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Controlled aqueous polymerization of acrylamides and acrylates and “*in-situ*” depolymerization in the presence of dissolved CO₂

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Aqueous copper-mediated radical polymerization of acrylamides and acrylates in carbonated water resulted in high monomer conversions ($t < 10$ min) before undergoing depolymerisation ($60 \text{ min} > t > 10 \text{ min}$). Regenerated monomer was characterised and repolymerised following deoxygenation of the resulting solutions to reyield polymers in high conversions and that exhibit low dispersities.

Depolymerization of polymers from radical and chain growth polymerizations is often desirable for recycling but can be problematic due to the high kinetic energy barrier and low depropagation rate constants. For many systems, high reaction temperatures can be employed to reach the ceiling temperature (T_c)¹⁻³ threshold which are often highly energy intensive processes.⁴⁻⁷ In an attempt to overcome these limitations, research has focused on the formation of polymeric materials derived from reformable monomers and the synthesis of stimuli responsive polymers.⁸⁻¹⁰ Indeed, Zhu *et al.* recently reported the low temperature (0 °C) depolymerization of poly(*N*-isopropyl acrylamide) (pNIPAm) in aqueous media.¹¹ In this work, depolymerization was achieved by the addition of either TEMPO or 1,4-benzoquinone, which was proposed to proceed *via* abstraction of the terminal halide. Both the polymerization and depolymerization processes exhibited the lack of control associated with a free radical polymerization.

Reversible-deactivation radical polymerization (RDRP) techniques such as reversible addition-fragmentation chain transfer (RAFT)¹²⁻¹⁴ polymerization, nitroxide-mediated polymerization (NMP)¹⁵, and transition-metal mediated living radical polymerization (TMM-LRP)¹⁶⁻¹⁹, have significantly expanded our arsenal for polymer synthesis and have substantially increased the availability of well-defined

polymers. In particular, the development of a Cu(0)-mediated aqueous RDRP system²⁰ allows for excellent control over the polymerization of acrylamides²⁰⁻²⁴, acrylates^{22, 25} and other water-soluble monomers²⁶ which previously, were almost exclusively restricted to RAFT polymerizations.²⁷⁻²⁹ The robustness of this technique has later been demonstrated through the polymerization of NIPAm in a variety of diverse media such as blood serum³⁰, and commercially available alcoholic beverages.³¹ In this case, a proportion of the beverages contained carbon dioxide (CO₂) and it was hypothesized that conventional deoxygenation using an inert gas such as nitrogen (N₂) was an unnecessary step in these reactions. To that end, CO₂ (an abundant, non-toxic and usually inert reagent) present in carbonated water was utilized as a source of oxygen free solvent for the polymerization of NIPAm, *N*-hydroxyethyl acrylamide (HEAm) and 2-hydroxyethyl acrylate (HEA).

Initially, through the use of the *in-situ* disproportionation of [Cu⁰Br/Me₆TREN] at 0 °C in carbonated water prior to the addition of monomer and initiator, a rapid ($t < 10$ minutes; >99 % conversion) and controlled polymerization of NIPAm was observed, as expected in line with our previous reports²⁰ ($M_n = 3200 \text{ g mol}^{-1}$; $\mathcal{D}_m = 1.16$ (Fig. 1)). However, when the crude reaction mixture was kept under formal polymerization conditions, a reduction in molecular weight was observed by SEC ($M_n = 1600 \text{ g mol}^{-1}$; $\mathcal{D}_m = 1.16$) (Table 1, Fig. 1, Fig. S1 ESI⁺), as well as the noticeable re-appearance of vinyl peaks in the ¹H NMR spectrum (Fig. 1, Fig. S2 ESI⁺). Integration of the reformed vinyl protons (5.6 ppm) against the isopropyl methine proton present in the reformed monomer and remaining polymer (3.9 ppm) indicated that > 50 % depolymerization had occurred within 60 minutes. The presence of regenerated monomer was confirmed by gas chromatography (GC) (Fig. S3, ESI⁺) and GC-MS (Fig. S4-S5, ESI⁺) and identified as being identical to that of NIPAm indicating that “*in-situ*” depolymerization had occurred. It is important to note that the extent of depolymerization remained unchanged after allowing the reaction to proceed for 24 hours, thus indicating that depolymerization occurs over a relatively short time period

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and then ceases. Although it is unclear the reason for this cessation of the depolymerisation we can speculate it is due to reaching an equilibrium position or due to hydrolysis of the bromine end group which results in the presence of a double bond or hydroxyl group at the ω -end of the polymer.

