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Rapid Synthesis of Well-Defined Polyacrylamide by Aqueous Cu(0)-Mediated Reversible-Deactivation Radical Polymerization

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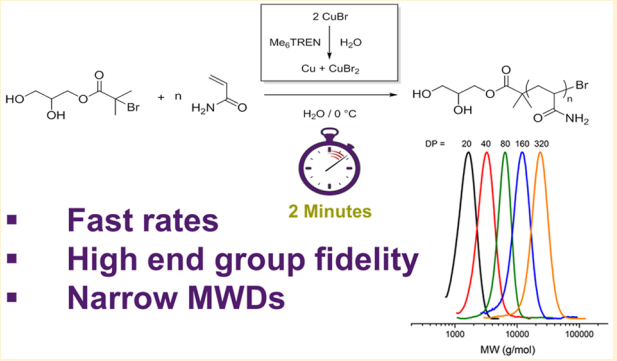
Supporting Information

ABSTRACT: Atom transfer radical polymerization (ATRP) of acrylamide (AM) has proved challenging, typically exhibiting low conversions and broad molecular weight distributions (MWDs). Herein, we report the synthesis of well-defined polyacrylamide (both homo and block copolymers) via aqueous copper(0)-mediated reversible-deactivation radical polymerization (Cu(0)-RDRP), exploiting the *in situ* disproportionation of Cu(I)Br in the presence of Me_6Tren to yield insoluble Cu(0) and Cu(II)Br_2 which acts as a deactivator. Careful optimization of the levels of Cu(I)Br and Me_6TREN allowed for the synthesis of polyacrylamide of a range of molecular weights (DP_n = 20−640) proceeding to quantitative conversion within just a few minutes (typically full conversion is attained within 15 min of reaction time) and exhibiting narrow MWDs (*Đ* as low as 1.09), which represents a significant improvement over transitional-metal-mediated approaches previously reported in the literature. This optimized approach was subsequently utilized to perform *in situ* chain extensions and block copolymerizations with hydroxyethyl acrylamide, yielding block copolymers of low dispersity and quantitative monomer conversions in a time frame of minutes.



INTRODUCTION

Polyacrylamide belongs to a highly versatile group of polymers that can find use in a wide range of applications including wastewater treatment,[1] oil recovery,[2,3] soil conditioning, agriculture,[4] biochemistry, and biomedical applications[5,6] and even as a subdermal filler for aesthetic surgical procedures.[7] The toxicity of these polymers has also attracted considerable attention as some of the aforementioned applications include direct contact with either humans or animal livestock. The concentration of the residual monomer in particular has to be in ppm levels (~500 ppm), and hence polymerization reactions that can afford quantitative monomer conversion are highly desired.[8,9]

Free radical polymerization has been utilized for the synthesis of AM homopolymers and statistical block copolymers. However, the need for enhanced control over the MWDs and sophisticated architectures facilitated the employment of controlled radical polymerization methods (CRP). Reversible-deactivation radical polymerization of acrylamide and derivatives has been until recently an area dominated by reversible addition−fragmentation chain transfer (RAFT) methodology with well-defined polyacrylamide and derivatives as well as excellent sequence control being demonstrated.[10−15] Although RAFT gives good control over the MWDs, the reaction generally requires 24 h to reach 94% conversion at ambient temperature while *in situ* chain extensions and block copolymers from a polyacrylamide macroinitiator were not reported under the conditions employed.[10,12]

The other most promising methodology of reversible-deactivation radical polymerization, transition-metal-mediated reversible-deactivation polymerization (TMMRDRP),[16−19] (usually utilizing copper) has proved challenging for acrylamide, cited as being due to low equilibrium constants and numerous side reactions involving radical abstraction and combination.[19,20] Atom transfer radical polymerization (ATRP) of acrylamide and its derivatives has been attempted in various organic solvents[21,22] as well as mixed aqueous media[23−27] with varying degrees of success; however, research into transition-metal-mediated polymerization of acrylamide in particular has been limited and has proved relatively unsuccessful compared to more established protocols for the polymerization of acrylates and methacrylates.[16,28−31]

