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## Aqueous electrochemically-triggered atom transfer radical polymerization†

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Simplified electrochemical atom transfer radical polymerization (seATRP) using  $\text{Cu}^{\text{I}}\text{-N-propyl pyridineimine complexes } (\text{Cu}^{\text{I}}(\text{NPPI})_2)$  is reported for the first time. In aqueous solution, using oligo(ethylene glycol) methyl ether methacrylate (OEGMA), standard electrolysis conditions yield POEGMA with good control over molecular weight distribution ( $\bar{D}_m < 1.35$ ). Interestingly, the polymerizations are not under complete electrochemical control, as monomer conversion continues when electrolysis is halted. Alternatively, it is shown that the extent and rate of polymerization depends upon an initial period of electrolysis. Thus, it is proposed that seATRP using  $\text{Cu}^{\text{I}}(\text{NPPI})_2$  follows an electrochemically-triggered, rather than electrochemically mediated, ATRP mechanism, which distinguishes them from other  $\text{Cu}^{\text{II}}\text{L}$  complexes that have been previously reported in the literature.

## Introduction

Electrochemical intervention in synthesis and catalysis has received renewed interest over the last 5–10 years.<sup>1–6</sup> From a synthetic point of view, the use of an applied potential/current enables accurate control over the thermodynamics and/or kinetics of electron transfer processes.<sup>7,8</sup> This can enhance the selectivity of chemical transformations and confer spatiotemporal control over synthetic and catalytic reactions of small and macromolecular organic molecules/polymers, amongst others.

In the context of reversible deactivation radical polymerization (RDRP) electrochemical intervention has been employed to regulate polymer synthesis through control of the dynamic equilibrium between dormant and active (radical) species which allows the overall radical concentration to be accurately controlled.<sup>9–11,53</sup> In atom transfer radical polymerization (ATRP)<sup>12,13</sup> the equilibrium ( $K_{\text{ATRP}}$ ) is between a dormant alkyl ( $\text{R-X}$ ) or macromolecular ( $\text{P}_n\text{-X}$ ) halide and propagating radicals ( $\text{R}^\bullet/\text{P}_n^\bullet$ ) which undergo reversible redox reactions with transition metal complexes.

In 2011, Matyjaszewski and co-workers showed that the redox nature of the Cu-mediated ATRP mechanism could lend itself to electrochemical manipulation and control.<sup>10</sup> The active, yet oxidatively labile  $\text{Cu}^{\text{I}}\text{L}$  complex was formed *in situ* when a reducing potential ( $E_{\text{app}}$ ) was applied at the working electrode (WE) to induce a one electron reduction of an inactive  $\text{Cu}^{\text{II}}\text{L}$  precursor. Activation of the dormant species ( $\text{R-X}/\text{P}_n\text{-X}$ ) in the reaction media then generated the radical species ( $\text{R}^\bullet/\text{P}_n^\bullet$ ), and the Cu-complex in a higher oxidation state ( $\text{X-Cu}^{\text{II}}\text{L}$ ). Well

controlled polymerization of methyl acrylate was reported suggesting that the deactivation step of the equilibrium, between the propagating radical ( $\text{P}_n^\bullet$ ) and  $\text{X-Cu}^{\text{II}}\text{L}$ , reforming the dormant species ( $\text{P}_n\text{-X}$ ) and  $\text{Cu}^{\text{I}}\text{L}$  respectively, was not perturbed by the electrochemical intervention. In fact, it was shown that by switching the  $E_{\text{app}}$  at the WE to an oxidizing potential the polymerization could be completely switched off, conferring high fidelity on-off spatiotemporal control over polymer synthesis in solution.

In the 10 years since this discovery, eATRP has been employed for the synthesis of polymers with a variety of compositions and architectures including block copolymers, bioconjugates, star and graft (co)polymers.<sup>14–22</sup> It is compatible with aqueous<sup>23,24</sup> and organic<sup>10</sup> media whilst heterogeneous systems such as mini-emulsion<sup>25–28</sup> and surface-initiated (seATRP)<sup>29–32</sup> polymerizations have also been reported. Furthermore, the complex reaction set-up, initially involving a 3-electrode divided electrochemical cell, has been simplified by the use of sacrificial counter electrodes (typically Al-wire), enabling undivided cells to be used in either 3-electrode (potential controlled) or 2-electrode (current controlled) configurations giving rise to simplified electrochemical atom transfer radical polymerisation (seATRP).<sup>33</sup> This development is significant as it enables the chemistry to be performed using commercial, standardized hardware.<sup>24</sup>

The most widely studied systems for aqueous eATRP employ  $\text{Cu}^{\text{II}}\text{X}$  salts with tetradentate ligands *tris*(2-(dimethylamino)ethyl)amine ( $\text{Me}_6\text{-Tren}$ )<sup>10,34,35</sup> or *tris*(2-pyridylmethyl)amine (TPMA).<sup>33,36,37</sup> They form more active complexes, having high  $K_{\text{ATRP}}$  values.<sup>38</sup> The ligands stabilize  $\text{Cu}^{\text{II}}$  more than  $\text{Cu}^{\text{I}}$  with cyclic voltammetry (CV) indicating that  $\text{Cu}^{\text{I}}\text{Me}_6\text{-Tren}$  and  $\text{Cu}^{\text{I}}\text{TPMA}$  are strongly reducing complexes, leading to fast activation ( $k_{\text{act}}$ ) of  $\text{R-X}/\text{P}_n\text{-X}$ .<sup>39,40</sup> The  $k_{\text{act}}$  (and  $K_{\text{ATRP}}$ ) can

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increase by orders of magnitude when aqueous media is employed, which in the absence of appropriate conditions and/or external control of active catalyst generation, can result in high radical concentrations which has a detrimental effect on the polymerization.<sup>41,42</sup> A great deal of discovery and optimization, of which eATRP is one example, has resulted in the development of efficient, well controlled aqueous ATRP reactions using these highly active complexes.<sup>9,43</sup>

