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# Aqueous copper(II) photoinduced polymerization of acrylates: Low copper concentration and the importance of sodium halide salts

Glen R. Jones,<sup>a</sup> Richard Whitfield,<sup>a</sup> Athina Anastasaki,<sup>\*a,b</sup> David M. Haddleton<sup>\*a,b</sup>

*a - University of Warwick, Chemistry Department, Library road, CV4 7AL, Coventry, United Kingdom.*

*b- ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Monash Institute of Pharmaceutical Sciences, Monash University (Parkville Campus), 399 Royal Parade, Parkville, Victoria 3152, Australia*

*DMH: d.m.haddleton@warwick.ac.uk, AA: a.anastasaki@warwick.ac.uk*

## Abstract

Photoinduced metal mediated radical polymerization is a rapidly developing technique which allows for the synthesis of macromolecules with defined molecular weight and narrow molecular weight distributions, although typically exhibiting significant limitations in aqueous media. Herein we demonstrate that the presence of alkali metal halide salts in conjunction with low copper concentration and UV irradiation, allows for the controlled polymerization of water soluble acrylates in aqueous media, yielding narrow molecular weight distributions and high conversions. Despite the aqueous environment which typically compromises polymer end group fidelity, chain extensions have also been successfully performed and different degrees of polymerization were targeted. Importantly, no conversion was observed in the absence of UV light and the polymerization could be switched “on” and “off” upon demand as demonstrated by intermittent light and dark periods and thus allowing access to spatiotemporal control.

## Introduction

The development of reversible-deactivation radical polymerization (RDRP) techniques such as atom transfer living radical polymerization (ATRP)<sup>1-5</sup>, Cu(0) mediated reversible deactivation radical polymerization (Cu(0)-RDRP)<sup>6-9</sup>, nitroxide-mediated radical polymerization (NMP)<sup>10-12</sup> and reversible addition-fragmentation chain transfer (RAFT)<sup>13-16</sup> has allowed for the

synthesis of polymers of targeted molecular weight, macromolecular architecture, end group functionality and narrow molecular weight distributions. These techniques work by establishing an equilibrium between dormant and active species in which the dormant state is predominant; as a result of this the concentration of free radicals is very low which suppresses termination reactions. ATRP in polar media such as water has traditionally proved challenging typically exhibiting a lower degree of control. This has been attributed to higher values of  $K_{\text{ATRP}}$ , the equilibrium constant that defines the balance between active and dormant species, resulting in higher radical concentrations and consequently higher probability of termination reactions. A range of new processes have been developed, such as initiators for continuous activator regeneration (ICAR) ATRP<sup>17</sup>, activators regenerated by electron transfer (ARGET) ATRP<sup>18</sup> and aqueous Cu(0)-RDRP<sup>7,9,19,20</sup> in an attempt to attain a higher degree of control over polymerization in aqueous media. Although progress has been made by these approaches, significant drawbacks such as low conversions or high catalyst concentrations still remain a challenge and possibly limit the scope of such techniques.

Within recent years considerable focus has been placed on developing RDRP and other polymerization systems in which the equilibrium between dormant and active species is mediated by various external stimuli such as allosteric<sup>21,22</sup>, electrochemical<sup>23</sup>, mechanochemical<sup>24</sup> and photochemical control.<sup>23,25-29</sup> Such external stimuli allow for dynamic control over polymerizations thus introducing new opportunities for advanced materials synthesis. Photochemical mediation is of increasing interest due to its wide availability, being environmental benign. Photochemistry also allows for lower activation energy pathway processes such as initiation and repeat reactivation of dormant chains, faster rates of polymerization, and temporal control achieved by simply removing the light source.

Among the various RDRP techniques, ATRP has become a popular photopolymerization route. The emergence of photoinduced RAFT polymerization is also noted with Boyer and co-workers reporting some excellent examples of Photoinduced Electron Transfer RAFT polymerization (PET-RAFT).<sup>30-37</sup> Cu-mediated photoinduced ATRP systems both in the presence and absence of photosensitizers and photoinitiators have been developed by Yagci and co-workers.<sup>38,39</sup> In a bulk polymerization of MMA using *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) and Cu(II)Br<sub>2</sub> it was proposed that a Cu(II)X<sub>2</sub>/L complex can be directly reduced to Cu(I)X/L which can rapidly generate carbon-centred radicals from alkyl bromide initiators. Addition of a small amount of methanol to the system was reported to enhance control over molecular weights and yield narrower MWD's, this is

attributed to better solubility of Cu(II) species and the *in situ* generation of hydroxymethyl radicals that act as reducing agents.<sup>40</sup> Konkolewicz *et al.* has reported a Cu based photoinduced ATRP system using Cu(II)Br<sub>2</sub> with Tris(2-pyridylmethyl)amine (TPMA) based ligands. The polymerization of both MMA and methyl acrylate (MA) were shown to proceed with a high degree of control ( $\bar{D}$  as low as 1.05) at parts per million (ppm) catalyst loadings.<sup>41</sup> A series of control experiments lead to the conclusion that photoreduction of Cu(II) occurs via ligand to metal charge transfer in an excited state, with a later mechanistic study concluding that the main route of radical (re)generation occurs via reduction of Cu(II) complexes by free amines (uncomplexed ligand).<sup>42</sup> Recently Matyjaszewski and coworkers expanded the scope of this technique to aqueous media for the polymerization of PEG methacrylates, whilst control was demonstrated over the polymerization conversions were limited, hence chain extension required purification of a macroinitiator as opposed to an in-situ chain growth approach.<sup>43</sup>

