Electronic Supporting Information for:

Thermosensitive Spontaneous Gradient Copolymers with Block- and Gradient-like Features

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The VAc and NIPAM conversions were calculated by comparing the integral areas of the protons of the double-bond peaks (signals *b* at δ = 4.75 ~ 4.90 ppm and *e* at δ = 5.51 ~ 5.62 ppm for respectively) in reference to the protons peaks of the internal standard 1,3,5-trioxane at δ = 5.16 ppm. (Figure S1)

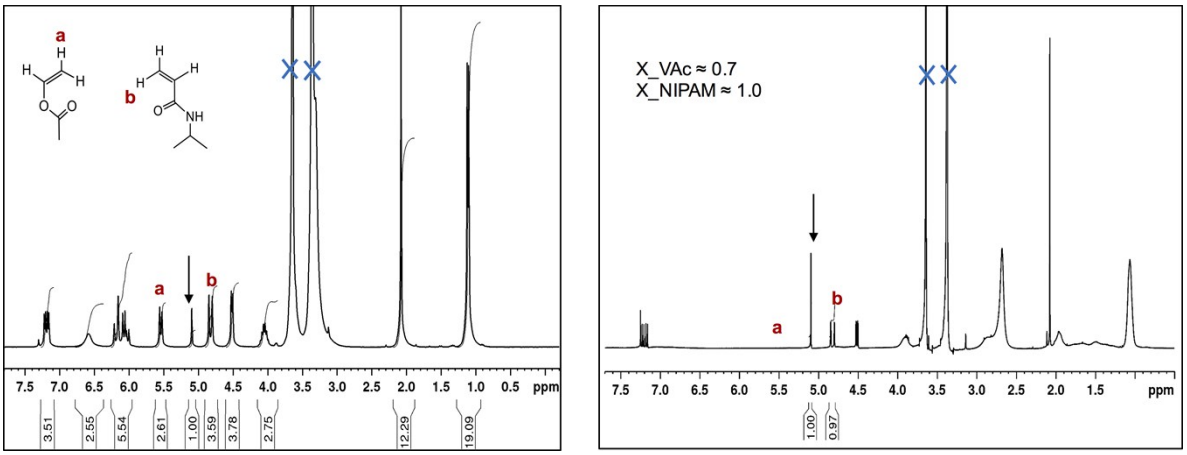

Figure S1. ^{1}H NMR spectra of sample $A_{40/60}$ at t=0 (left) and t=6 h (right) (in $CDCl_3$)

