Electronic Supplementary Material (ESI) for Polymer Chemistry.

Sequence-controlled multi-block copolymerization of acrylamides *via* aqueous SET-LRP at 0 °C

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Materials

N-Isopropylacrylamide (NIPAM, 97%) was purchased from commercial supplier (Sigma-Aldrich) and was purified by recrystallization from hexane to remove the inhibitor. 2-Hydroxyethyl acrylamide (HEAA, 97%, Sigma-Aldrich), *N*,*N*-Dimethyl acrylamide (DMA, 99%, Sigma-Aldrich), *N*,*N*-Diethylacrylamide (DEA, 99%, Sigma-Aldrich) and 4-acryloylmorpholine (NAM, 97%, Sigma-Aldrich) were passed over a column filled with basic alumina to remove the inhibitor prior to use.

HPLC grade water (H_2O, VWR international, LLC) was used as the solvent for disproportionation and polymerizations.

The water soluble initiator 2, 3-dihydroxypropyl 2-bromo-2-methylpropanoate was prepared as reported in the literature.[1]

Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized according to literature procedures and stored under nitrogen prior to use.[2,3]

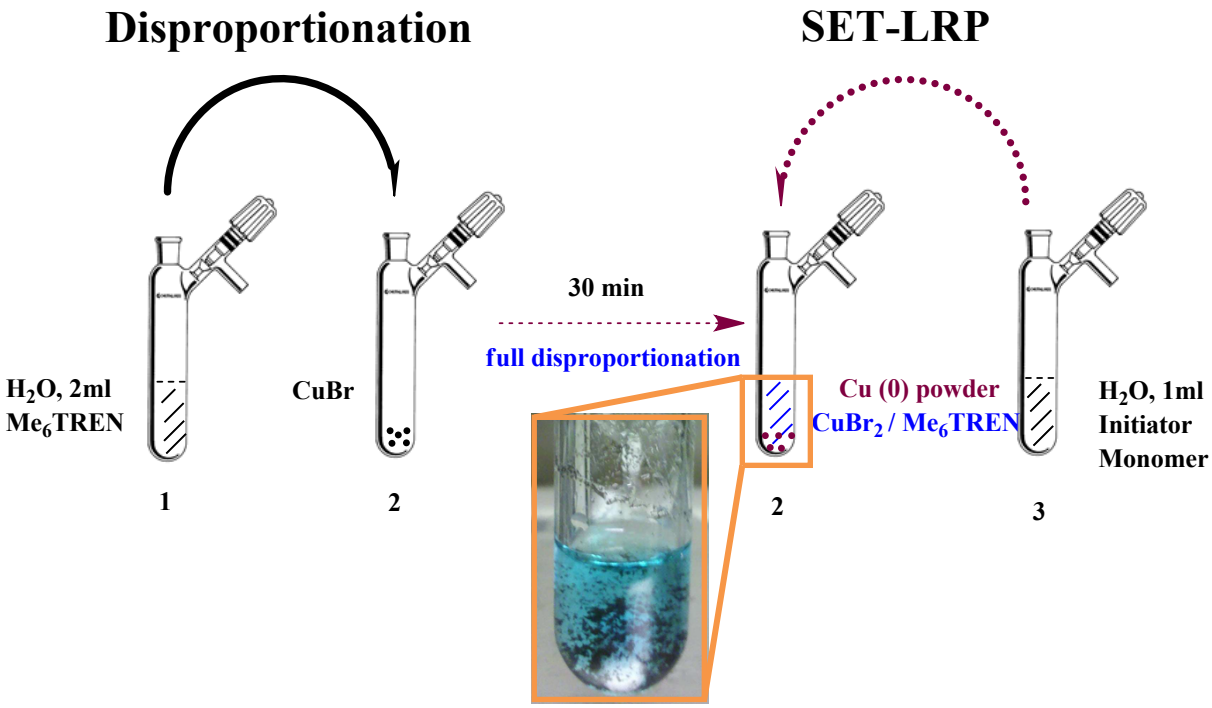
Copper(I) bromide (CuBr, 98%, Sigma-Aldrich) was sequentially washed with acetic acid and ethanol and dried under vacuum.[4]

Instruments and analysis

Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on Bruker DPX-300 and DPX-400 spectrometers using deuterated solvents obtained from Aldrich. Monomer conversion for NIPAM, HEAA, DMA, DEA and NAM homopolymerization was determined, comparing the integral of vinyl protons with isopropyl, ethyl, dimethyl, diethyl, morphline protons, respectively.

Size-exclusion chromatography (SEC) was conducted on Varian 390-LC system using DMF as the mobile phase (5 mM NH_4BF_4) at 50 °C, equipped with refractive index, UV and viscometry detectors, 2 × PLgel 5 mm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Commercial narrow linear poly (methyl methacrylate) standards in range of 200 to 1.0 × 10^6 g · mol^{-1} were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis.

All reactions were carried out under an inert atmosphere of oxygen-free nitrogen, using standard Schlenk techniques.



Scheme S1: Schematic of a typical aqueous SET-LRP proceeding with disproportionation of CuBr/Me_6TREN *prior* to monomer/initiator addition in pure water at 0 °C.

General procedure for homopolymerization by aqueous SET-LRP (DP_n = 10)

To a Schlenk tube fitted with a magnetic stir bar and a rubber septum, H_2O (2 mL) and Me_6TREN (0.1 mmol) were charged and the mixture was bubbled with nitrogen for 15 min. CuBr (0.1 mmol) was then carefully added under slight positive pressure of nitrogen. The mixture immediately became blue (Cu^{II}) and a purple/red precipitate (Cu^0) was observed. In a separate vial fitted with a magnetic stir bar and a rubber septum monomer (2.5 mmol) was dissolved in H_2O (1.0 mL) prior to addition of initiator (2,3-dihydroxypropyl 2-bromo-2-methylpropanoate, 0.25 mmol) and the resulting mixture was bubbled with nitrogen for 15 min.

The degassed monomer / initiator aqueous solution was then transferred *via* cannula to the Schlenk tube containing Cu(0) / $CuBr_2$ / Me_6-Tren catalyst. The Schlenk tube was sealed and the mixed solution was allowed to polymerize at 0 °C. Sample of the reaction mixture were then removed for analysis. The sample for ^1H NMR was directly diluted with D_2O. Catalyst residues were removed by filtering through a column of neutral alumina prior to DMF SEC analysis.

General procedure for homopolymerization by aqueous SET-LRP (DP_n = 100)

To a Schlenk tube fitted with a magnetic stir bar and a rubber septum, H_2O (2 mL) and Me_6TREN (28 μmol) were charged and the mixture was bubbled with nitrogen for 15 min. CuBr (56 μmol) was then carefully added under slight positive pressure of nitrogen. The mixture immediately became blue (Cu^{II}) and a purple/red precipitate (Cu^0) was observed. In a separate vial fitted with a magnetic stir bar and a rubber septum monomer (7.0 mmol) was dissolved in H_2O (4.0 mL) prior to addition of initiator (2,3-dihydroxypropyl 2-bromo-2-methylpropanoate, 0.07 mmol) and the resulting mixture was bubbled with nitrogen for 15 min. The degassed monomer / initiator aqueous solution was then transferred *via* cannula to the Schlenk tube containing Cu (0) / $CuBr_2$ / Me_6TREN catalyst. The Schlenk tube was sealed and the mixed solution was allowed to polymerize at 0 °C. Samples of the reaction mixture were then removed for analysis. The sample for ^1H NMR was directly diluted with D_2O. Catalyst residues were removed by filtering through a column of neutral alumina prior to DMF SEC analysis.

General procedure for kinetic investigation of aqueous SET-LRP polymerization

Reactions were performed in triplicate. The general procedure for homopolymerization by aqueous SET-LRP was followed. Homopolymer conversions were monitored by regular sampling to accurately determine the time at which full monomer conversion was reached according to ^1H NMR (D_2O). In subsequent experiments (also performed in triplicate) hompolymerization was allowed to proceed to this time and a sample was taken, in order to confirm the anitcipated full conversion, *prior* to addition of freshly deoxygenated aqueous solutions of monomer (DP_n eq). Regular sampling was again employed to identify the time required to reach full monomer conversion. This was repeated until conversion and/or molecular weight distributions were compromised by termination. Samples taken for ^1H NMR were directly diluted with D_2O. Catalyst residues were removed by filtering through a column of neutral alumina prior to DMF SEC analysis.

General procedure for chain extension/multi-block copolymerization by aqueous SET-LRP

The general procedure for homopolymerization by aqueous SET-LRP was followed. At specific times determined by control experiments a sample was taken for conversion analysis before addition of freshly deoxygenated aqueous solutions of monomer (DP_n eq). This process was repeated until conversion and/or molecular weight distributions were compromised by termination. Samples taken for ^1H NMR were directly diluted with D_2O. Catalyst residues were removed by filtering through a column of neutral alumina prior to DMF SEC analysis.

Supplementary tables and figures

Table S1: Preparation of multi-block homopolymers prepared by sequential addition of deoxygenated aliquots of aqueous NIPAM (10 eq) to PNIPAM during SET-LRP at 0 C in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Entry	Block number	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$
1	Block 1	100	60 (60)	1400	2900	1.06
2	Block 2	100	240 (300)	2500	4800	1.07
3	Block 3	100	320 (620)	3600	6700	1.08
4	Block 4	0	1200 (1820)	4700	6900	1.08

[a] Cumulative time in parentheses. [b] DMF SEC, calibrating with PMMA standard.

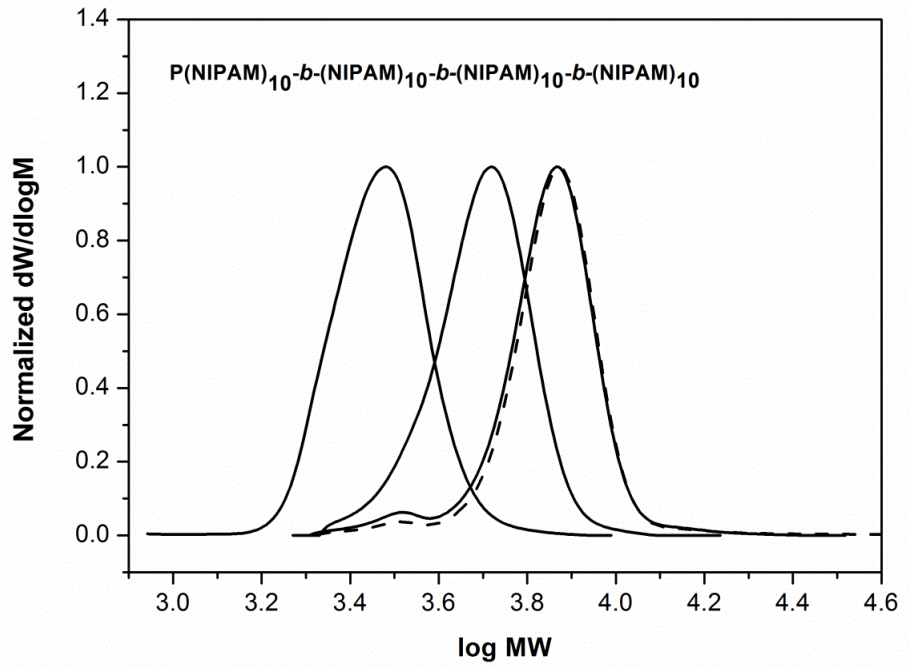


Figure S1: Preparation of multi-block homopolymers (unoptimized) prepared by sequential addition of deoxygenated aliquots of aqueous NIPAM (10 eq) to PNIPAM via SET-LRP at 0 ℃ in D_2O (a) and evolution of block molecular weight by DMF SEC (b) $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

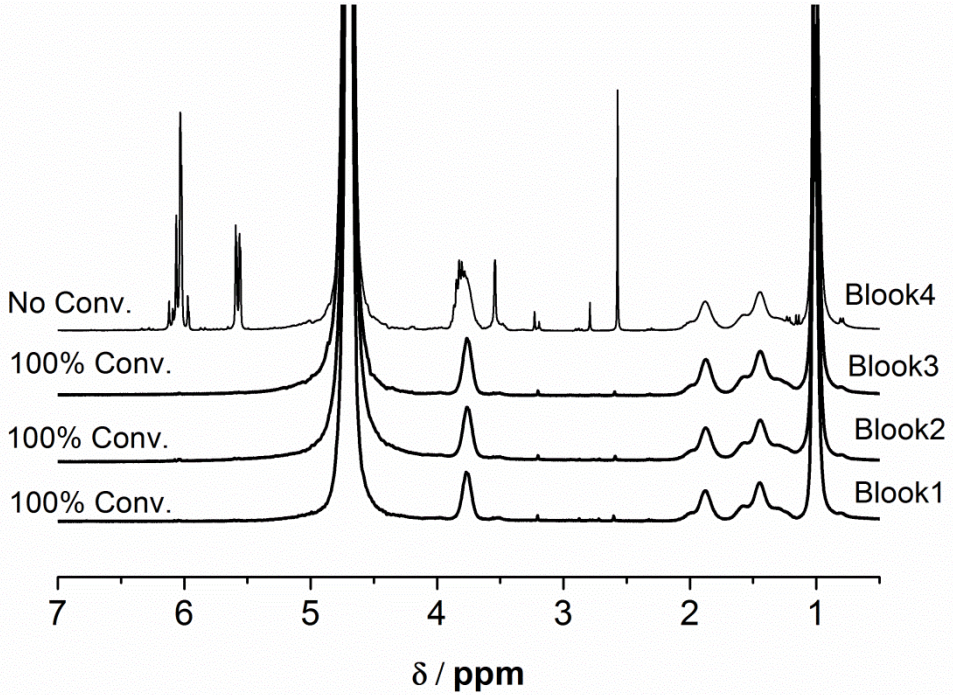


Figure S2: ^1H NMR (D_2O) show the conversion during multi-block homopolymerization (unoptimized) of NIPAM. $[M]_0 : [I]_0 : [CuBr] : [Me_6\text{-Tren}] = [10] : [1] : [0.04] : [0.04]$.