When the dissolved CO_2 was removed *via* N_2 purging post-depolymerization, the regenerated monomer was quantitatively repolymerized within 30 minutes in a controlled manner ($M_n = 3500 \text{ g mol}^{-1}$; $\mathcal{D}_m = 1.23$) (Fig. 1) with the resulting polymer remaining stable towards depolymerization at 100 % conversion for at least 1 day. The repolymerization of recycled monomer alongside the retention of low dispersities implies that this system harbors a degree of control and is, to the best of our knowledge, unlike any previous system.

Importantly, when the polymerization of NIPAm is carried out in HPLC grade water with N_2 deoxygenation, no depolymerization resulted as previously reported (Fig. S6, ESI[†]).²⁰ Considering the observation of depolymerization in carbonated water, an initial assessment of the two systems was conducted which investigated either CO_2 or the presence of dissolved minerals as potential triggers for depolymerization. To investigate the role of the former upon this process, HPLC grade water was carbonated (and thus deoxygenated) using dry ice as the source of carbonation and subsequently used as the solvent for the polymerization of NIPAm. Within 10 minutes, high conversion was obtained (94 %; $M_n = 3600 \text{ g mol}^{-1}$) (Fig. S7-S8, ESI[†]) with depolymerization occurring after the reaction was allowed to proceed further ($t = 24 \text{ hours}$; 34 % depolymerization; $M_n = 2800 \text{ g mol}^{-1}$; $\mathcal{D}_m = 1.12$) (Fig. S7-S8, ESI[†]). Despite the extent of depolymerization being less than that which was observed before, it was evident that CO_2 is the cause of the depolymerization. Additionally, given the purity of HPLC grade water, it is likely that the mineral additives present within carbonated water do not significantly contribute towards depolymerization. In order to verify this, commercially available carbonated water was decarbonated and the polymerization was conducted in the presence of N_2 to yield 100 % conversion after 10 minutes ($M_n = 5300 \text{ g mol}^{-1}$; $\mathcal{D}_m = 1.10$) (Fig. S9, ESI[†]) with no evidence of depolymerization by SEC or ^1H NMR after a further 1 hour under formal polymerization conditions.

Depolymerization occurs following the carbonation of water and therefore we felt it was important to consider the carbonation process. Industrially, water is carbonated under a pressure ranging from 1.5 to 2.5 bar and as a result, the effect of “high” pressure upon the polymerization/depolymerization system was investigated. The polymerization of NIPAm was conducted at a range of pressures ranging from 2 bar to 100 bar in a steel autoclave (typically used for conducting polymerizations in supercritical carbon dioxide (scCO_2)).^{32, 33} It was found that for all of the applied pressures; uncontrolled polymerizations resulted (e.g. $M_n = 3600 \text{ g mol}^{-1}$; $\mathcal{D}_m = 2.85$) alongside an absence of depolymerization (Fig. S10-S11, ESI[†]). Conversely, when an “open top” polymerization (in an unsealed vial under atmospheric conditions) of NIPAm was performed, a maximum of 98 % conversion was achieved after

10 minutes ($M_n = 4200 \text{ g mol}^{-1}$; $\mathcal{D}_m = 2.25$) (Fig. S12-S13, ESI[†]) with further sampling of the reaction yielding a stable polymer.

When CO_2 is dissolved in water it exists in chemical equilibrium with carbonic acid (Eq. S1-4, ESI[†]) resulting in acidic conditions ($\text{pH} = 4.72$) when compared to HPLC grade water ($\text{pH} = 6.28$). Therefore the pH of the polymerization

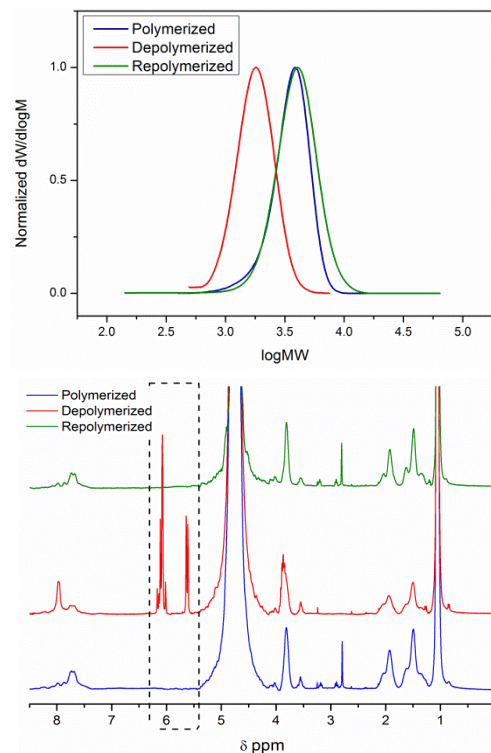
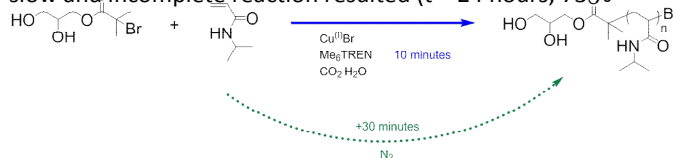


