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Electronic Supplementary Information

for

Controlled aqueous polymerization of acrylamides and acrylates and *"in-situ"* depolymerization in the presence of dissolved CO_2

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Experimental Details

Materials:

N-Isopropylacrylamide (NIPAm, Sigma-Aldrich, 97 %), water (HPLC grade, VWR), deionized water (RO grade), hydrochloric acid (HCl, Sigma-Aldrich, 37%), MilliQ water (18.2 MΩcm) and sodium hydrogen carbonate ($NaHCO_3$, Fisher Scientific, 99.7 %) were used without further purification. Cuprisorb™ resin was purchased from Seachem. Commercially bought carbonated water (Highland Spring sparkling and Perrier water) was used as received (Table S1).

	Highland Spring Carbonated Water	Highland Spring Still Water	Perrier Carbonated Water
Bicarbonate	150	150	390
Calcium	40.5	40.5	147.3
Chloride	6.1	6.1	21.5
Magnesium	10.1	10.1	3.4
Nitrates	3.1	3.1	4.3
Potassium	0.7	0.7	0.6
Sodium	5.6	5.6	9.0
Sulphates	5.3	5.3	33
pH	4.72	7.8	5.46

Table S1 Average mineral analysis at the source (mg/L) for Highland Spring carbonated and still water and Perrier water

N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, Sigma-Aldrich, 99 %) was distilled under reduced pressure (55 °C, 10^{-1} mbar), deoxygenated, and stored in an ampule under nitrogen protection at 4 °C prior to use. 2-Hydroxyethyl acrylate (HEA, BASF, 96 %) and *N*-hydroxyethyl acrylamide (HEAm, Sigma-Aldrich, 97 %) were uninhibited using basic alumina prior to use in the polymerizations. 3-Dihydroxypropyl 2-bromo-2-methylpropanoate was synthesized according to the literature procedure.[1] *N,N,N',N',N'',N''*-Hexamethyl-[tris(aminoethyl)amine] (Me_6TREN) was synthesized according to the literature procedure[2], deoxygenated, and stored in an ampule at 4 °C under nitrogen protection. Copper$^{(I)}$bromide ($Cu^{(I)}Br$, Aldrich, > 98 %) was purified according to the method detailed by Keller and Wycoff.[3]

Instrument and analysis:

^{1}H NMR spectra were recorded on a Brüker AV-250, DPX-400 and HD-500 spectrometer using deuterated solvents obtained from Sigma-Aldrich. IR spectra were collected on a Brüker VECTOR-22 FT-IR spectrometer using a Golden Gate diamond attenuated reflection cell. GC-FID was performed using a Varian 450 fitted with a FactorFourTM capillary column VF-1ms, of 15 m x 0.25 mm I.D. and film thickness 0.25 μm, utilizing methanol as the sample solvent. The oven temperature was programmed as follows: 40 °C (allowed to hold for 1 minute) then increased by 25 °C min^{-1} to 200 °C. The injector was operated at 200 °C with the FID at 220 °C and nitrogen was used as the carrier gas at a flow rate of 1 mL min^{-1}. Gas chromatography – mass spectrometry (GC-MS) was conducted on a Varian 4000 GC equipped with an ion trap mass spectrometer and a non-polar column (Varian Factor Four VF5, 30 m x 0.25 mm x 0.25 μm) with a splitless injector operated at 325 °C. Size exclusion chromatography (SEC) measurements were performed on an Agilent PL50 equipped with 2 Agilent Polargel L Columns eluting with dimethylformamide containing 0.1 M LiBr as an additive at 50°C. The flow rate was 1 mL min^{-1} and detection was achieved using simultaneous refractive index (RI) and UV (λ = 280 nm) detectors. Molecular weights were calculated relative to narrow PMMA standards. All samples were stirred in the presence of Cuprisorb™ resin to remove residual copper species, dissolved in the appropriate eluent and filtered through disposable 0.45 μm PTFE filters before analysis. Molecular weight data was analyzed using Agilent GPC software and plotted using OriginPro 8.5. UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis in the range of 200 – 1100 nm using a cuvette with a 10 mm optical path length. All pH measurements were conducted using a SevenGo™ pH – SG2 meter (Fisher Scientific) equipped with a pH semi-micro tip electrode (Thermo Scientific Orion).

The percentage conversion of NIPAm was calculated *via* ^{1}H NMR through integration of the vinyl group (5.6 ppm, 1H, d) and integration of the $C\underline{H}(CH_3)_2$ peak (3.9 ppm, 1H, m). The conversion of HEAm was calculated by ^{1}H NMR through integration of the vinyl group (5.65 ppm, 1H, d) and integration of the C$\underline{H_2}$NH peak (3.93 ppm, 2H, q). For HEA, the conversion was calculated *via* ^{1}H NMR through integration of the vinyl group (6.95 ppm, 1H, d) and integration of the C$\underline{H_2}$OH peak (3.75 ppm, 2H, q).

Where referred to, % depolymerization refers to the quantity of polymer which has undergone depolymerization

Experimental procedures:

Typical procedure for the polymerization and depolymerization of NIPAm in the presence of Me_6TREN

Me_6TREN (23.6 µL, 0.4 eq.) was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}$Br (12.7 mg, 0.4 eq.) was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of $Cu^{(I)}$Br to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate (53.3 mg, 1.0 eq.) and NIPAm (500 mg, 20 eq.) were dissolved in Highland Spring carbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period, the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}$Br. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

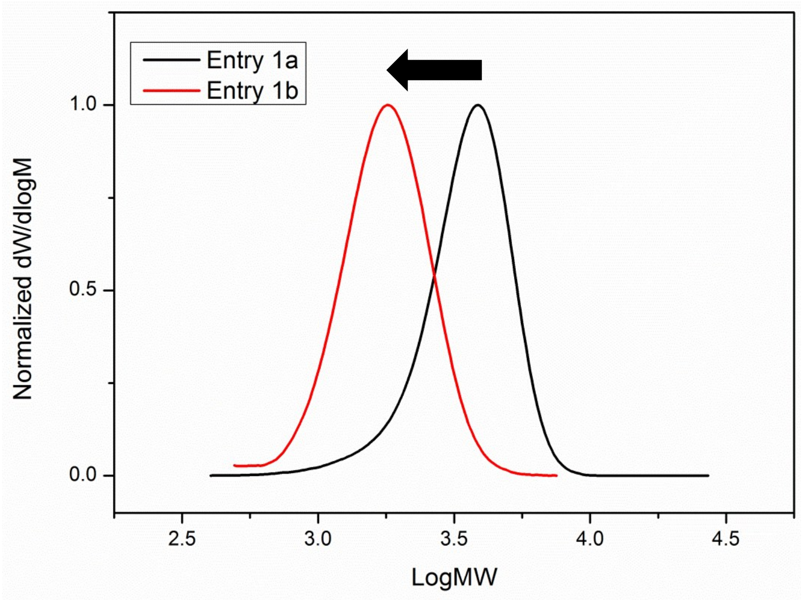


Fig. S1 Molecular weight distributions for the polymerization (entry 1a, black) and depolymerization (entry 1b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

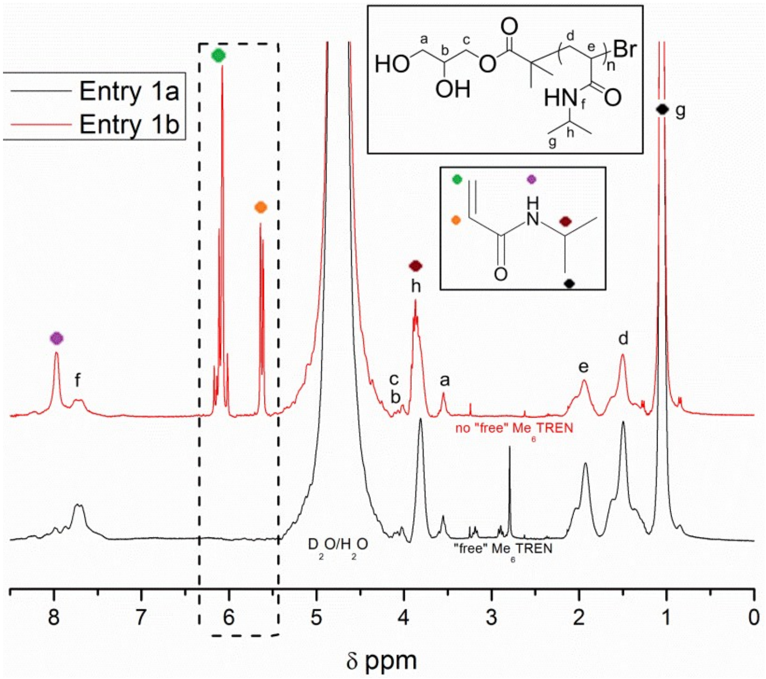


Fig. S2 ^{1}H NMR spectra (D_2O) for the polymerization (entry 1a, black) and depolymerization (entry 1b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Code	Retention Time (minutes)
NIPAm standard	2.76
Depolymerized pNIPAm	2.75

Table S2 Results for the GC analysis of depolymerized pNIPAm (green) and a NIPAm standard (black).

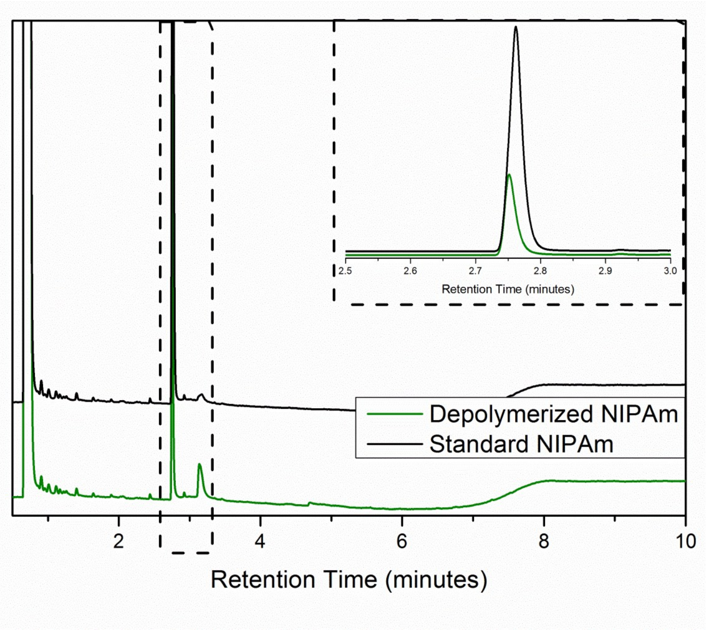


Fig. S3 GC traces for the reaction mix post-depolymerization (green); [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4] and standard NIPAm (black) in methanol (MeOH).