Prior to this, less active complexes composed of bidentate ligands such as bipyridine (bpy) and *N*-alkyl pyridine imines (NAPI) were more suitable for aqueous ATRP.<sup>44-49</sup> They stabilize Cu<sup>I</sup> more than Cu<sup>II</sup>, form less reducing Cu<sup>I</sup> complexes and have lower  $k_{\text{act}}$  and  $K_{\text{ATRP}}$  leading to lower radical concentrations. On one hand, this means that larger catalyst concentrations are required to mediate well controlled ATRP. On the other hand, it can also be beneficial for polymerizations carried out in aqueous media wherein increased  $k_{\text{act}}$  and  $K_{\text{ATRP}}$  can lead to higher radical concentrations when more active complexes are employed. For example, 20 years ago, Haddleton and Perrier described in detail the efficient, well controlled polymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) using Cu<sup>I</sup>(NAPI)<sub>2</sub> complexes in water.<sup>44-46</sup> The rates of reaction and control over the polymerization were optimized with respect to [Cu<sup>I</sup>(NAPI)<sub>2</sub>]/[Cu<sup>II</sup>(NAPI)<sub>2</sub>] which was controlled from the outset by using known amounts of Cu<sup>I</sup>Br and Cu<sup>II</sup>Br<sub>2</sub> to form a mixed complex system. To accurately achieve the target [Cu<sup>I</sup>(NAPI)<sub>2</sub>]/[Cu<sup>II</sup>(NAPI)<sub>2</sub>] ratio's careful handling of oxidatively labile Cu<sup>I</sup> complexes and thoroughly deoxygenated reaction conditions were required. Looking back at this work, we considered the possibility of controlling [Cu<sup>I</sup>(NAPI)<sub>2</sub>]/[Cu<sup>II</sup>(NAPI)<sub>2</sub>] electrochemically, thus avoiding the need to handle the oxidatively labile Cu<sup>I</sup> complexes. There are currently no reports of eATRP using Cu(NAPI)<sub>2</sub> complexes, in either organic or aqueous media in the literature. We were inspired to investigate these complexes with a view to mediate eATRP at less reducing potentials and currents. Long term, we hope this will help to overcome some of the initial limitations associated with oxygen reduction (at more reducing potentials) in our related work in scanning electrochemical probe directed eATRP.<sup>50</sup>

To this end, herein we report for the first time the use of the *N*-propyl pyridineimine (NPPI) ligand to form Cu<sup>II</sup>(NPPI)<sub>2</sub> complexes for eATRP of OEGMA<sub>300</sub>. Well controlled polymerization (*P*<sub>m</sub> ≈ 1.30) is possible and initial investigations into the mechanism suggest that an alternative electrochemically-triggered process is prevalent for these less-active copper complexes.

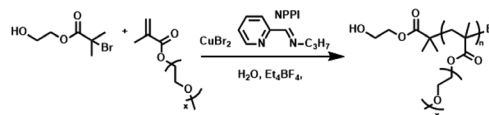
## Results and discussion

Comparative CV of Cu<sup>II</sup>L complexes; Cu<sup>II</sup>TPMA, Cu<sup>II</sup>Me<sub>6</sub>Tren and Cu<sup>II</sup>(NPPI)<sub>2</sub> were initially performed in solutions of the reaction mixture (10% (v/v) OEGMA<sub>300</sub> in H<sub>2</sub>O) in the absence and presence of the initiator, hydroxyethyl-2-bromoisobutyrate (HEBiB) (Fig. S1–S3†). In the absence of HEBiB, each complex exhibited the [Cu<sup>II</sup>L]/[Cu<sup>I</sup>L] redox process and as expected the standard reduction potential ( $E^0 \approx E_{1/2} = E_{\text{pc}} + E_{\text{pa}}/2$ ) shifted to

less reducing potentials (vs. Ag/AgCl) going from  $\text{Cu}^{\text{II}}\text{Me}_6\text{Tren}$  ( $E_{1/2} = -0.40$  V) to  $\text{Cu}^{\text{II}}\text{TPMA}$  ( $E_{1/2} = -0.21$  V) to  $\text{Cu}^{\text{II}}(\text{NPPI})_2$  ( $E_{1/2} = +0.02$  V) respectively. In the presence of HEBiB the voltammograms of the  $\text{Cu}^{\text{II}}\text{Me}_6\text{Tren}$  and  $\text{Cu}^{\text{II}}\text{TPMA}$  complexes show a coupled increase in the cathodic current intensity ( $E_{\text{pc}}$ ) and decrease in the anodic current intensity ( $E_{\text{pa}}$ ). This is indicative of electrochemical reduction of  $\text{Cu}^{\text{II}}\text{L}$  to  $\text{Cu}^{\text{I}}\text{L}$  followed by fast activation of HEBiB by the  $\text{Cu}^{\text{I}}\text{L}$  on the timescale of the CV ( $0.1 \text{ V s}^{-1}$ ). In the case of  $\text{Cu}^{\text{II}}(\text{NPPI})_2$  the coupled change in  $E_{\text{pc}}$  and  $E_{\text{pa}}$  was not observed. The currents decrease in both the cathodic and anodic scan suggesting that although the presence of HEBiB has an effect on the kinetics of electron transfer, the activation of HEBiB by  $\text{Cu}^{\text{I}}(\text{NPPI})_2$  is slow on the timescale of the CV. These results are in agreement with the literature that suggests that with respect to  $k_{\text{act}}$ , complexes with  $\text{Me}_6\text{Tren} > \text{TPMA} \gg \text{NPPI}$ .<sup>35,38</sup>

Potentiostatic seATRP reactions using each complex were performed in undivided cells using an IKA ElectraSyn device. A commercial Pt-coated electrode (IKA) was employed as the cathode (WE), the anode (CE) was Al-wire and the reference electrode (RE) was  $\text{Ag}^+/\text{AgCl}$ . For the bidentate NPPI ligand a ratio of  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$  was used. When  $E_{\text{app}} = E_{1/2} = +0.02$  V the resistance in the system was too high preventing the IKA ElectraSyn from operating. However, when an overpotential of 60 mV was applied ( $E_{\text{app}} = -0.04$  V) polymerization was complete within 2 h yielding POEGMA<sub>300</sub> with  $M_{n,\text{SEC}} = 9200$  g mol<sup>-1</sup> and  $D_m = 1.31$  (Table 1, entry 1, Fig. S4†).

**Table 1** seATRP of OEGMA<sub>300</sub> in H<sub>2</sub>O. [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25]; room temperature<sup>a</sup>



Entry	$E_{\text{app}}/\text{V}$	Time/h	Conv <sup>k</sup>	$M_{\text{n,th}}^{l}/\text{g mol}^{-1}$	$M_{\text{n,SEC}}^m/\text{g mol}^{-1}$	$\mathcal{D}_m^m$
1	−0.04	2	100%	6211	9200	1.31
2	−0.08	2	96%	5971	11 000	1.30
3	−0.12	2	96%	6211	12 800	1.29
4	−0.16	2	99%	6211	10 200	1.32
5 <sup>b</sup>	−0.16	2	100%	6211	10 000	1.28
6 <sup>c</sup>	−0.16	2	100%	6211	9000	1.26
7 <sup>d</sup>	−0.16	2	96%	5971	18 200	1.50
8 <sup>e</sup>	−0.16	2	67%	4231	21 800	1.98
9 <sup>f</sup>	−0.16	2	96%	9811	14 600	1.30
10 <sup>g</sup>	−0.16	6.5	67%	14 951	14 900	1.23
11 <sup>h</sup>	−0.16	2	98%	3151	7800	1.31
12 <sup>i</sup>	−0.16	2	90%	11 011	14 000	1.33
13 <sup>j</sup>	−0.16	2	95%	23 011	21 500	1.33

