Electronic Supplementary Information

for

Aqueous Copper(0) Mediated Reversible Deactivation Radical Polymerization of 2-Hydroxyethyl Acrylate

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Trace EGDA residue by GC

Table S1. GC programming profile for EGDA residue measurement

Temperature(°C)	Rate (°C/min)	Hold (min)	Total (min)
50	-	2.15	2.15
110	15	1.00	7.15
113	0.5	1.00	14.15
250	15	2.00	25.28

Calibration curve of standard EGDA samples:

Using acetone as the solvent, different concentrations of ethylene glycol diacrylate (90%, technical grade, Sigma-Aldrich) were added to prepare standard EGDA samples as shown below in Table S2.

Table S2. GC standard EGDA samples

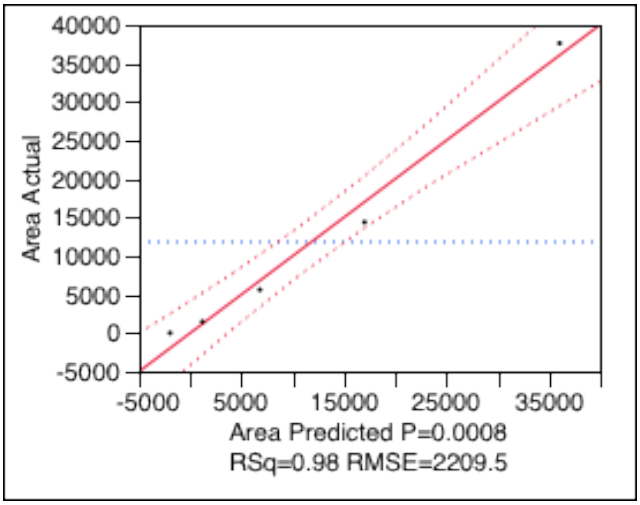
Standard Sample No.	EGDA Concentration(weight ppm)	Integral Area
Blank	0	0
1	80.82	1467
2	224.55	5616
3	486	14382
4	973.98	37610

(EGDA has a retention time of 16.6-16.7 min; HEA has a retention time of 9.4 min; Acetone has a retention time of 2.5-2.6 min.)

JMP software was used to do linear regression (details shown below).

$Y = aX + b + \varepsilon$ (Regression model; Y denotes area and X denotes concentration.)

Fig. S1 Actual versus predicted value plot for GC calibration of EGDA content



Analysis of variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	942428215	942428215	193.0384
Error	3	14646229	4882076.2	Prob > F
C. Total	4	957074444		0.0008*

Parameter estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-1967.141	1400.144	-1.40	0.2547
Concentration	39.035152	2.809532	13.89	0.0008*

The regression expression is Y =39.035152 X – 1967.141. (SE1)

Measurement of EGDA residue in the HEA:

Table S3. EGDA in the HEA used in the experiments

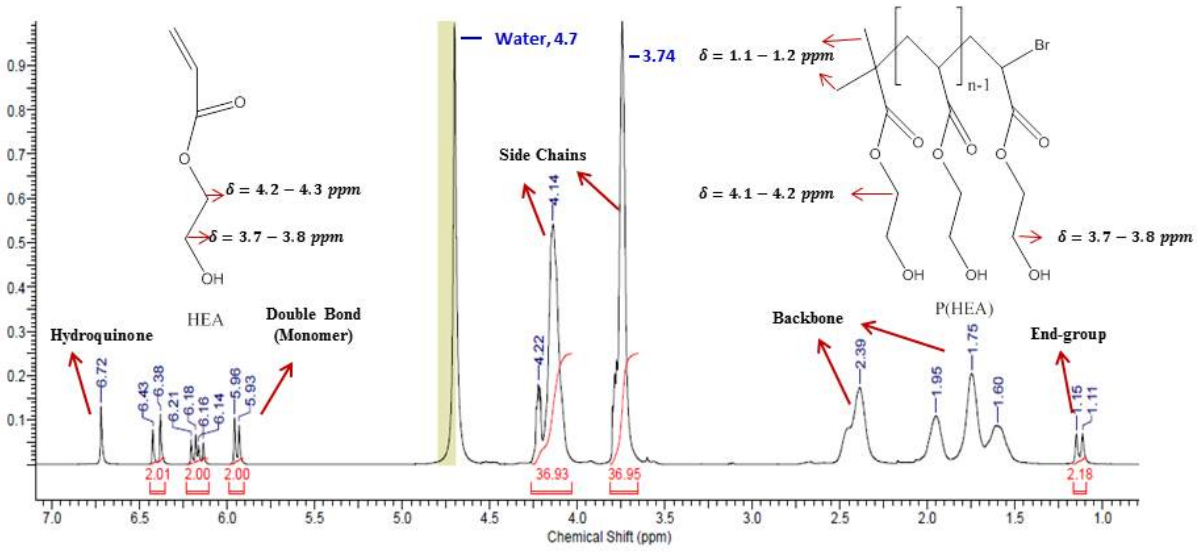
Sample	Integral Area	Total Amount Sample (mg)	HEA (mg, containing EGDA)	Calculated x	Calculated (wt.%)
Batch 1	10954	4351.2	868.5	331.01	0.166
Commercial HEA	39204	4526.5	754.4	1054.72	0.633
Batch 2	3184	4340.0	1047.7	131.96	0.055
Batch 3	8798	4553.4	1125.1	275.78	0.112