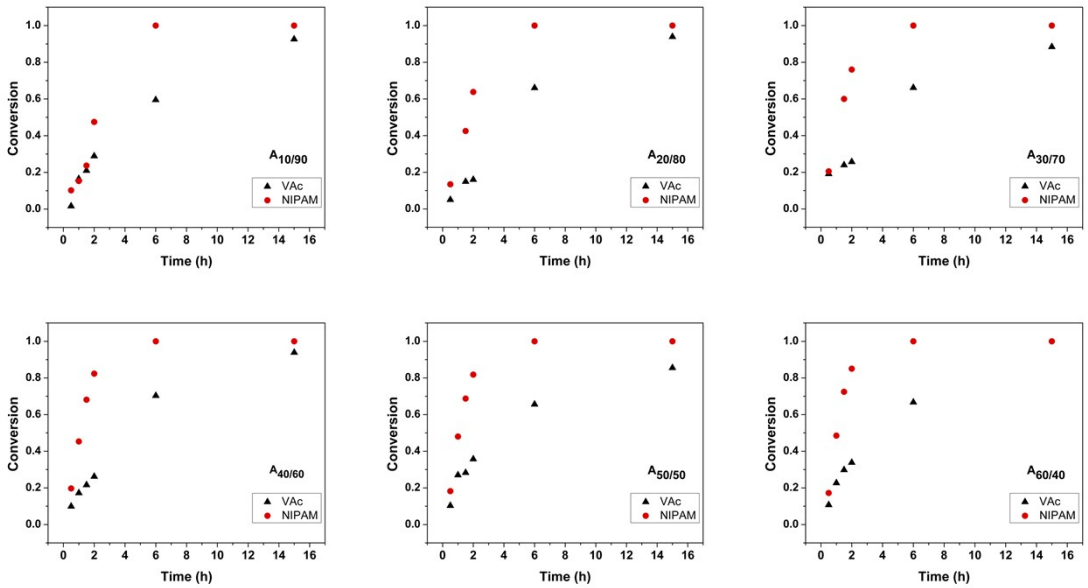

Figure S2. Monomer conversion as a function of time for all compositions of series A.

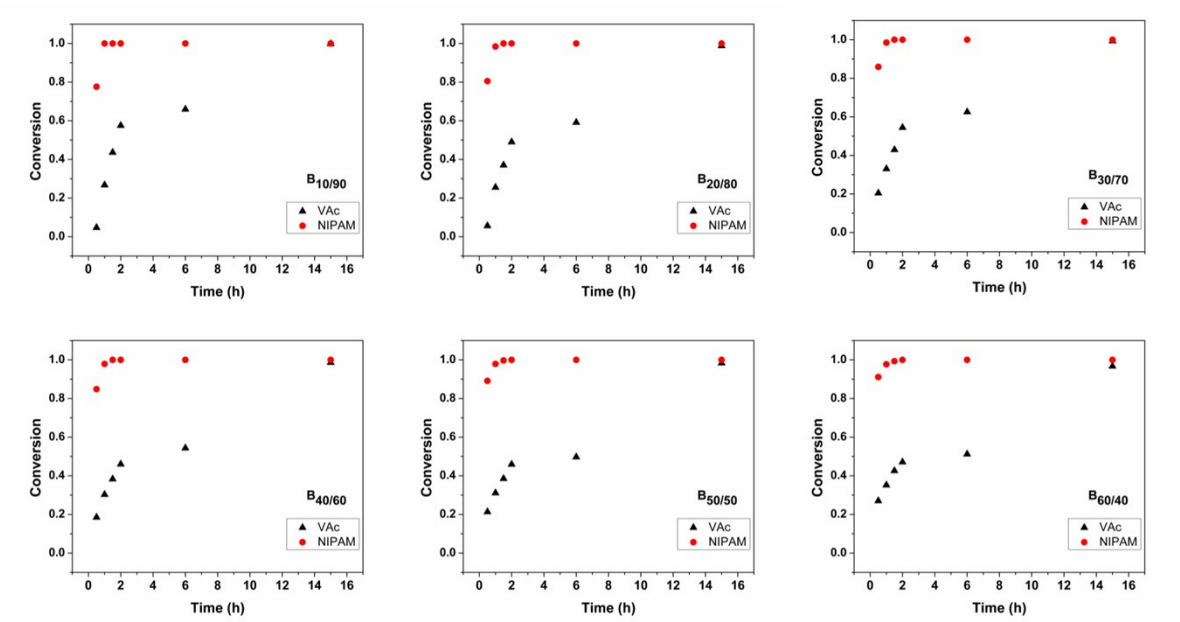

Figure S3. Monomer conversion as a function of time for all compositions of series B.

Table S1 Overview of the selected reaction conditions used for the additional copolymerizations of VAc and NIPAM performed on automated parallel synthesizer (Series C)

Entry	[M/RAFT]	[RAFT/AIBN]	$f_{VAc, ini}$	$f_{NIPAM, ini}$	$\eta_{VAc, ini}$ (mmol)	$\eta_{NIPAM, ini}$ (mmol)
C1	100	1/0.05	0.8	0.2	16	4.0
C2	100	1/0.05	0.8	0.2	16	4.0
C3	100	1/0.13	0.8	0.2	16	4.0
C4	250	1/0.13	0.8	0.2	16	4.0
C5	100	1/0.01	0.5	0.5	10	10
C6	100	1/0.05	0.5	0.5	10	10
C7	100	1/0.13	0.5	0.5	10	10