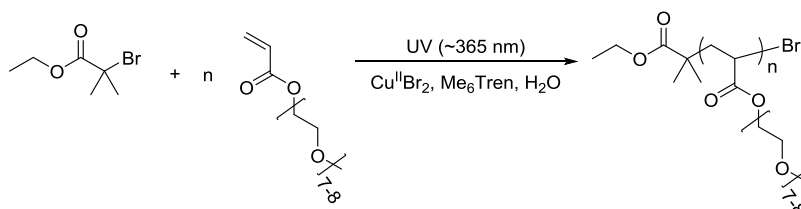
Hawker and co-workers have demonstrated the controlled radical polymerization of methacrylates and acrylates using an iridium photoredox catalyst.<sup>44,45</sup> The catalyst is proposed to proceed by absorption of visible light by *fac*-[Ir(III)(ppy)<sub>3</sub>] to give an excited state which can abstract bromide from a conventional alkyl bromide initiator. Polymerization of methyl methacrylate (MMA) was demonstrated to proceed with a high degree of control over MWD's ( $\bar{D}$ ~1.2) at low catalyst loadings (0.005 mol%). The technique was also demonstrated to work efficiently using photo-masking on surface grafted initiators to give three-dimensional polymer brush nanostructures<sup>46</sup> and in a flow system.<sup>47</sup> In 2014 Hawker, Fors and co-workers reported for the first time a metal-free ATRP system utilising phenothiazine as a photoredox catalyst.<sup>48</sup> Control over the molecular weight and low dispersities were reported for methacrylates along with excellent spatiotemporal control, demonstrated by kinetic analysis with repeated cyclization of light and dark conditions. Furthermore the synthesis of a variety of well controlled block copolymers was demonstrated by both concurrent metal-free ATRPs and a combination of metal-free, copper and iridium based systems. This metal-free approach was later expanded upon by Matyjaszewski to include the synthesis of poly(acrylonitrile) with predictable molecular weights, low dispersities and high preservation of chain-end functionality.<sup>49</sup> The use of exotic catalytic systems potentially limits the applicability of these techniques, as well as relatively low conversions, necessitating purification for the synthesis of block copolymers. Liu *et al.* also showed photoinduced ATRP of MMA can be mediated using fluorescein in the presence of triethylamine (TEA), albeit with a lower degree of control of MWD's.<sup>50</sup>

Haddleton and co-workers recently reported on the photoinduced polymerization of acrylates mediated by low concentrations of Cu(II)Br<sub>2</sub> and the aliphatic tertiary amine ligand tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>Tren) in UV and visible light.<sup>51</sup> A range of acrylate and methacrylate monomers were successfully polymerized with excellent control over MWD's, quantitative conversions and near perfect end-group fidelity. This approach has been subsequently applied to the synthesis of a range of sequence-controlled materials including high order multiblock copolymers, telechelic, and methacrylate-acrylate block copolymers, and utilised in flow based systems.<sup>52-54</sup> Junkers and coworkers have reported the synthesis of sequence controlled materials as well as acrylate-methacrylate blocks via ligand switching.<sup>55-58</sup> The use of Cu(II) formate complexes has also be shown to polymerize (meth)acrylates in a controlled manner, with the distinct benefit of using stable, discrete catalyst complexes as opposed to those generated *in situ*, and enhanced spatiotemporal control.<sup>59,60</sup> Efficient control over polymerization has been reported in DMSO, DMF, IPA, toluene/methanol mixtures, and a range of ionic liquids.<sup>51,54,61</sup> However, attempts at utilizing aqueous media has until now proved challenging, furnishing polymers with broad MWD's.

Herein we report the controlled polymerization of PEGA in aqueous medium utilizing a photo-induced polymerization approach. The addition of sodium bromide results in a significant enhancement of the control over the molecular weight distributions in the presence of ppm concentration of copper. Quantitative conversions can be achieved without compromising the high end group fidelity which is assessed through successful *in situ* chain extensions. The ability of our approach to exhibit spatiotemporal control is also evaluated via intermediate “on” and “off” cycles and the synthesis of higher MW polymers is also attempted.