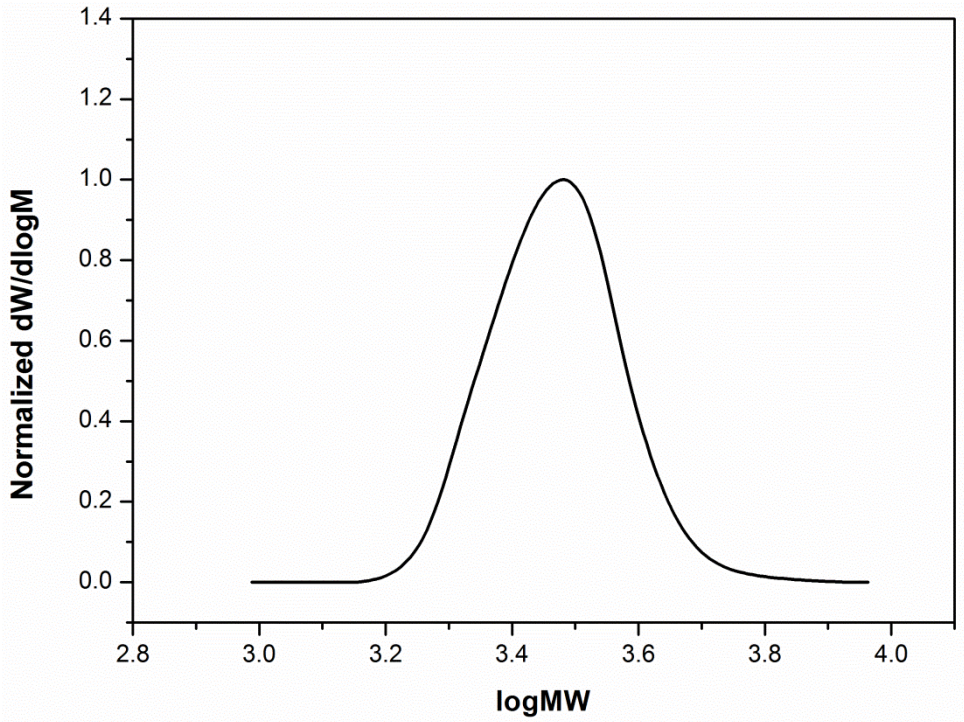
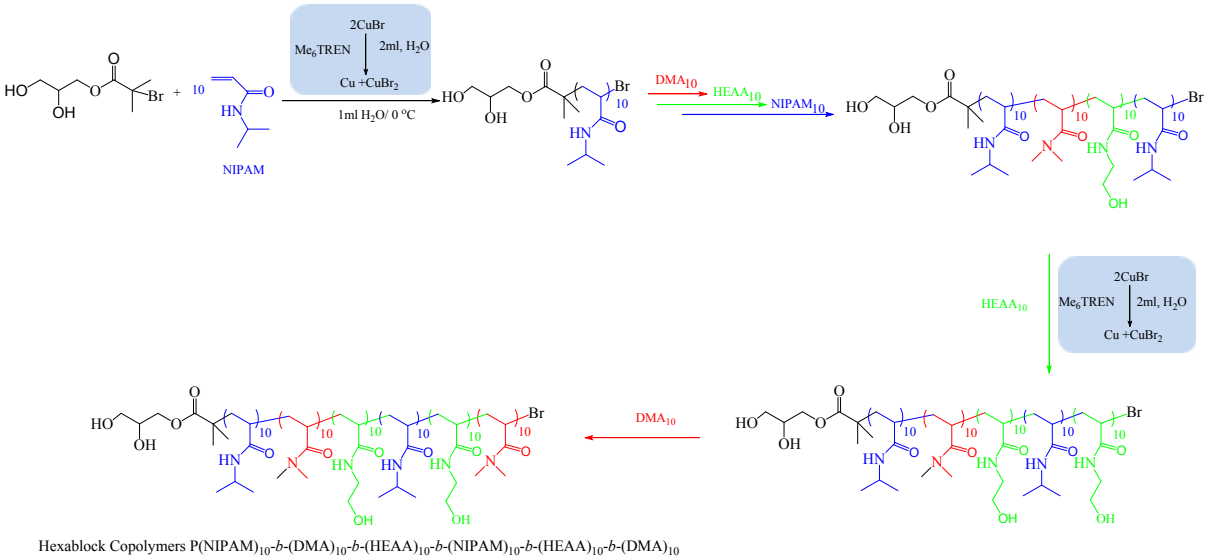


Figure S3: DMF SEC for the homopolymerization of NIPAM by aqueous SET-LRP [NIPAM] : [I] : [CuBr] : [Me_6-Tren] = [10] : [1] : [0.04] : [0.04].



Scheme S2: Synthesis of multi-block copolymers composed of NIPAM, DMA and HEAA by iterative SET-LRP in H_2O with an additional feed of catalyst with the 5th monomer addition. $[M]_0$: $[I]_0$: [CuBr] : [Me_6-Tren] = [10] : [1] : [0.04] : [0.04].

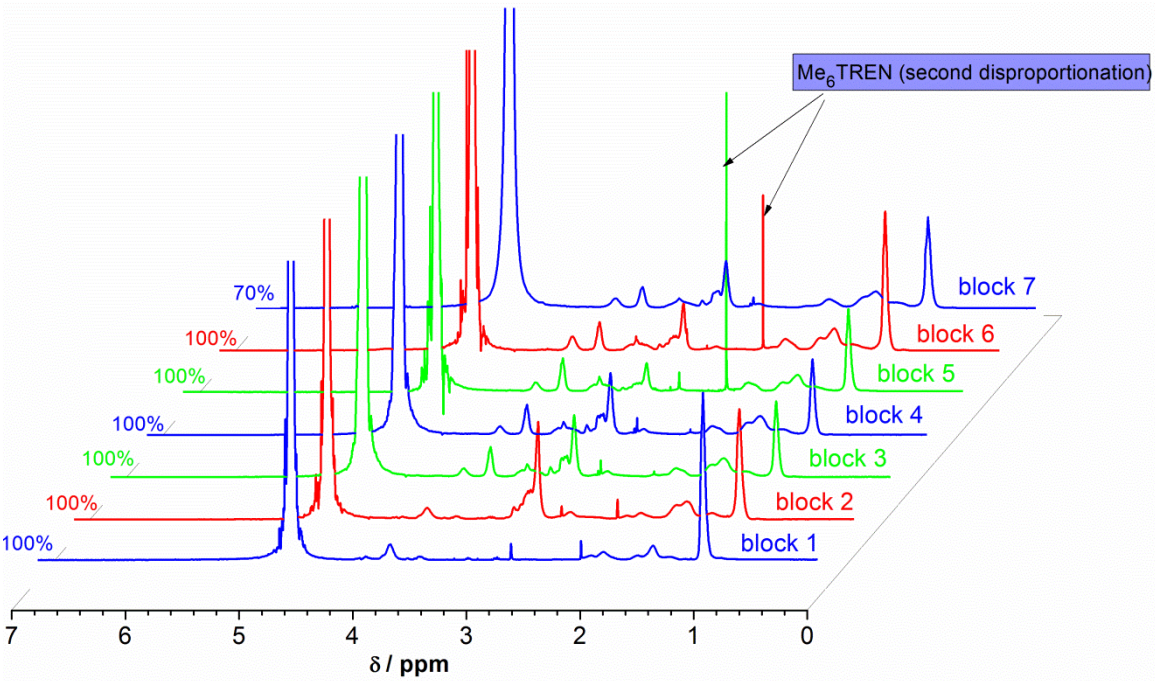


Figure S4: ^{1}NMR (D_2O) of multi-block copolymers composed of NIPAM, DMA and HEAA by iterative SET-LRP in H_2O with an additional feed of catalyst with the 5th monomer addition. $[M]_0 : [I]_0 : [CuBr] : [Me_6\text{-Tren}] = [10] : [1] : [0.04] : [0.04]$.

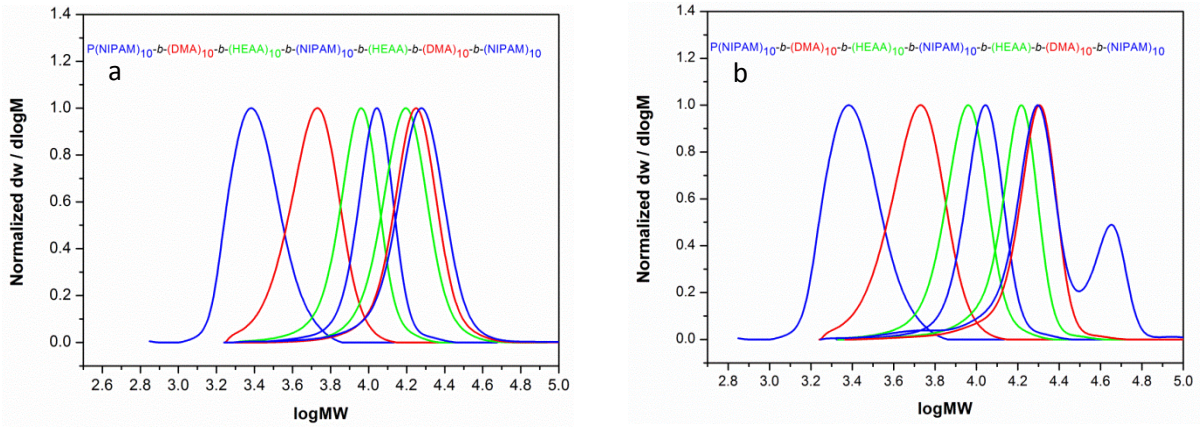
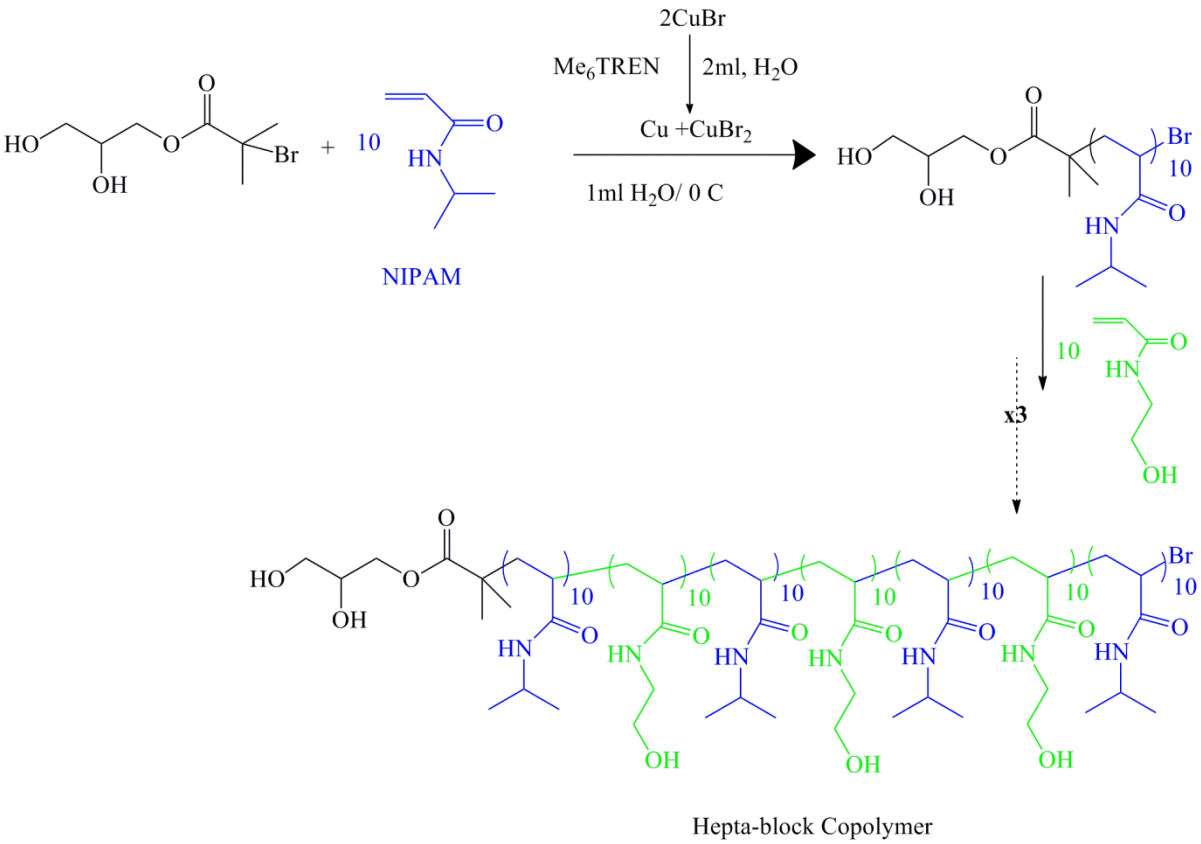


Figure S5. DMF SEC for mulitblock copolymers composed of NIPAM, HEAA and DMA (a) and NIPAM, HEAA and DMA with an addition feed of catalyst (b) in H_2O at 0 °C. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Table S2: Preparation of multi-block copolymers composed of NIPAM, DMA and HEAA by iterative SET-LRP in H_2O with an additional feed of catalyst with the 5th monomer addition. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Entry	Block number	Conv. (%)	Monomer	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	Block 1	100	NIPAM	11 (11)	1400	2700	1.09
2	Block 2	100	DMA	6 (17)	2400	4800	1.11
3	Block 3	100	HEAA	25 (42)	3500	8300	1.09
4	Block 4	100	NIPAM	40 (82)	4600	10200	1.07
5	Block 5	100	HEAA	45 (127)	5800	14500	1.09
6	Block 6	100	DMA	70 (197)	6800	17400	1.11
7	Block 7	70	NIPAM	overnight	7900	18700	1.37

[a] Cumulative time in parentheses. [b] DMF SEC, , calibrating with PMMA standard



Scheme S3: Synthesis of alternating block copolymers composed of NIPAM and HEAA by iterative SET-LRP in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Table S3: Preparation of alternating block copolymers composed of NIPAM and HEAA by iterative SET-LRP in H_2O. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Entry	Block number	Monomer	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	Block 1	NIPAM	100	11 (11)	1400	2600	1.05
2	Block 2	HEAA	99	25 (36)	2600	5100	1.10
3	Block 3	NIPAM	100	20 (56)	3800	7100	1.09
4	Block 4	HEAA	98	24 (80)	5000	9900	1.10
5	Block 5	NIPAM	100	30 (110)	6200	12200	1.08
6	Block 6	HEAA	98	50 (160)	7400	15600	1.10
7	Block 7	NIPAM	100	60 (240)	8600	18800	1.07