<sup>a</sup> [Cu<sup>II</sup>Br<sub>2</sub>] = 8.8 mM. <sup>b</sup> [OEGMA<sub>300</sub>] = 20% v/v. <sup>c</sup> [OEGMA<sub>300</sub>] = 30% v/v. <sup>d</sup> [Cu<sup>II</sup>Br<sub>2</sub>] = 4.4 mM. <sup>e</sup> [Cu<sup>II</sup>Br<sub>2</sub>] = 2.2 mM. <sup>f</sup> OEGMA<sub>500</sub> used. <sup>g</sup> OEGMA<sub>1100</sub> used. <sup>h</sup> [M]/[I] = 10. <sup>i</sup> [M]/[I] = 40. <sup>j</sup> [M]/[I] = 80. <sup>k</sup> Determined *via* <sup>1</sup>H NMR of reaction samples performed in D<sub>2</sub>O. <sup>l</sup> M<sub>500,th</sub> = [(conv./100 × DP<sub>n,th</sub>) × 300/500(e)/1100(f)] + 211. <sup>m</sup> From THF SEC.

When Me<sub>6</sub>Tren and TPMA were employed as ligands ([OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [L] = [20] : [1] : [0.5] : [0.6]),  $E_{app} = E_{1/2}$  was sufficient for the ElectraSyn to operate. In both cases, conversions were limited to <80% after 4 h and the control over the polymerization was poor ( $D_m > 4$ , Table S1†). This is likely due to the stoichiometry of Cu<sup>II</sup>Br<sub>2</sub> employed which equates to [Cu<sup>II</sup>Br<sub>2</sub>] = 8.8 mM. Although, this is suitable for the less active Cu<sup>II</sup>/NPPI system, it is much higher than is required for the so-called highly active complexes leading to higher than necessary [Cu<sup>I</sup>L] and [R<sup>•</sup>/P<sup>•</sup><sub>n</sub>] due to rapid over activation when  $E_{app} = E_{1/2}$  which ultimately compromises the outcome of the polymerization.

Incrementally increasing the overpotential by 40 mV had little effect on the rate of the polymerization with conversions remaining high (>95%), and control being retained with  $D_m \approx 1.30$  (Table 1, entries 2–4, Fig. S5–S7†). The  $E_{app}$  was then fixed at –0.16 V and [OEGMA<sub>300</sub>] was increased to 20% and 30% v/v respectively (Table 1, entries 5–6). There was no significant change in the control over the polymerization with low dispersities ( $D_m < 1.30$ ) obtained (Fig. S8 and S9†). Kinetic analysis showed that quantitative conversions were obtained with 2 h. However, the semi-log plot showed that whilst the pseudo first order kinetics were observed at [OEGMA<sub>300</sub>] = 10% v/v, distinct

deviations were apparent at the higher concentrations (Fig. S10†). The observed increase in rate throughout the reaction is in agreement with Haddleton and Perrier who attributed it to water and monomer competing with the ligand for coordination at the Cu centre thus affecting the Cu<sup>II</sup>/Cu<sup>I</sup> equilibrium.<sup>44</sup> With this in mind, the remaining reactions were performed at [OEGMA<sub>300</sub>] = 10% v/v.

Decreasing the [Cu] from 8.8 mM to 4.4 mM and 2.2 mM had a detrimental effect on the control over the polymerization ( $D_m > 1.50$ , Table 1, entries 7–8). Increasing the length of the OEGMA monomer using OEGMA<sub>500</sub> and OEGMA<sub>1100</sub> had little effect on the control over the polymerization, with low dispersities retained ( $D_m < 1.30$ , Fig. S11 and S12†), though the rate of polymerization for OEGMA<sub>1100</sub> was slower than OEGMA<sub>300/500</sub> reaching 67% within 6.5 h (Table 1, entries 9–10).

Under the conditions established above ( $E_{app} = -0.16$  V; [M] = 10% v/v), the  $DP_{n,th}$  was varied such that [M] : [I] = [10]/[20]/[40]/[80] : [1]. The polymerizations reached 90–98% conversion within 2 h, proceeding with good control over  $M_n$  and dispersity ( $D_m < 1.35$ ; Table 1, entries 4, 11–13). An overlay of the SEC chromatograms shows the expected shift in the narrow molecular weight distributions to higher molecular weights as a function of [M]/[I] (Fig. 1A). A plot of  $M_{n,SEC}$  vs. [M]/[I] indicates