## Results and Discussion

### The effect of altering the relative copper and ligand concentrations



**Scheme 1:** Homopolymerization of PEGA<sub>480</sub> under UV irradiation using a simple, inexpensive photoreactor.

Initially, the homopolymerization of PEGA (targeted  $DP_n = 20$ ) was attempted in water (50% v/v) with 0.02 equivalents of Cu(II)Br<sub>2</sub> and 0.12 equivalents of Me<sub>6</sub>Tren using an inexpensive UV lamp with a broad low intensity emission centred at approximately 365 nm (entry 1, table 1) (scheme 1, figure S1, SI) as described previously.<sup>51</sup> Sampling after 8 hours showed full monomer conversion by <sup>1</sup>H NMR, however, SEC analysis revealed an uncontrolled polymerization process with the polymer showing a dispersity of 3.75 (Figure S3 (a), SI). This is not surprising for aqueous systems with low copper concentrations as the lack of control could be attributed to insufficient deactivation. In order to assess this further the copper content was initially increased to 0.04 equivalents (twofold increase, entry 2, table 1) resulting in slightly lower dispersities, although the process was still lacking control. A further increase of the copper content up to five fold (0.10 equivalents, entry 3, table 1) gave rise to a significant lowering of the dispersity ( $D = 1.28$ ), confirming that a higher copper(II) concentration is essential in order to maintain good control over the molecular weight distributions. It should be noted that a potential increase of the [copper(II)] solely would be impossible without also adjusting the [ligand] as when [copper]:[ligand] is equal or < 1, there is no excess of ligand to facilitate the reduction of Cu(II) into the active species and hence the polymerization stops.<sup>51</sup> As this was demonstrated only for the case of organic solvents (in DMSO no polymerization is reported when [Cu(II)]:[L]=[0.02]:[0.02]), we were interested in replicating the experiment in aqueous media. As expected, no polymerization occurred at this ratio even when the reaction was left to proceed for 24 h highlighting the necessity of an excess of Me<sub>6</sub>Tren in the polymerization mixture (entry 4, table 1), which is in agreement with the mechanistic studies of Frick *et al.*<sup>62</sup> Identical results were obtained when higher amounts of copper and ligand were utilized (Cu(II):[L]=[0.12]:[0.12]), concluding that regardless of the chosen amount of copper and ligand, equimolar amounts result in cessation of the polymerization (entry 5, table 1). Thus, in order to reach higher levels of copper, the [ligand] should also be adjusted. However, increasing the concentration of both Me<sub>6</sub>Tren and Cu(II)Br<sub>2</sub> by 5 fold showed an increase in dispersity ( $D = 1.60$ ), (entry 6, table 1), attributed to extended termination events due to the excess of the ligand, in line with previous investigations.<sup>63</sup> In order to use a higher copper content but also maintain the ligand concentration at moderate levels, we subsequently utilized the ratio of [Cu]:[L]=[0.20]:[0.25] which resulted in a further decrease in the dispersity value from 1.28 to 1.11 (entry 6, table 1). Hence, it was concluded that the polymerization of acrylates in aqueous media can be facilitated in the presence of high concentrations of copper and ligand resulting in narrow MWDs at quantitative conversions.

## The effect of the addition of sodium bromide

Although our investigations show that higher [Cu(II)] and [ligand] can effectively control the polymerization of PEGA in aqueous media, the excess of those compounds should be reduced, if not eliminated, as they can potentially induce undesired toxicity and/or colour to the final material. In addition, Me<sub>6</sub>Tren is a relatively expensive compound and thus its usage should be reduced to the minimum. The addition of halide salts has previously been reported to increase the control of ATRP processes by effectively increasing the concentration of deactivating species without disrupting the equilibrium between [Cu(I)] and [Cu(II)].<sup>43,64,65</sup> This approach is also beneficial as it allows for a much lower concentration of copper species to be utilized. In order to assess whether the presence of halide salts would be compatible with this photoinduced polymerization method, we conducted the polymerization of PEGA in the presence of various concentrations of sodium bromide (NaBr). The addition of 0.5 equivalents of NaBr with respect to the initiator gave rise to an improved dispersity (1.25) when compared to entry 1, where the absence of the salt resulted in a complete lack of control. Thus, the presence of an external deactivator resulted in better control over the MWDs. A further increase of NaBr to 1, 2 and 3 equivalents led to a gradual reduction of the dispersity with the best result achieving 1.12 despite reaching full monomer conversion. By maintaining a relative high salt content, we were also able to further lower the copper content down to 67 ppm, although slightly broader MWD's resulted (entry 12, table 1). Dispersity was shown to increase as [copper] was further reduced to 26 ppm and 13 ppm (entries 13 and 14, table 1). It is quite remarkable that in the presence of just 26 ppm of copper the dispersity value is still as low as 1.26 and thus demonstrates good control over the MWDs despite such a low concentration of catalytic species. Nevertheless, in order to maintain a good balance between copper concentration and control, 250 ppm of copper was chosen for the remaining polymerizations (subsequent section).

**Table 1:** Polymerization of PEGA<sub>480</sub> with various Cu(II)Br<sub>2</sub>, Me<sub>6</sub>TREN and NaBr concentrations.

Corresponding SEC traces can be found in figure S3, supporting information (SI).

Entry	[PEGA <sub>480</sub> ]:[I]:[Cu(II)Br <sub>2</sub> ]:[Me <sub>6</sub> TREN]	[NaBr]	Time (hours)	Conversion	M <sub>n</sub> (Theo.) (Da)	M <sub>n</sub> (SEC) (Da)	D
1	20 : 1 : 0.02 : 0.12	-	8	>99%	9800	17500	3.75