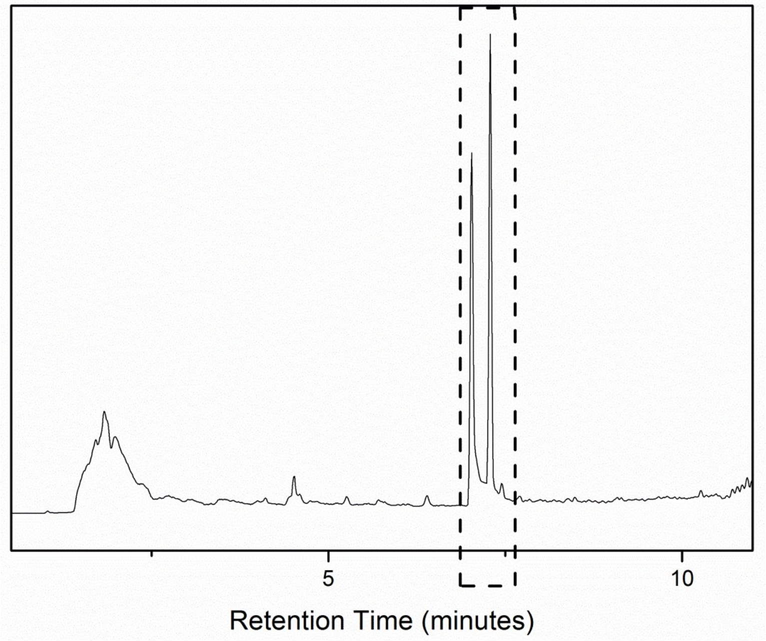


Fig. S4 GC trace for the depolymerized pNIPAm reaction mix in methanol (MeOH); [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

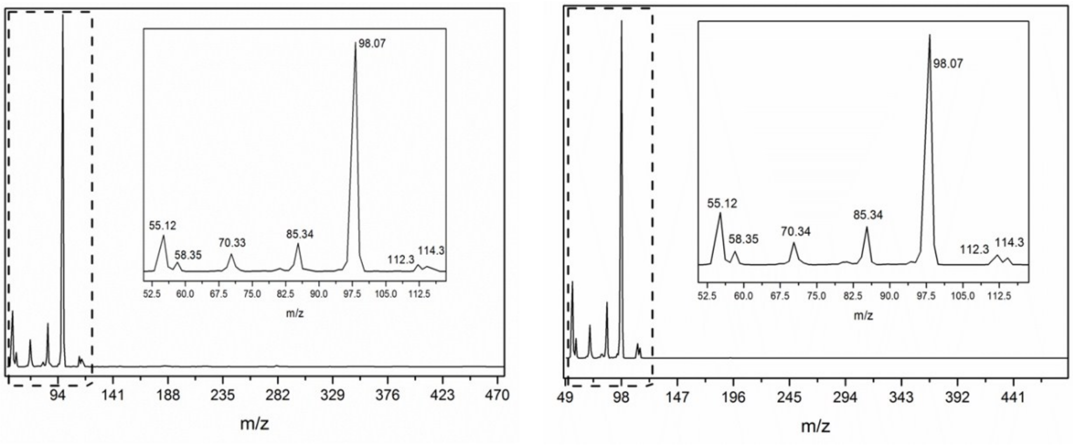
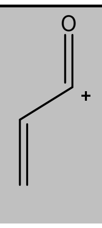
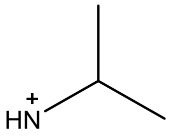
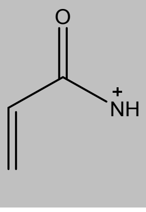
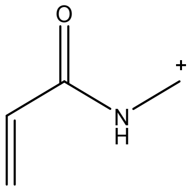
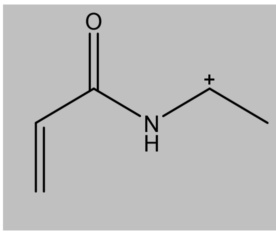
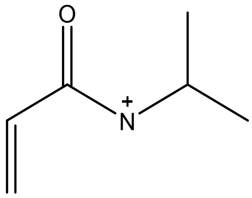
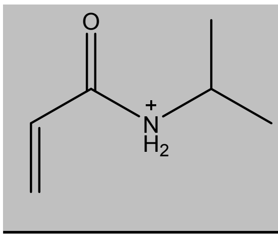


Fig. S5 Mass spectrum for the depolymerized pNIPAm reaction mix (peak 1, left) (peak 2, right); [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Fragmentation Structure	Theoretical m/z	Peak 1 m/z (rt = 7.02 minutes)	Peak 2 m/z (rt = 7.27 minutes)
	55.02	55.12	55.12
	58.10	58.35	58.35
	70.03	70.33	70.34
	85.05	85.34	85.34
	98.06	98.07	98.07
	112.08	112.30	112.30
	114.09	114.30*	114.30*

*denotes the molecular ion [M+]

Table S3 GC-MS analysis of the depolymerized pNIPAm reaction mixture.

Procedure for the repolymerization of pNIPAm following depolymerization

For the repolymerization of depolymerized pNIPAm, the reaction mixture was deoxygenated with N_2 for 15 minutes and left under a nitrogen atmosphere for 30 minutes before analysis *via* SEC and ^1H NMR.

Typical procedure for the aqueous Cu-mediated RDRP of NIPAm in the presence of Me_6TREN

To a Schlenk tube equipped with a magnetic stirring bar, HPLC grade water (3 mL) and Me_6TREN were added and purged of oxygen *via* nitrogen (N_2) bubbling for 2 minutes. The mixture was placed into an ice/water bath to regulate the temperature (0 °C) after which $Cu^{(I)}Br$ was added under an N_2 atmosphere. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The resulting solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in water (2 mL) and bubbled with nitrogen for 15 minutes. At the end of the deoxygenation period the initiator-monomer solution was transferred *via* a nitrogen purged syringe and needle into the Schlenk tube. Samples for NMR and GPC were taken using a nitrogen purged syringe, filtered through an alumina column, and diluted in the appropriate solvents.

The amounts and equivalents of the reagents for the polymerizations are provided in Table S4.

Code	**Targeted DP**	**Monomer (mg)**	**Initiator (eq.)**	**Initiator (mg)**	**Ligand (eq.)**	**Ligand (µL)**	**$Cu^{(I)}Br$ (mg)**	**$Cu^{(I)}Br$ (eq.)**
Entry 2	20	500.0	1.0	53.3	0.4	23.6	0.4	12.7

Table S4 Conditions used to synthesize pNIPAm in HPLC grade water to a targeted DP = 20 in the presence of $Cu^{(I)}Br/Me_6TREN$.

Code	Targeted DP	Time (minutes)	Conversion (%)	$M_{n,th}$ g mol^{-1}	$M_{n,GPC}$ g mol^{-1}	$Đ_m$
Entry 2	20	60	100	2500	4300	1.09

Table S5 ^{1}H NMR and SEC results for the synthesis of pNIPAm in HPLC grade water to a targeted DP = 20.

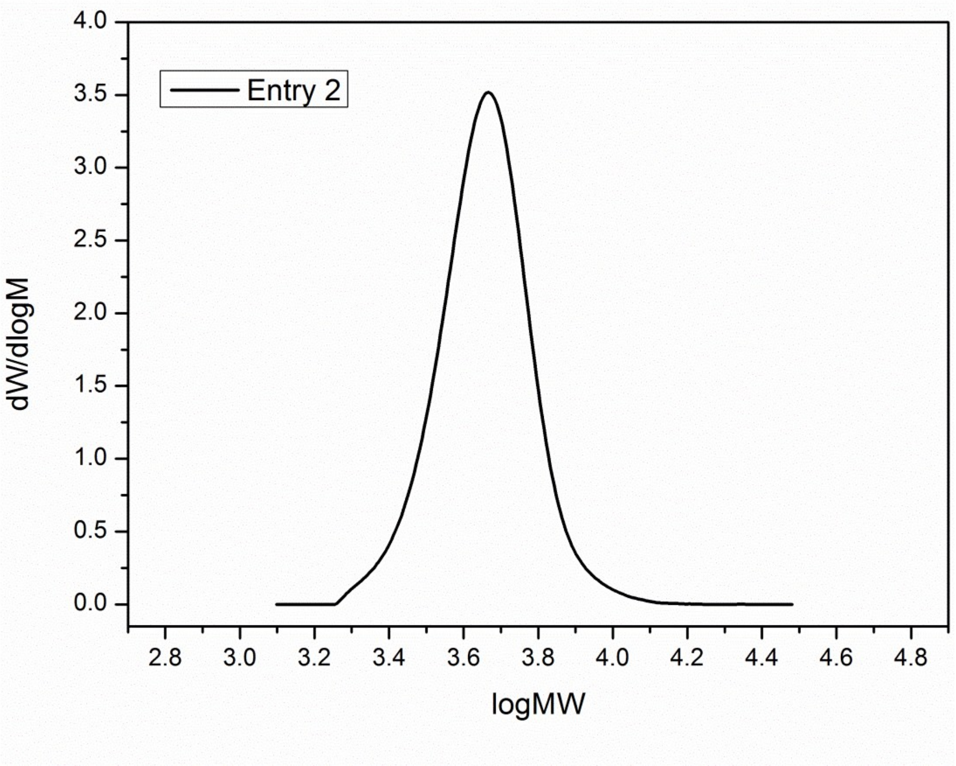


Fig. S6 Molecular weight distributions for the polymerization of NIPAm in HPLC grade water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me_6TREN] = [20] : [1] : [0.4] : [0.4].

Procedure for the polymerization and depolymerization of pNIPAm conducted in HPLC grade water carbonated with dry ice

0.5 g of dry ice was charged to a vial containing 20 mL of water (HPLC grade) and sealed with a latex balloon. After complete dissolution of the dry ice pellet, the balloon was removed and the carbonated water used as a solvent for the polymerization of DP20 NIPAm. Me_6TREN was added to a 14 mL glass vial containing carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in carbonated HPLC grade water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 3a	20	10	94	-	2400	3600	1.16
Entry 3b	20	next day	60	34	1500	2800	1.12

Table S6 ^{1}H NMR and SEC results for the polymerization (entry 3a) and depolymerization (entry 3b) of pNIPAm in water carbonated using dry ice as the source of carbonation.