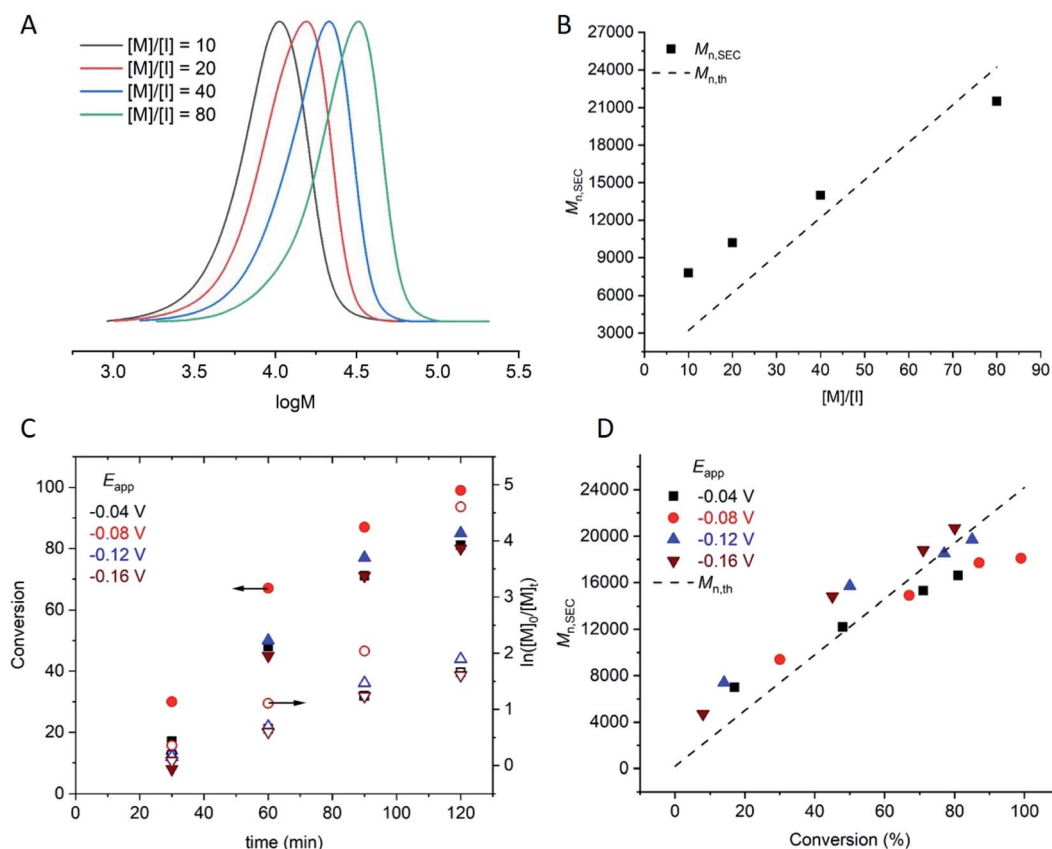


Fig. 1 For seATRP of [OEGMA<sub>480</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [M] : [1] : [0.5] : [1.25]; (A) SEC in THF showing a shift in molecular weight distributions as for [M] = 10,  $M_n = 7800$  g mol<sup>-1</sup>,  $D_m = 1.31$ ; [M] = 20,  $M_n = 10\,200$  g mol<sup>-1</sup>,  $D_m = 1.32$ ; [M] = 40,  $M_n = 14\,000$  g mol<sup>-1</sup>,  $D_m = 1.33$ ; [M] = 80,  $M_n = 21\,500$  g mol<sup>-1</sup>,  $D_m = 1.33$ . (B) Plot of  $M_{n,SEC}$  as a function of [M]/[I] for [M] = 10, 20, 40, 80, [I] = 1, ( $E_{app} = -0.16$  V). (C) Conversion and pseudo first order kinetic plots as a function of  $E_{app}$ . (D) Evolution of the  $M_{n,SEC}$  with conversion during polymerizations performed at different  $E_{app}$  ([M]/[I] = 80).



a linear increase in  $M_{n,SEC}$  as a function of  $[M]/[I]$ , with slight deviations in  $M_{n,SEC}$  and  $M_{n,th}$  converging as  $[M]/[I]$  increased (Fig. 1B).

Kinetic analyses of the polymerizations performed with  $[M] : [I] = [80] : [1]$  revealed that the apparent rate constant for propagation was  $k_p^{app} = 0.0167 \text{ min}^{-1}$  at  $E_{app} = -0.04 \text{ V}$  (Fig. 1C). Initially, more reducing potentials ( $E_{app} = -0.08 \text{ V}$ ) resulted in a small increase in the rate of polymerization ( $k_p^{app} = 0.0456 \text{ min}^{-1}$ ). However, at higher overpotentials ( $E_{app} = -0.12 \text{ V}$ ,  $-0.16 \text{ V}$ ), the rate decreased back to  $k_p^{app} = 0.0201 \text{ min}^{-1}$  and  $0.0174 \text{ min}^{-1}$  respectively. At these potentials,  $E_{app}$  is close to  $E_{pc}$  at which point the reduction of  $\text{Cu}^{II}/\text{L}$  to  $\text{Cu}^I/\text{L}$  is not governed by the electrode potential and is limited by the rate of diffusion of accumulated  $\text{Cu}/\text{L}$  species to and from the electrode surface to and from the bulk. Irrespective of  $E_{app}$ , a linear increase in  $M_{n,SEC}$  as a function of conversion was observed with good agreement with the theoretical molecular weight ( $M_{n,th}$ ) (Fig. 1D).

A hallmark of eATRP is the temporal control conferred by switching the potential/current on and off. At reducing potentials  $\text{Cu}^{II}/\text{L}$  is reduced to  $\text{Cu}^I/\text{L}$  leading to activation of dormant chains which can undergo propagation and subsequent deactivation events *via* the proposed ATRP mechanism. If the potential is switched off, or an oxidising potential is applied, reduction of  $\text{Cu}^{II}/\text{L}$  no longer occurs so activation of the dormant chains stops and the polymerization is halted. Conducting this experiment using  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$  and applying  $E_{app} = -0.16 \text{ V}$  ( $[M] = 10\% \text{ v/v}$ ), conversion reached  $>50\%$  within 20 min (Fig. 2). The potential was then switched off ( $E_{app} = 0 \text{ V}$ ) and stirring was continued for a further 20 min, after which conversion unexpectedly increased to  $>80\%$ . The polymerization reached  $>90\%$  conversion through an additional 'on' (20 min) and 'off' (20 min) cycle, indicating that  $\text{Cu}^{II}(\text{NPPI})_2$  lacked the temporal control associated with eATRP. The lack of temporal control with this less active catalyst system is in agreement with reported differences in temporal control related to catalyst activity observed in photo-ATRP.<sup>51</sup>

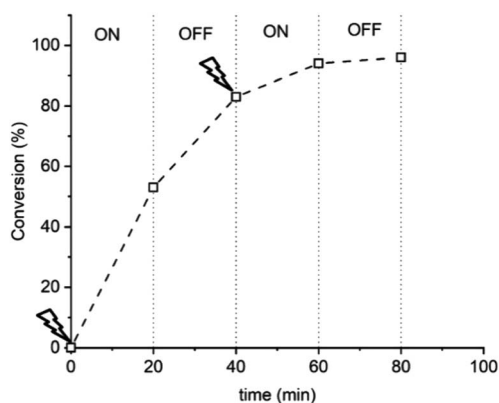


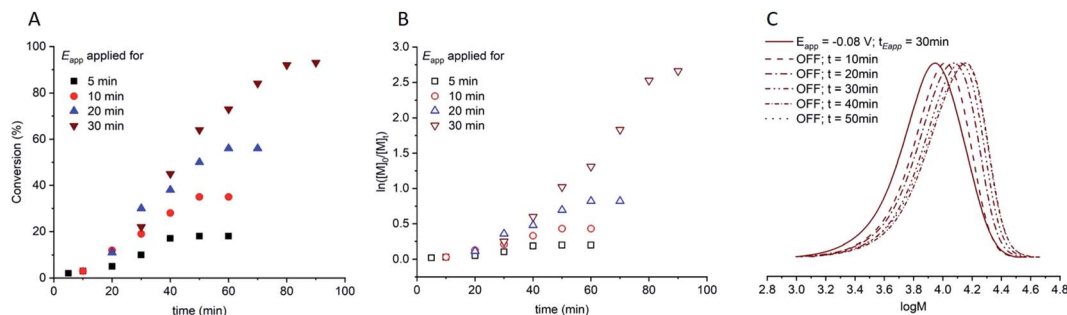
Fig. 2 Conversion vs. time plot demonstrating a lack of temporal control afforded by seATRP with  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25] : [0.15]$ ;  $E_{app} = -0.16 \text{ V}$ .