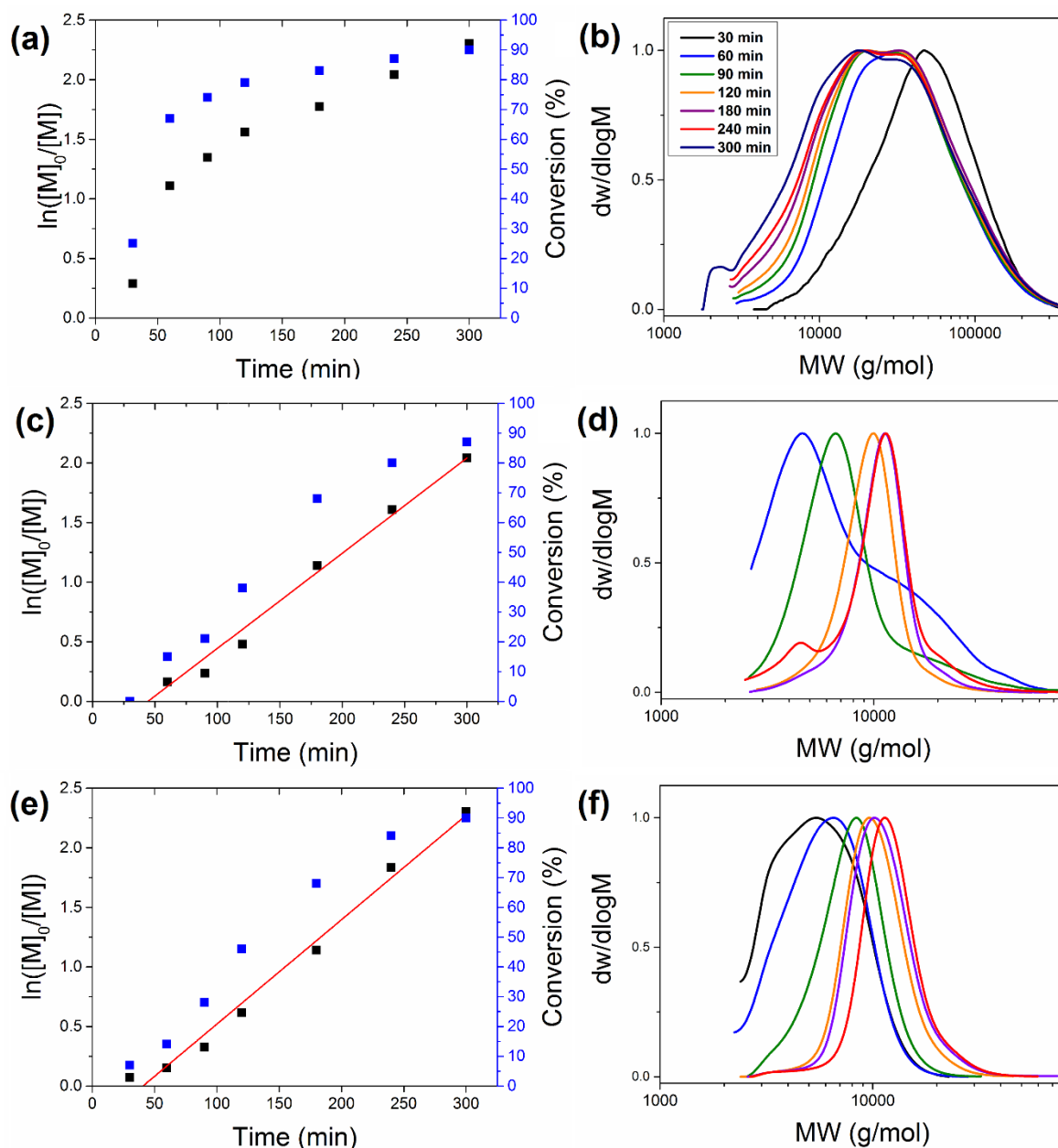
2	20 : 1 : 0.04 : 0.12	-	8	>99%	9800	12500	2.14
3	20 : 1 : 0.10 : 0.12	-	8	>99%	9800	12600	1.28
4	20 : 1 : 0.02 : 0.02	-	24	-	-	-	-
5	20 : 1 : 0.12 : 0.12	-	24	-	-	-	-
6	20 : 1 : 0.10 : 0.60	-	8	>99%	9800	10800	1.60
7	20 : 1 : 0.20 : 0.25	-	8	>99%	9800	12500	1.11
8	20 : 1 : 0.02 : 0.12	0.5	8	>99%	9800	12700	1.25
9	20 : 1 : 0.02 : 0.12	1	8	>99%	9800	12300	1.16
10	20 : 1 : 0.02 : 0.12	2	8	>99%	9800	12000	1.13
11	20 : 1 : 0.02 : 0.12	3	8	>99%	9800	12200	1.12
12	20 : 1 : 0.01 : 0.12	3	16	>99%	9800	14300	1.17
13	20 : 1 : 0.005 : 0.12	3	16	>99%	9800	14500	1.26
14	20 : 1 : 0.001 : 0.12	3	16	>99%	9800	15000	1.57
15	40 : 1 : 0.02 : 0.12	3	8	>99%	19400	21600	1.18
16	40 : 1 : 0.02 : 0.12	6	8	>99%	19400	19900	1.14
17	80 : 1 : 0.02 : 0.12	3	8	>99%	38600	34000	1.24
18	80 : 1 : 0.02 : 0.12	12	8	>99%	38600	35500	1.58
19	160 : 1 : 0.02 : 0.12	3	8	>99%	77000	gel	-
20	160 : 1 : 0.02 : 0.12	24	8	>99%	77000	gel	-
21	10 : 1 : 0.02 : 0.12	3	8	>99%	5000	6700	1.13

### Kinetic analysis in the presence and absence of sodium bromide

The lack of control in the presence of low copper concentrations and the absence of NaBr prompted us to perform a careful kinetic study in order to attest the *livingness* of the system. As expected from the final broad MWDs, the kinetic analysis revealed a non-linear first order kinetics throughout the polymerization accompanied by the initial formation of high molecular species (1.9). However, as the polymerization proceeds the molecular weight decreases probably due to the gradual accumulation of Cu(II)Br<sub>2</sub> as a result of pronounced termination events, although the accumulated Cu(II)Br<sub>2</sub> is still not efficient to facilitate a controlled polymerization yielding broad bimodal distributions throughout the reaction. In order to verify this assumption, the kinetic analysis of higher copper content was also performed. Following the typical small induction period observed in this system, the inclusion of more copper resulted in linear first order kinetics and significantly less pronounced termination during the initial stage of the polymerization. The good correlation between the theoretical and the experimental molecular weights further attests to the controlled/living character of the system, confirming that the presence of higher concentrations of deactivator is essential in order to establish the desired equilibrium. Similarly, the inclusion of NaBr, as opposed to higher copper content,