Specifically, in 2003 Jewrajka and Mandal reported on the ATRP of acrylamide in both water and a glycerol−water medium.[24] Using both chlorine- and bromine-containing initiators and a copper bipyridine complex as catalyst, Jewrajka

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et al. found that addition of CuX_2 reduced the dispersity of the resultant polyacrylamide. However, even under optimized conditions the dispersity was relatively high (~1.7), with size exclusion chromatography (SEC) traces revealing low molecular weight tailing, thus indicating extensive termination events; it is noted that this ligand will stabilize copper(I) due to the presence of low-lying π^* orbitals accepting electron density from the metal. These results were further optimized in a later report by utilizing aqueous glycerol media with a CuX/pentamethyldiethylenetriamine (PMDETA)-based catalyst.[25] Although lower dispersity was reported ($Đ$ = 1.24) for a bromine-based initiating system, monomer conversion and molecular weight were severely limited (9%, M_n = 1200, in 48 h).

In a further report, Jiang et al. investigated the preparation of polyacrylamide by ATRP using a chloride initiator and tetramethylethylenediamine (TMEDA) as ligand.[26,27] Low dispersity polyacrylamides ($Đ$ = 1.19−1.57) were obtained in aqueous and mixed aqueous media; however, similar to Jewrajka and Mandal's work, monomer conversion was found to be low, less than 20% in most cases, even after long reaction times (>48 h). In addition to this, the experimental molecular weights were significantly deviating from the theoretical values, indicating severe termination. ATRP in aqueous media using a Cu(I)X/tris[2-(dimethylamino)ethyl]amine (Me_6TREN) catalyst system was also performed by Broekhuis and co-workers in 2012.[32] The molecular weight was demonstrated to evolve linearly with conversion, and monomer conversion was found to be significantly higher than previously reported. However, the dispersities of the resultant polyacrylamides (>1.4) were higher than those typically reported for the ATRP of acrylates and methacrylates.

Perhaps the most recent example of polyacrylamide synthesis by ATRP was published in 2015 by Matyjaszewski and co-workers.[23] Using electrochemistry (eATRP) to tune redox parameters, acrylamide was polymerized from a poly(ethylene glycol) macroinitiator showing good agreement between theoretical and experimentally determined molecular weights and dispersity as low as 1.09 for lower targeted molecular weight species. However, a water/DMF mixture was used (not pure water), and the integrity of the reported diblock copolymer was compromised when the macroinitiator reached a conversion of only 84% prior to the subsequent monomer addition.

Cu(0)-RDRP, commonly referred to as single electron transfer living radical polymerization (SET-LRP),[33−45] of acrylamides has also been attempted. However, the introduction of high contents of water in the solvent composition resulted in significant broadening of the MWDs, suggesting inefficient deactivation under the conditions used.[43,46−48] In 2013, Haddleton and co-workers introduced a novel protocol for the polymerization of acrylamide monomers in aqueous solution in the presence of Cu(0).[49] The key to the success of the polymerizations was to utilize the fast and complete disproportionation of Cu(I)Br to Cu(0) and Cu(II) species in an aqueous solution of Me_6TREN *prior* to the addition of either monomer and initiator. We have demonstrated that this technique is an extremely powerful tool for the synthesis of both polyacrylamides and other water-soluble monomers such as PEG-based acrylates over very short time scales. Poly(*N*-isopropylacrylamide) (PNiPAM), poly(*N*,*N*-dimethylacrylamide), poly(poly(ethylene glycol) acrylate), poly(2-hydroxyethyl acrylate) (PHEA), poly(*N*-acryloylmorpholine) (PNAM),[50] and polymers from an acrylamido glyco monomer[51] were all synthesized with narrow MWDs ($Đ$ < 1.10 in many cases). The robust nature of the system was further demonstrated by successful polymerizations of NiPAM in complex mixed solvent systems (beverages) as well as polymerizations in biologically relevant media (blood serum).[52−56]