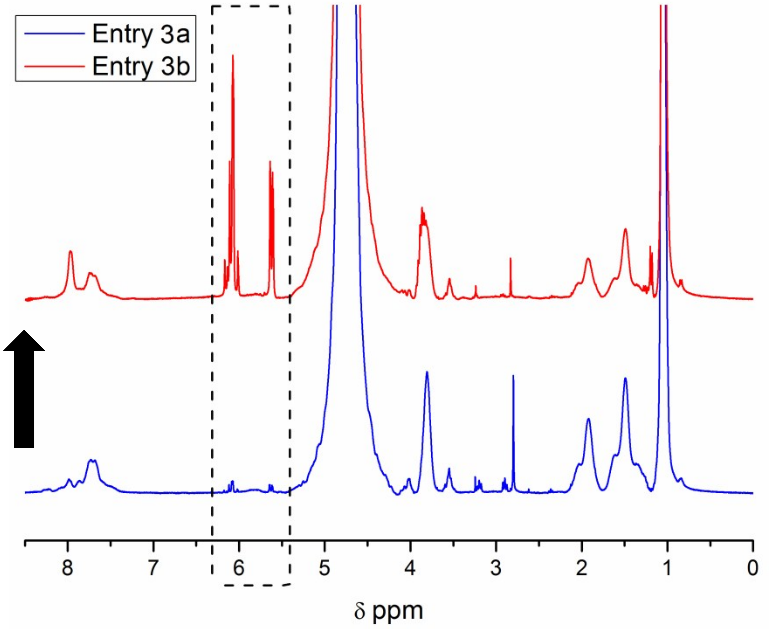


Fig. S7 ^{1}H NMR spectra (D_2O) for the polymerization (entry 3a, blue) and depolymerization (entry 3b, red) of pNIPAm in carbonated water at 0 °C using dry ice as the source of carbonation; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

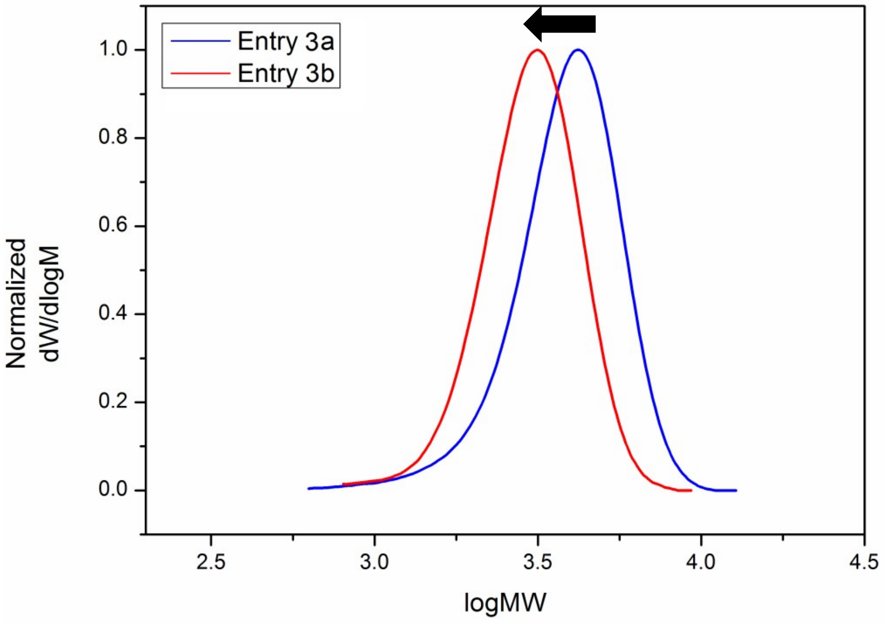


Fig. S8 Molecular weight distributions for the polymerization (entry 3a, blue) and depolymerization (entry 3b, red) of pNIPAm in carbonated water at 0 °C using dry ice as the source of carbonation; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Procedure for the polymerization of pNIPAm conducted in decarbonated carbonated water

20 mL of Highland Spring sparkling water was subjected to three rigorous freeze-thaw cycles, followed by 30 minutes of sonication to ensure that complete removal of CO_2 had been achieved. Me_6TREN was added to a 14 mL glass vial containing decarbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ was rapidly added to the ligand-water mix, the vial re-sealed and deoxygenated with N_2 for 10 minutes. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in decarbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period, the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 4	20	10	100	-	2500	5300	1.10

Table S7 ^1H NMR and SEC results for the polymerization of DP = 20 pNIPAm in the presence of $Cu^{(I)}Br/Me_6TREN$ in decarbonated commercial water.

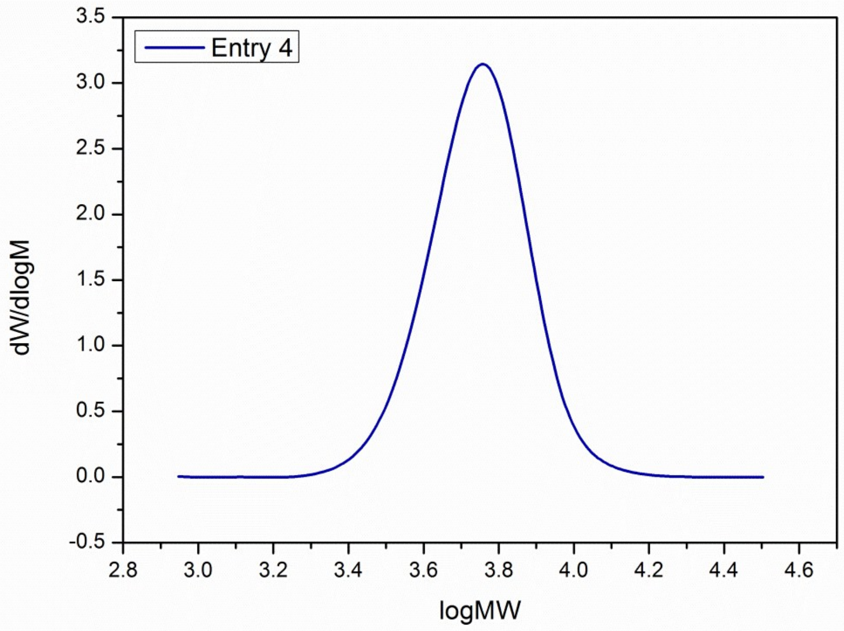


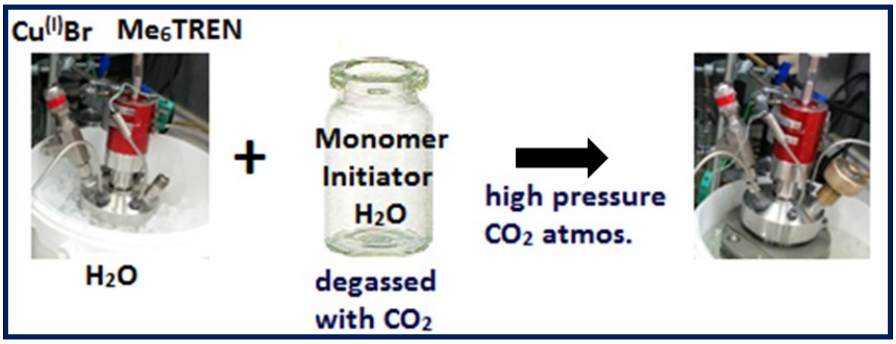
Fig. S9 Molecular weight distributions for the polymerization of NIPAm in decarbonated commercial water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Typical procedure for the high pressure polymerization DP = 20 NIPAm in carbonated water

Cu$^{(I)}$Br (12.7 mg, 0.4 eq.), Me$_6$TREN (23.6 µL, 0.4 eq.) and deionized water (3 mL) were charged to a high-pressure steel autoclave. The vessel was partially sealed and placed into an ice/water bath. The resulting catalytic solution was subsequently degassed *via* CO$_2$ purging at 2 bar for 10 minutes. During this time, deionized water (2 mL), NIPAm (500 mg, 20.0 eq.), and 3-dihydroxypropyl 2-bromo-2-methylpropanoate (53.3 mg, 1.0 eq.) were degassed in a sealed vial with carbon dioxide. After 10 minutes the monomer-initiator solution was transferred *via* a degassed syringe to the autoclave. At this point, the vessel was fully sealed and a range of pressures (10 bar, 24 bar, 48 bar and 100 bar) were applied. The reaction mixture was then stirred at 250 rpm for 10 minutes after which the reaction was terminated by freezing the solution in an acetone/dry ice bath. When completely frozen, the pressure was reduced by venting the autoclave over a period of ~ 30 minutes and a sample was removed and thawed. The reaction was repeated with the polymerization being left for 1 hour before termination. All samples were diluted in an appropriate solvent and analyzed using NMR and GPC.

Code	Pressure (bar)	Time (minutes)	Conversion (%)	Depolymerization (%)	$M_{n,th}$ g mol^{-1}	$M_{n,GPC}$ g mol^{-1}	$Đ_m$
Entry 5a	10	10	100	-	2500	3600	2.85
Entry 5b	10	60	100	-	2500	3300	1.89
Entry 6a	100	10	98	-	2500	6200	4.74
Entry 6b	100	60	100	-	2500	3400	1.91

Table S8 ^{1}H NMR and SEC results for the polymerization of NIPAm in carbonated water under high pressure.



Scheme S1 General scheme for the polymerization of pNIPAm in carbonated water under high pressure.

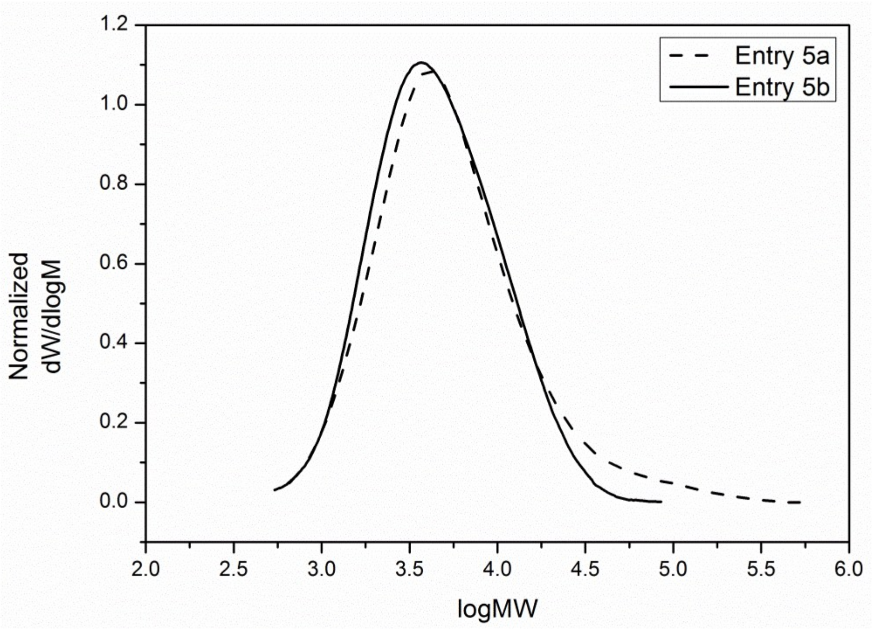


Fig. S10 Molecular weight distributions for the polymerization of NIPAm in carbonated deionized water at 0 °C under a pressure of 10 bar; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

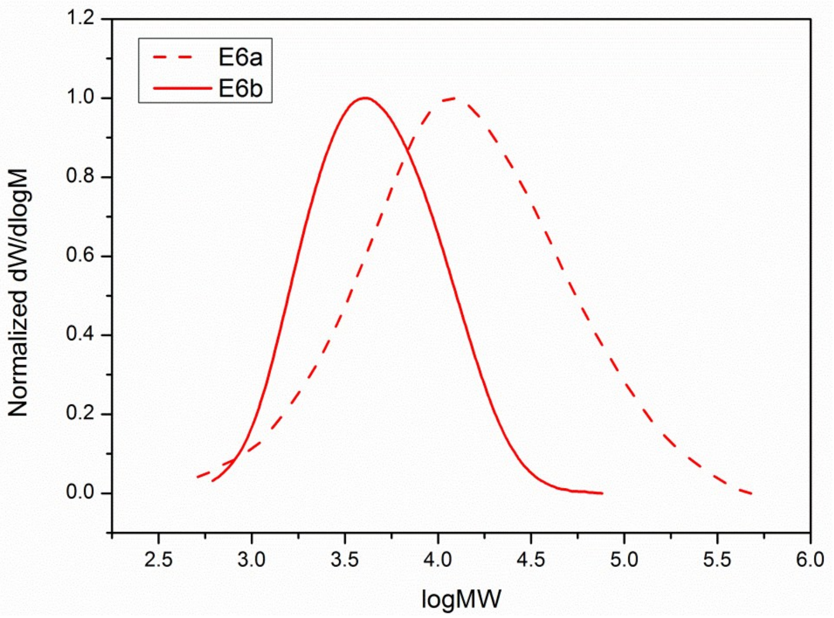


Fig. S11 Molecular weight distributions for the polymerization of NIPAm in carbonated deionized water at 0 °C under a pressure of 100 bar; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Procedure for the open top polymerization of DP = 20 NIPAm in carbonated water

Me_6TREN (23.6 µL, 0.4 eq.) was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), left unsealed and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ (12.7 mg, 0.4 eq.) was rapidly added to the ligand-water mix. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate (53.3 mg, 1.0 eq.) and NIPAm (500 mg, 20.0 eq.) were dissolved in Highland Spring carbonated water (2 mL), left unsealed, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 7a	20	10	99	-	2500	4200	2.25
Entry 7b	20	60	98	-	-	-	-

Table S9 ^{1}H NMR and SEC results for the open top polymerization of NIPAm in carbonated water.