x denotes EGDA concentration (ppm) in the sample.

Conversion and end-group method to calculate $M_{n,NMR}$ via ^{1}H-NMR spectra

Using Experiment TCL50-3 (Table 2, entry 6) as an example, the conversion and $M_{n,NMR}$ calculations are shown as below.

Fig. S2 ^{1}H-NMR Spectrum of Sample (Experiment TCL50-3) using D_2O solvent.



δ (ppm): 1.11, 1.15 [6H, 2(CH_3)C], 5.93-6.43 (3H, CH_2=CH), 3.74, 4.14-4.22 [4H, COO(CH_2CH_2)OH]

Conversion=1- (molar of monomer residue)/(molar of monomers participated in the polymers)

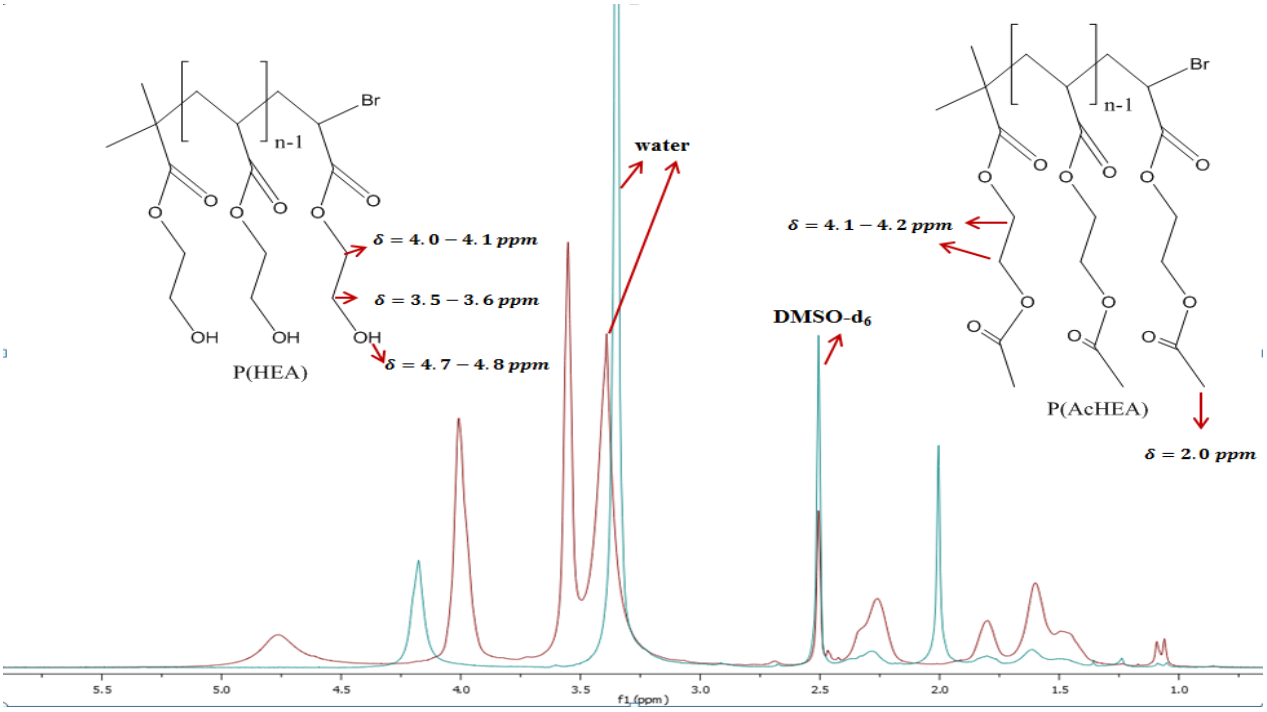
=1-[(2.01+2.00+2.00)/3]/[(36.93+36.95)/4]= 89.2%