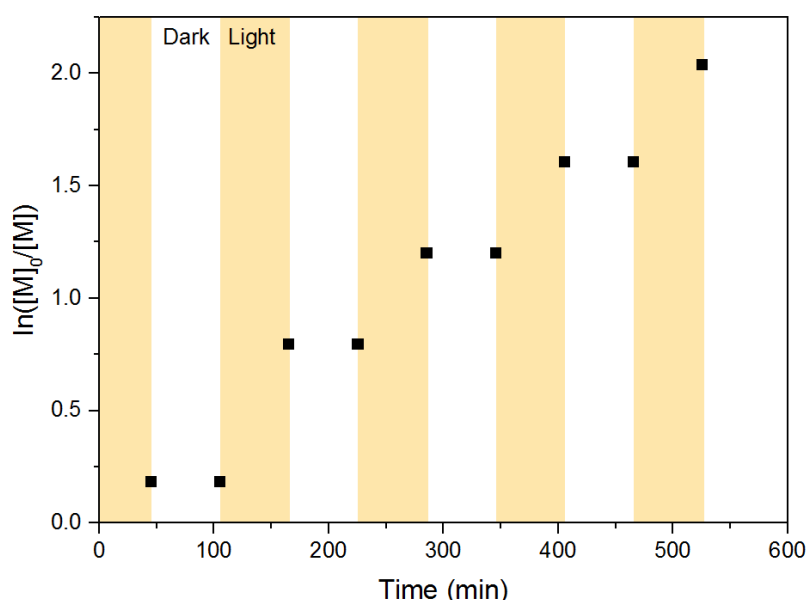
gave rise to identical data with the  $\ln([M]/[M_0])$  increasing linearly with time consistent with a constant concentration of radicals, the molecular weight is increasing linearly with conversion and the dispersity values decreasing throughout the polymerization. Hence, under our optimized conditions all the criteria of a living polymerization have been maintained.



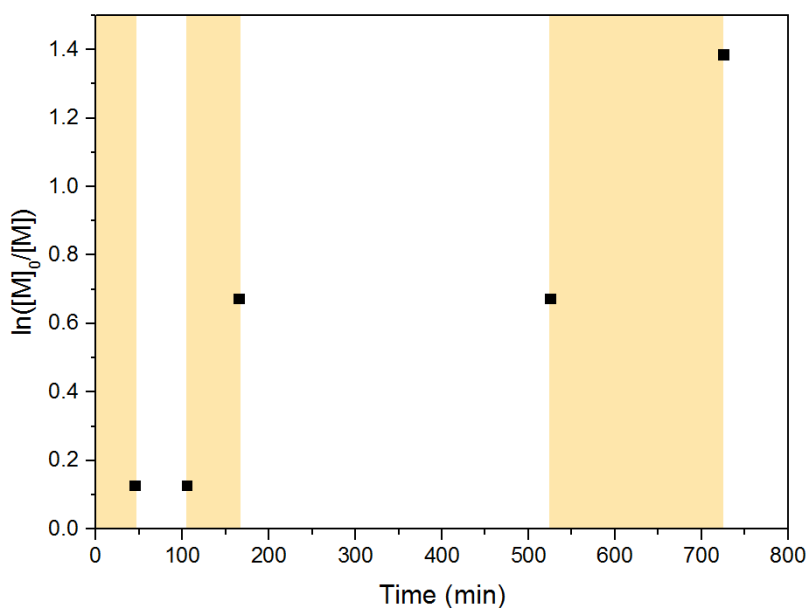
**Figure 1:** (a) Kinetic plot of polymerization of PEGA<sub>480</sub>, conditions from entry 1, table 1, (b) molecular weight evolution for plot (a), (c) kinetic plot of polymerization of PEGA<sub>480</sub> with increased copper and ligand concentration, conditions from entry 3, table 1, (d) molecular weight evolution for plot (c), (e) kinetic plot of polymerization of PEGA<sub>480</sub> in the presence of 3 eq. of NaBr, conditions from entry 11, table 1, (f) molecular weight evolution for plot (e).

### Demonstrating temporal control

In order to demonstrate “on/off” temporal control a polymerization was carried out with intermittent exposure to both light and dark periods. PEGA ( $DP_n = 20$ ) (conditions from entry 11, table 1) was polymerized in a UV light box for an initial 45 minutes, followed by 1 hour periods cycled between a dark room and the light box, with samples taken for NMR and SEC analysis at every change of light/dark conditions. The total time the reaction was exposed to light was 285 minutes (final conversion = 85%,  $M_n = 10,000$  Da,  $D = 1.12$ ), Figure 2. It can be seen that there was no conversion observed during dark periods, demonstrating the necessity of UV irradiation for both initiation and propagation allowing for the possibility of temporal control. In order to investigate this further, an experiment was carried out in which a longer dark period was employed in order to demonstrate reactivation of alkyl halides after a prolonged inactive period. A reaction was exposed to UV light for 45 minutes, followed by an hour dark period and a second hour in light. The reaction was then placed in a dark room for six hours, after which it was sampled and placed back into UV light for a final time. No conversion is observed during dark periods, including a prolonged exposure to dark conditions, furthermore reinitiation was found to occur and the polymerization proceeds in a controlled manner ( $D = 1.12$ ), Figure 3. It is noted that temporal control in aqueous media appears to be significantly enhanced when compared to similar reactions in DMSO, in which a slight increase in conversion during dark periods is observed;<sup>51</sup> this is attributed to the increased concentration of NaBr in solution.