Herein, a thorough investigation on the polymerization of AM via aqueous Cu(0)-RDRP is presented. Careful tuning of the ratio of [Cu(I)Br]:[Me_6Tren] allows for the rapid, quantitative, and controlled polymerization of AM to a range of chain lengths (DP_n = 20−640). Under well-optimized conditions polyacrylamides could be obtained within 15 min, in a quantitative manner (>99% conversion) with narrow molecular weight distributions ($Đ$ ~ 1.10 in most cases). Kinetic experiments were also performed to assess the living character and the polymerization rate, which was found to be completed in <3 min. The control retained during polymerization has been subsequently exemplified by *in situ* chain extensions and block copolymerizations furnishing higher molecular weight polymers within 30 min (>99% conversion) while maintaining the low dispersities.

METHODS AND MATERIALS

Materials. Acrylamide (≥99% for electrophoresis) and *N*-hydroxyethyl acrylamide (97%) were obtained from Sigma-Aldrich. Me_6TREN was synthesized according to literature procedure[57] and stored under nitrogen and refrigerated prior to use. The water-soluble initiator, 3-dihydroxypropyl 2-bromo-2-methylpropanoate, was synthesized according to literature protocol.[58] Copper(I) bromide (Cu(I)Br, 98%) was purchased from Sigma-Aldrich and sequentially washed with acetic acid and ethanol and dried *in vacuo* to remove Cu(II) impurities.

Instruments and Analysis. NMR spectra were recorded on Bruker AV-250 and DPX-400 spectrometers using deuterated solvents purchased from Sigma-Aldrich and Cambridge Isotope Laboratories. Monomer conversion was calculated by comparison of vinyl protons with polymer backbone protons, as described in the Supporting Information. NMR spectra for the water-soluble initiator were conducted on a Bruker AV III-500 HD spectrometer using a cryoprobe. Aqueous SEC was conducted on an Agilent Technologies Infinity 1260 MDS instrument equipped with a differential refractive index (DRI), light scattering (LS), and viscometry (VS) and UV detectors. The column set used were Agilent PL aquagel OH30 * 2 and a 5 μm Aquagel guard column. The mobile phase used was 0.1 M $NaNO_3$. Column oven and detector temperatures were regulated to 35 °C, flow rate 1 mL/min. Poly(ethylene oxide) standards (Agilent EasyVials) were used for calibration (100−30 000 g mol^{-1}). Analyte samples were filtered through a hydrophilic membrane with 0.22 μm pore size before injection. Experimental molar mass ($M_{n,SEC}$) and dispersity ($Đ$) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

Experimental Section. *Typical Polymerization Protocol.* Poly(acrylamide) DP_n = 80. H_2O (1 mL) and Me_6TREN (8.7 μL, 32.6 μmol, 0.6 equiv) were charged to a 25 mL Schlenk tube with a magnetic stirrer bar and a rubber septum. The solution was deoxygenated by bubbling with nitrogen for 2 min. Cu(I)Br (6.2 mg, 43.4 μmol, 0.8 equiv) was added with rapid stirring, and disproportionation was seen to occur after a few seconds. The disproportionated solution was placed in an ice bath and deoxygenated for a further 15 min. Simultaneously, a vial was charged with 3-dihydroxypropyl 2-bromo-2-methylpropanoate (13.1 mg, 54.3 μmol), acrylamide (0.5 g, 4.34 mmol, 80 equiv), and 3.5 mL of H_2O. The vial was fitted with a septum, stirred, and degassed with nitrogen in an ice bath for 15 min. Subsequently the deoxygenated monomer/initiator solution was transferred into the Schlenk tube containing the disproportionated solution via degassed syringe. The polymerization mixture was allowed to react for 15 min, after which a sample (~0.1

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mL) was taken for analysis. The sample for SEC was filtered through a plug of neutral alumina to remove catalyst residues prior to analysis. The sample for ^{1}H NMR analysis was diluted with D_2O.