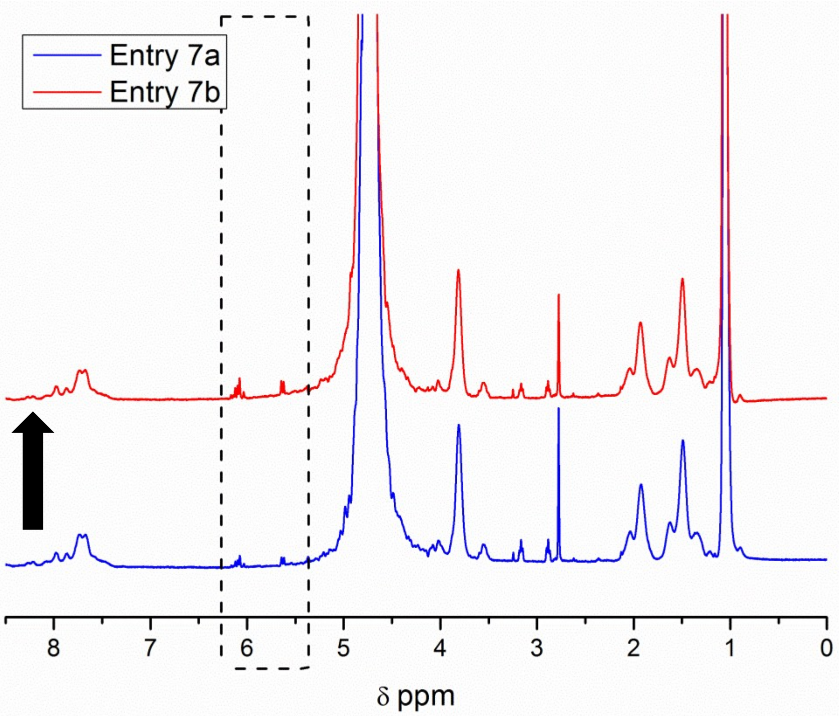


Fig. S12 ^{1}H NMR spectra (D_2O) for the "open top" polymerization (entry 7a, blue) and depolymerization (entry 7b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

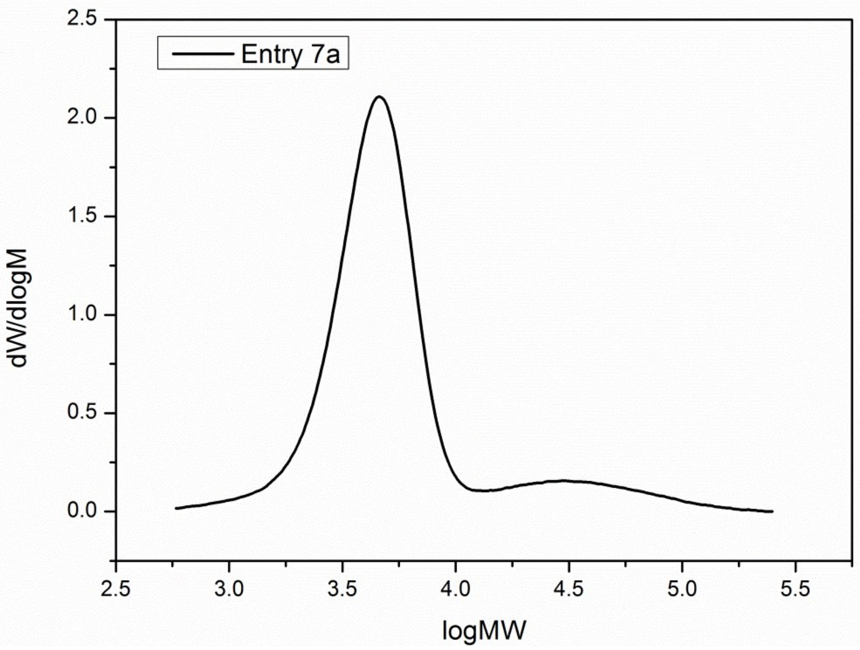


Fig. S13 Molecular weight distribution for the "open top" polymerization of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

pH monitoring of the polymerization and depolymerization process

Me_6TREN (11.8 µL, 0.4 eq.) was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ (6.3 mg, 0.4 eq.) was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate (26.6 mg, 1.0 eq.) and NIPAm (500 mg, 40 eq.) were dissolved in Highland Spring carbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents. The pH of the reaction mix was monitored immediately upon sampling of the reaction with all samples being frozen and thawed for NMR following the measurements.

Code	**Time (minutes)**	**pH**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 8a	1	6.40	99	-	4700	4700	1.52
Entry 8b	5	6.48	94	-	4500	5900	1.29
Entry 8c	10	6.53	98	-	4700	6300	1.24
Entry 8d	30	6.94	35	65	1700	2700	1.35

Table S10 ^1H NMR and SEC results for the polymerization/depolymerization of DP = 40 pNIPAm in carbonated water with pH measurements recorded for each sample.

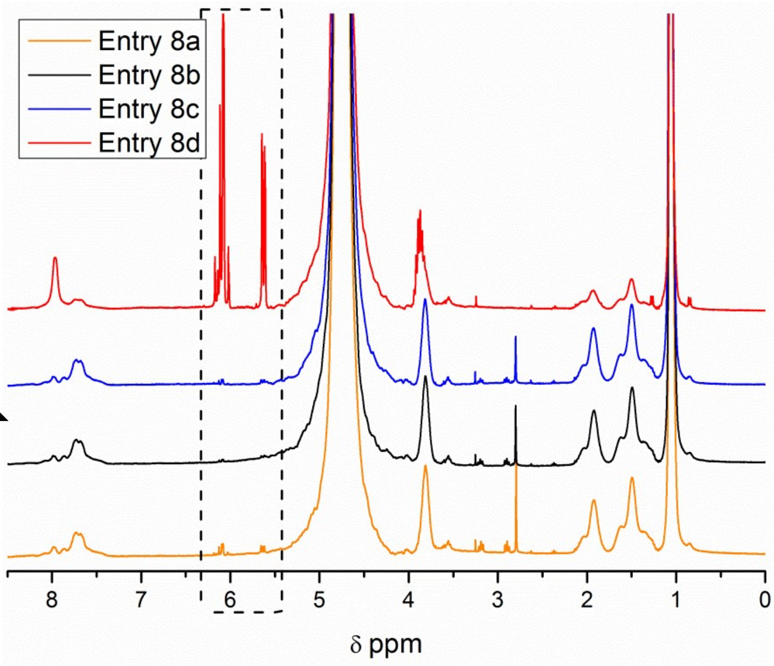


Fig. S14 ^1H NMR spectra (D_2O) for the polymerization (entries 8a-c) and depolymerization (entry 8d) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [40] : [1] : [0.4] : [0.4].

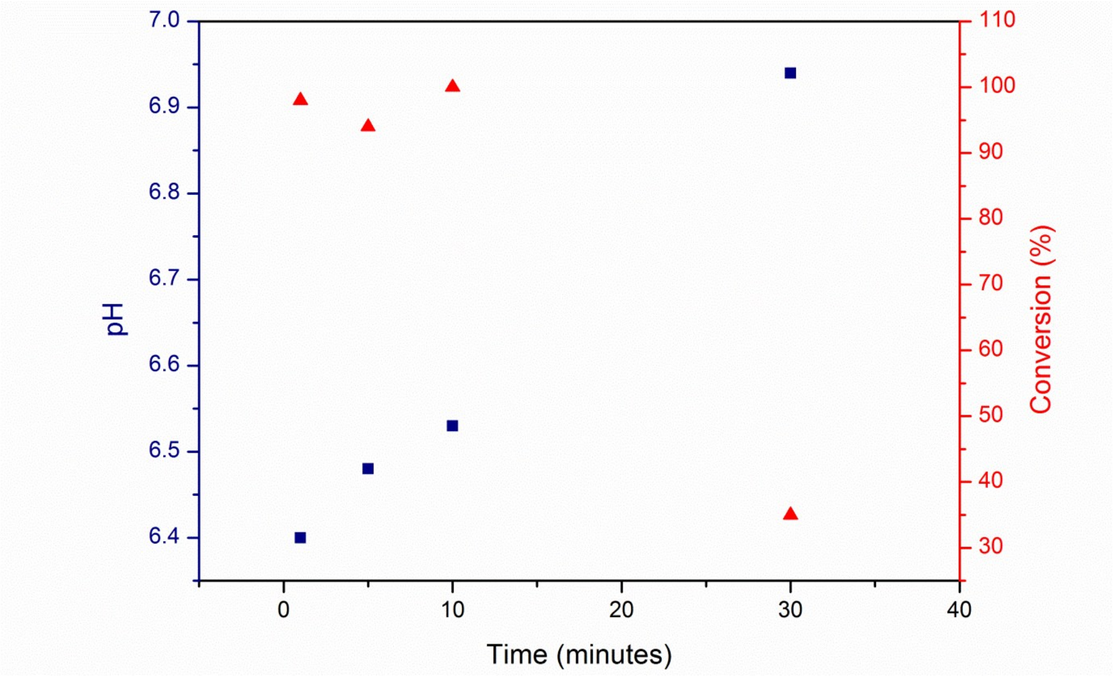


Fig. S15 Plot of pH vs time (blue) and conversion vs time (red) for the polymerization and depolymerization of DP = 40 pNIPAm.