Fig. 1 – SEC traces (top) and ^1H NMR spectra (bottom) for NIPAm polymerization ($t = 10 \text{ min}$), depolymerization ($t = 60 \text{ min}$) and repolymerization ($t = 105 \text{ min}$).

reaction media, in carbonated water, was investigated as a function of time and conversion. The data obtained from monitoring the process (Fig. S14-16, ESI[†]) revealed that there was little change in pH during both the polymerization ($\text{pH} = 6.40$) and depolymerization ($\text{pH} = 6.94$) processes ($\Delta\text{pH} = 0.54$).

To further investigate the role of pH in depolymerization, HPLC grade water was acidified to $\text{pH} 5.55$ and used as the solvent for the polymerization of NIPAm. Unsurprisingly, a slow and incomplete reaction resulted ($t = 24 \text{ hours}$; 73%



Monomer	Process	Conv. ^b (%)	M_n^a (g mol^{-1})	\mathcal{D}_m
NIPAm	Polymerization	100	3200	1.16
	Depolymerization	52	1600	1.16

Repolymerization	100	3500	1.23
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Table 1 - Summary of the polymerization, depolymerization and repolymerization of pNIPAm in water in the presence of dissolved CO₂. "a" conversion was calculated by ¹H NMR. "b" M_n values were determined using SEC.

conversion; M_n = 1600 g mol⁻¹; Đ_m = 1.25) (Fig. S17, ESI[†]), which can be ascribed to the protonation of the ligand in the Cu^(II)Br₂/Me₆TREN complex and the occurrence of termination events.³⁴ Conversely, when the pH of carbonated water was adjusted to 8 using NaHCO₃, near quantitative conversion was obtained alongside an absence of depolymerization (97 % conversion after 48 hours) (Fig. S18-19, ESI[†]). Thus it is apparent that in the presence of CO₂, depolymerization is sensitive to pH.

It was thought that depolymerization might arise due to modification of the Cu^(II)Br₂/Me₆TREN complex as a consequence of the co-ordination sphere around copper being altered by ligand protonation. Monitoring the effect of pH on [Cu^(II)Br₂/Me₆TREN] by UV-Vis spectroscopy revealed the loss of the weak d-d transition at 680 nm³⁵ in both the acidified water (pH 5.55) and the carbonated water (pH 5.45) when compared to water with a pH of 8.89 (Fig. S20 ESI[†]). Interestingly, when carbonated water was deoxygenated with N₂ to mimic the treatment of the depolymerization system prior to repolymerization, the band reappeared and the spectra followed that of the Cu^(II)Br₂/Me₆TREN complex in HPLC grade water (Fig. S20 ESI[†]). Further to this, when 100 μL conc. hydrochloric acid (HCl) was added to the reaction prior to depolymerization (t = 10 minutes; 100% conversion; Đ_m = 1.22) (Fig. S21-22, ESI[†]) a noticeable colour change was observed, accompanied by a decrease in the absorbance observed by UV-Vis (Fig. S23, ESI[†]). Upon allowing the reaction to proceed, depolymerization was observed (t = 60 minutes; 54 % depolymerization; Đ_m = 1.17) (Fig. S21-S22, ESI[†]) and as a result, the effect of changing the co-ordination sphere around copper was studied further.

N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA) is an *N*-donating tridentate ligand which co-ordinates to copper in a different manner when compared to the *N*-donating, tetradentate tris[2-(dimethylamino)ethyl]amine (Me₆TREN) ligand.^{35, 36} When used for the polymerization of NIPAm in HPLC grade water *via* copper(0)-mediated RDRP, 96 % conversion can be obtained within 30 minutes (M_n = 2000 g mol⁻¹; Đ_m = 1.74) (Fig. S24, ESI[†]). However, when utilized as the ligand for the polymerization of NIPAm in carbonated water, a bimodal mass distribution was attained (88 % conversion; M_n = 6100 g mol⁻¹; Đ_m = 1.62) and no depolymerization was observed after 1 hour (82 % conversion) (Fig. S25-S26, ESI[†]). The absence of depolymerization when PMDETA is employed as the ligand supports the earlier theory of a modified complex causing depolymerization.

In order to investigate the scope of this system, higher molecular weight polymers (> 12,800 g mol⁻¹) were also attempted. When polymers with a targeted DP = 120 were tried, with a 0.4 eq. of Me₆TREN and Cu^(II)Br, low conversions were attained. However, utilizing 2.4 eq. of both components enabled 100 % conversion to be achieved within 10 minutes,

followed by 43 % depolymerization within 1 hour (Table 2, Fig. S27-28, ESI[†]).

