 of Table 5), DP = 485 (—, Entry 2 of Table 5) and DP = 970 (—, Entry 3 of Table 5).

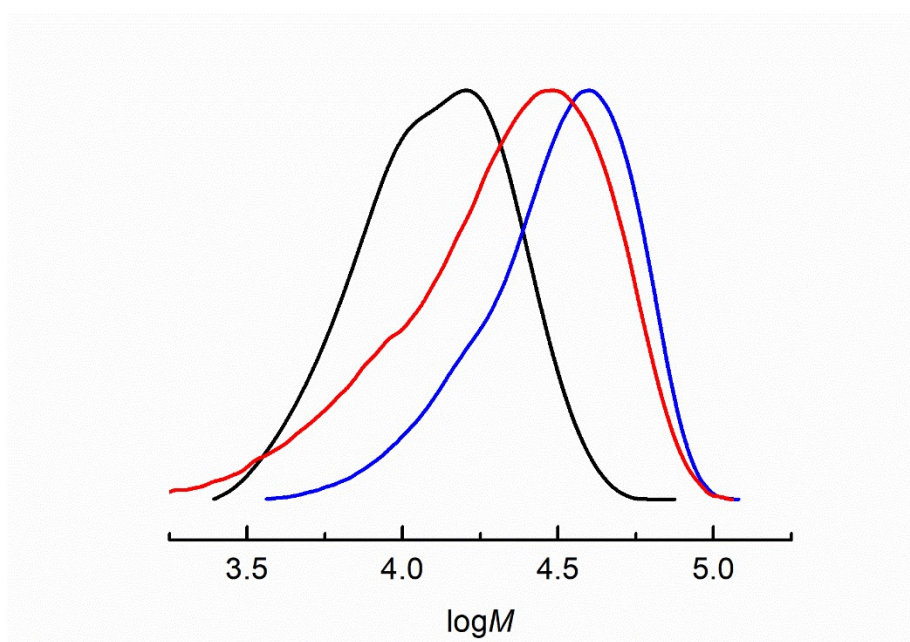


Fig. S16. Molecular weight distributions of PVC-Br obtained by *e*ATRP in DMSO at $T = 40$ °C catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$. $C_{\text{Cu}} = 10^{-3}$ M (—, Entry 1 of Table 6), $C_{\text{Cu}} = 5 \times 10^{-4}$ M (—, Entry 2 of Table 6) and $C_{\text{Cu}} = 2.5 \times 10^{-4}$ M (—, Entry 3 of Table 6).