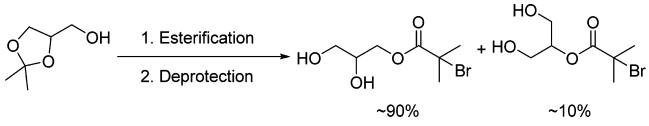
Typical Polymerization Protocol for Chain Extension. Poly(acrylamide)$_{40}$-*b*-poly(acrylamide)$_{80}$. H_2O (1 mL) and Me_6TREN (18.8 μL, 70.4 μmol, 0.4 equiv) were charged to a 25 mL Schlenk tube with a magnetic stirrer bar and a rubber septum. The solution was deoxygenated by bubbling with nitrogen for 2 min. Cu(I)Br (10.1 mg, 70.4 μmol, 0.4 equiv) was added with rapid stirring, and disproportionation was seen to occur after a few seconds (visually observed by the formation of a red/purple metallic precipitate and a deep blue solution, corresponding to Cu(0) particles and Cu(II) species, respectively.) The ensuing solution was placed in an ice bath and deoxygenated for a further 15 min. Simultaneously, a glass vial was charged with 3-dihydroxypropyl 2-bromo-2-methylpropanoate (13.1 mg, 54.3 μmol), acrylamide (0.5 g, 7.03 mmol, 40 equiv), and 3.5 mL of H_2O. The vial was fitted with a septum, stirred, and deoxygenated by bubbling with nitrogen in an ice bath for 15 min. Subsequently the deoxygenated monomer/initiator solution was transferred into the Schlenk tube containing the disproportionated solution via a degassed syringe. The reaction mixture was sampled after 15 min and analyzed by SEC and NMR. Immediately after this a deoxygenated solution of acrylamide (1 g, 14.06 mmol, 80 equiv in 2 mL of H_2O) was transferred into the reaction vessel by degassed syringe.

For further experimental details please see the Supporting Information.

RESULTS AND DISCUSSION

Initiator Synthesis. During this work it was noticed that the initiator contained an impurity which was seen in ^{1}H NMR in D_2O but did not show up in organic solvents, including DMSO. A thorough NMR investigation employing ^{13}C, ^{1}H, COSY, and HMQC correlation showed the presence of up to 10% of a structural isomer (Scheme 1, Figures S1–S4, Supporting Information). As the initiator is prepared from the protected glycerol, solketal, it is suggested that isomerization occurs during the deprotection of the acetonide. However, it is noted that this is also a dihydroxyl water-soluble initiator which will lead to a very similar product and is expected to have very similar rates of initiation. As separation of the two isomers is difficult, and due to the similarity of the reactivity of the final products, it was decided to continue with the mixed initiator.

Scheme 1. Synthesis of Water-Soluble Initiator Showing the Main Product and Isomer



Optimization of Homopolymerizations of Acrylamide DP_n = 20–320. Homopolymerizations of AM (Scheme 2) were initially carried out using a ratio of [AM]:[I]:[Cu(I)Br]:[Me_6TREN] of [20]:[1]:[0.4]:[0.4]; note the 1:1 ratio of Cu(I)/ligand which is very important for a successful polymerization. Full monomer conversion was attained within 15 min, as determined by the integration of the vinyl protons (~5.75–6.5 ppm) (see Supporting Information). Aqueous SEC analysis revealed an excellent agreement between the theoretical and the experimental molecular weights and a symmetrical molecular weight distribution ($Đ$ ~ 1.10, entry 1, Table 1, Figure 1). Identical conditions ([40]:[1]:[0.4]:[0.4]) were subsequently applied targeting a degree of polymerization of 40. ^{1}H NMR revealed again near quantitative conversion (>99%) in 15 min, and SEC showed a low dispersity polymer ($Đ$ ~ 1.12, Figure 1).