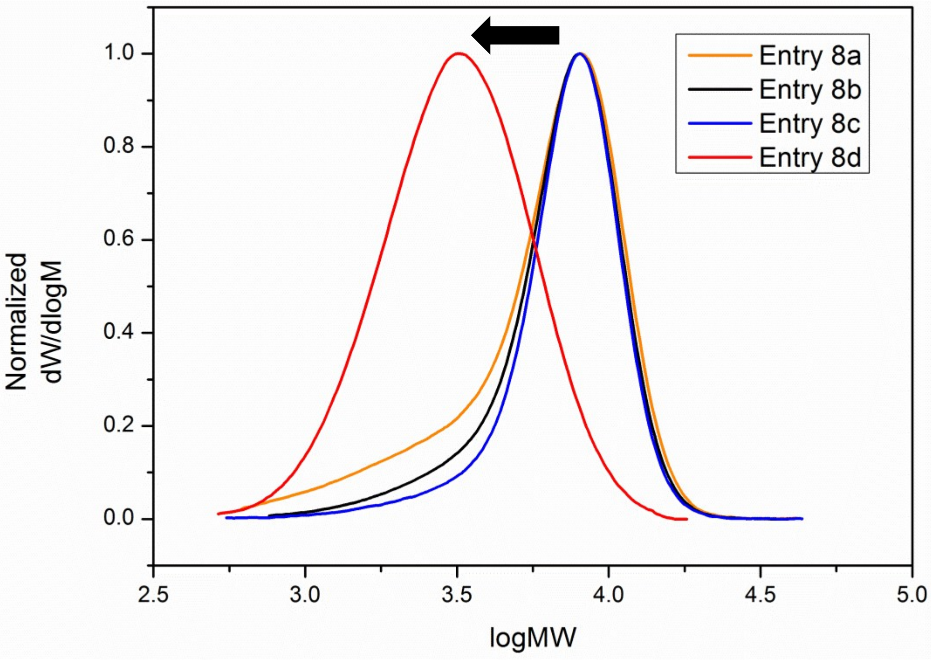


Fig. S16 Molecular weight distributions for the polymerization (entry 8a-c) and depolymerization (entry 8d) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [40] : [1] : [0.4] : [0.4].

Supplementary equations for the dissolution of carbon dioxide in water (Eq. S1 - 4)

$$CO_2\,(g) \leftrightarrow CO_2\,(l)$$

Dissolution of carbon dioxide **(Equation 1)**

$$CO_2\,(l) + H_2O\,(l) \leftrightarrow H_2CO_3(aq)$$

Equilibrium between dissolved carbon dioxide and water **(Equation 2)**

$$H_2CO_3(aq) + H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + HCO_3^-\,(aq)$$

Dissociation of carbonic acid **(Equation 3)**

$$HCO_3^-\,(aq) + H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$

Dissociation of carbonic acid **(Equation 4)**

Procedure for the aqueous Cu-mediated RDRP of NIPAm in the presence of Me_6TREN at pH 5.55

To a Schlenk tube equipped with a magnetic stirring bar, acidified HPLC grade water (3 mL) and Me_6TREN were added and purged of oxygen *via* nitrogen (N_2) bubbling for 2 minutes. The mixture was placed in an ice/water bath to regulate the temperature (0 °C) after which $Cu^{(I)}Br$ was added under an N_2 atmosphere. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The resulting solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in acidified water (2 mL) and bubbled with nitrogen for 15 minutes. At the end of the deoxygenation period, the initiator-monomer solution was transferred *via* a nitrogen purged syringe and needle into the Schlenk tube. Samples for NMR and GPC were taken using a nitrogen purged syringe, filtered through an alumina column, and diluted in the appropriate solvents.

The amounts and equivalents of the reagents for the polymerizations are provided in Table S11.

Code	Targeted DP	Monomer (mg)	Initiator (eq.)	Initiator (mg)	Ligand (eq.)	Ligand (μL)	$Cu^{(I)}Br$ (mg)	$Cu^{(I)}Br$ (eq.)
Entry 9	20	500.0	1.0	53.3	0.4	23.6	0.4	12.7

Table S11 Conditions used to synthesize pNIPAm in acidified HPLC grade water to a targeted DP = 20 in the presence of $Cu^{(I)}Br/Me_6TREN$ and carbonated water.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 9a	20	10	33	-	800	1400	1.53
Entry 9b	20	30	39	-	1000	1900	1.47
Entry 9c	20	next day	73	-	1800	1600	1.25

Table S12 ^{1}H NMR and SEC results for the polymerization of NIPAm in acidified HPLC grade water (pH 5.55).

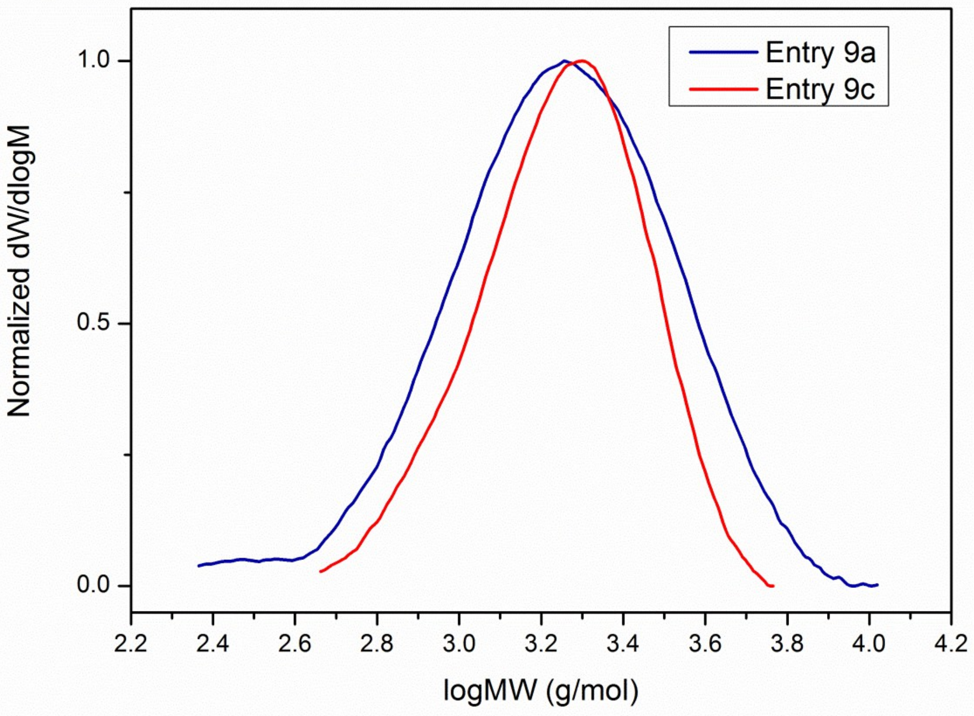


Fig. S17 Molecular weight distributions for the polymerization of pNIPAm in acidified HPLC grade water (pH 5.55) at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

Procedure for the polymerization and depolymerization of DP = 20 NIPAm in the presence of Me_6TREN at pH 8

Me_6TREN was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), the pH adjusted to 8 with $NaHCO_3$, and sealed with a rubber septum. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ was rapidly added to the ligand-water mix, the vial was re-sealed and the resulting solution stirred at 250 rpm for 1 minute. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in Highland Spring carbonated water (2 mL), the pH adjusted to 8 with $NaHCO_3$, and sealed with a rubber septum. The resulting solution was stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 10a	20	10	100	-	2500	3500	1.23
Entry 10b	20	60	100	-	2500	3700	1.17
Entry 10c	20	next day	97	-	2500	-	-

Table S13 ^{1}H NMR and SEC results for the polymerization of NIPAm conducted in pH 8 carbonated water.

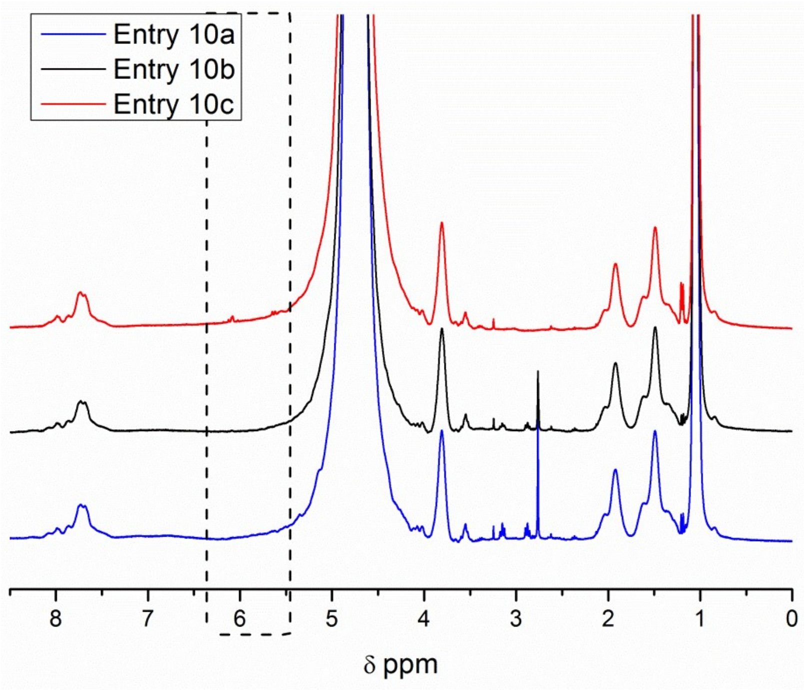


Fig. S18 ^{1}H NMR spectra (D_2O) for the polymerization at 0 °C of pNIPAm in carbonated water adjusted to pH 8 using $NaHCO_3$; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

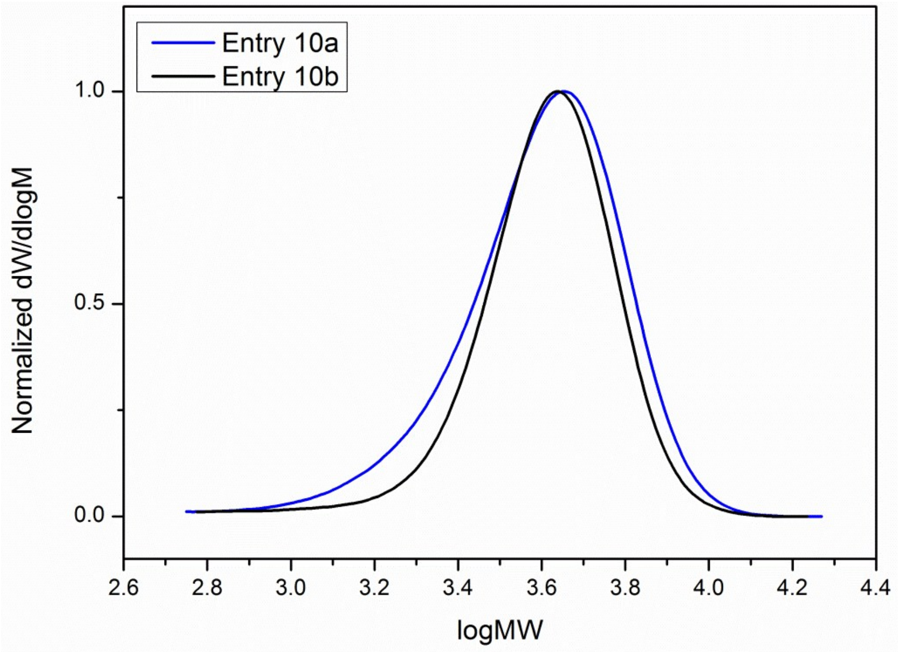


Fig. S19 Molecular weight distributions for the polymerization at 0 °C of pNIPAm in carbonated water adjusted to pH 8 using $NaHCO_3$; [NIPAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [20] : [1] : [0.4] : [0.4].