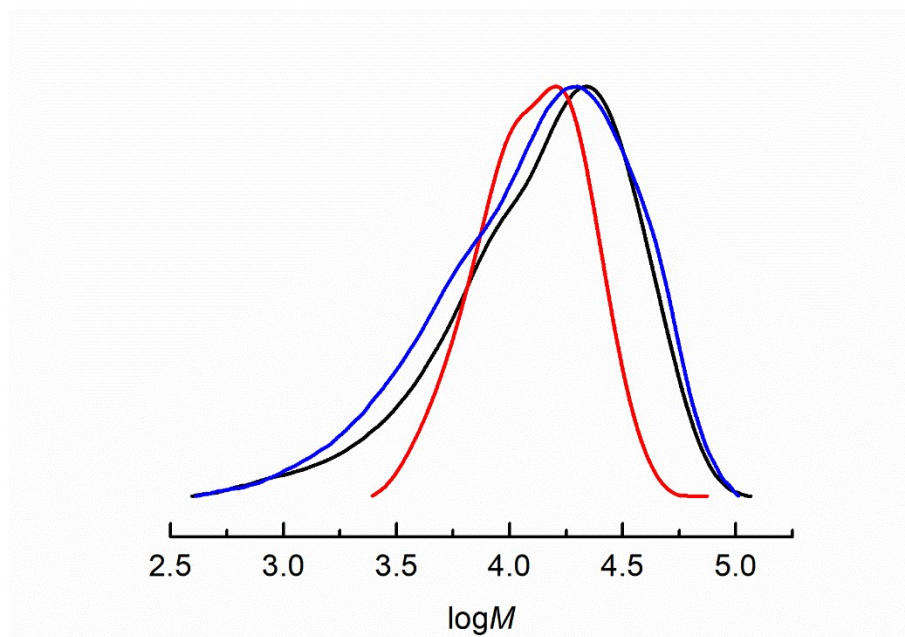


Fig. S17. Molecular weight distributions of PVC-Br obtained by *e*ATRP in DMSO at $T = 40\text{ }^{\circ}\text{C}$ catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$. $C_{\text{VC}} = 75\text{ vol\%}$ (—), $25\text{ vol\%}$ (—) and $50\text{ vol\%}$ (—).

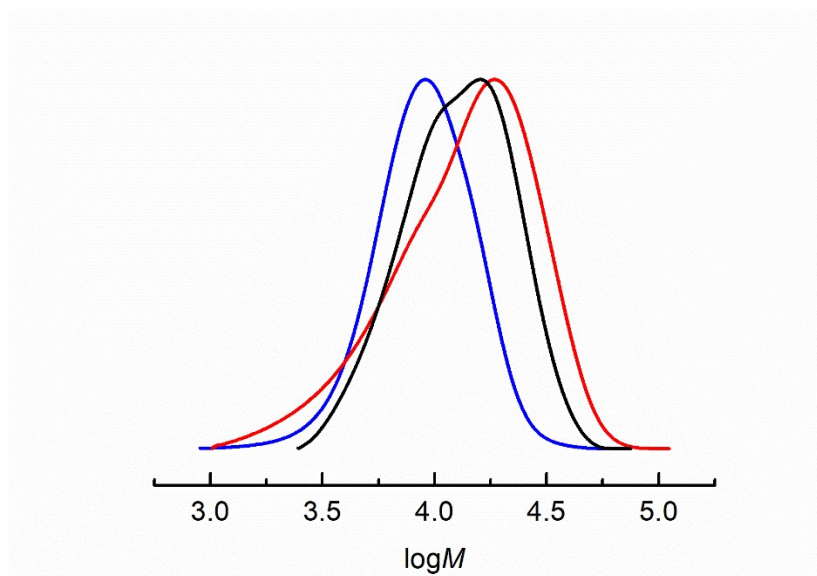


Fig. S18. Molecular weight distributions of PVC-Br obtained by *e*ATRP in DMSO at $T = 40\text{ }^{\circ}\text{C}$ catalyzed by $[\text{Cu}^{\text{II}}\text{TREN}]^{2+}$. $\text{RX} = 1.5 \times 10^{-2}\text{ M MBP}$ (—, Entry 3 of Table 8), $1.5 \times 10^{-2}\text{ M CHBr}_3$ (—, Entry 1 of Table 8) and $1.5 \times 10^{-2}\text{ M EBiB}$ (—, Entry 2 of Table 8).

S4. Description of the reactor

The SS304 stainless steel vessel is a home-made reactor built to host reactions with gaseous or liquid monomers (*e.g.* vinyl chloride and methyl acrylate respectively) or for high temperature reactions. The reactor consists of two sections: body and head (Fig. S19). The body, a single piece, was lathed from a single rod of steel to avoid welding and has an inner volume of 40 mL. Housings for an optional platinum (or any other electronic conductor) working electrode (serving as a cathode) and an aluminum rod anode are mounted on the head. Electric and chemical insulation is ensured by PEEK and fluorinated O-rings. When in operation, the sealing is provided by four orthogonal SS304 threaded screws. Stirring is operated by a rare-earth octahedral magnet.



Fig. S19. The SS304 reactor used for *e*ATRP of vinyl chloride at the Department of Chemical Engineering of University of Coimbra.

Supporting References

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