**Figure 2:** Kinetic plot demonstrating temporal control over the polymerization of PEGA<sub>480</sub> (conditions from entry 11, table 1), dark periods (white), light periods (yellow).

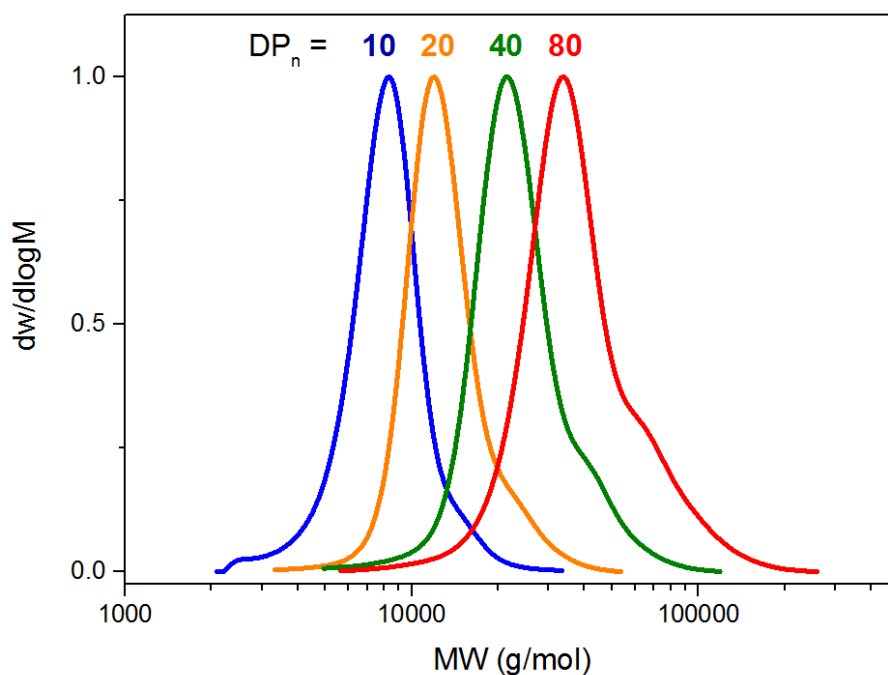


**Figure 3:** Kinetic plot demonstrating temporal control over the polymerization of PEGA<sub>480</sub> (conditions from entry 11, table 1) during a prolonged dark period (white), light periods (yellow).

### Optimization of homopolymerization of PEGA DP<sub>n</sub> = 10-80

Homopolymerization of PEGA of various targeted molecular weights were attempted using the optimized conditions found during the investigation into copper, ligand and halide salt concentrations. The conditions for DP<sub>20</sub> (1 : 0.02 : 0.12 : 3, I : Cu(II) : L : NaBr) were applied to targeted degrees of polymerization of 10, 40, 80, and 160. For DP<sub>10</sub> the polymerization reaches quantitative conversion (entry 21, table 1), and SEC analysis revealed a narrow MWD ( $\mathcal{D} = 1.13$ , figure 4.) DP<sub>40</sub> (>99% conversion,  $M_n = 21600$  Da,  $\mathcal{D} = 1.18$ ) and DP<sub>80</sub> (>99% conversion,  $M_n = 34000$  Da,  $\mathcal{D} = 1.24$ ) were also successfully targeted (entries 15 and 17, table 1). Keeping the vol% of monomer constant (50 vol%) results in lower molar concentrations of Cu, L and NaBr (as low as 62 ppm levels of Cu(II)Br<sub>2</sub>). In order to ascertain whether this reduction in NaBr concentration has an effect on the dispersity of the resultant polymer, reactions targeting DP<sub>40</sub> and DP<sub>80</sub> were carried out under the same conditions but with double and quadruple the amount of NaBr, giving the same effective concentration of salt in solution as the optimized DP<sub>20</sub> conditions (entries 16 and 18, table 1). It can be seen that a higher concentration of NaBr gives a similar result to entry 15, table 1 (DP<sub>40</sub>), however when targeting a higher molecular weight (DP<sub>80</sub>) the higher salt concentration results in a broader dispersity product. Attempts to polymerize PEGA to higher molecular weight (entries 19 and 20, table 1) resulted in the formation of a “covalent hydrogel”; this is postulated to be due to the presence of diacrylate impurity in the monomer, further supported by the appearance of the high

molecular weight shoulders, figure 4, which become more prevalent at higher degrees of polymerization.