[a] Cumulative time in parentheses. [b] DMF SEC, , calibrating with PMMA standard

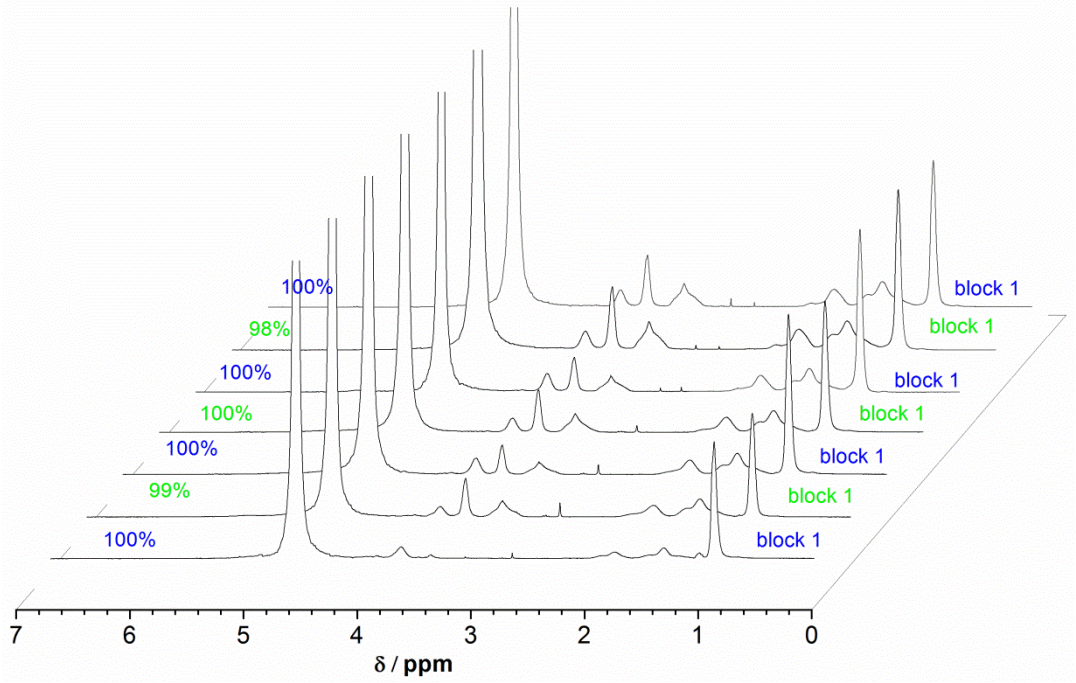


Figure S6: ^{1}H NMR (D_2O) showing the conversions for alternating block copolymers composed of NIPAM and HEAA by iterative SET-LRP in H_2O. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Table S4: Preparation of alternating block copolymers composed of NIPAM and DMA by iterative SET-LRP in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Entry	Block number	Monomer	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	Block 1	NIPAM	100	11 (11)	1400	2600	1.06
2	Block 2	DMA	100	6 (17)	2400	5200	1.09
3	Block 3	NIPAM	99	20 (37)	3500	7600	1.07
4	Block 4	DMA	99	15 (52)	4500	10900	1.10
5	Block 5	NIPAM	99	40 (92)	5600	13400	1.12
6	Block 6	DMA	90	180 (272)	6600	15400	1.22
7	Block 7	NIPAM	0	180 (452)	7700	16300	1.21

[a] Cumulative time in parentheses. [b] DMF SEC, , calibrating with PMMA standard

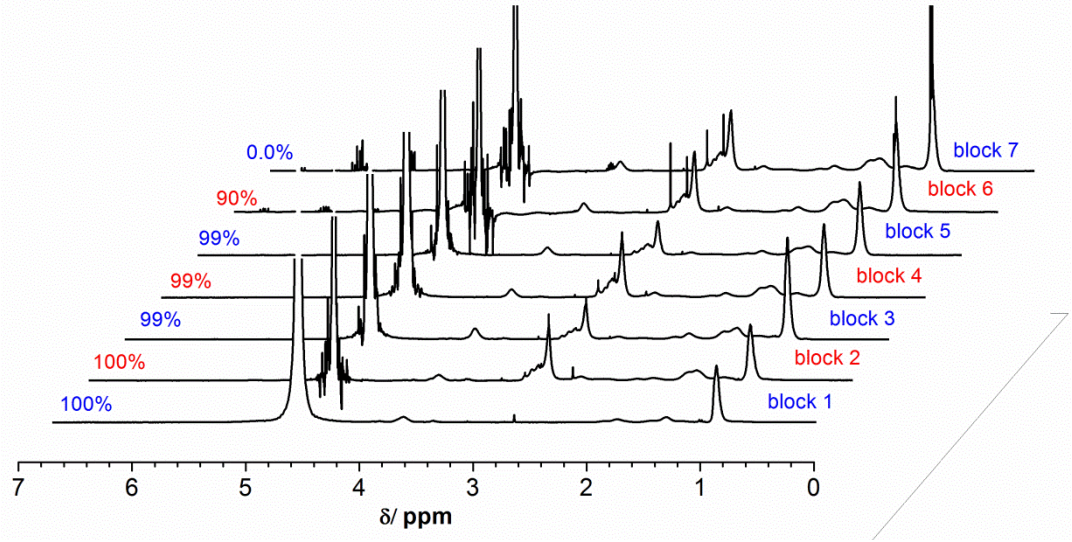


Figure S7: ^1H NMR (D_2O) showing the conversions for alternating block copolymers composed of NIPAM and DMA by iterative SET-LRP in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

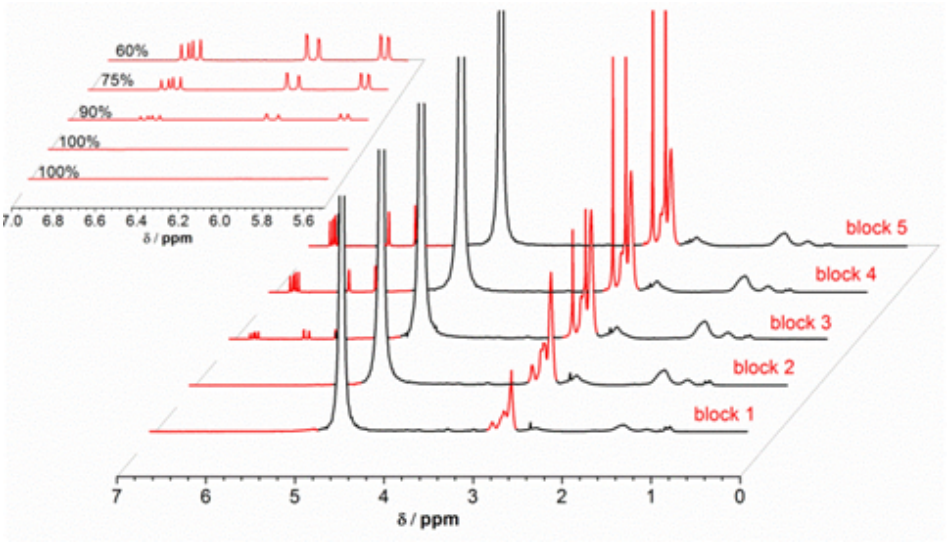


Figure S8. ^{1}H NMR analyses for aqueous SET-LRP of multi-block homopolymers of DMA (a, b). $[M]_0 : [I]_0 : [CuBr] : [Me_6$

TREN] = [10] : [1] : [0.04] : [0.04].

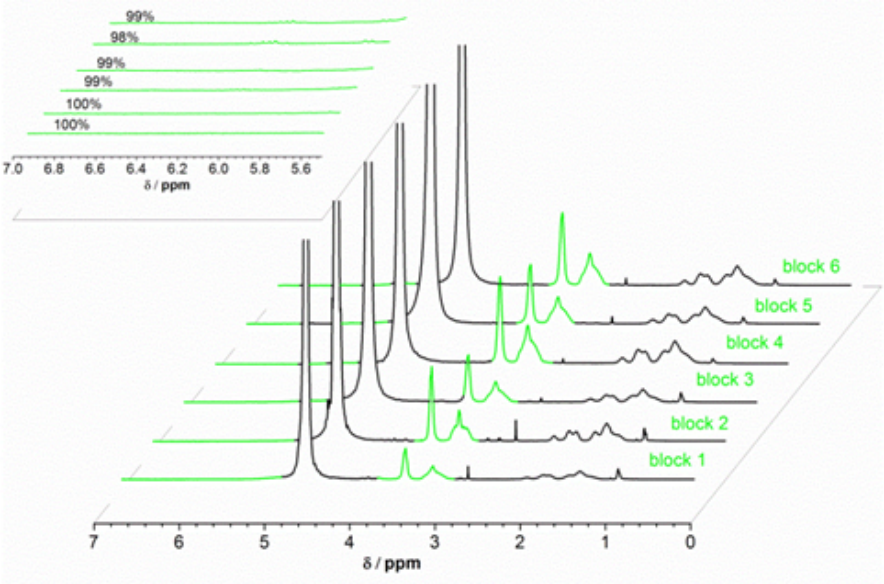


Figure S9. ^{1}H NMR analyses for aqueous SET-LRP of multi-block homopolymers of HEAA. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

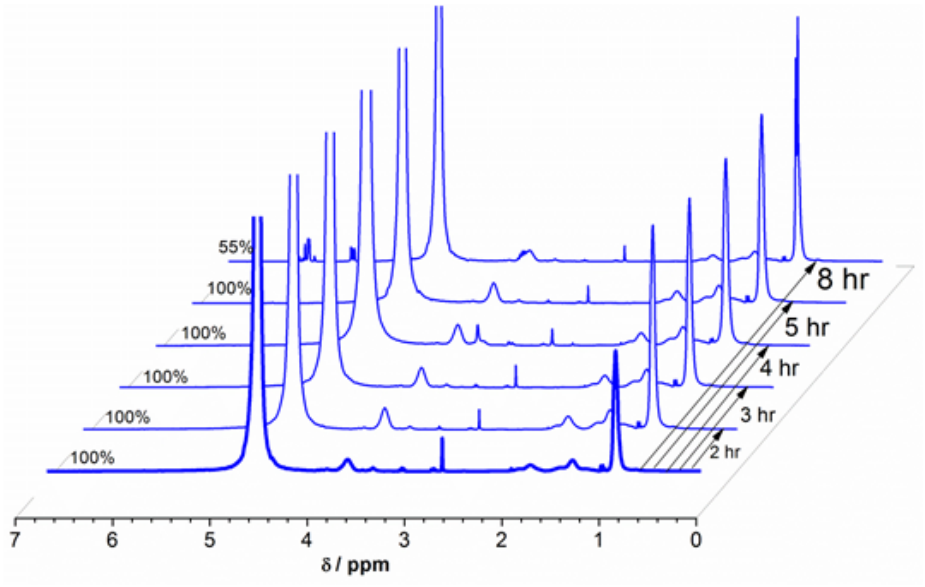


Figure S10. Assessment of the chain end fidelty of PNIPAM by in situ chain extension using deoxygenated NIPAM (10 eq). ^{1}H NMR following chain extension at delayed feed times. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Table S5: Preparation of multi-block homopolymers prepared by sequential additon of deoxygenated aliquots of aqueous HEAA (10 eq) to PHEAA during SET-LRP at 0 °C in H_2O. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Entry	Monomer	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	HEAA	100	25 (25)	1400	4500	1.08
2	HEAA	100	20 (45)	2500	7200	1.09
3	HEAA	99	20 (65)	3700	10700	1.06
4	HEAA	99	20 (85)	4800	13700	1.05
5	HEAA	98	70 (155)	6000	16900	1.06
6	HEAA	100	70 (225)	7100	20900	1.07

[a] Cumulative time in parentheses. [b] DMF SEC, calibrating with PMMA standard.

Table S6: Preparation of multi-block homopolymers prepared by sequential additon of deoxygenated aliquots of aqueous DMA (10 eq) to PDMA during SET-LRP at 0 °C in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Entry	Monomer	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	DMA	98	6 (6)	1200	3100	1.08
2	DMA	100	20 (26)	2200	5100	1.10
3	DMA	90	20 (46)	3200	8000	1.17
4	DMA	74	20 (66)	4200	90010	1.25
5	DMA	60	120 (186)	5200	10200	1.30

[a] Cumulative time in parentheses. [b] DMF SEC, calibrating with PMMA standard.

Table S7: Investigating the effect of time of chain end fidelity of PNIPAM under aqueous SET-LRP conditions. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[a] g.mol^{-1}	$Đ$[a]
1	NIPAM	100	2	1400	2600	1.05
	NIPAM	100	overnight	2500	4500	1.09
2	NIPAM	100	3	1400	2600	1.05
	NIPAM	100	overnight	2500	4300	1.07
3	NIPAM	100	4	1400	2600	1.05
	NIPAM	100	overnight	2500	4200	1.11
4	NIPAM	100	5	1400	2600	1.05
	NIPAM	100	overnight	2500	4600	1.08
5	NIPAM	100	8	1400	2600	1.05
	NIPAM	50	overnight	2500	3500	1.16

[a] DMF SEC, calibrating with PMMA standard.