Unlike in eATRP reactions using  $\text{Cu}^{II}(\text{Me}_6\text{Tren})$  and  $\text{Cu}^{II}(\text{TPMA})$  complexes, it was observed that the reaction solutions containing  $\text{Cu}^{II}(\text{NPPI})_2$  changed colour, from green to brown, during electrolysis (Fig. S14†). The brown colour resembled that reported in early aqueous ATRP using  $\text{Cu}^I(\text{NAP})_2$  complexes.<sup>44–46</sup> Thus, it was hypothesized that the overpotentials applied and the less activating nature of the  $\text{Cu}^I(\text{NPPI})_2$  complex, resulted in accumulation of stable  $\text{Cu}^I(\text{NPPI})_2$  in the reaction media which was capable of continuing to mediated the polymerization of OEGMA when  $E_{app}$  was removed.

To explore this hypothesis, the temporal control experiment was repeated using  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$ . After the electrolysis period ( $E_{app} = -0.08 \text{ V}$ ;  $t_{E_{app}} = 30 \text{ min}$ ), the reaction solution was brown, indicative of  $\text{Cu}^I(\text{NPPI})_2$  accumulation, and conversion had reached 33% (Fig. S15A†). Concurrently, electrolysis was stopped and sparging with compressed air was commenced to rapidly introduce  $\text{O}_2$  into the reaction solution to stop the polymerization. The solution quickly changed colour from brown to green, indicative of oxidation of  $\text{Cu}^I(\text{NPPI})_2$  to  $\text{Cu}^{II}(\text{NPPI})_2$  and no further conversion was observed (Fig. S15B†). In an attempt to re-initiate the polymerization, the reaction solution was sparged for second time, this time with  $\text{N}_2$  to displace the  $\text{O}_2$  previously added to the solution, prior to a second period of electrolysis. Pleasingly, re-initiation was observed ( $E_{app} = -0.08 \text{ V}$ ;  $t_{E_{app}} = 30 \text{ min}$ ) with the polymerization reaching 64% conversion (Fig. S15C†), yielding  $\text{POEGMA}_{300}$  with  $M_{n,SEC} = 9800 \text{ g mol}^{-1}$  and  $D_m = 1.25$  (Fig. S16†) which is comparable to the  $\text{POEGMA}_{300}$  obtain during the constant electrolysis reactions.

A series of experiments was then performed in which reaction solutions ( $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$ ) were electrolyzed at constant potential ( $E_{app} = -0.08 \text{ V}$ ) for increasing periods of time ( $t_{E_{app}} = 5, 10, 20, 30 \text{ min}$ ) before the potential was removed ( $E_{app} = 0 \text{ V}$ ). Samples were taken for analysis after electrolysis and at regular intervals after the potential was removed. Increasing the initial electrolysis times led to an increase in initial conversion from 2% ( $E_{app} = -0.08 \text{ V}$ ;  $t_{E_{app}} = 5 \text{ min}$ ) to 22% ( $E_{app} = -0.08 \text{ V}$ ;  $t_{E_{app}} = 30 \text{ min}$ ). In all experiments monomer conversion continued upon removal of  $E_{app}$  (Fig. 3A). At shorter electrolysis times, conversion continued up to a total reaction time of 60 min resulting in final conversions of 18% and 35% when  $t_{E_{app}} = 5$  and 10 min respectively. Increasing the initial electrolysis time to 20 min yielded initial conversions of 11% with monomer conversion continuing thereafter to reach a final conversion of 56% after a total reaction time of 70 min. When the reaction solution was electrolyzed for 30 min monomer conversion continued for a total reaction time of 90 min, reaching 93% conversion. Kinetic analysis of these reactions revealed that the rate of the reaction also increased from  $k_p^{app} = 0.0028 \text{ min}^{-1}$  when  $t_{E_{app}} = 5 \text{ min}$  to  $k_p^{app} = 0.0425 \text{ min}^{-1}$  when  $t_{E_{app}} = 30 \text{ min}$  (Fig. 3B). An overlay of the SEC chromatograms shows that the polymerization continues after the initial electrolysis period with the molecular weight distributions shifting to higher molecular weights as a function of time (Fig. 3C). The final polymer





**Fig. 3** For triggered seATRP of [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25]; (A) conversion vs. time plot for polymerizations with different  $t_{E_{app}}$ . (B) Pseudo first order kinetic plots for polymerizations for  $t_{E_{app}} = 5$  min,  $k_p^{app} = 0.0028$  min<sup>-1</sup>;  $t_{E_{app}} = 10$  min,  $k_p^{app} = 0.0046$  min<sup>-1</sup>;  $t_{E_{app}} = 20$  min,  $k_p^{app} = 0.0218$  min<sup>-1</sup>;  $t_{E_{app}} = 30$  min,  $k_p^{app} = 0.0425$  min<sup>-1</sup>. (C) SEC in THF showing the evolution of the molecular weight distribution after electrolysis ( $E_{app} = -0.08$  V,  $t_{E_{app}} = 30$  min, solid line) and at 10 minutes intervals after the potential was removed ( $E_{app} = 0$  V, dashed lines, final  $M_{n,SEC} = 9300$  g mol<sup>-1</sup>,  $D_m = 1.33$ ).

obtained ( $E_{app} = -0.08$  V;  $t_{E_{app}} = 30$  min) was comparable to the polymer obtained by uninterrupted electrolysis (Table 1; entry 2) with  $M_{n,SEC} = 9300$  g mol<sup>-1</sup> and  $D_m = 1.33$ .