$$\bar{N} = [(36.93+36.95)/4-(2.01+2.00+2.00)/3-2.18/6]/(2.18/6) = 16.10333$$

$$M_{n,NMR} = M_{HEA} \times \bar{N} + M_{initiator} = 116.12*16.10333+211 = 5358$$

Verification of complete acetylation of P(HEA) *via* ^{1}H-NMR spectra

Fig. S3 Comparison ^{1}H-NMR Spectra of P(HEA) in red and P(AcHEA) in cyan with DMSO-d_6 solvent.



P(HEA) δ (ppm): 4.76 (1H, OH), 3.55,4.01 [4H, $COO(CH_2CH_2)OH$]

P(AcHEA) δ (ppm): 2.00 (3H, $COCH_3$), 4.18 [4H, $COO(CH_2CH_2)OOC$]

Recipes for different target chain length (TCL) with two-step Cu(0) *in situ* mediated RDRP

Table S4. Details of recipes for different target chain length with two-step Cu(0) *in situ* mediated RDRP

TCL ($[M]_0$:$[I]_0$:$[C]_0$:$[L]_o$/$[NaBr]_0$)	Components in tube A (m mole)	Components in tube B (m mole)
20 (20:1:0.4:0.4)	Me_6TREN: 0.14 D_2O: 2.0 mL CuBr: 0.14 -	HEA: 7 HEBiB: 0.35 - D_2O: 2 mL
20 (20:1:0.1:0.1/1.2)	Me_6TREN: 0.035 D_2O: 2.0 mL CuBr: 0.035 -	HEA: 7 HEBiB: 0.35 NaBr:0.42 D_2O: 2.0 mL
50 (50:1:0.4:0.4)	Me_6TREN: 0.056 D_2O: 2.0 mL CuBr: 0.056 -	HEA: 7 HEBiB: 0.14 - D_2O: 2.0 mL
50 (50:1:0.4:0.4/4.8)	Me_6TREN: 0.56 D_2O: 2.0 mL CuBr: 0.56 -	HEA: 7 HEBiB: 0.14 NaBr: 0.672 D_2O: 2.0 mL
50 (50:1:0.1:0.1/1.2)	Me_6TREN: 0.014 D_2O: 2.0 mL CuBr: 0.014 -	HEA: 7 HEBiB: 0.14 NaBr: 0.168 D_2O: 2.0 mL
100 (100:1:0.4:0.4)	Me_6TREN: 0.056 D_2O: 2.0 mL CuBr: 0.056 -	HEA: 14 HEBiB: 0.14 - D_2O: 2.0 mL
100 (100:1:0.1:0.1)	Me_6TREN: 0.014 D_2O: 2.0 mL CuBr: 0.014 -	HEA: 14 HEBiB: 0.14 - D_2O: 2.0 mL

100 (100:1:0.1:0.1/1.2)	Me_6TREN: 0.014 D_2O: 2.0 mL CuBr: 0.014 -	HEA: 14 HEBiB: 0.14 NaBr: 0.168 D_2O: 2.0 mL
200 (200:1:0.1:0.1/2.4)	Me_6TREN: 0.01 D_2O: 3.0 mL CuBr: 0.01 -	HEA: 20 HEBiB: 0.1 NaBr: 0.24 D_2O: 2.7 mL
400 (400:1:0.1:0.1/3.6)	Me_6TREN: 0.008 D_2O(H_2O): 4.5 mL CuBr: 0.008 -	HEA: 32 HEBiB: 0.08 NaBr: 0.288 D_2O(H_2O): 4.6 mL
800 (800:1:0.2:0.2/4.8)	Me_6TREN: 0.008 D_2O: 4.5 mL CuBr: 0.008 -	HEA: 32 HEBiB: 0.04 NaBr: 0.192 D_2O: 4.6 mL