Scheme 2. Homopolymerization of AM by Aqueous SET-LRP

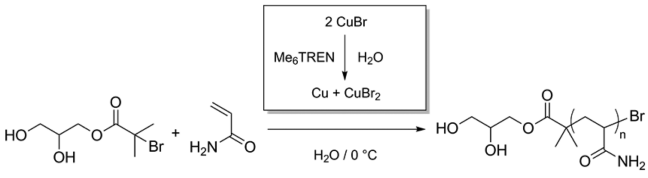


Table 1. Aqueous SET-LRP of Acrylamide with Varied Degree of Polymerization and Cu(I)Br and Me_6TREN Concentration

entry	[M]:[I]:[Cu(I)Br]:[Me_6TREN]	conv (%)	$M_{n(Theo)}$ (Da)	$M_{n(SEC)}$ (Da)	$Đ$
1	20:1:0.4:0.4	>99	1700	1500	1.10
2	40:1:0.4:0.4	>99	3100	2900	1.12
3	80:1:0.4:0.4	>99	5900	5500	1.17
4	80:1:0.8:0.4	93	5500	4900	1.11
5	80:1:0.8:0.6	>99	5900	5800	1.09
6	160:1:0.4:0.4	>99	11600	12900	1.46
7	160:1:0.8:0.4	96	11100	9700	1.07
8	160:1:0.8:0.6	>99	11600	11000	1.09
9	320:1:0.4:0.4	99	22700	18800	6.20
10	320:1:0.8:0.4	95	21800	18400	1.10
11	320:1:0.8:0.6	>99	22700	23100	1.12

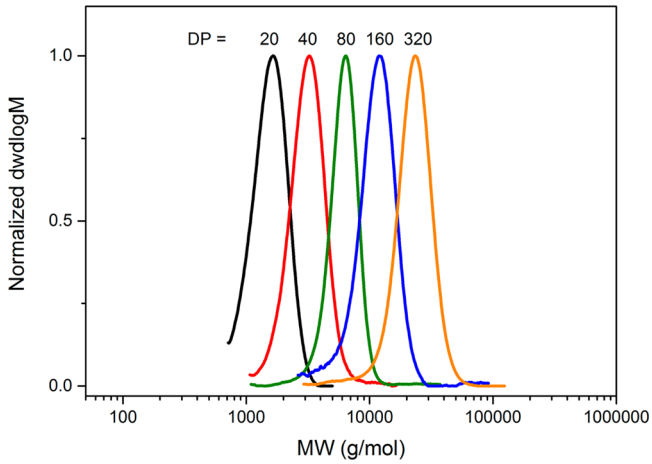


Figure 1. Molecular weight distributions of polyacrylamide (DP_n = 20, 40, 80, 160, and 320) synthesized under optimized conditions (Table 1) as measured by aqueous SEC.

Similar results were obtained for a targeted degree of polymerization of 80; however, a slight broadening of the molecular weight distribution was also observed (entry 3, Table 1; Figure S5a). Attributing this broadening to insufficient deactivation of propagating polymer chains the concentration of the copper was doubled to [I]:[Cu(I)Br]:[Me_6TREN] = [1]:[0.8]:[0.4], effectively giving a higher concentration of the deactivating species: [Cu(Me_6TREN)Br_2]. It is again noted that this ratio of 2:1 Cu/ligand is very different than "typical polymerization conditions" used in previous work where this ratio is between 1:6 and 1:20.[34,59] Table 1, entry 4, shows that

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the dispersity of the resultant polymer improved slightly ($Đ$ = 1.11 compared to $Đ$ = 1.17, Figure S5b), although conversion was somewhat limited (~93% vs >99% for a typical aqueous polymerization). This was attributed to the excess of deactivator that not only gives better control over the MWDs but also is compromising the rate of polymerization. It should be also noted that for aqueous systems propagation needs to be fast as exposure of the bromine end group to the aqueous media for prolonged periods can result in hydrolysis and other side reactions such as elimination.[53] It has also been shown that the concentration of the ligand relative to the copper is an essential parameter that needs to be carefully considered to afford a well-defined polymer at an acceptable polymerization rate.[60,61] Thus, in an attempt to strike an acceptable balance between control over polymerization and a rate at which higher conversions can be effectively reached, the relative concentration of ligand was increased to [0.8:0.6]. Table 1, entry 5, shows that the improved ratios yielded polyacrylamide of lower dispersity ($Đ$ = 1.09, Figure 1) and higher conversion (>99%; Figure S4) with excellent agreement between experimental and theoretical molecular weight. The necessity to tune the ratio between ligand and copper content was further highlighted when targeting even higher degrees of polymerization (DP_n = 160, 320). In both cases, the initial conditions ([Cu(I)Br]:[Me_6TREN] = [0.4]:[0.4]) yielded quite uncontrolled polymers with broad molecular weight distributions (entries 6 and 9, Table 1; Figures S6a and S7a) while when higher copper content relative to ligand was employed (generating more deactivating Cu(II)Br_2), lower conversions were evident and quantitative conversion could not be achieved, even when the reactions were left to proceed overnight (entries 7 and 10, Table 1; Figures S6b and S7b). However, when both the copper and ligand concentration were optimized, full conversion could be reached within 15 min with aqueous SEC revealing symmetrical, monomodal polymer peak distributions (Figure 1) and good agreement between the theoretical and experimental values.