Quantification of the end group fidelity using conventional <sup>1</sup>H NMR analysis was not possible as poly(methacrylates) do not contain an  $\omega$ -methine proton to integrate against signals at the  $\alpha$ -chain end. To exemplify end group fidelity, a chain extension experiment was performed. Homopolymerization of OEGMA<sub>300</sub> was performed using [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25] ( $E_{app} = -0.08$  V). After electrolysis for 30 min (Table 2, entry 1) and stirring at room temperature in the absence of electrolysis for an additional 90 min near quantitative conversion was obtained (Table 2, entry 2, Fig. S17†). At this point a second aliquot of OEGMA<sub>300</sub> (1 mL, [OEGMA<sub>300</sub>] : [POEGMA<sub>300</sub>-Br] = [20] : [1]) was added and electrolysis was again applied ( $E_{app} = -0.08$  V) for 30 min (Table 2, entry 3) followed by stirring in the absence of electrolysis for an additional 90 min reaching a final conversion of 81% (Table 2, entry 4). A clear shift in the molecular weight distribution was evident *via* SEC analysis (Fig. 4). The molecular weight of the final POEGMA<sub>300</sub> obtained ( $M_{n,SEC} = 16\,600$  g mol<sup>-1</sup>) was in reasonable agreement to the theoretical molecular weight ( $M_{n,th} = 12\,200$  g mol<sup>-1</sup>) relative to the homopolymerizations performed. Although this result exemplifies good chain-end

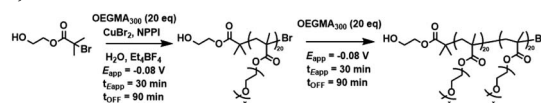
fidelity, there is scope for optimization based on a gradual increase in tailing to low molecular weight, which increased during the course of the reaction resulting in a gradual increase in dispersity ( $D_m = 1.27$ – $1.45$ , Table 2).

The electrochemically triggered reaction conditions were also compatible with polymerizations of OEGMA<sub>300</sub> targeting higher molecular weights. When  $DP_{n,th} = 200$ , the reaction solution was electrolyzed for 30 min ( $E_{app} = -0.08$  V) leading to 13% conversion. The reaction continued in the absence of electrolysis for an additional 90 min, reaching 89% conversion (Fig. S18†) furnishing POEGMA<sub>300</sub> with relatively low dispersity ( $D_m = 1.32$ , Fig. S19†). To expand the monomer scope, 2-*N*-morpholinoethyl methacrylate ( $DP_{n,th} = 200$ ) was electrolyzed for 30 min ( $E_{app} = -0.08$  V) resulting in 40% conversion. The reaction was allowed to continue in the absence of electrolysis for an additional 90 min, reaching 65% conversion (Fig. S20 and S21†).

To explore the mechanism, the polymerization using [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25] ( $t_{E_{app}} = 30$  min;  $E_{app} = -0.08$  V) was repeated and the electrochemical reduction of Cu<sup>II</sup>(NPPI)<sub>2</sub> to Cu<sup>I</sup>(NPPI)<sub>2</sub> followed by UV-vis spectroscopy (Fig. 5). Prior to electrolysis the reaction solution was green and the characteristic Cu<sup>II</sup>(NPPI)<sub>2</sub> absorbance band was present at  $\lambda = 670$  nm,

**Table 2** Electrochemically triggered seATRP of OEGMA<sub>300</sub> in H<sub>2</sub>O. [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25]; followed by *in situ* chain extension using OEGMA<sub>300</sub> (20 eq);  $E_{app} = -0.08$  V;  $t_{E_{app}} = 30$  min; room temperature<sup>a</sup>

Entry	$E_{app}$ /V	Time/min ( $t_{total}$ )	Conv <sup>b</sup>	$M_{n,th}$ /g mol <sup>-1</sup>	$M_{n,SEC}$ <sup>e</sup> /g mol <sup>-1</sup>	$D_m$ <sup>e</sup>
1	-0.08	30 (30)	33%	2191 <sup>c</sup>	7300	1.26
2	—	90 (120)	>99%	6211 <sup>c</sup>	11 300	1.31
3	-0.08	30 (150)	57%	9631 <sup>d</sup>	13 800	1.34
4	—	90 (240)	81%	11 071 <sup>d</sup>	16 600	1.45



<sup>a</sup> [Cu<sup>II</sup>Br<sub>2</sub>] = 8.8 mM. <sup>b</sup> Determined *via* <sup>1</sup>H NMR of reaction samples performed in D<sub>2</sub>O. <sup>c</sup>  $M_{n,th} = [(conv./100 \times DP_{n,th}) \times 300] + 211$ . <sup>d</sup>  $M_{n,th} = [(conv./100 \times DP_{n,th}) \times 300] + 6211$ . <sup>e</sup> From THF SEC.

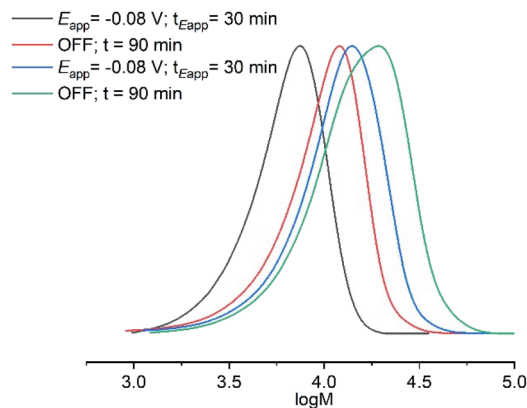


Fig. 4 SEC in THF showing the evolution of the molecular weight distribution during electrochemically triggered eATRP of OEGMA<sub>300</sub> ([OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25];  $E_{app} = -0.08$  V;  $t_{eATRP} = 30$  min) and chain extension ([OEGMA<sub>300</sub>]-[POEGMA<sub>300</sub>-Br] = [20] : [1];  $E_{app} = -0.08$  V;  $t_{eATRP} = 30$  min) (Table 2).

assigned to the d-d transitions of the Cu<sup>II</sup> centre. After electrolysis the reaction solution was brown in colour, qualitatively confirming the reduction of Cu<sup>II</sup>(NPPI)<sub>2</sub> to Cu<sup>I</sup>(NPPI)<sub>2</sub>. UV-vis of the reaction solution immediately after electrolysis showed disappearance of the absorbance band at  $\lambda = 670$  nm and appearance of a new, strong absorbance band at  $\lambda = 465$  nm, confirming reduction of Cu<sup>II</sup>(NPPI)<sub>2</sub> to Cu<sup>I</sup>(NPPI)<sub>2</sub>. The absorbance at  $\lambda = 465$  nm was assigned to MLCT between the Cu<sup>I</sup> centre and the  $\pi^*$  of the surrounding NPPI ligands, as reported for other bipyridyl and/or diimine based complexes of Cu<sup>I</sup>.<sup>52</sup>

In order to quantify the concentration of Cu<sup>I</sup>(NPPI)<sub>2</sub> present after electrolysis, a calibration plot of Cu<sup>I</sup>(NPPI)<sub>2</sub> was used to determine the molar extinction coefficient of Cu<sup>I</sup>(NPPI)<sub>2</sub> ( $\epsilon = 1359$  M<sup>-1</sup> cm<sup>-1</sup>, Fig. S22†). Prior to electrolysis, the concentration of Cu<sup>II</sup>(NPPI)<sub>2</sub> in the reaction solution was 8.8 mM. After electrolysis for 30 min, conversion reached 24% (Fig. 5A) and [Cu<sup>I</sup>(NPPI)<sub>2</sub>] was measured and found to be 4.94 mM (Fig. 5B). The reaction was again allowed to continue in the absence of an applied potential ( $E_{app} = 0$  V). Though the polymerization continued, the colour of the reaction solution gradually

changed from brown back to green over the course of the reaction. Further UV-vis analysis of the reaction solution allowed [Cu<sup>I</sup>(NPPI)<sub>2</sub>] to be followed, revealing a steady decrease over time eventually reaching 1.37 mM after 30 min at which point the reaction had reached 72% conversion.