UV-Vis comparison of the $Cu^{(II)}Br_2/Me_6TREN$ complex in carbonated and HPLC grade water

Code	pH
$Cu^{(II)}$/L in pure water [a]	8.89
$Cu^{(II)}$/L in carbonated water [a]	5.45
$Cu^{(II)}$/L in acidified water [a]	5.55

[a] 1 mg/mL Cu(II)Br_2 , 2 eq. Me_6TREN

Table S14 pH measurements for the solutions analyzed by UV-Vis spectroscopy.

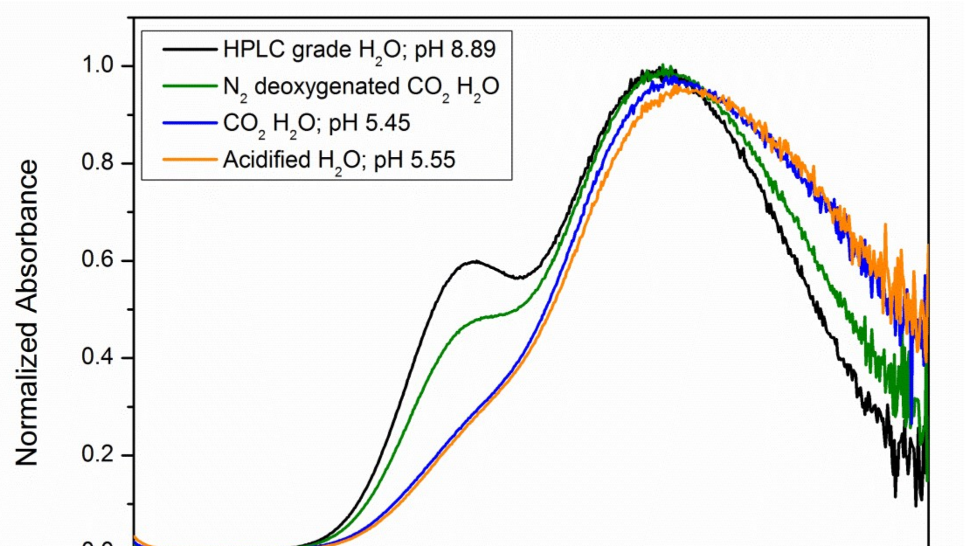


Fig. S20 UV-Vis spectra for [$Cu^{(II)}Br_2$/Me_6TREN] in HPLC grade water (black), N_2 deoxygenated carbonated water (green), carbonated water (blue) and acidified HPLC grade water (orange).

Procedure for the polymerization and depolymerization of NIPAm in the presence of Me_6TREN with addition of HCl *prior* to depolymerization

Me_6TREN (23.6 µL, 0.4 eq.) was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. $Cu^{(I)}Br$ (12.7 mg, 0.4 eq.) was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate (53.3 mg, 1.0 eq.) and NIPAm (500 mg, 20 eq.) were dissolved in Highland Spring carbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and $Cu^{(I)}Br$. After 10 minutes, 100 µL concentrated hydrochloric acid (HCl) (37 %, Sigma Aldrich) was added to the reaction mix. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	Targeted DP	Time (minutes)	Conversion (%)	Depolymerization (%)	$M_{n,th}$ g mol^{-1}	$M_{n,GPC}$ g mol^{-1}	$Đ_m$
Entry 11a	20	10	100	-	2500	3900	1.22
Entry 11b	20	60	46	54	1200	2600	1.17

Table S15 ^{1}H NMR and SEC results for the polymerization and depolymerization of NIPAm with the addition of HCl *prior* to depolymerization.

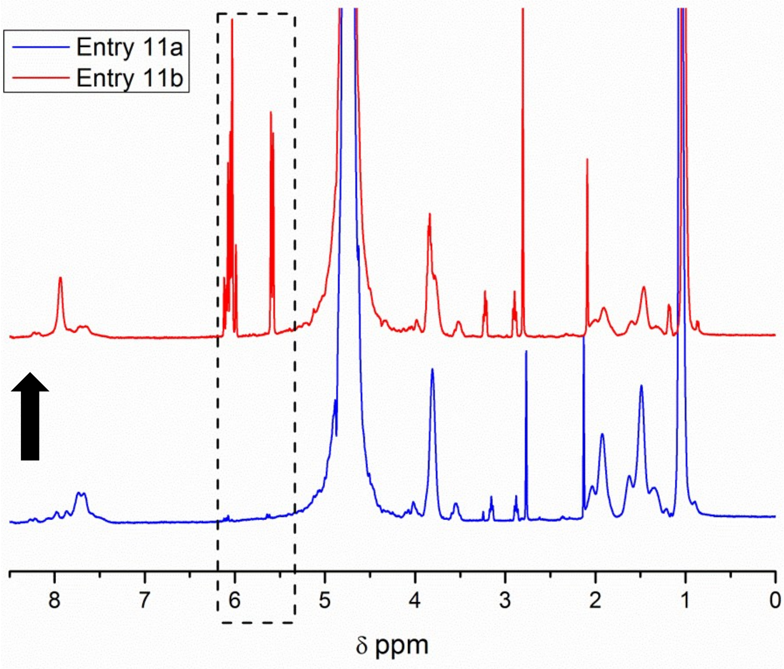


Fig. S21 ^{1}H NMR spectra (D_2O) for the polymerization (entry 11a, blue) and depolymerization (entry 11b, red) of pNIPAm in carbonated water at 0 °C with the addition of HCl *prior* to depolymerization; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

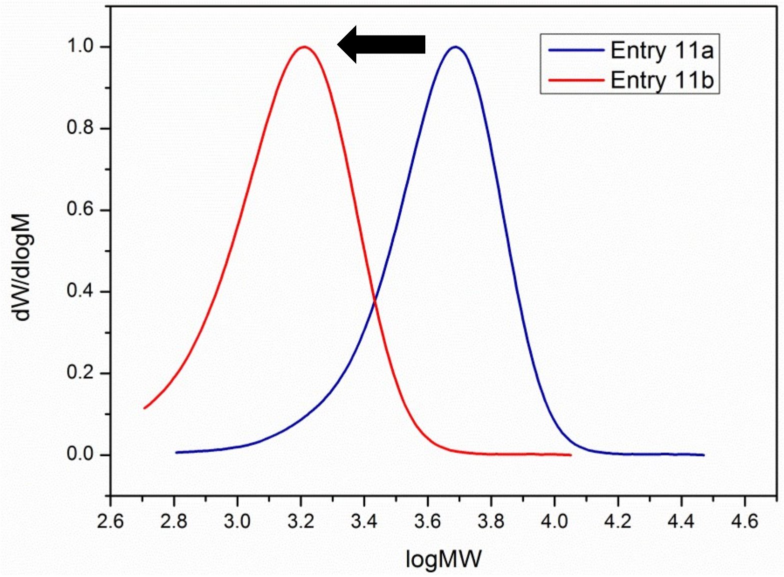


Fig. S22 Molecular weight distributions for the polymerization (entry 11a, blue) and depolymerization (entry 11b, red) of pNIPAm in carbonated water at 0 °C with the addition of HCl *prior* to depolymerization; [NIPAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [20] : [1] : [0.4] : [0.4].

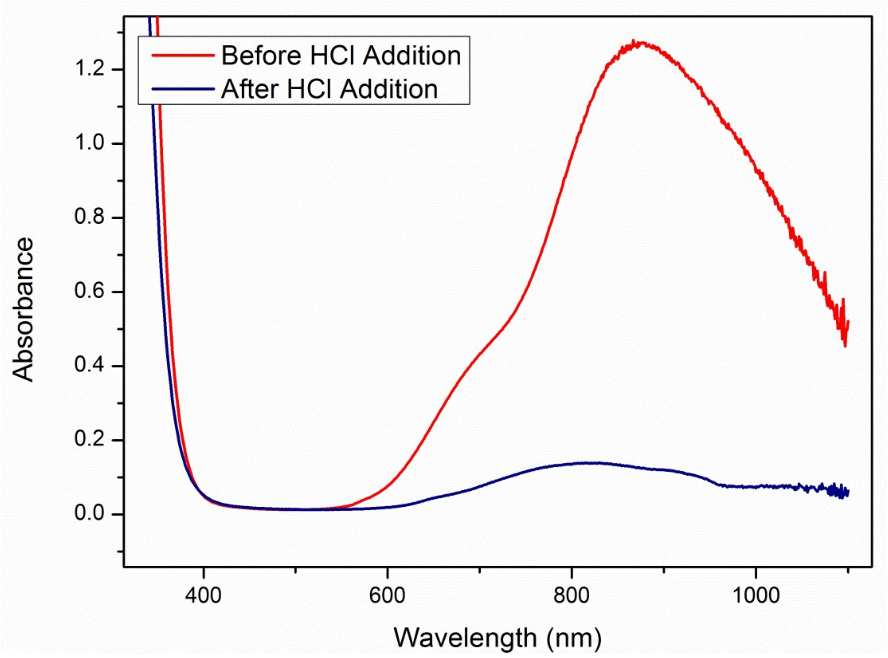


Fig. S23 UV-Vis chromatogram for the polymerization and depolymerization of NIPAm with the addition of HCl *prior* to depolymerization.

Typical procedure for the aqueous Cu-mediated RDRP of DP = 20 NIPAm in the presence of PMDETA

To a Schlenk tube equipped with a magnetic stirring bar, HPLC grade water (3 mL) and PMDETA (18.5 μL, 0.4 eq.) were added and purged of oxygen *via* nitrogen (N_2) bubbling for 2 minutes. The mixture was placed in a ice/water bath to regulate the temperature (0 °C) after which $Cu^{(I)}Br$ (12.7 mg, 0.4 eq.) was added under an N_2 atmosphere. Upon addition of $Cu^{(I)}Br$ to the ligand-water mix, a coloured solution formed and red/brown $Cu^{(0)}$ particles were visible. The resulting solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate (53.3 mg, 1eq.) and NIPAm (0.5 g, 20 eq.) were dissolved in water (2 mL) and bubbled with nitrogen for 15 minutes. At the end of the deoxygenation period the initiator-monomer solution was transferred *via* a nitrogen purged syringe and needle into the Schlenk tube. Samples for NMR and GPC were taken using a nitrogen purged syringe, filtered through an alumina column, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 12a	20	30	96	2400	2000	1.74
Entry 12b	20	60	100	-	-	-

Table S16 ^{1}H NMR and SEC results for the polymerization of NIPAm in HPLC grade water utilizing PMDETA as the ligand.