It is worth noting that when 2.4 eq. of Me₆TREN and Cu^(II)Br were utilized for DP = 20 pNIPAm, no depolymerization resulted (Fig. S29-30, ESI[†]) and characterization by SEC

Monomer	Process	Conv. ^b (%)	M _n ^a (g mol ⁻¹)	Đ _m
NIPAm	Polymerization	100	20,600	1.18
	Depolymerization	43	12,400	1.11
HEAm	Polymerization	98	6300	1.09
	Depolymerization	71	3200	1.10
HEA	Polymerization	93	7100	1.16
	Depolymerization	34	5800	1.13

Table 2 - Summary of the polymerization and depolymerization of water soluble acrylamides and acrylates in water in the presence of dissolved CO₂. "a" conversion was calculated by ¹H NMR. "b" M_n values were determined using SEC.

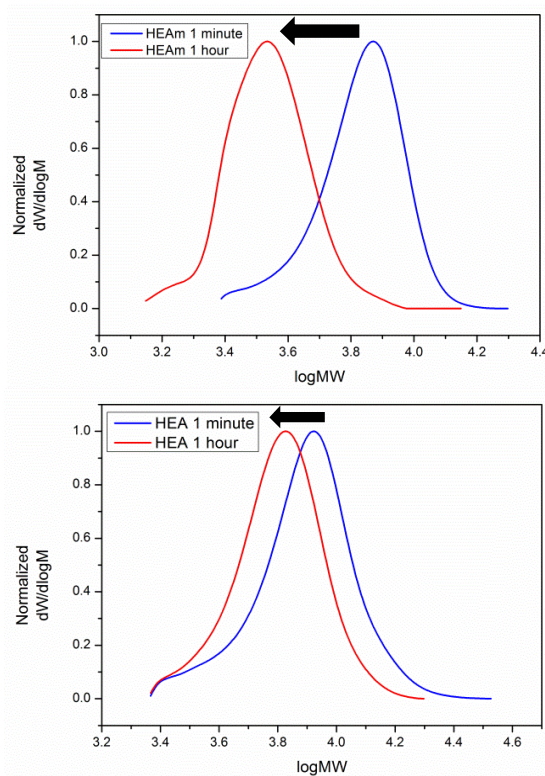


Fig. 2 – Polymerization and depolymerization SEC traces for DP = 20 HEAm (top) and DP = 20 HEA

revealed a deviation from the symmetrical Poisson-like distribution previously attained for DP = 20 pNIPAm. According to the proposed mechanism for copper(0)-mediated RDRP by Percec *et al.*^{17, 18} (the mechanism is currently under debate in the literature³⁷⁻³⁹), the addition of excess copper and ligand results in a loss of control over the polymerization, an increase in termination, and hence, a loss of end group fidelity from the polymer chains.

In order to investigate if depolymerization was more widely observed than for NIPAm, a second water soluble acrylamide, HEAm was polymerized in carbonated water. In a similar

manner to that of NIPAm, a rapid and near quantitative conversion (~ 98 %) was achieved within 1 minute and was accompanied by controlled depolymerization (71 % depolymerization; $M_n = 3200 \text{ g mol}^{-1}$; $\bar{D}_m = 1.10$) (Fig. S31, ESI[†]) within 60 minutes (Table 2, Fig. 2); resulting in this system being applicable to more than one monomer.

Furthermore, for the purpose of establishing whether this system was only viable for acrylamides, the water soluble acrylate, HEA was polymerized in carbonated water ($t = 1$ minute; 93% conversion) (Fig. S32, ESI[†]). Upon continuation of the reaction, depolymerization of HEA occurred within 30 minutes with a maximum point being reached after 1 hour (34 % depolymerization) and as such, both acrylamides and acrylates undergo depolymerization. Pleasingly, as with the acrylamides, narrow molecular weight distributions were maintained after depolymerization ($\bar{D}_m = 1.13$) (Table 2, Fig. 2).

In summary, we describe the low temperature depolymerization of water soluble poly(acrylamides) and poly(acrylates) in the presence of dissolved CO₂. **Whilst a mechanism has not been established the modification of the Cu^(II)Br₂/Me₆TREN coordination complex in the presence of dissolved CO₂ is only a potential explanation for depolymerization and we believe that providing a mechanism based on this would currently be speculation.** Unlike previously reported depolymerization systems, narrowly disperse, low molecular weight polymers are produced following depolymerization and are accompanied by the regeneration of monomer in a reversible process. Notably, through switching CO₂ with N₂, the controlled repolymerization of reformed monomer was achieved without sacrificing control over the molecular weight or mass distribution. This has led to the development of a low temperature aqueous system with conceivable potential, both commercially and environmentally, for the controlled reversal of acrylic/vinyl polymerizations.

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