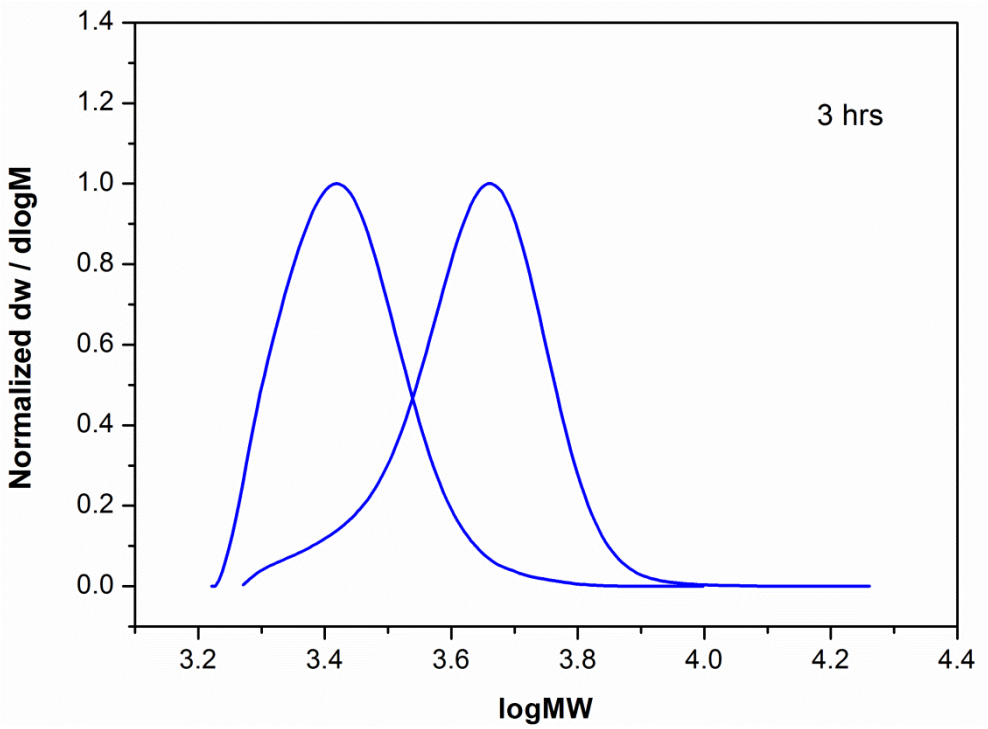


Figure S11: DMF SEC for the chain extension of PNIPAM with deoxygenated aqueous NIPAM (10 eq) after a 3 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

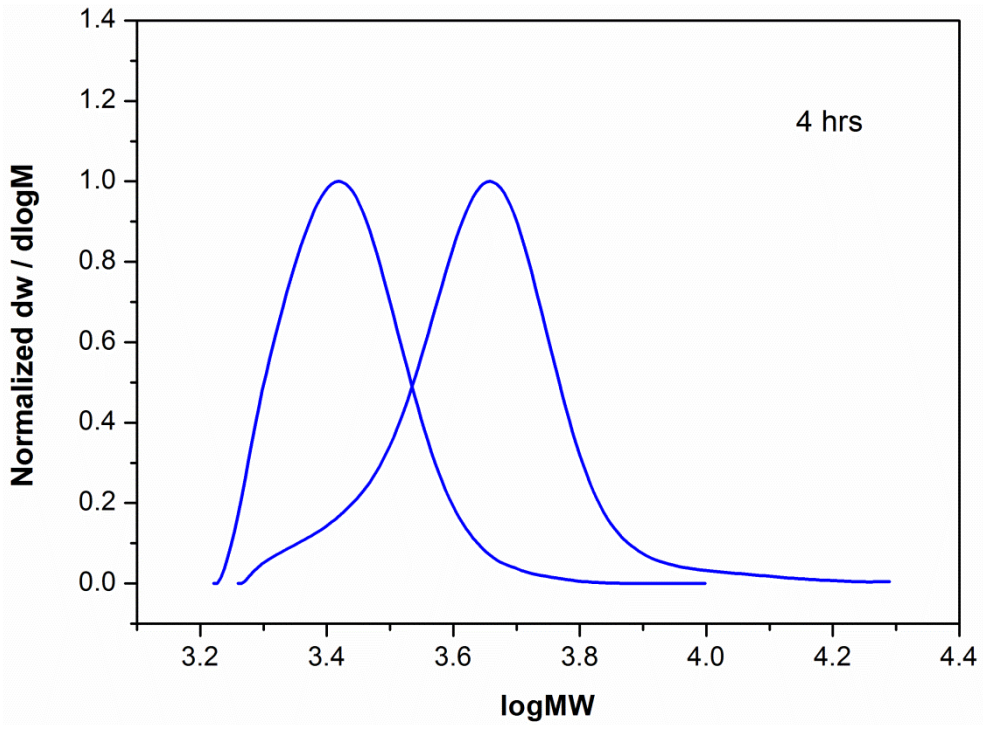


Figure S12: DMF SEC for the chain extension of PNIPAM with deoxygenated aqueous NIPAM (10 eq) after a 4 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

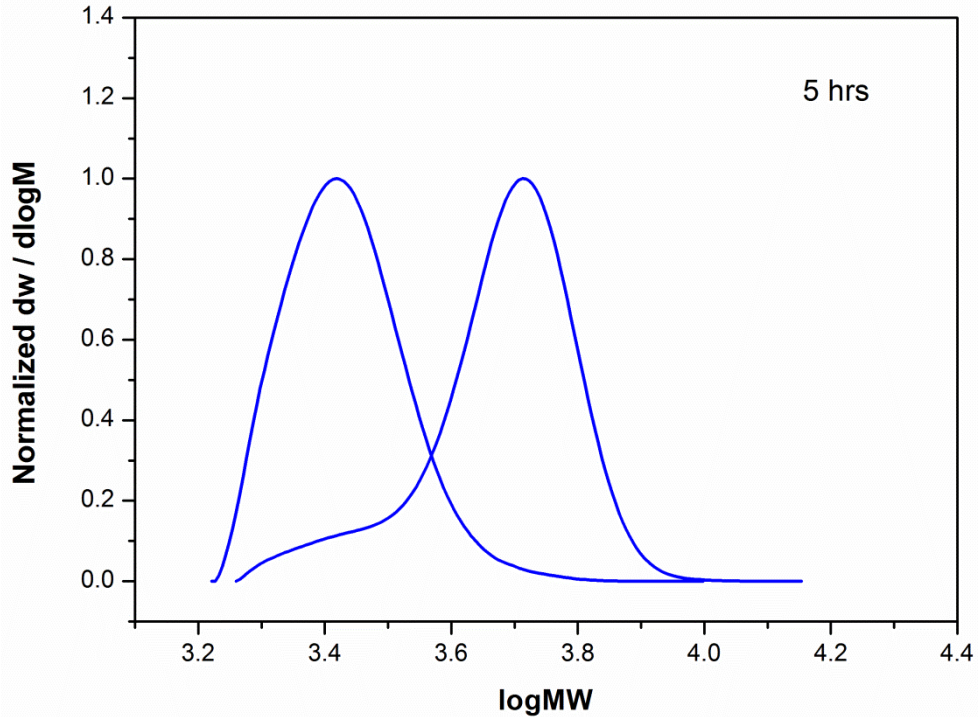


Figure S13: DMF SEC for the chain extension of PNIPAM with deoxygenated aqueous NIPAM (10 eq) after a 5 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Table S8: Investigating the effect of time of chain end fidelity of PHEAA under aqueous SET-LRP conditions. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	HEAA	100	2	1400	3600	1.07
	NIPAM	100	overnight	2500	5500	1.07
2	HEAA	100	3	1400	3600	1.09
	NIPAM	100	overnight	2500	4900	1.08
3	HEAA	100	4	1400	3600	1.07
	NIPAM	95	overnight	2500	5000	1.07
4	HEAA	100	5	1400	3600	1.07
	NIPAM	75	overnight	2500	4400	1.09

[a] DMF SEC, calibrating with PMMA standard.

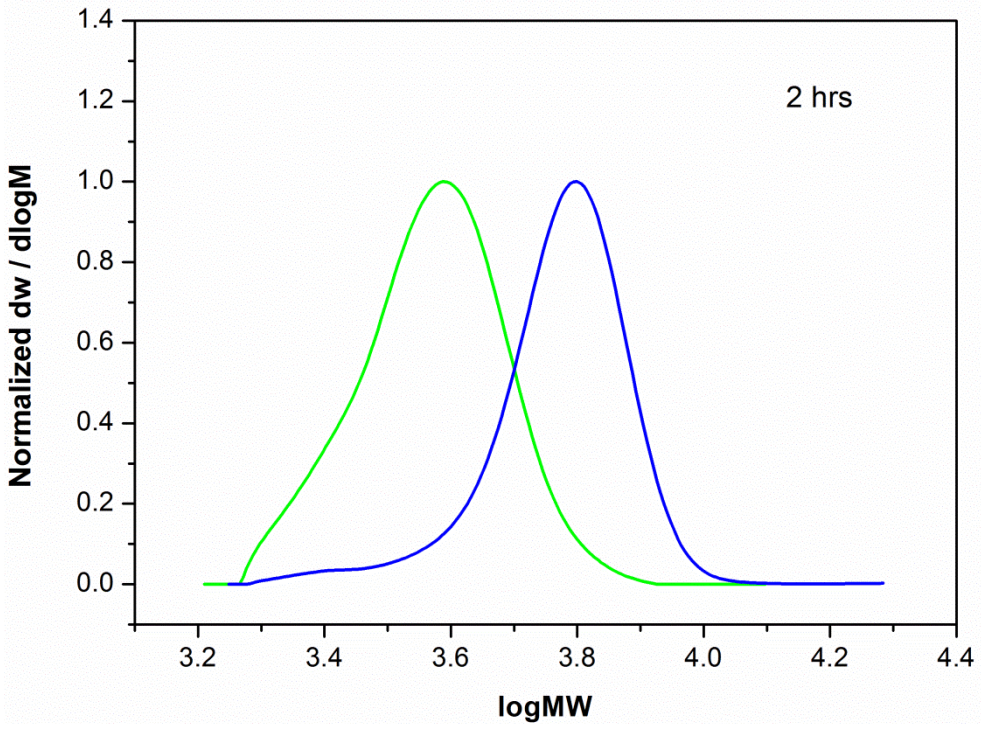


Figure S14: DMF SEC for the chain extension of PHEAA with deoxygenated aqueous NIPAM (10 eq) after a 2 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

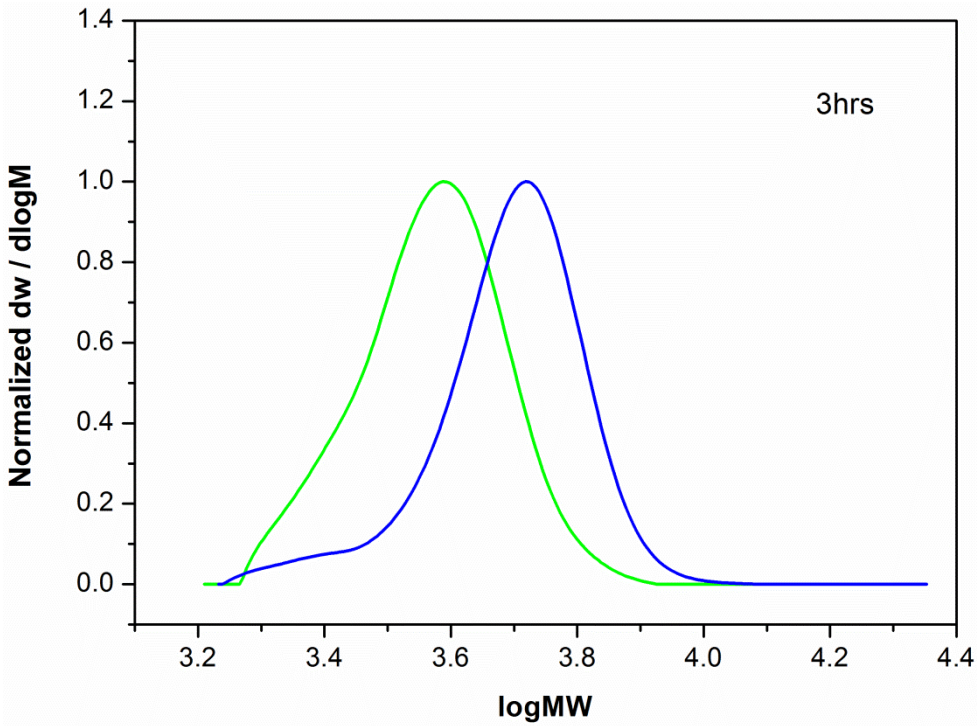


Figure S15: DMF SEC for the chain extension of PHEAA with deoxygenated aqueous NIPAM (10 eq) after a 3 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

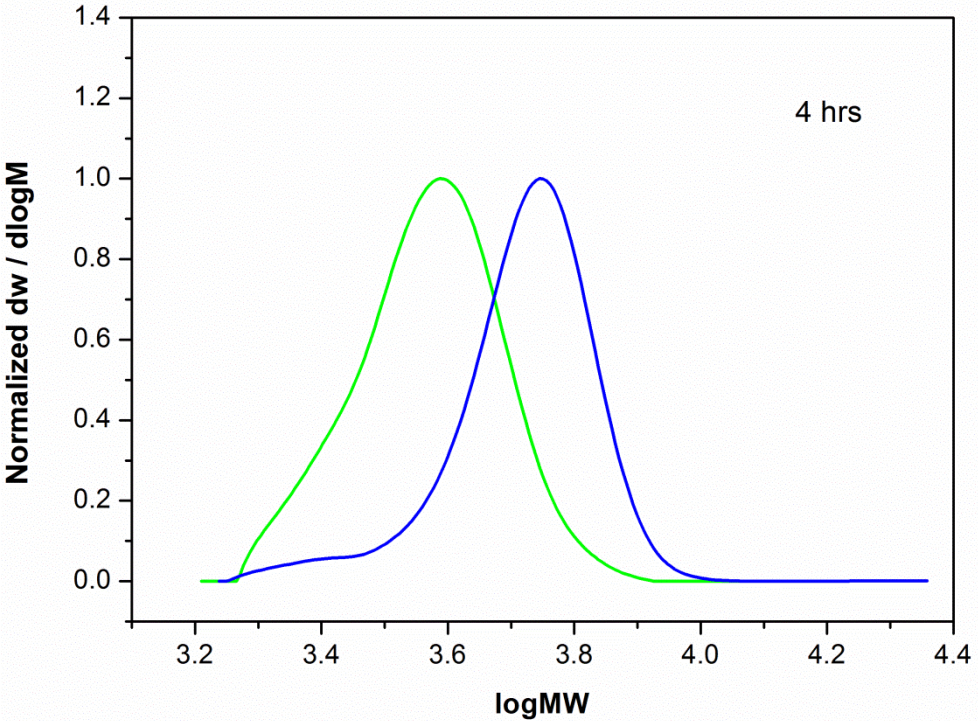


Figure S16: DMF SEC for the chain extension of PHEAA with deoxygenated aqueous NIPAM (10 eq) after a 4 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