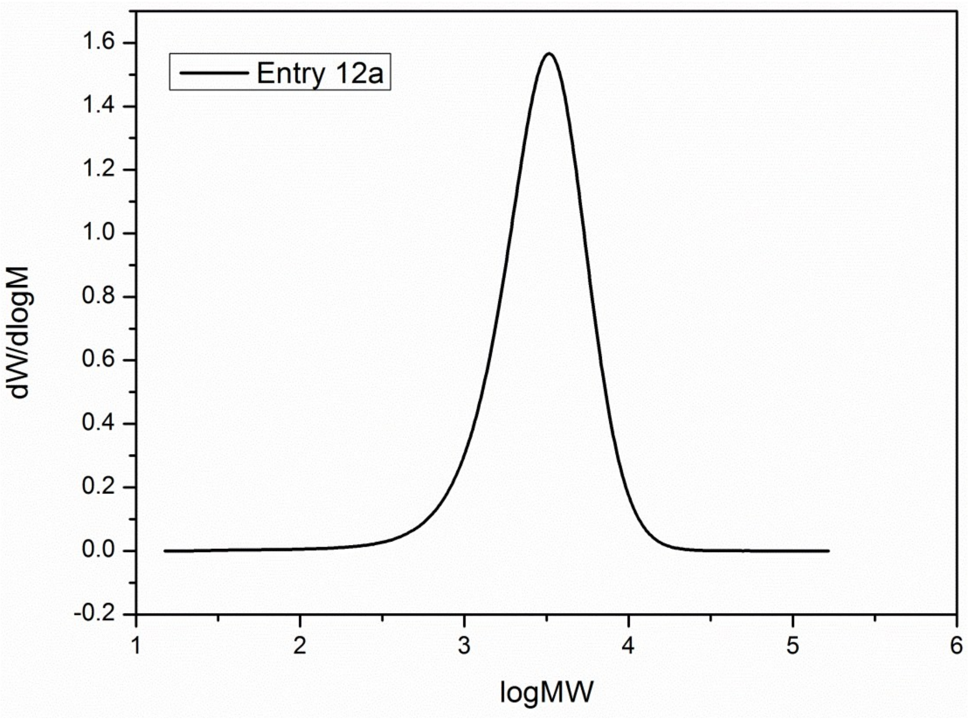


Fig. S24 Molecular weight distributions for the polymerization of NIPAm in HPLC grade water employing PMDETA as the ligand (entry 12a); [NIPAm] : [I] : [Cu$^{(I)}$Br] : [PMDETA] = [20] : [1] : [0.4] : [0.4].

Typical procedure for the polymerization of DP = 20 NIPAm in the presence of PMDETA and carbonated water

PMDETA (18.5 µL, 0.4 eq.) was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. Cu$^{(I)}$Br (12.7 mg, 0.4 eq.) was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of Cu$^{(I)}$Br to the ligand-water mix, a coloured solution formed and red/brown Cu$^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-

methylpropanoate (53.3 mg, 1.0 eq.) and NIPAm (500 mg, 20.0 eq.) were dissolved in Highland Spring carbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and Cu$^{(I)}$Br. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

Code	**Targeted DP**	**Time (minutes)**	**Conversion (%)**	**Depolymerization (%)**	**$M_{n,th}$ g mol^{-1}**	**$M_{n,GPC}$ g mol^{-1}**	**$Đ_m$**
Entry 13a	20	10	88	-	2200	-	-
Entry 13b	20	60	82	-	2100	6100	1.62

Table S17 ^{1}H NMR and SEC results for the polymerization of NIPAm in carbonated water utilizing PMDETA as the ligand.

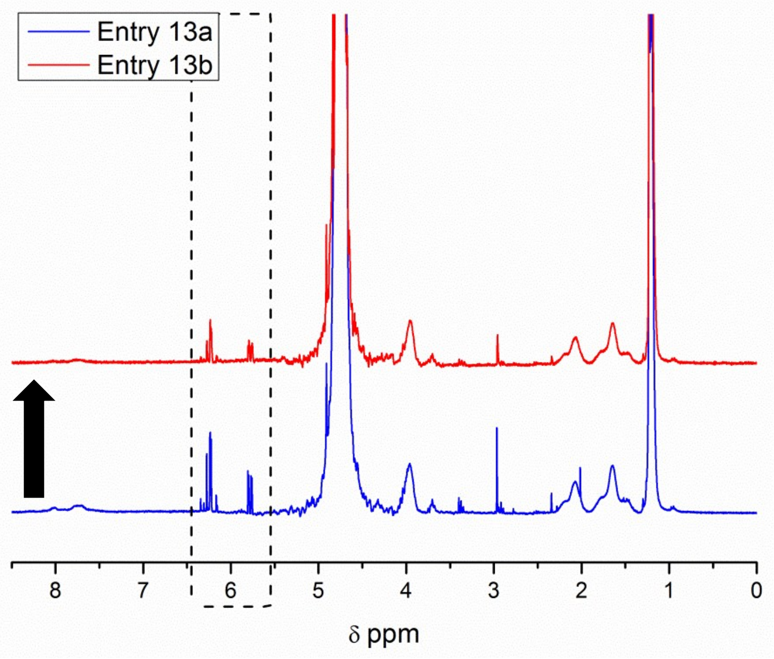


Fig. S25 ^{1}H NMR spectra (D_2O) for the polymerization of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [PMDETA] = [20] : [1] : [0.4] : [0.4].

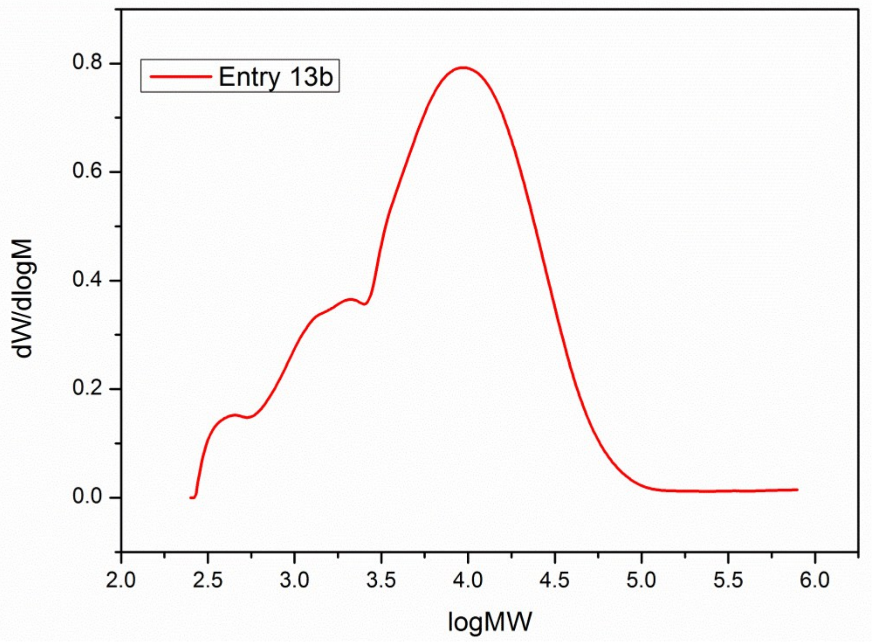


Fig. S26 Molecular weight distributions for the polymerization of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [PMDETA] = [20] : [1] : [0.4] : [0.4].

Typical procedure for the polymerization and depolymerization of high molecular weight NIPAm in the presence of Me_6TREN

Me_6TREN was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. Cu$^{(I)}$Br was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of Cu$^{(I)}$Br to the ligand-water mix, a coloured solution formed and red/brown Cu$^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and NIPAm were dissolved in Highland Spring carbonated water (2 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and Cu$^{(I)}$Br. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

The amounts and equivalents of the reagents for the polymerizations are provided in Table S18.

Code	Targeted DP	Monomer (mg)	Initiator (eq.)	Initiator (mg)	Ligand (eq.)	Ligand (µL)	$Cu^{(I)}Br$ (eq.)	$Cu^{(I)}Br$ (mg)
Entry 14	120	500.0	1.0	8.9	0.4	3.9	0.4	2.1
Entry 15	120	500.0	1.0	8.9	2.4	23.6	2.4	12.7
Entry 16	20	500.0	1.0	53.3	2.4	141.7	2.4	76.0

Table S18 Conditions used to synthesize pNIPAm in carbonated water to different degrees of polymerization (DP).

Code	Targeted DP	Time (minutes)	Conversion (%)	Depolymerization (%)	$M_{n,th}$ g mol^{-1}	$M_{n,GPC}$ g mol^{-1}	$Đ_m$
Entry 14a	120	10	0	-	-	-	-
Entry 14b	120	60	0	-	-	-	-
Entry 15a	120	10	100	-	13800	20600	1.18
Entry 15b	120	60	57	43	7900	12400	1.11
Entry 16a	20	10	100	-	2500	9300	1.16
Entry 16b	20	60	100	-	2500	9200	1.14

Table S19 ^{1}H NMR and SEC results for the polymerization (a) and depolymerization (b) of pNIPAm to different degrees of polymerization (DP) in the presence of varying amounts of Cu$^{(I)}$Br/Me$_6$TREN.

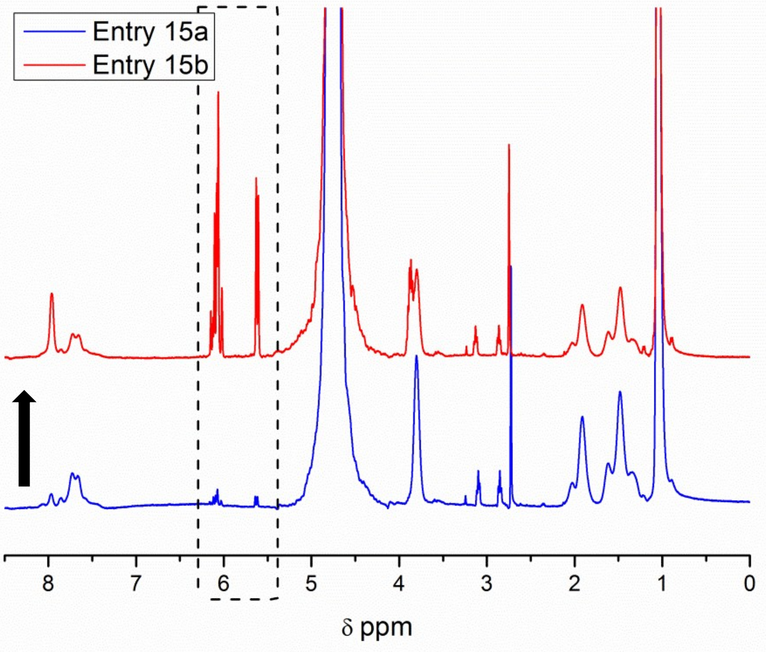


Fig. S27 ^{1}H NMR spectra (D$_2$O) for the polymerization (entry 15a, blue) and depolymerization (entry 15b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [120] : [1] : [2.4] : [2.4].