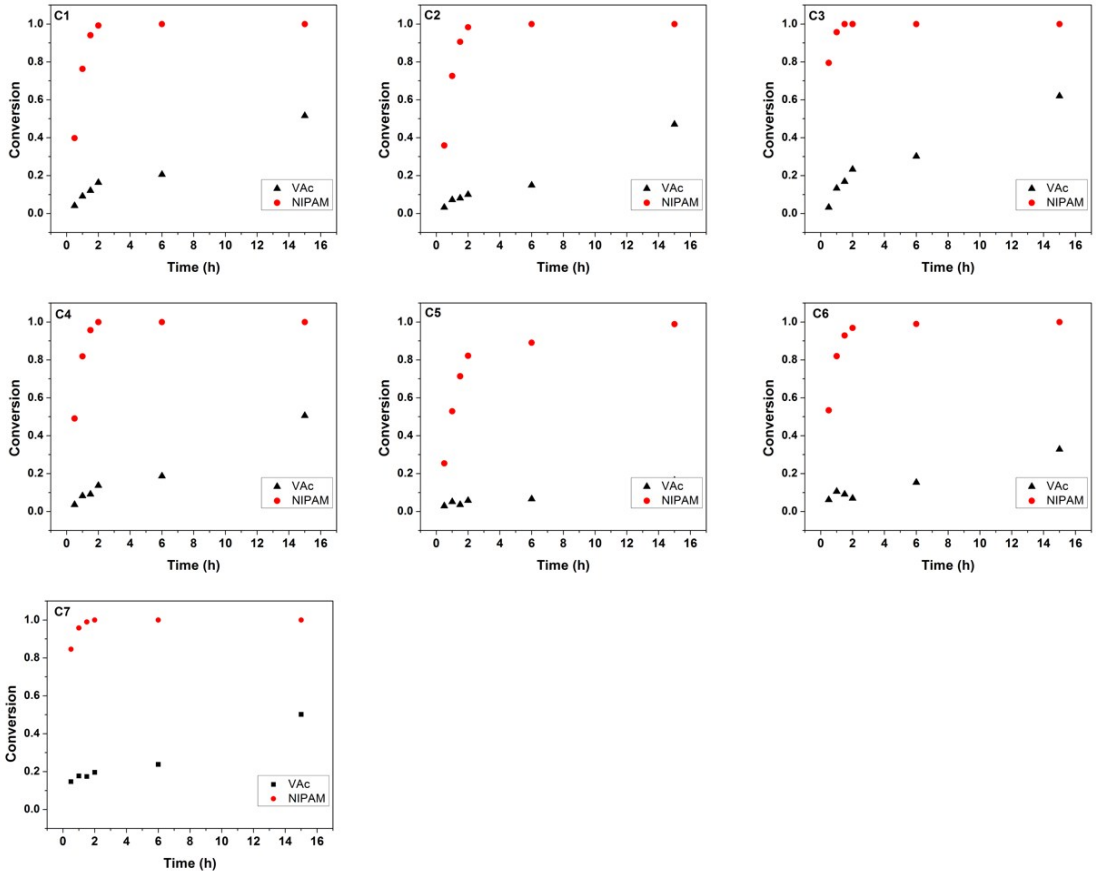

Figure S4. Monomer conversion as a function of time for all compositions of additional experiments (series C)