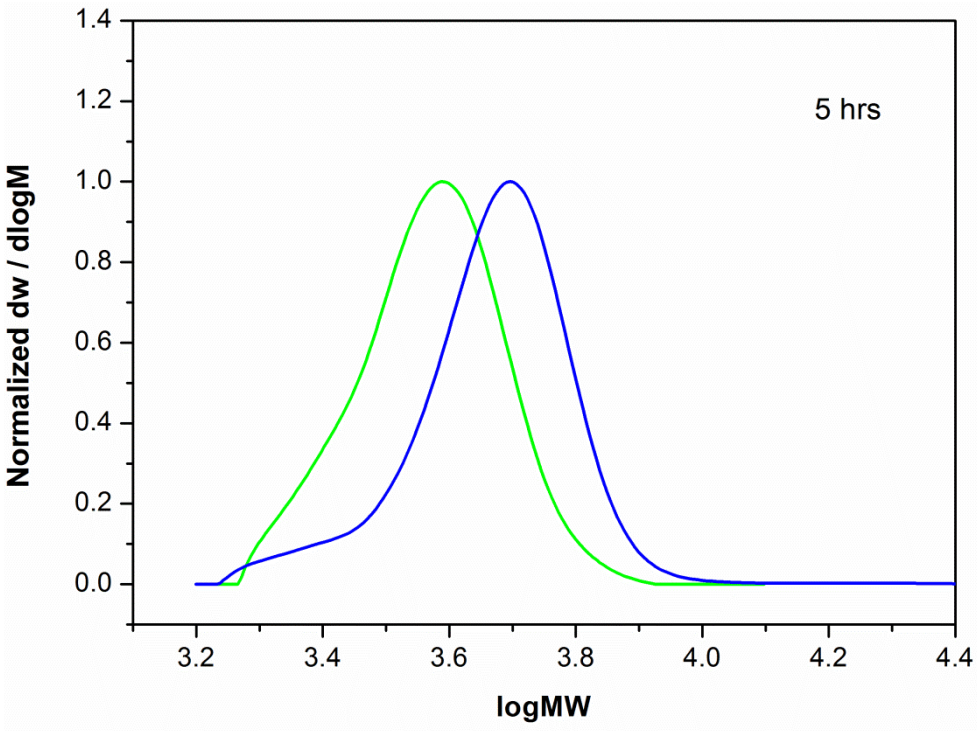


Figure S17: DMF SEC for the chain extension of PHEAA with deoxygenated aqueous NIPAM (10 eq) after a 5 hour delay. $[M]_0$: $[I]_0$: [CuBr] : $[Me_6TREN]$ = [10] : [1] : [0.04] : [0.04].

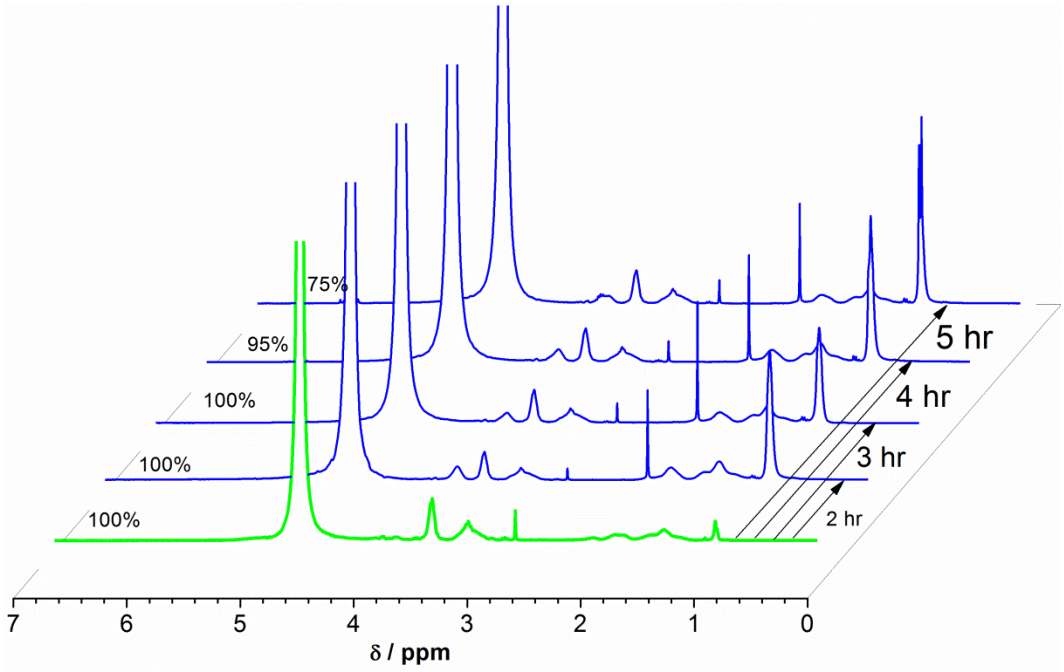


Figure S18: ^{1}NMR (D_2O) for the chain extension of PHEAA with deoxygenated aqueous NIPAM (10 eq) after various time delays.

Table S9: Investigating the effect of time of chain end fidelity of PDMA under aqueous SET-LRP conditions. $[M]_0$: $[I]_0$: [CuBr] : $[Me_6TREN]$ = [10] : [1] : [0.04] : [0.04].

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	DMA	100	0.5	1200	2400	1.04
	NIPAM	100	overnight	2300	4400	1.10
2	DMA	100	1	1200	2500	1.07
	NIPAM	20	overnight	2300	3100	1.11
3	DMA	100	2	1200	2600	1.07
	NIPAM	15	overnight	2300	2700	1.08

[a] DMF SEC, calibrating with PMMA standard.

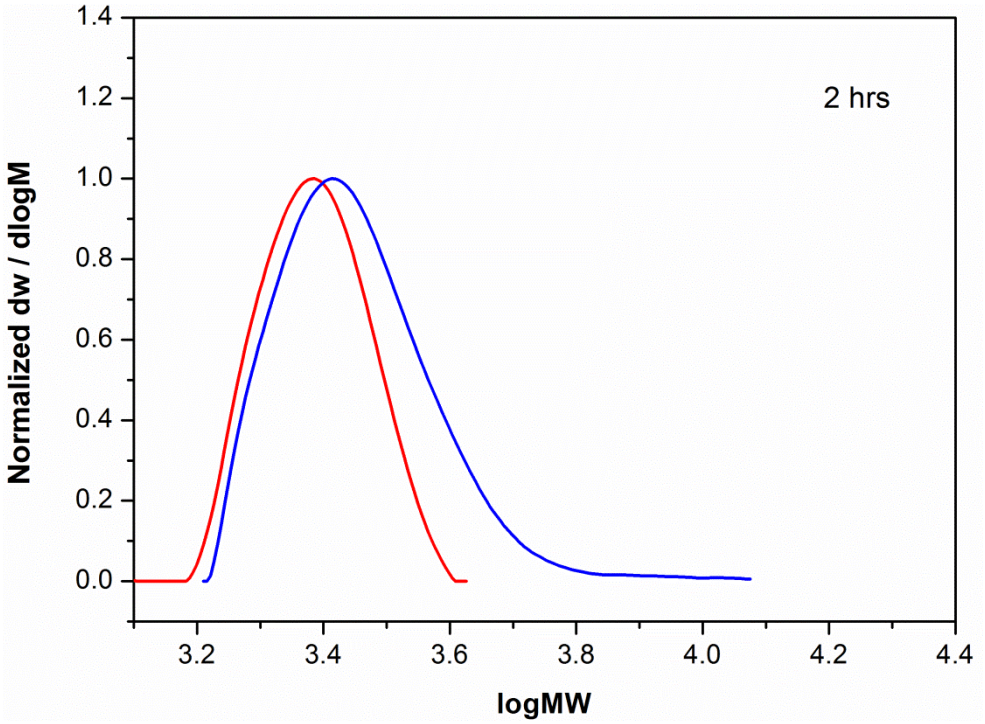


Figure S19: DMF SEC for the chain extension of PDMA with deoxygenated aqueous NIPAM (10 eq) after a 2 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

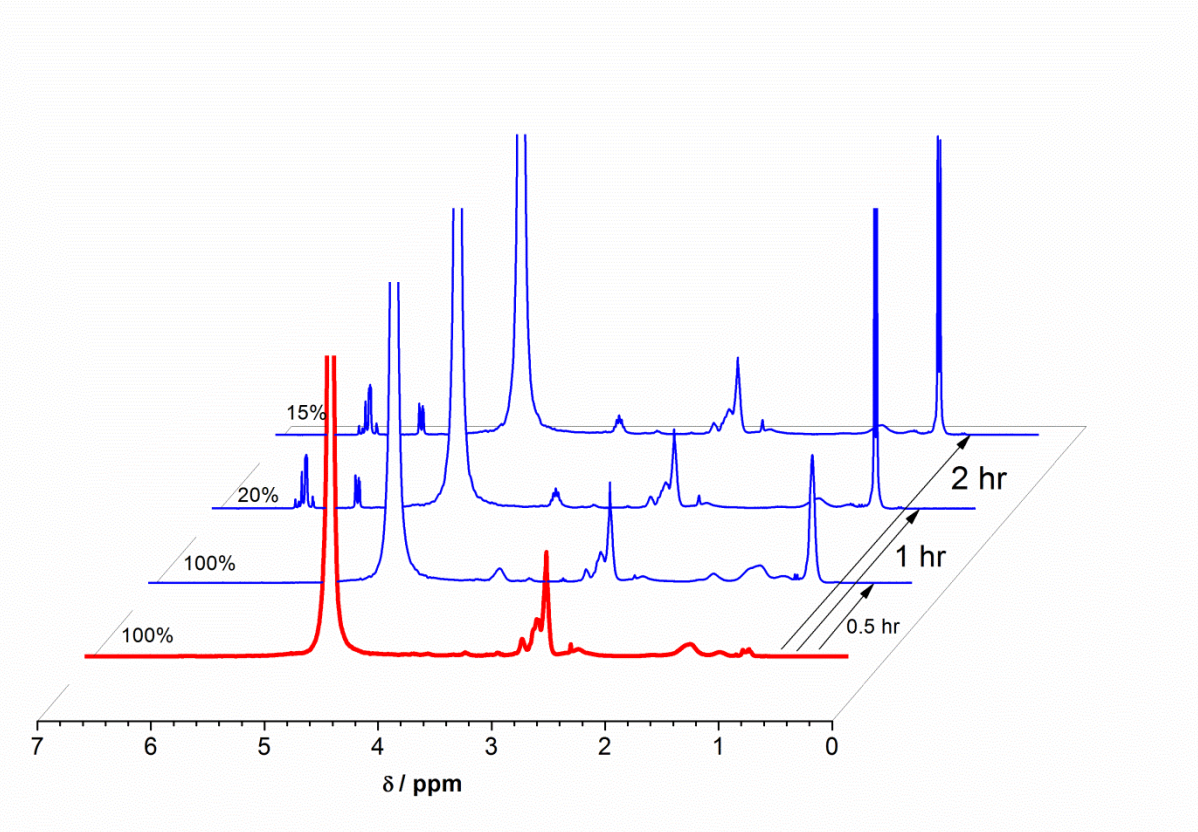


Figure S20: Assessment of the chain end fidelty of PDMA by in situ chain extension using deoxygenated NIPAM (10 eq).^{1}H NMR (c) following chain extension at delayed feed times. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Table S10: Investigating the effect of time of chain end fidelity of PNAM under aqueous SET-LRP conditions. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	NAM	100	0.5	1400	3400	1.09
	NIPAM	100	overnight	2500	6300	1.32
2	NAM	100	1	1400	3400	1.09
	NIPAM	45	overnight	2500	4500	1.30
3	NAM	100	2	1400	3500	1.06
	NIPAM	20	overnight	2500	3500	1.08

[a] DMF SEC, calibrating with PMMA standard.

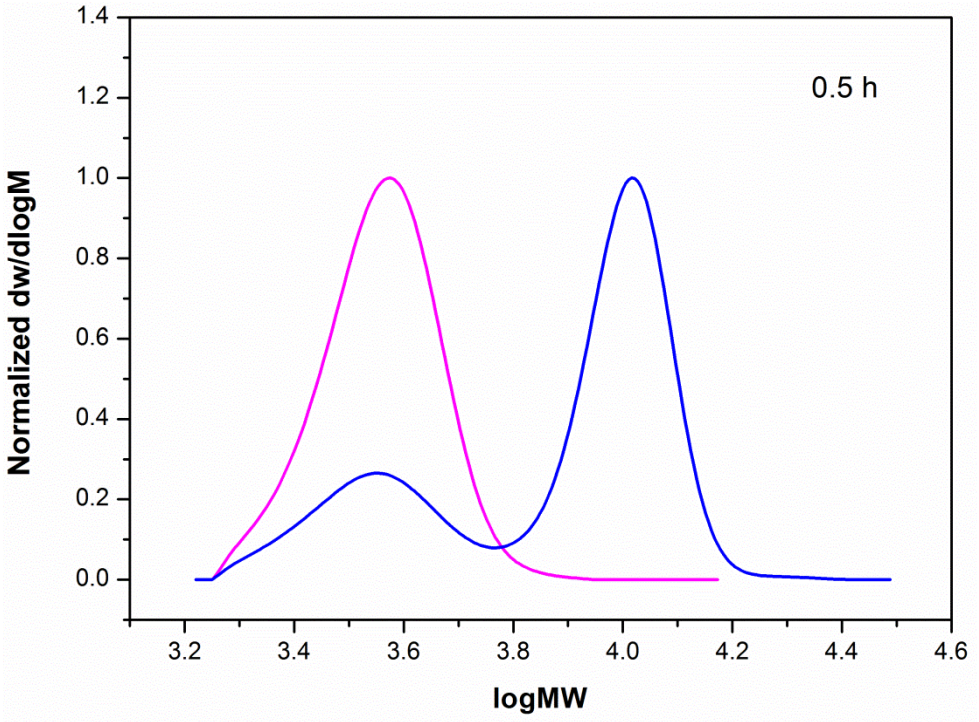


Figure S21: DMF SEC for the chain extension of PNAM with deoxygenated aqueous NIPAM (10 eq) after a 0.5 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