Targeting Higher Molecular Weight: DP_n = 640. In order to probe the potential of the technique to obtain higher molecular weight polyacrylamide, a reaction targeting DP_n = 640 was conducted. Because of the loss of control observed when lower copper and ligand concentrations were utilized, initial work into the synthesis of polyacrylamide of DP_n = 640 employed the previously optimized ratios of [1]:[0.8]:[0.6] ([I]:[Cu(I)Br]:[Me_6TREN]). These initial conditions successfully polymerized acrylamide to high conversion (>99%), once again with good agreement between theoretical and experimental molecular weights (Table 2, entry 1). However, the SEC analysis (Figure S8a) showed a much broader polymer peak distribution than those of lower molecular weights synthesized when identical conditions were employed (entry 1, Table 2). Increasing the copper ratio to the point of being in excess of initiator concentration results in a narrower molecular weight distribution ($Đ$ = 1.27 compared to $Đ$ = 1.41, Figure 2) while retaining high conversion and expected molecular weight, whereas increasing copper and ligand concentration results in a broadening of the MWD. The broader dispersity of $Đ$ = 1.27 (Figure 2) as compared to much lower values for lower molecular weights is either due to the use of a mixed type column as opposed to an aquagel column designed for differentiation between smaller differences in molecular weight or possibly due to more side reactions at prolonged reaction times (more monomer units being added per propagating chain). Attempts to further optimize the control over the MWDs were unsuccessful (Figure S8b), suggesting that the limits of the system had been reached (entry 3, Table 2).

Table 2. Homopolymerization of Acrylamide by Aqueous SET-LRP (DP_n = 640)

entry	[M]:[I]:[Cu(I)Br]:[Me_6TREN]	conv (%)	$M_{n(Theo)}$ (Da)	$M_{n(SEC)}$ (Da)	$Đ$
1	640:1:0.8:0.6	>99	44500	45700	1.41
2	640:1:1.2:0.6	>99	44500	42900	1.27
3	640:1:1.2:0.8	>99	44500	49400	1.60

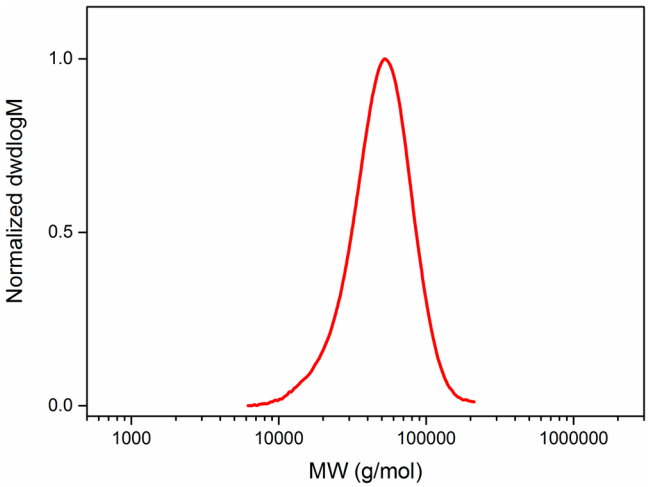

Figure 2. Molecular weight distributions of polyacrylamide (DP_n = 640) synthesized under optimized conditions (Table 2) as measured by aqueous SEC.