Identical analyses were performed during polymerization of OEGMA<sub>300</sub> using Cu<sup>II</sup>TPMA and Cu<sup>II</sup>Me<sub>6</sub>-Tren. Due to the tetradentate nature of TPMA and Me<sub>6</sub>-Tren, the reaction solutions were composed of [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [TPMA/Me<sub>6</sub>-Tren] = [20] : [1] : [0.5] : [0.6]. Both Cu<sup>II</sup>TPMA and Cu<sup>II</sup>Me<sub>6</sub>-Tren produced blue solutions prior to electrolysis. Qualitatively, no colour change was observed upon electrolysis. The  $E_{app}$  employed was selected based on the  $E_{1/2}$  (−0.2 V, TPMA; −0.4 V Me<sub>6</sub>-Tren; Fig. S1 and S2†) and electrolysis was initially performed for 30 min before the potential was removed and stirring continued at room temperature. The progress of the reactions was followed by <sup>1</sup>H NMR revealing ~5% conversion after the initial period of electrolysis. UV-vis analysis showed very little change in the absorbance spectra of each complex (Fig. 5C) and unlike the Cu<sup>II</sup>(NPPI)<sub>2</sub> system, no further conversion of monomer to polymer was observed when the reaction was continued for 30 min at  $E_{app} = 0$  V (Fig. 5A). This is perhaps unsurprising considering the relative activity of the Cu<sup>I</sup>TPMA and Cu<sup>I</sup>Me<sub>6</sub>-Tren complexes relative to Cu<sup>I</sup>(NPPI)<sub>2</sub>. Thus we repeated the reaction using bipyridine (bipy) to form Cu<sup>I</sup>(bipy)<sub>2</sub> *in situ* which has intermediate activity relative to the highly active complexes derived from Me<sub>6</sub>-Tren/TPMA and the less active complex derived from NPPI. Similar to Cu<sup>II</sup>(NPPI)<sub>2</sub>, initial conversion in the presence of Cu<sup>II</sup>(bipy)<sub>2</sub> increased with increasing electrolysis time ( $E_{app} = -0.08$  V;  $t_{eATRP} = 10$ –30 min). However, in the absence of electrolysis polymerization was only maintained for 10–20 min reaching only moderate final conversions (< 65%,  $E_{app} = -0.08$  V;  $t_{eATRP} = 30$  min, Fig. S23†). This suggests that the ability to conduct electrochemically triggered eATRP is directly related to the activity ( $k_{act}$  and  $K_{ATRP}$ ) of the Cu-complex employed.

Overall, these results consolidate the hypothesis that the less activating nature of the Cu<sup>I</sup>(NPPI)<sub>2</sub> complex, and its stability in water results in its accumulation in the reaction media. The accumulated Cu<sup>I</sup>(NPPI)<sub>2</sub> is then capable of mediating the

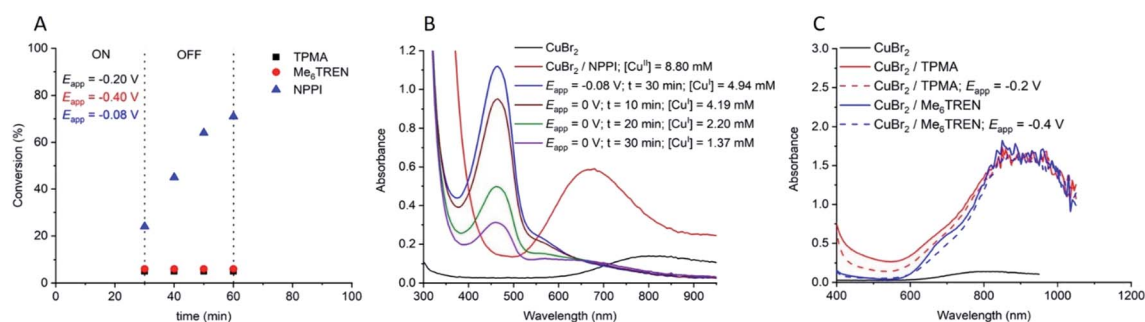


Fig. 5 (A) Conversion vs. time plot for seATRP of [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [L] = [20] : [1] : [0.5] : [L]. For NPPI [L] = [1.25] and for TPMA and Me<sub>6</sub>Tren [L] = [0.6] ( $t_{eATRP} = 30$  min). (B) UV-vis traces showing the reduction of Cu<sup>II</sup>(NPPI)<sub>2</sub> to Cu<sup>I</sup>(NPPI)<sub>2</sub> and the change in [Cu<sup>I</sup>(NPPI)<sub>2</sub>] during the triggered seATRP of [OEGMA<sub>300</sub>] : [HEBiB] : [CuBr<sub>2</sub>] : [NPPI] = [20] : [1] : [0.5] : [1.25]. Using  $\epsilon = 1359$  M<sup>-1</sup> cm<sup>-1</sup> [Cu<sup>I</sup>(NPPI)<sub>2</sub>] was quantified at each point (see ESI† for calibration and calculation details). (C) UV-vis traces of Cu<sup>II</sup>(TPMA) and Cu<sup>II</sup>(Me<sub>6</sub>Tren) before and after electrolysis.  $E_{app,TPMA} = -0.20$  V,  $E_{app,Me6Tren} = -0.40$  V,  $t_{eATRP} = 30$  min.

polymerization of OEGMA when  $E_{\text{app}}$  was removed. We therefore propose that Cu complexes containing pyridine-imine ligands ( $\text{Cu}^{\text{II}}(\text{NAPI})_2$ ) follow an electrochemically-triggered, rather than electrochemically mediated, ATRP mechanism wherein  $E_{\text{app}}$  is only required in order to generate the required  $[\text{Cu}^{\text{I}}(\text{NAPI})_2]$  to initiate and maintain the polymerization reaction.