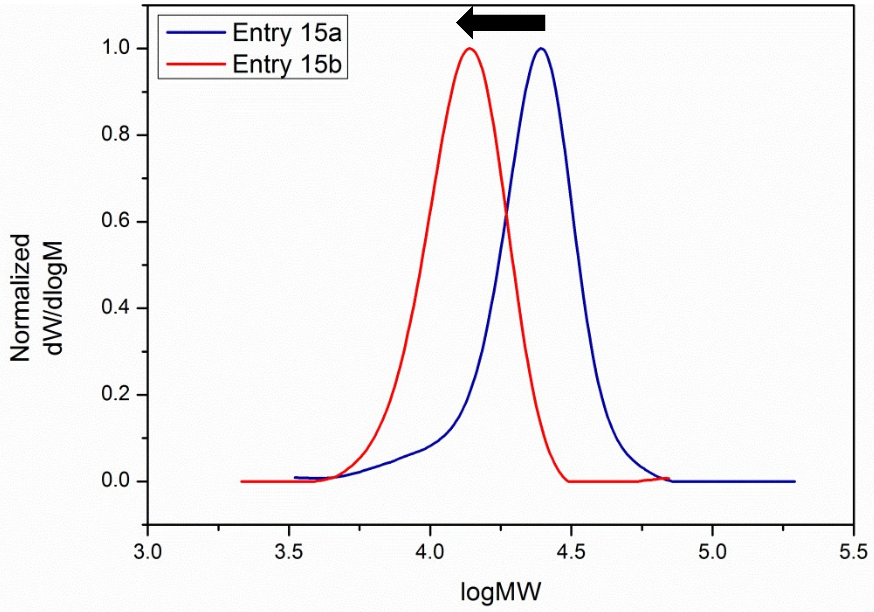


Fig. S28 Molecular weight distributions for the polymerization (entry 15a, blue) and depolymerization (entry 15b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [120] : [1] : [2.4] : [2.4].

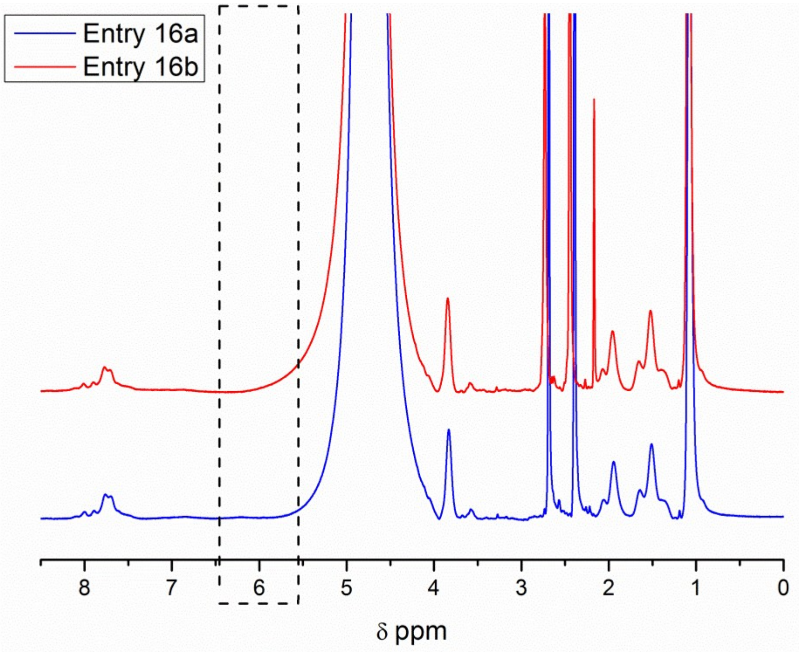


Fig. S29 ^1H NMR spectra (D_2O) for the polymerization (entry 16a, blue) and depolymerization (entry 16b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [20] : [1] : [2.4] : [2.4].

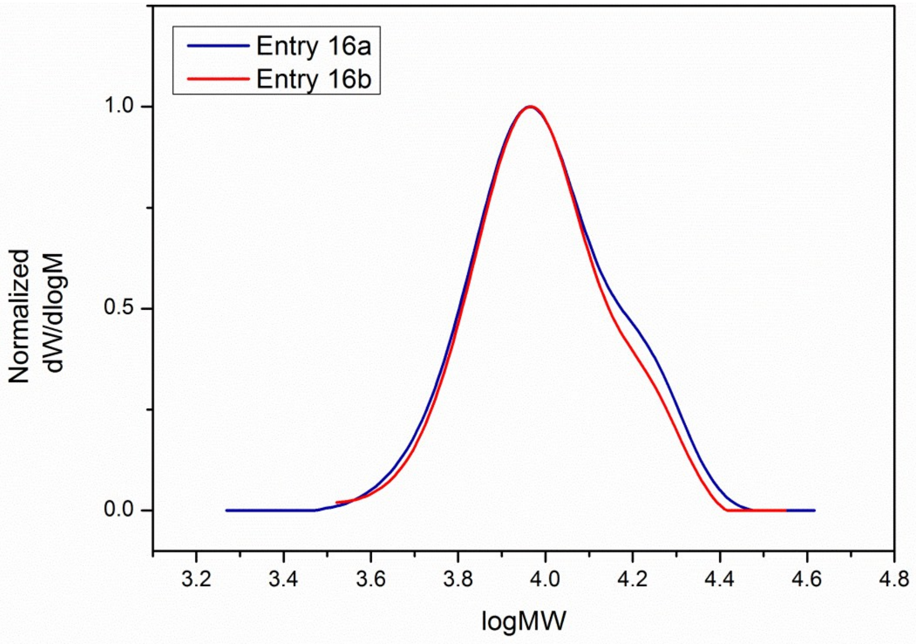


Fig. S30 Molecular weight distributions for the polymerization (entry 16a, blue) and depolymerization (entry 16b, red) of pNIPAm in carbonated water at 0 °C; [NIPAm] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [2.4] : [2.4].

Typical procedure for the polymerization and depolymerization of other water soluble monomers in the presence of Me$_6$TREN

Me$_6$TREN was added to a 14 mL glass vial containing Highland Spring carbonated water (3 mL), sealed with a rubber septum and stirred at 250 rpm for 1 minute. The glass vial was then placed into an ice/water bath to regulate the temperature and supress the rate of hydrolysis. Cu$^{(I)}$Br was rapidly added to the ligand-water mix and the vial was re-sealed. Upon addition of Cu$^{(I)}$Br to the ligand-water mix, a coloured solution formed and red/brown Cu$^{(0)}$ particles were visible. The solution was allowed to stir and disproportionate whilst 3-dihydroxypropyl 2-bromo-2-methylpropanoate and uninhibited monomer were dissolved in Highland Spring carbonated water (1 mL), sealed with a rubber septum, and stirred at 250 rpm for 10 minutes. At the end of this period the initiator-monomer solution was transferred *via* a syringe and needle into the glass vial containing the disproportionated ligand and Cu$^{(I)}$Br. Samples for NMR and GPC were taken using a syringe, frozen in liquid nitrogen, thawed, and diluted in the appropriate solvents.

The amounts and equivalents of the reagents for the polymerizations are provided in Table S20.

Code	Targeted DP	Monomer (mg)	Initiator (eq.)	Initiator (mg)	Ligand (eq.)	Ligand (μL)	$Cu^{(I)}Br$ (mg)	$Cu^{(I)}Br$ (eq.)
Entry 17	20	500.0	1.0	52.4	0.4	23.2	0.4	12.5
Entry 18	20	500.0	1.0	51.9	0.4	23.0	0.4	12.3

Table S20 Conditions used to synthesize DP = 20 pHEAm (entry 17) and pHEA (entry 18) in carbonated water.

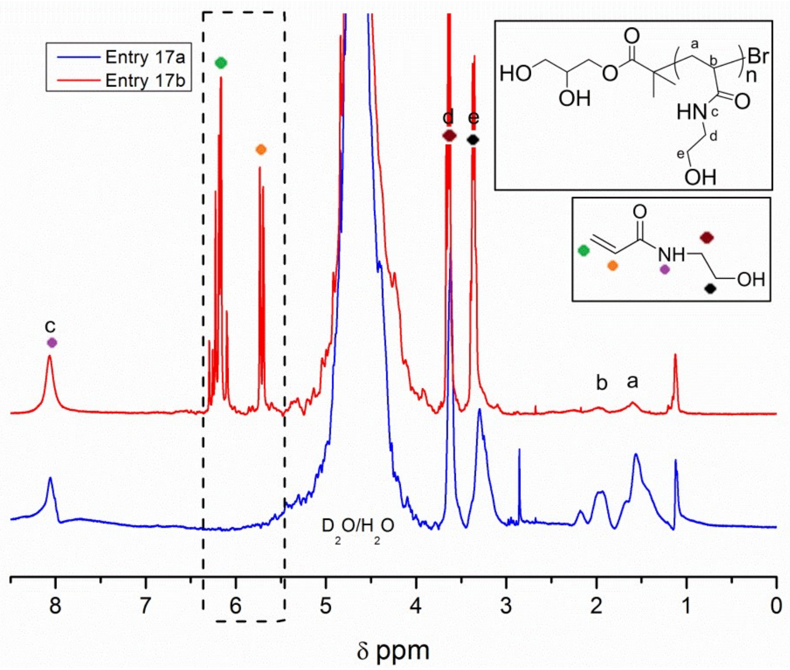


Fig. S31 ^1H NMR spectra (D_2O) for the polymerization (entry 17a, blue) and depolymerization (entry 17b, red) of pHEAm in carbonated water at 0 °C; [HEAm] : [I] : [$Cu^{(I)}Br$] : [Me_6TREN] = [20] : [1] : [0.4] : [0.4].

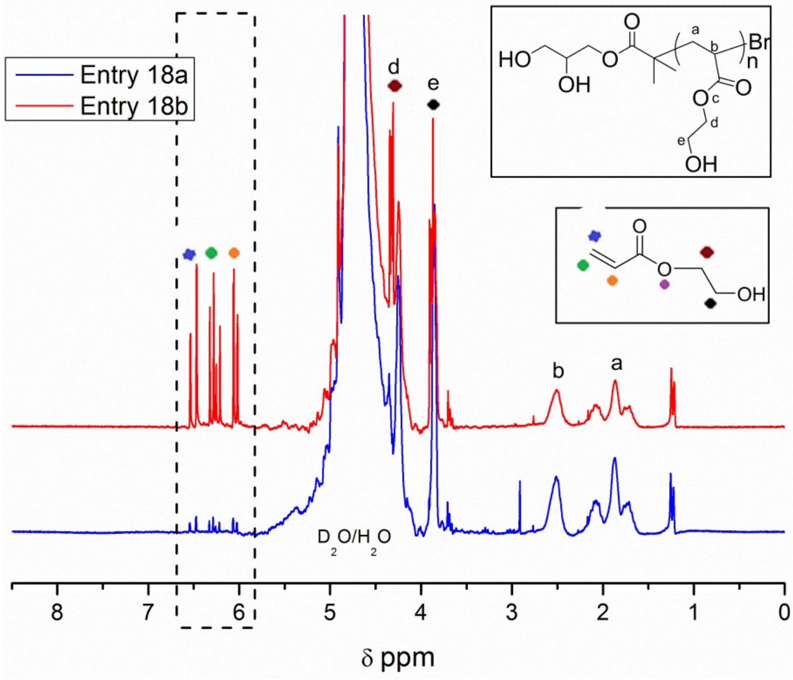


Fig. S32 ^{1}H NMR spectra (D_2O) for the polymerization (entry 18a, blue) and depolymerization (entry 18b, red) of pHEA in carbonated water at 0 °C; [HEA] : [I] : [Cu$^{(I)}$Br] : [Me$_6$TREN] = [20] : [1] : [0.4] : [0.4].

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