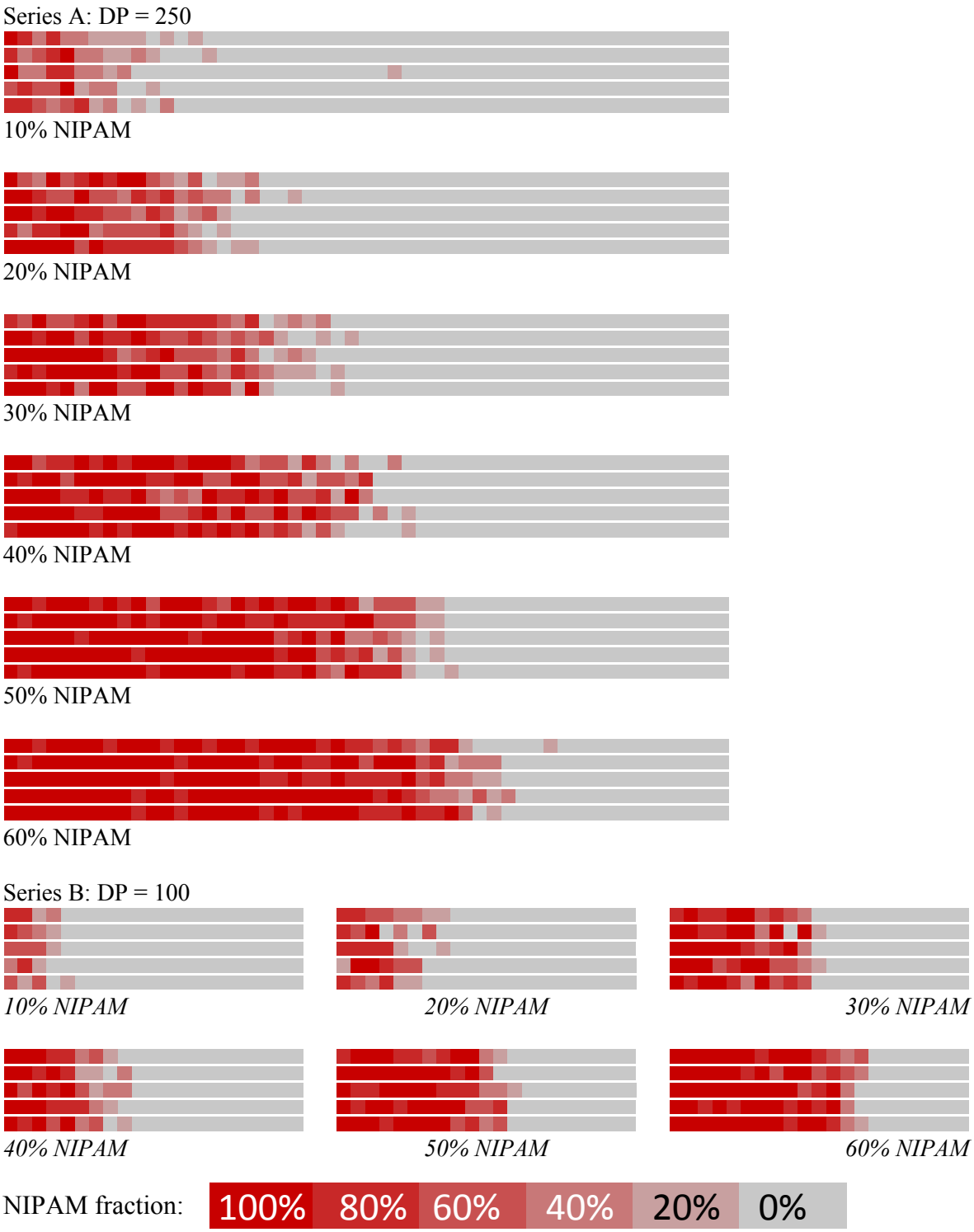

Figure S5. Simulated polymer chains for series A (DP = 250) and Series B (DP = 100) showing distribution of NIPAM units expected for $r_{NIPAM} = 26$, $r_{VAc} = 0.062$. Each square represents a block of five monomer units, and is colored according to the fraction of NIPAM units it contains.