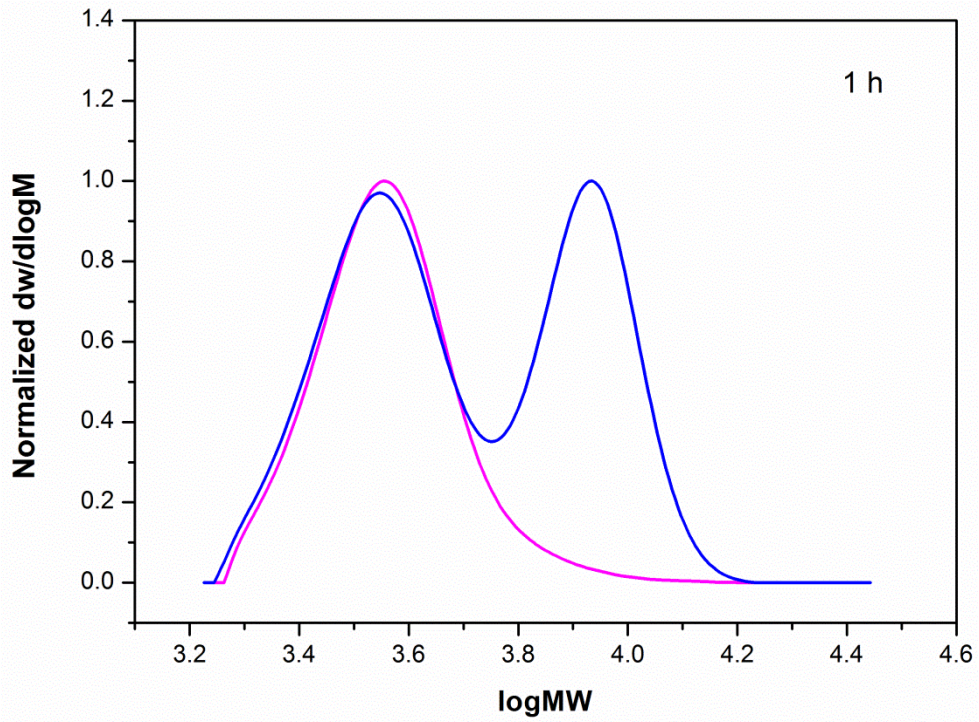


Figure S22: DMF SEC for the chain extension of PNAM with deoxygenated aqueous NIPAM (10 eq) after a 1 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

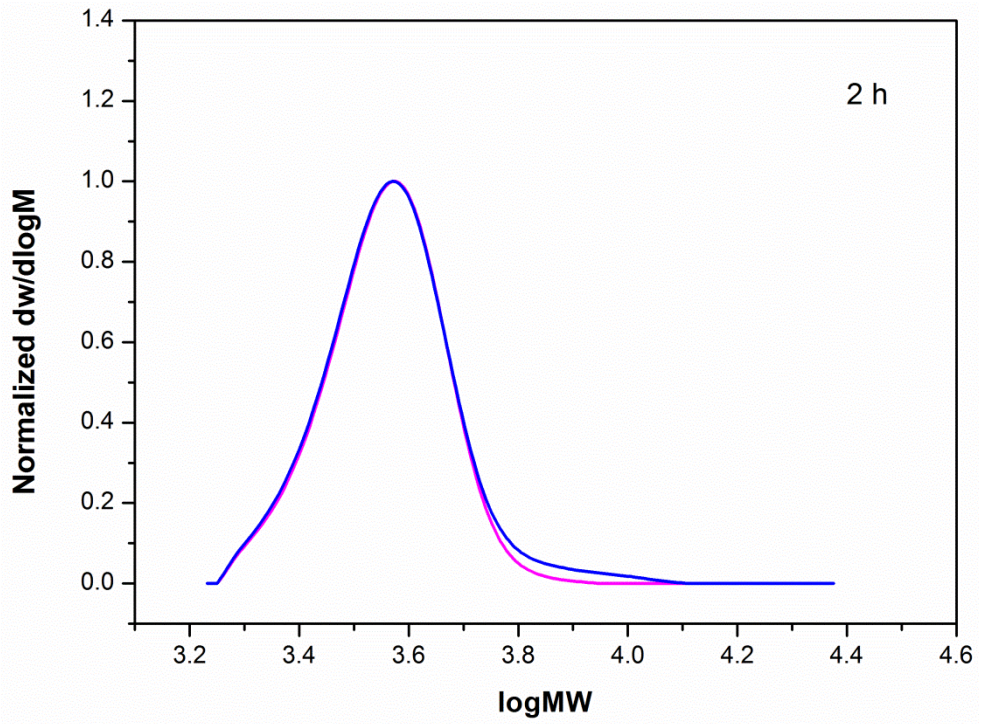


Figure S23: DMF SEC for the chain extension of PNAM with deoxygenated aqueous NIPAM (10 eq) after a 2 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

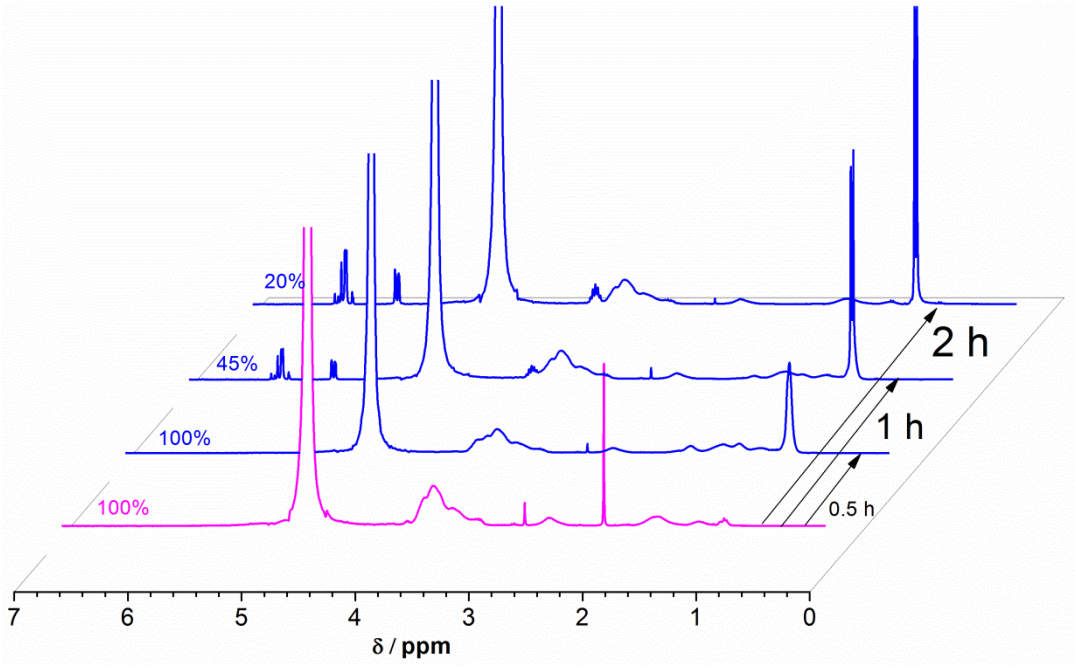


Figure S24: ^{1}NMR (D_2O) for the chain extension of PNAM with deoxygenated aqueous NIPAM (10 eq) after various time delays.

Table S11: Investigating the effect of time of chain end fidelity of PDEA under aqueous SET-LRP conditions. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	DEA	100	0.5	1500	2600	1.53
	NIPAM	98	overnight	2600	3200	1.15
2	DEA	100	1	1500	2600	1.51
	NIPAM	65	overnight	2600	3300	1.40
3	DEA	100	2	1500	2600	1.53
	NIPAM	30	overnight	2600	2600	1.54

[a] DMF SEC, calibrating with PMMA standard.

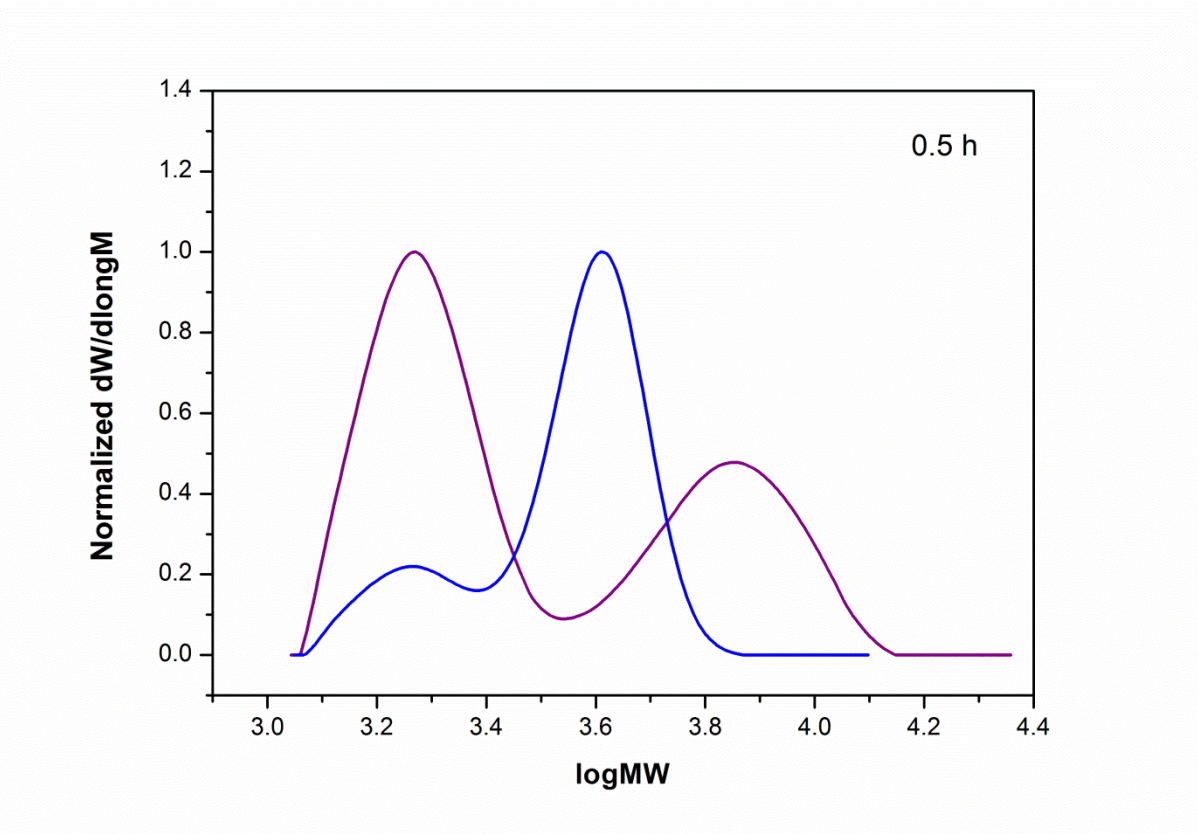


Figure S25: DMF SEC for the chain extension of PDEA with deoxygenated aqueous NIPAM (10 eq) after a 0.5 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

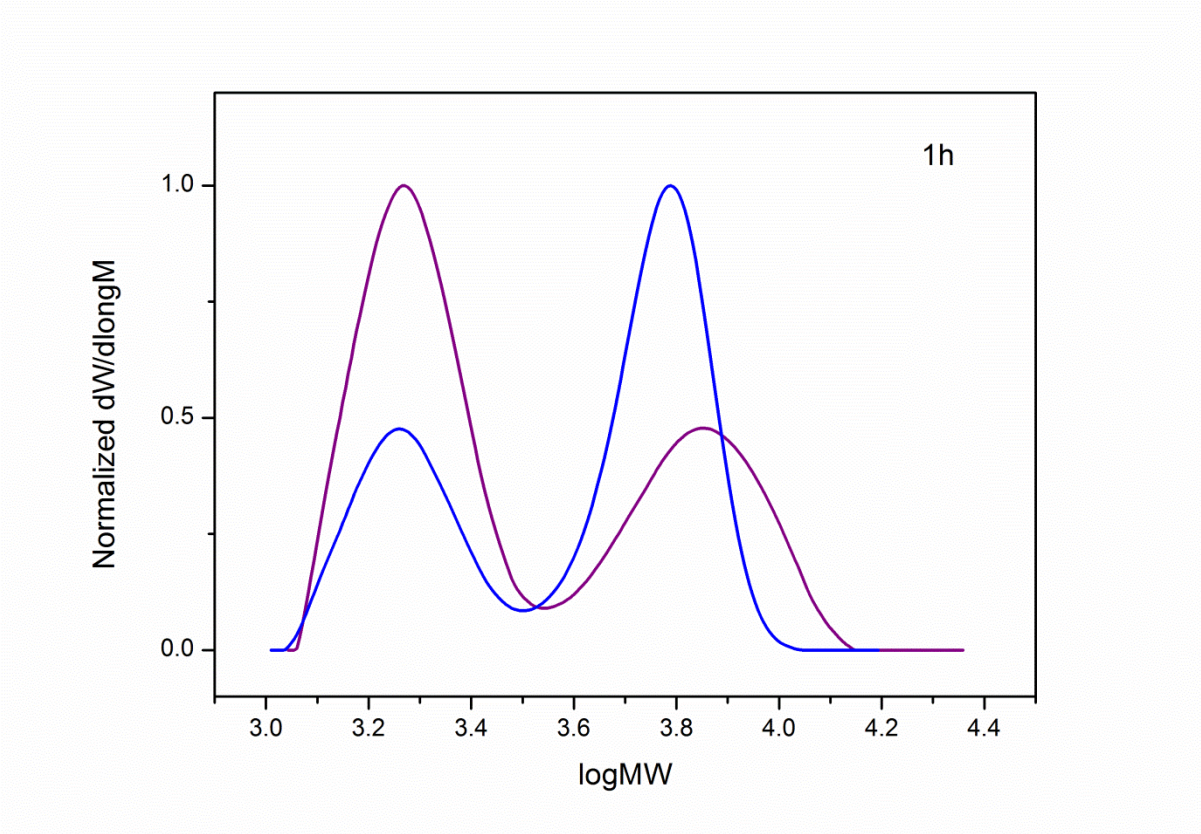


Figure S26: DMF SEC for the chain extension of PDEA with deoxygenated aqueous NIPAM (10 eq) after a 1 hour delay. $[M]_0$: $[I]_0$: [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04].