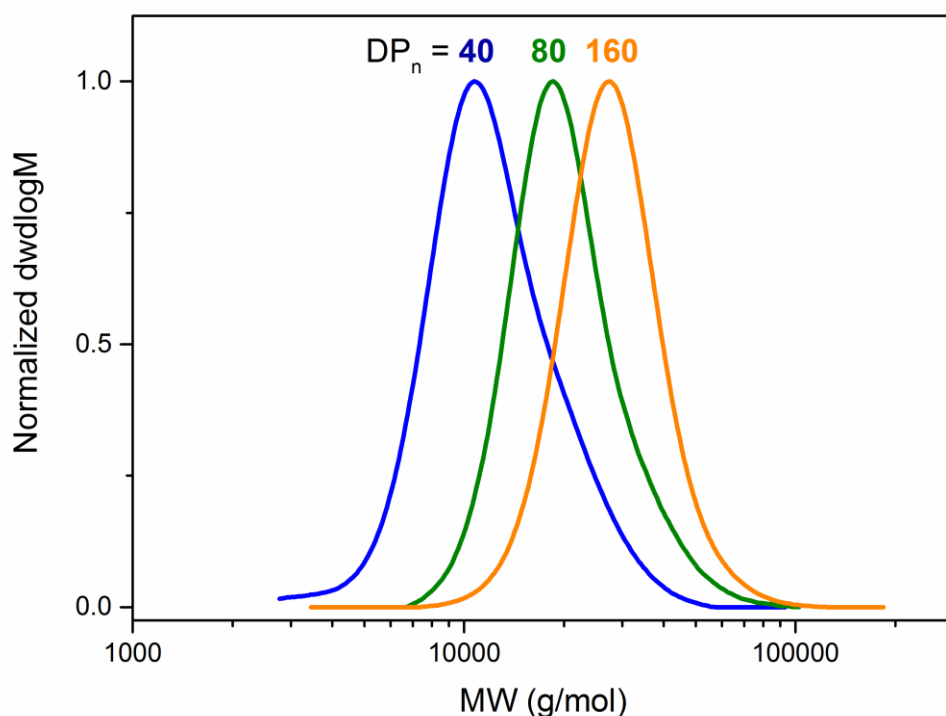


**Figure 4:** Molecular weight distributions of poly(PEGA) ( $DP_n = 10, 20, 40, 80$ ) synthesized under optimized conditions (entry 21, 11, 15, 17, table 1) as measured by DMF SEC.

### Monomer scope

In addition to PEGA, other water soluble functional acrylates can be successfully polymerized in the presence of UV light and halide salts. The homopolymerization of hydroxyethyl acrylate (HEA)  $DP_n = 40-160$  was targeted using 1 : 0.02 : 0.12 : 3, I : Cu(II) : L : NaBr in a similar manner to polymerizations of PEGA (see table S6, SI). In the case of  $DP_{40}$  the reaction reached 96% conversion in 8 hours; and SEC analysis showed a monomodal peak ( $M_n = 10900$  Da,  $\mathcal{D} = 1.20$ , figure 5).  $DP_{80}$  (95% conversion,  $M_n = 18700$  Da,  $\mathcal{D} = 1.16$ ) and  $DP_{160}$  (82% conversion,  $M_n = 26000$  Da,  $\mathcal{D} = 1.13$ ) were also successfully targeted using the same conditions showing good control over the MWDs. The polymerization of a monomer salt, 3-sulfopropyl acrylate potassium salt was also attempted. It was found that the initiator used in previous polymerizations, EBiB, was insoluble in aqueous mixtures of the sulfonate monomer so the alternative water soluble initiator 2,3-dihydroxypropyl 2-bromo-2-methyl propanoate was utilized. Targeting a DP of 20 using 1 : 0.02 : 0.12 : 3, I : Cu(II) : L : NaBr yielded conversion of 83% after 8 hours ( $M_n = 9500$  Da,  $\mathcal{D} = 1.24$  by aqueous GPC, figure S4, SI). Successful controlled polymerization of PEG<sub>500</sub> methacrylate proved more challenging, with

reactions reaching quantitative conversions but exhibiting broad dispersities ( $D > 3.0$ ) under the optimized conditions for PEGA. By using tris(2-pyridylmethyl)amine (TPMA) as the ligand instead of Me<sub>6</sub>TREN conversion was limited to just a few percent after 24 hours. However when the reaction was left in ambient light the reaction proceeded to near full conversion (>99%,  $M_n = 9500$  Da,  $D = 1.27$ , figure S5, SI).