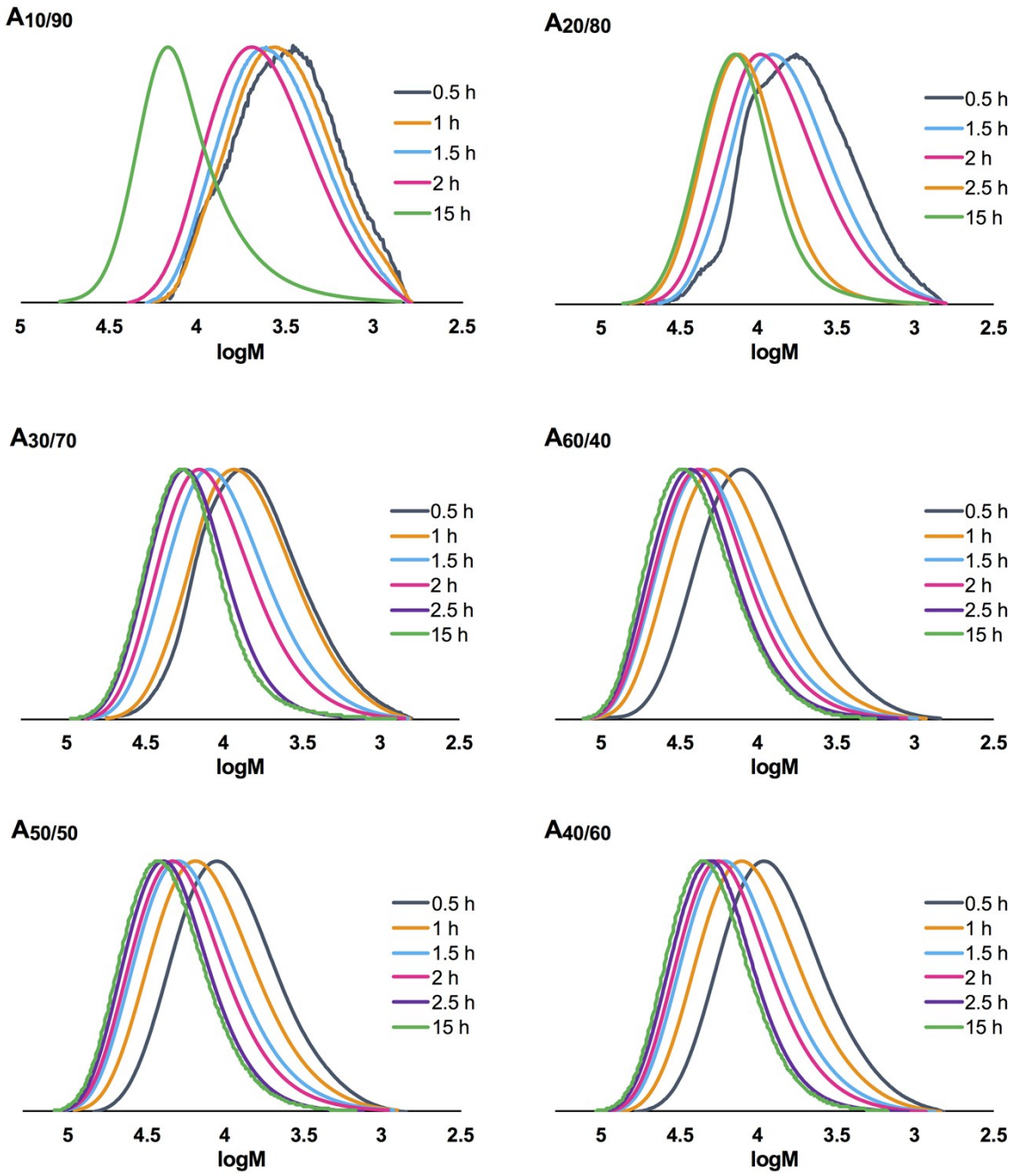

Figure S6. SEC traces as a function of time of reaction – Series A.