Investigating the Rate of Polymerization of Acrylamide by Aqueous SET-LRP. We recently highlighted aqueous SET-LRP as a tool for the synthesis of sequence controlled multiblock copolymers in which it was demonstrated that chain extension is much more efficient if sequential monomer addition is performed at or as close to full conversion as possible, so as to minimize exposure to conditions at which monomer concentration is low.[53] To this end a kinetic investigation revealed that quantitative monomer conversion is obtained in just 11 min for the polymerization of NiPAM.

By placing a digital probe thermometer into the Schlenk tube during polymerization in an ice bath under optimized conditions, it could be seen that in the case of the polymerization of acrylamide (DP_n = 80) the reaction exotherms to reach ~6 °C. Attempts at a full kinetic analysis of this system proved challenging due to the extremely fast reaction, with regular sampling compromising the reaction yielding incomplete conversion. This was attributed to the heterogeneous nature of the system as multiple samples could disrupt the polymerization equilibrium (e.g., by removing random amounts of Cu(0) per sample the concentration of active species is inconsistent). Scaling up the reaction in order to overcome this was also found to be unconducive to kinetic analysis as the speed of the reaction coupled with the need to add a large volume of monomer and initiator solution effectively yields monomer feeding conditions, and propagation is already occurring while the solution is still being added. Taking single samples from a smaller scale reaction revealed 95% conversion in just 2 min. We find it quite remarkable that

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polymers with such narrow MWDs can be obtained in almost quantitative yield in such a short time frame.

Chain Extensions and Block Copolymers of Polyacrylamide. Although obtaining such low dispersity polymers in a matter of minutes is impressive and indicated excellent control over the molecular weight, it, however, offers no insight into the end group fidelity of the resultant polymers. In order to assess the living nature of the polymerization, chain extension experiments were performed by a sequential monomer addition. Acrylamide (DP_n = 40) was polymerized as previously mentioned, sampled after 5 min (a time frame long enough for quantitative conversion to be reached), and a second aliquot of degassed acrylamide solution was immediately transferred into the reaction vessel via degassed syringe (Scheme S2). The reaction mixture was sampled again after 30 min and analyzed by ^{1}H NMR and SEC. Conversion of both the first and second block was found to be >99% (Figures S9 and S10). Aqueous SEC traces (Figure 3) show the first block to have a narrow, symmetrical, monomodal peak ($Đ$ = 1.14). The chain extended polyacrylamide is also found to have a narrow, monomodal molecular weight distribution ($Đ$ = 1.12). The clear shift to higher molecular weight shows only a very small amount noticeable tailing, thus indicating that the vast majority of polymer chains were able to further react with additional monomer, demonstrating the excellent end group fidelity of the polymerization.

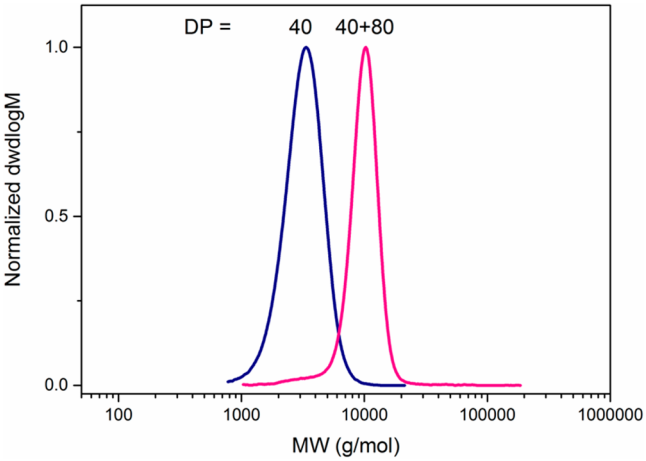

Figure 3. Molecular weight distribution of poly(acrylamide) (DP_n = 40) ($Đ$ = 1.14) and poly(acrylamide)$_{40}$-*b*-poly(acrylamide)$_{80}$ as measured by aqueous SEC ($Đ$ = 1.12).