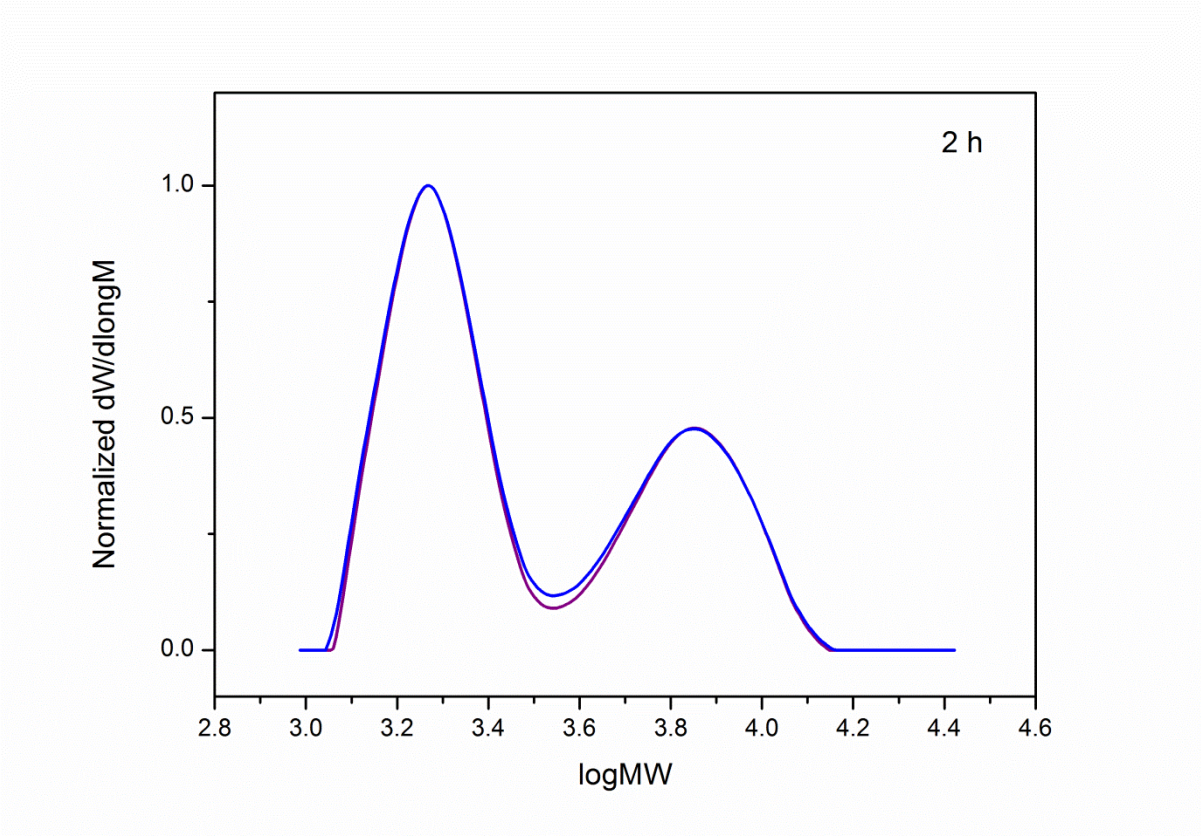


Figure S27: DMF SEC for the chain extension of PDEA with deoxygenated aqueous NIPAM (10 eq) after a 2 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

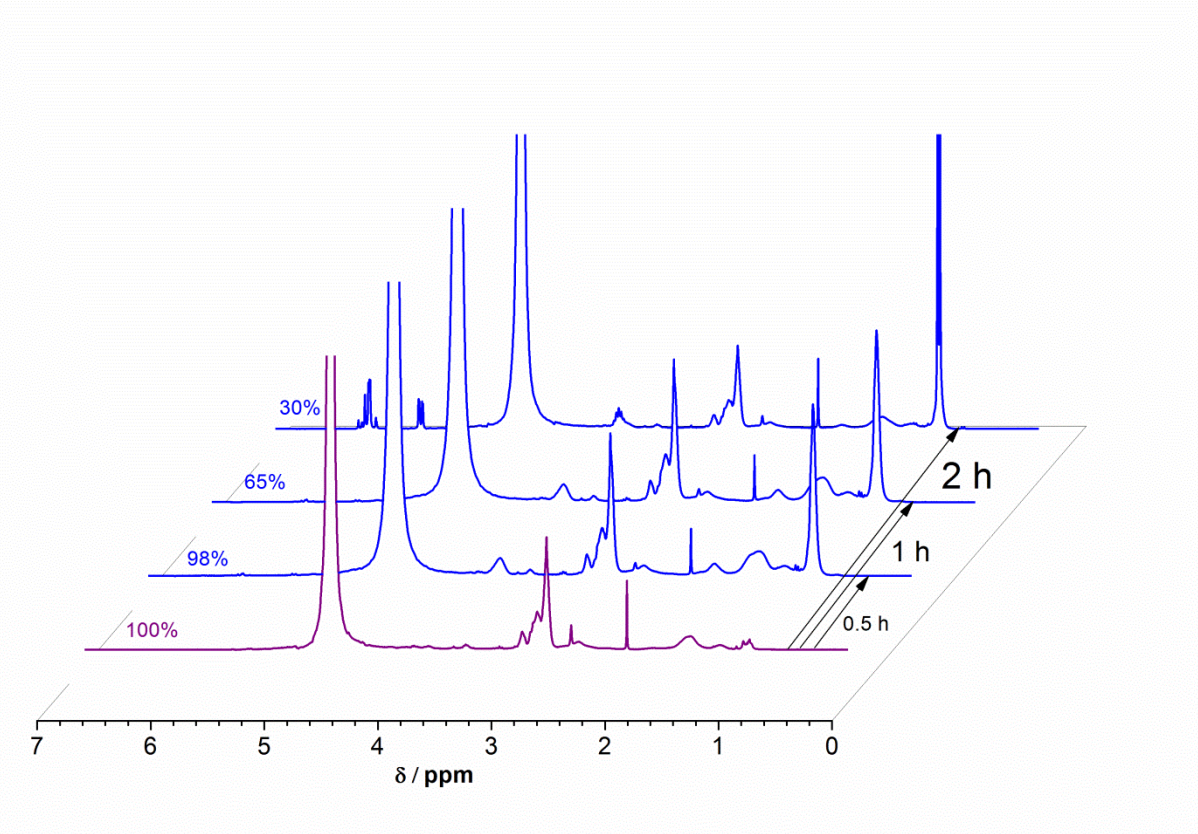


Figure S28: ^{1}NMR (D_2O) for the chain extension of PDEA with deoxygenated aqueous NIPAM (10 eq) after various time delays.

Table S12: Investigating the effect of time of chain end fidelity of PNIPAM under aqueous SET-LRP conditions. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	NIPAM	100	2	1400	2400	1.07
	DMA	100	overnight	2400	4600	1.07
2	NIPAM	100	3	1400	2400	1.09
	DMA	97	overnight	2400	5200	1.11
3	NIPAM	100	4	1400	2400	1.07
	DMA	28	overnight	2400	3800	1.12
4	NIPAM	100	10	1400	2400	1.07
	DMA	00	overnight	2400	2500	1.09

[a] DMF SEC, calibrating with PMMA standard.

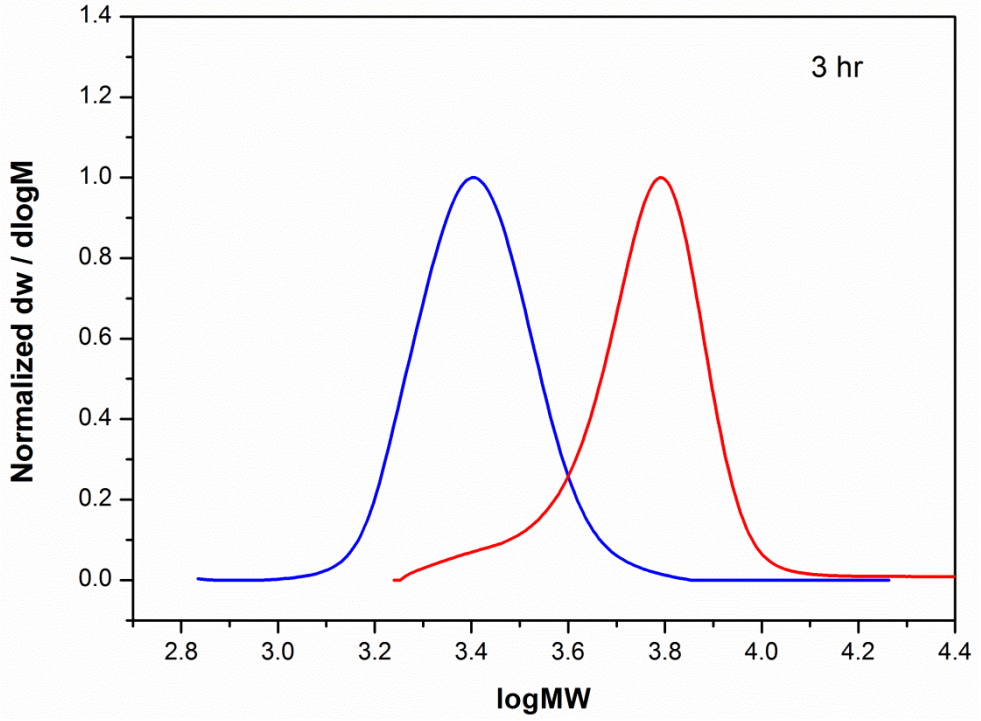


Figure S29: DMF SEC for the chain extension of PNIPAM with deoxygenated aqueous DMA (10 eq) after a 3 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

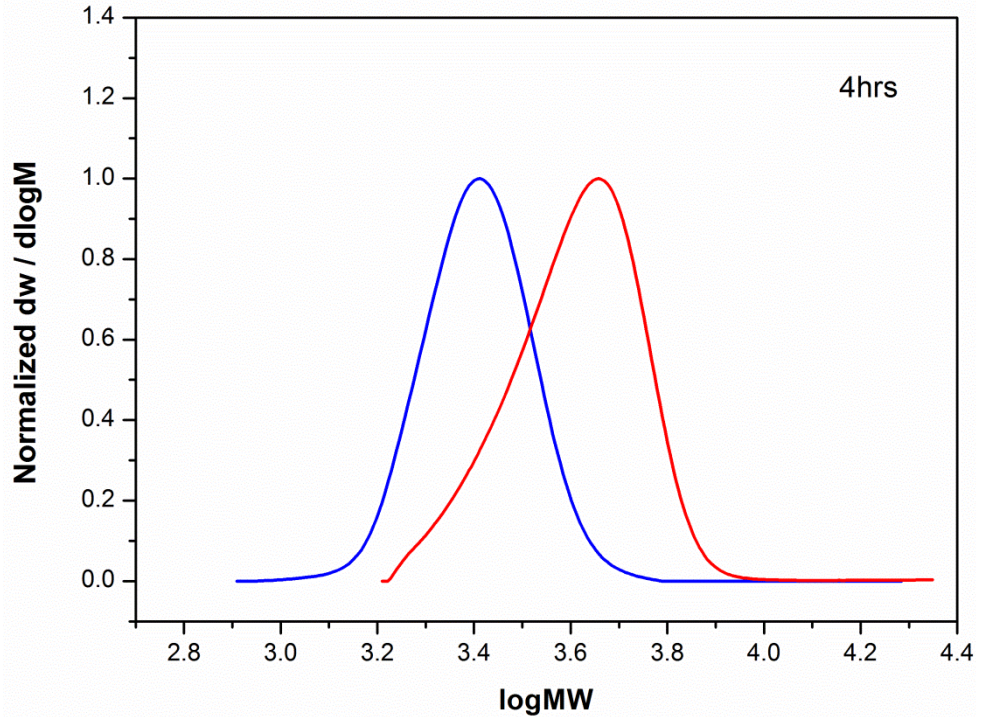


Figure S30: DMF SEC for the chain extension of PNIPAM with deoxygenated aqueous DMA (10 eq) after a 4 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

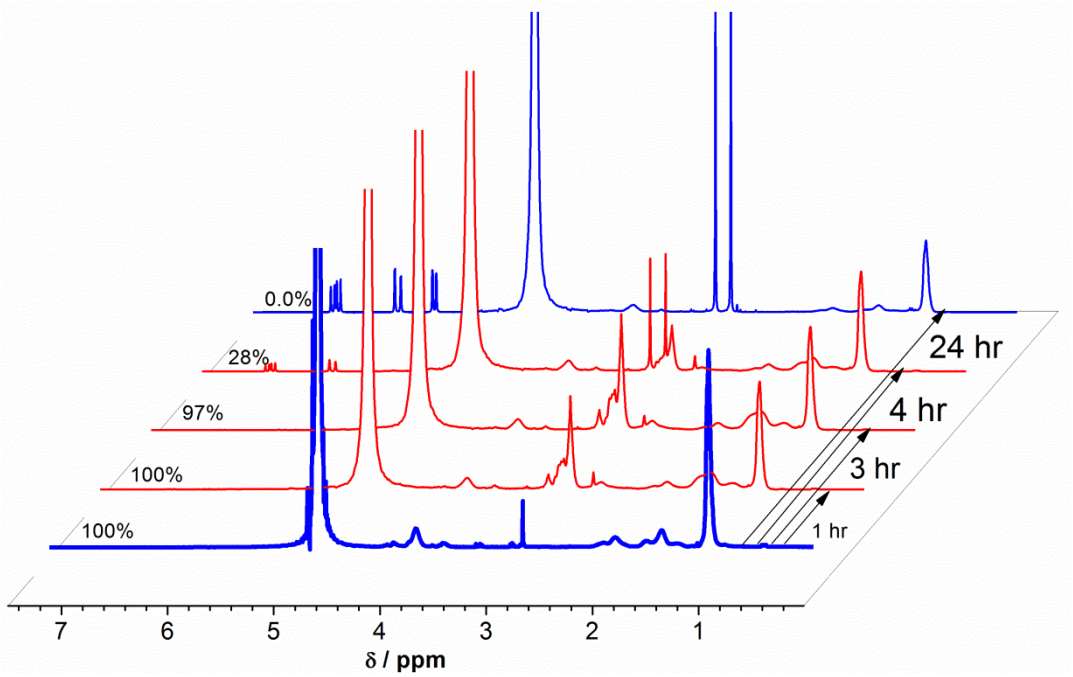


Figure S31: ^{1}NMR (D_2O) for the chain extension of PNIPAM with deoxygenated aqueous DMA (10 eq) after various time delays.