Finally, to simplify the reaction set up further, current vs. time ( $I$  vs.  $t$ ) graphs obtained from reactions performed under potentiostatic conditions (Fig. 6A) were used to design a step-wise current profile to enable the electrochemically triggered polymerizations to be performed using a 2-electrode current controlled configuration. Using  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$ , a 3-step current profile was initially applied over 30 min ( $I_{\text{app}} = -3.5$  mA, 8 min;  $-1.9$  mA, 7 min;  $-0.5$  mA, 15 min) resulting in 12% conversion. At this point the reaction continued in the absence of electrolysis for a further 120 min reaching 80% conversion (Fig. S24†) with comparable control ( $M_{n,\text{SEC}} = 11\,600$  g mol $^{-1}$ ;  $D_m = 1.25$ , Fig. 6B) to the polymerizations performed with a potentiostatic trigger. Considering future translation to flow electrolysis, it would be beneficial to trigger these reactions using a single current, truly galvanostatic reaction configuration. With this in mind the reaction was repeated with  $I_{\text{app}} = -2.0$  mA leading to 16% conversion after the 30 min electrolysis period reaching 95% after a further 120 min stirring in the

absence of electrolysis (Fig. S25†). This is very promising for intensification to flow electrolysis, though it should be noted that under these conditions, a higher overall charge is passed during the reaction which has an effect on the outcome of polymerization. Whilst the control respect to the dispersity is retained ( $D_m = 1.28$ , Fig. S26†), the  $M_{n,\text{SEC}}$  (14 300 g mol $^{-1}$ ) and  $M_{n,\text{th}}$  (6211 g mol $^{-1}$ ) diverge relative the potentiostatic and step-wise current profile triggered reactions, leaving scope for optimisation in future. We attribute the divergence in the  $M_{n,\text{SEC}}$  and  $M_{n,\text{th}}$  to the gradual increase in the potential (required to maintain  $I_{\text{app}}$ ) during the initial electrolysis period. This leads to an increase in  $[\text{Cu}^{\text{I}}(\text{NPPI})_2]$  and subsequently  $[\text{P}'_n]$ , leading to increased termination and reduced initiator efficiency, relative to the potentiostatic and step-wise current profile triggered polymerizations.

## Conclusions

In summary, seATRP using  $\text{Cu}(\text{NPPI})_2$  complexes in aqueous solution has been reported for the first time. Typical electrolysis conditions require less reducing potentials ( $E_{\text{app}} = -0.08$  V) than complexes derived from  $\text{Me}_6\text{Tren}$  and TPMA. Using OEGMA $_{300}$  as monomer, a range of molecular weights have been targeted with the polymerizations typically complete within 2 h, yielding POEGMA $_{300}$  with good control over the molecular weight distribution ( $D_m < 1.35$ ). However, the defining 'on-off' control experiment revealed that the polymerizations were not under complete electrochemical control, as monomer conversion continued in the absence of  $E_{\text{app}}$ . This is contrary to previous reports using more active  $\text{Cu}^{\text{II}}\text{L}$  complexes. Through electrochemically triggered control experiments and UV-vis spectroscopy we have been able to propose that these less activating complexes, that stabilize  $\text{Cu}^{\text{I}}$  more than  $\text{Cu}^{\text{II}}$ , follow an alternative, previously unreported, electrochemically-triggered polymerization pathway. The polymerizations proceed with good control enabling a range of molecular weights to be targeted ( $\text{DP}_{n,\text{th}} = 20\text{--}200$ ). *In situ* chain extension is also possible alluding to potential application to the synthesis of block copolymers. The reaction set-up can also be further simplified to a 2-electrode, galvanostatic configuration which is promising for future intensification through translation to flow electrolysis. However, though suitable for eATRP at reduced catalyst loadings, more active ligands such as  $\text{Me}_6\text{Tren}$ , TPMA and bipy do not support the electrochemically-triggered polymerization pathway. Indeed, the ability to conduct electrochemically triggered eATRP seems to be directly related to the activity of the Cu-complex and can be related to the  $k_{\text{act}}$  and  $K_{\text{ATRP}}$  of the complexes employed. Thus, it is possible that other ligands that stabilize  $\text{Cu}^{\text{I}}$  over  $\text{Cu}^{\text{II}}$  (e.g. other substituted NAPI and 1,4-diazabutadiene ligands) could also follow or favour this electrochemically triggered pathway.

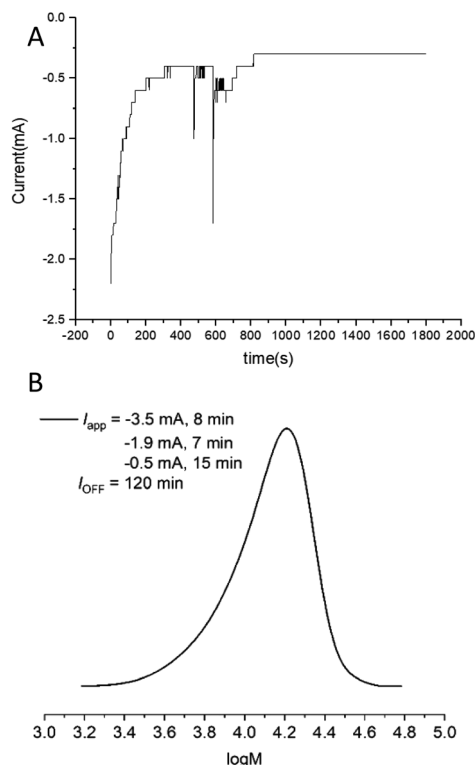


Fig. 6 (A)  $I$  vs.  $t$  plot for the electrochemically triggered seATRP reaction of OEGMA $_{300}$  performed under potentiostatic conditions  $[\text{OEGMA}_{300}] : [\text{HEBiB}] : [\text{CuBr}_2] : [\text{NPPI}] = [20] : [1] : [0.5] : [1.25]$ ;  $E_{\text{app}} = -0.08$  V;  $t_{\text{app}} = 30$  min,  $Q = 0.78$  C). (B) Molecular weight analysis of the final polymer formed from the same reaction performed using step-wise current profile min ( $I_{\text{app}} = -3.5$  mA, 8 min;  $-1.9$  mA, 7 min;  $-0.5$  mA, 15 min). SEC in THF  $M_{n,\text{SEC}} = 11\,600$  g mol $^{-1}$ ,  $D_m = 1.25$ .

## Data availability

Experimental procedures and data supporting the research, not presented in the main manuscript, is included in the ESI.† Raw data files are available from the Warwick Research Archive

Portal (WRAP, <https://wrap.warwick.ac.uk>) and from the corresponding author on request.

## Author contributions

Boyu Zhao: investigation; methodology; formal Analysis; validation; visualization; writing – original draft. Fred Pashley-Johnson: investigation; methodology; formal analysis; validation; visualization; writing – original draft. Bryn Jones: Methodology; formal analysis; supervision; writing – review and editing. Paul Wilson: conceptualization; funding acquisition; investigation; methodology; project administration; resources; supervision; writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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