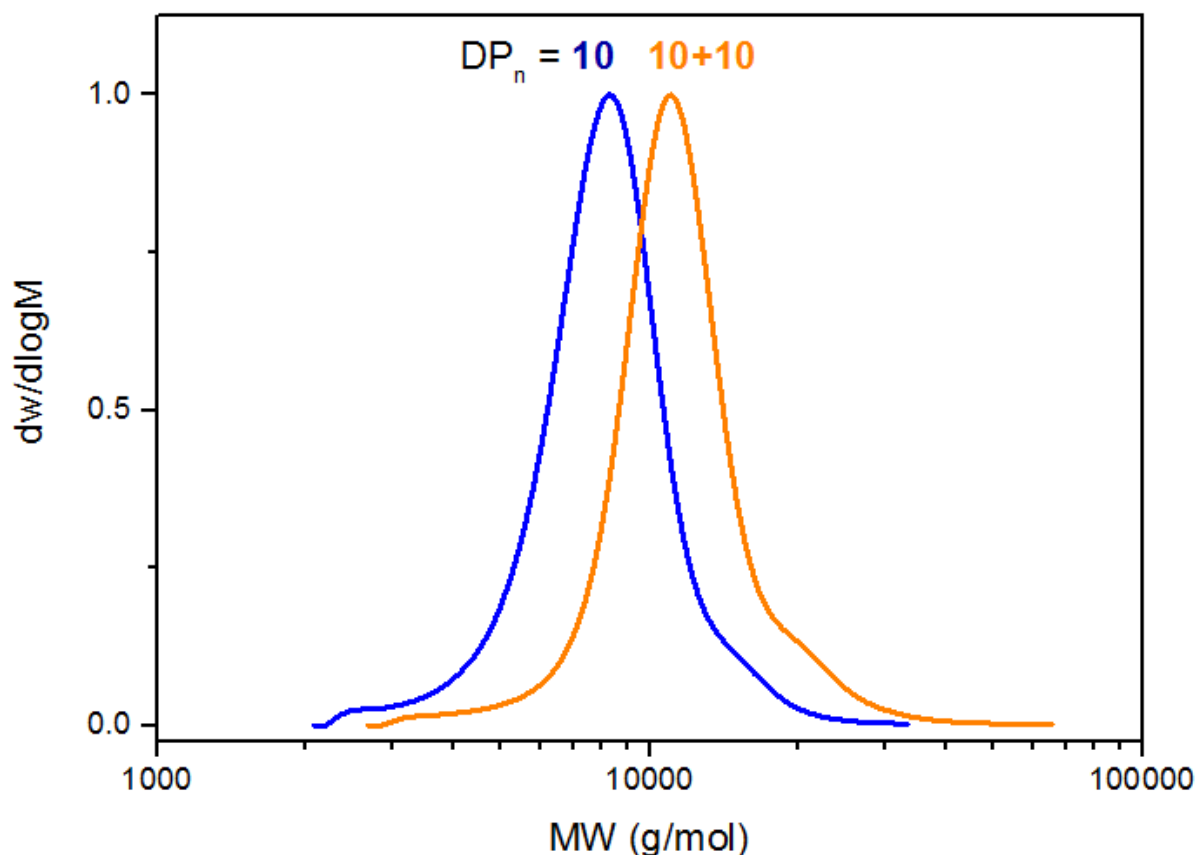


**Figure 5:** Molecular weight distributions of poly(HEA) ( $DP_n = 40, 80, 160$ ) synthesized under optimized conditions (table S5, SI) as measured by DMF SEC.

### **In-situ chain extension of poly(PEGA)**

In an attempt to demonstrate the end group fidelity of this aqueous polymerization technique an in-situ chain extension of poly(PEGA) was attempted. Poly(PEGA)<sub>10</sub> was targeted using 3eq. of NaBr and when the reaction reached full monomer conversion (>99% conversion,  $M_n = 7600$  Da,  $D = 1.12$ , figure 6) a second aliquot of PEGA was subsequently added. The reaction was then allowed to proceed overnight, yielding a chain extended polymer (>99% conversion,  $M_n = 11000$  Da,  $D = 1.11$ , figure 6.) The synthesis of double hydrophilic block copolymers was also demonstrated by in-situ chain extension of Poly(PEGA)<sub>10</sub> (>99%

conversion,  $M_n = 6400$  Da,  $D = 1.12$ , figure S6, SI) with HEA (targeted DP = 20), added as an aqueous solution with 0.02 eq. of Cu(II)Br<sub>2</sub> and 0.12 eq. of ligand with respect to the PPEGA macroinitiator. (66% conversion,  $M_n = 14700$  Da,  $D = 1.20$ , figure S6, SI).



**Figure 6:** Molecular weight distributions of poly(PEGA) ( $DP_n = 10$ ) and in-situ chain extension ( $DP_n = 10+10$ ) as measured by DMF SEC.

## Conclusions

In summary, we present a new methodology to effectively expand the scope of photoinduced copper mediated RDRP to include the controlled polymerization of water soluble acrylates in aqueous media at relatively low copper concentrations. Addition of NaBr was demonstrated to give effective control over the polymerization ( $D$  as low as 1.11) with high conversions (>99% by NMR). These optimized conditions have also been demonstrated to control the polymerization of HEA and sulfopropyl acrylate potassium salt. Furthermore, the reaction was shown to have a high degree of temporal control, exemplified by ‘on-off’ experiments in which the reaction was exposed to intermittent periods of light and dark conditions. The technique was demonstrated to apply to a range of monomers, targeted molecular weights and exhibit high end group fidelity, exemplified by in-situ chain extensions.

## Supporting Information

Details of experimental procedures, supplementary figures, SEC data and tables.

## Acknowledgements

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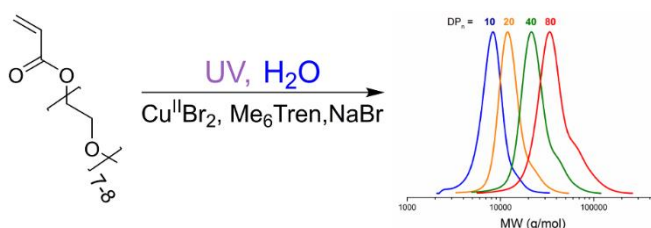
## Aqueous copper(II) photoinduced polymerization of acrylates: Low copper concentration and the importance of sodium halide salts

Glen R. Jones,<sup>a</sup> Richard Whitfield,<sup>a</sup> Athina Anastasaki,<sup>\*a,b</sup> David M. Haddleton<sup>\*a,b</sup>

*a* - University of Warwick, Chemistry Department, Library road, CV4 7AL, Coventry, United Kingdom.

*b*- ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, Monash Institute of Pharmaceutical Sciences, Monash University (Parkville Campus), 399 Royal Parade, Parkville, Victoria 3152, Australia

DMH: [d.m.haddleton@warwick.ac.uk](mailto:d.m.haddleton@warwick.ac.uk), AA: [a.anastasasaki@warwick.ac.uk](mailto:a.anastasasaki@warwick.ac.uk)



**Low [Cu] + NaBr :  
Controlled polymerization in Water**