Table S13: Investigating the effect of time of chain end fidelity of PNIPAM under aqueous SET-LRP conditions. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

Reaction No.	Monomer	Conv. (%)	Time per block (hr)	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}{}^{a}$ g.mol^{-1}	$Đ^{a}$
1	DMA	100	0.5	1200	2800	1.08
	DMA	100	overnight	2200	5600	1.27
2	DMA	100	1	1200	2700	1.06
	DMA	50	overnight	2200	40000	1.34
3	DMA	100	2	1200	2700	1.06
	DMA	15	overnight	2200	2800	1.15

[a] DMF SEC, calibrating with PMMA standard.

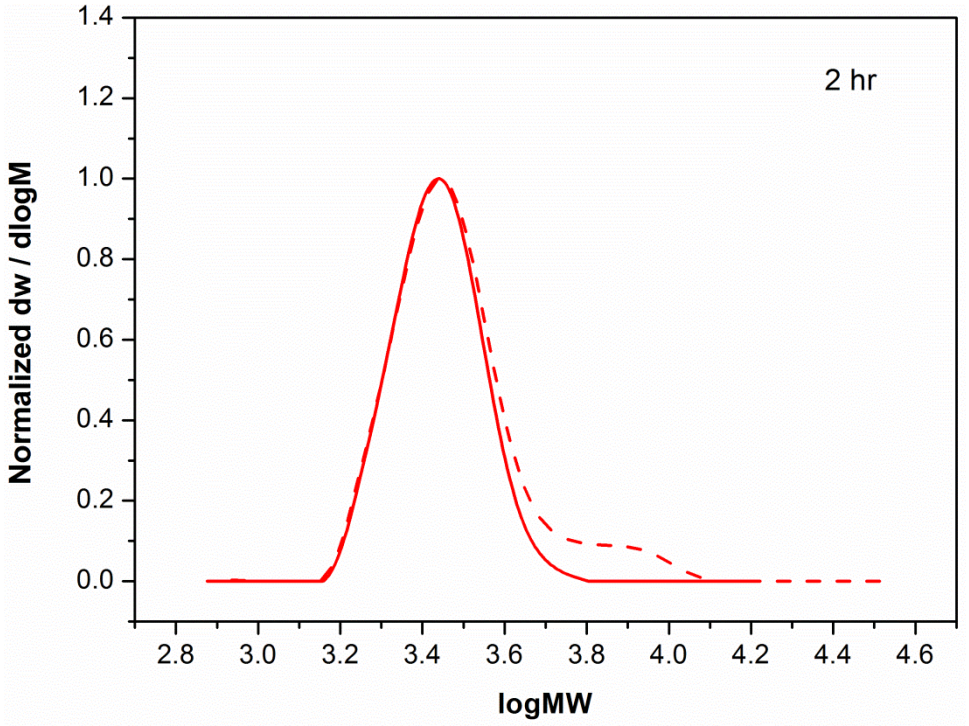


Figure S32: DMF SEC for the chain extension of PDMA with deoxygenated aqueous DMA (10 eq) after a 2 hour delay. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [10] : [1] : [0.04] : [0.04]$.

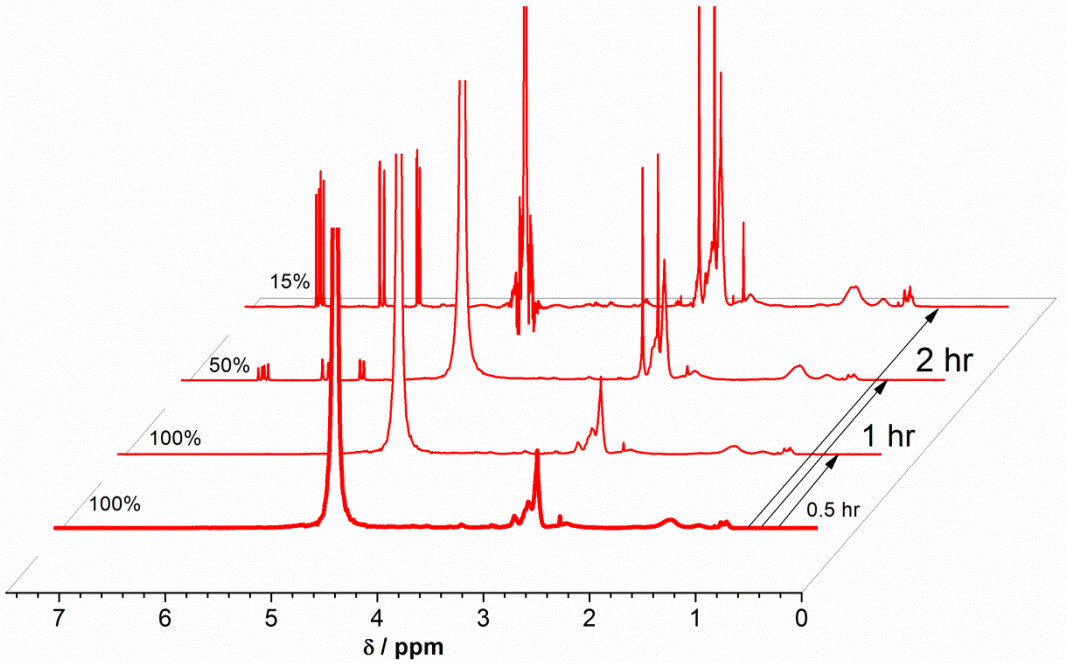


Figure S33: ^{1}NMR (D_2O) for the chain extension of PDMA with deoxygenated aqueous DMA (10 eq) after various time delays

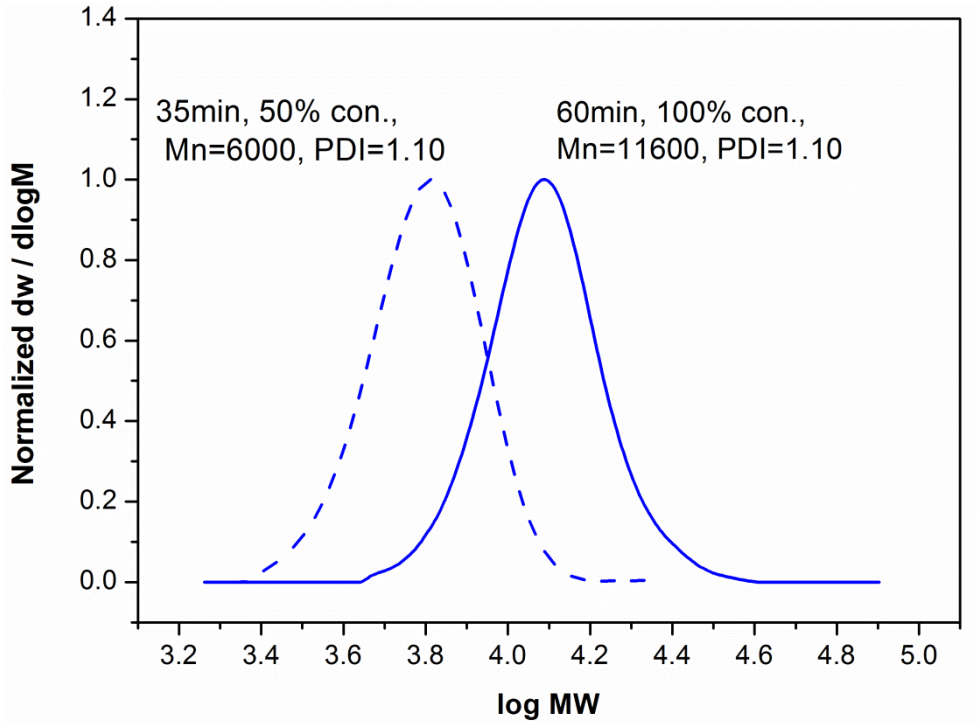


Figure S34: DMF SEC of higher molecular weight PNIPAM prepared by aqueous SET-LRP. [M] : [I] : [CuBr] : [Me_6TREN] = [100] : [1] : [0.008] : [0.004]

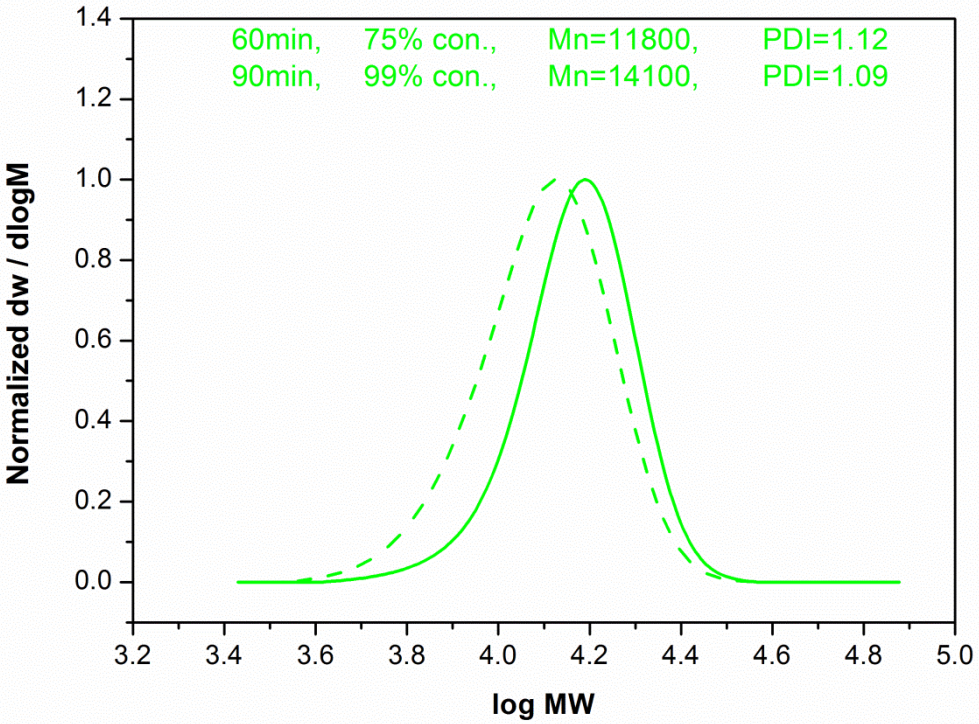


Figure S35: DMF SEC of higher molecular weight PHEAA prepared by aqueous SET-LRP. [M] : [I] : [CuBr] : [Me_6TREN] = [100] : [1] : [0.008] : [0.004]

Table S14: Preparation of higher molecular weight triblock homopolymer prepared by sequential additon of deoxygenated aliquots of aqueous NIPAM (100 eq) to PNIPAM during SET-LRP at 0 C in H_2O. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [100] : [1] : [0.008] : [0.004]$.

Entry	Block number	Monomer	Conv. (%)	Time per block (min)[a]	$M_{n,th}$ g.mol^{-1}	$M_{n,SEC}$[b] g.mol^{-1}	$Đ$[b]
1	Block 1	NIPAM	100	60 (60)	11600	11600	1.11
2	Block 2	NIPAM	100	90 (150)	22900	19800	1.09
3	Block 3	NIPAM	100	Overnight	34200	38800	1.08

[a] Cumulative time in parentheses. [b] DMF SEC, calibrating with PMMA standard.

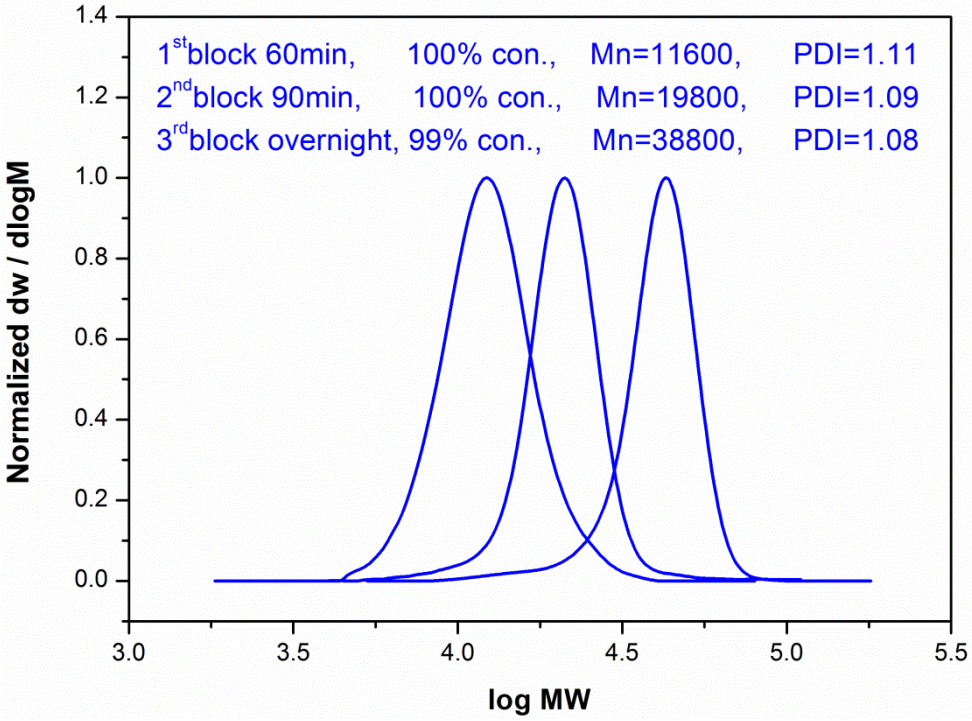


Figure S36: Evolution of block molecular weight by DMF SEC for high molecular weight triblock of PNIPAM. $[M]_0 : [I]_0 : [CuBr] : [Me_6TREN] = [100] : [1] : [0.008] : [0.004]$

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