Similarly, efficient one-pot block copolymerization by sequential addition of hydroxyethyl acrylamide (poly(acrylamide)$_{40}$-*b*-poly(hydroxyethyl acrylamide)$_{80}$) could also be achieved. SEC traces, shown in Figure 4a, show a shift in molecular weight, retaining a narrow monomodal distribution with little evidence of unreacted polyacrylamide homopolymer, with conversion >99% for both blocks (Figures S11 and S12). The reverse one-pot block copolymerization utilizing poly(hydroxyethyl acrylamide) this time as the macroinitiator was also investigated. Pleasingly, the final diblock copolymer was attained within 30 min presenting narrow MWDs, even at quantitative conversions demonstrating the versatility of the approach (Figure 4b; Figures S13 and S14).

CONCLUSIONS

In summary, the synthesis of well-defined poly(acrylamide) has been demonstrated utilizing aqueous SET-LRP. A range of molecular weights has been targeted (DP_n = 20−640) demonstrating narrow MWDs ($Đ$ ∼ 1.10 in most cases) and rapid polymerization rates (full conversion within 15 min). An investigation into the rate of polymerization of acrylamide of targeted DP = 80 revealed that >95% conversion could be attained in 2 min, further highlighting the speed of the reaction without compromising the control over the molecular weight distributions. Careful optimization of the copper-to-ligand ratio proved critical to afford polymers with high end group fidelity as exemplified by *in situ* chain extensions and block copolymerizations providing access to the facile synthesis of hydrophilic materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01994.

Additional NMR, SEC spectra, and experimental details (PDF)

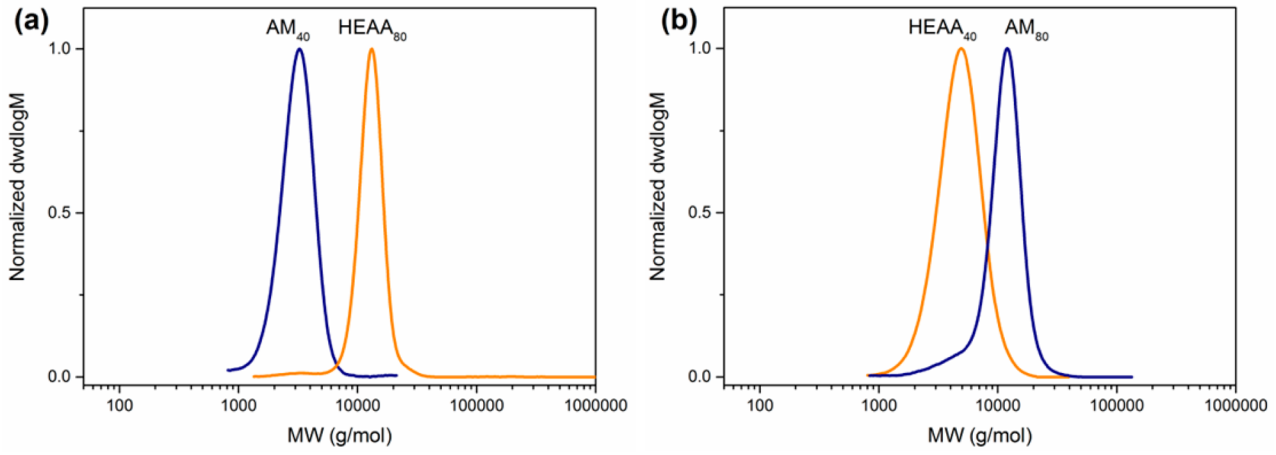

Figure 4. (a) Molecular weight distribution of poly(acrylamide) (DP_n = 40) ($Đ$ = 1.13) and poly(acrylamide)$_{40}$-*b*-poly(hydroxyethyl acrylamide)$_{80}$ ($Đ$ = 1.09) as measured by aqueous SEC. (b) Molecular weight distribution of poly(hydroxyethyl acrylamide) (DP_n = 40) ($Đ$ = 1.19) and poly(hydroxyethyl acrylamide)$_{40}$-*b*-poly(acrylamide)$_{80}$ ($Đ$ = 1.19) as measured by aqueous SEC.

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Notes

The authors declare no competing financial interest.

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