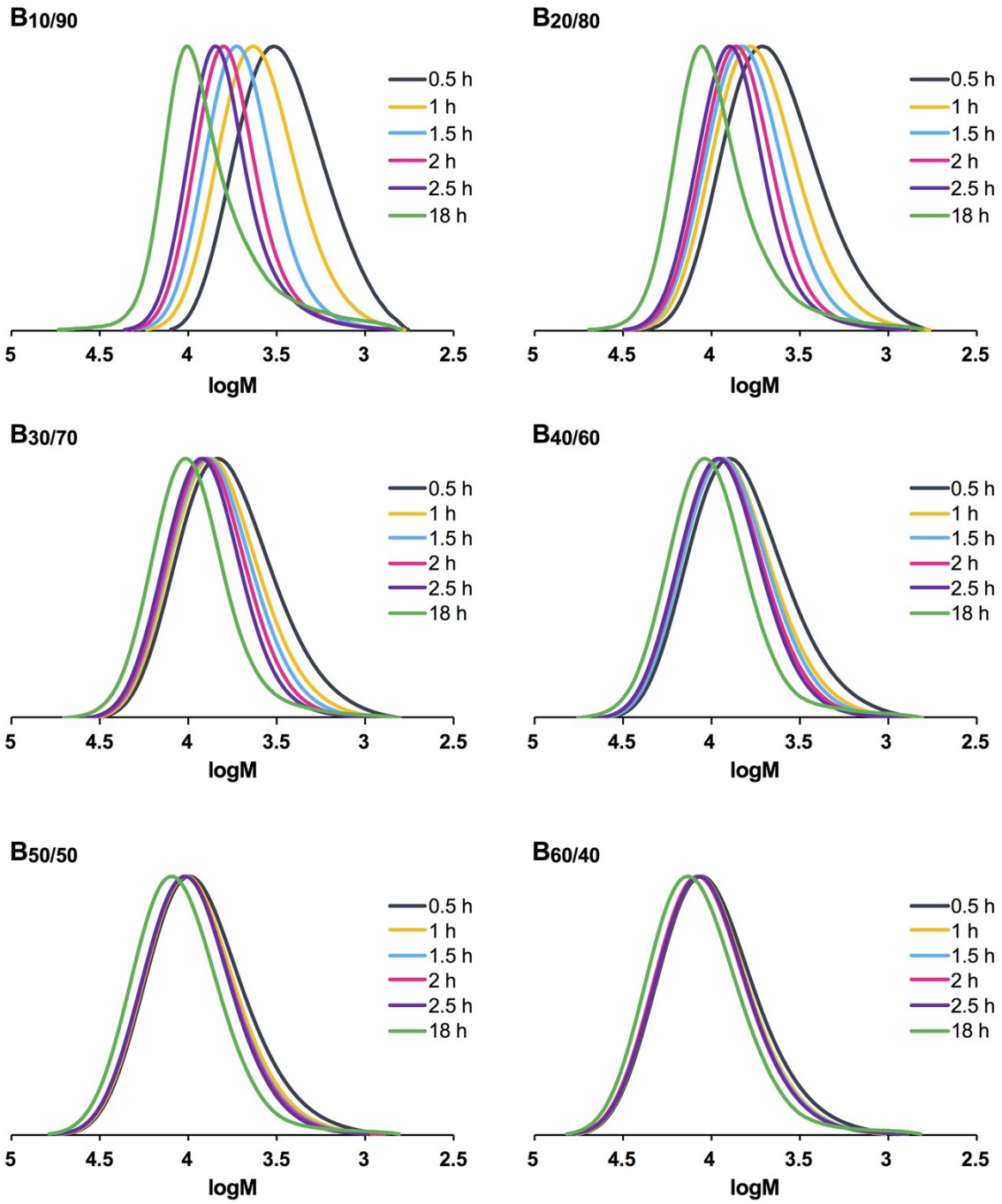

Figure S7. SEC traces as a function of time of reaction – Series B.

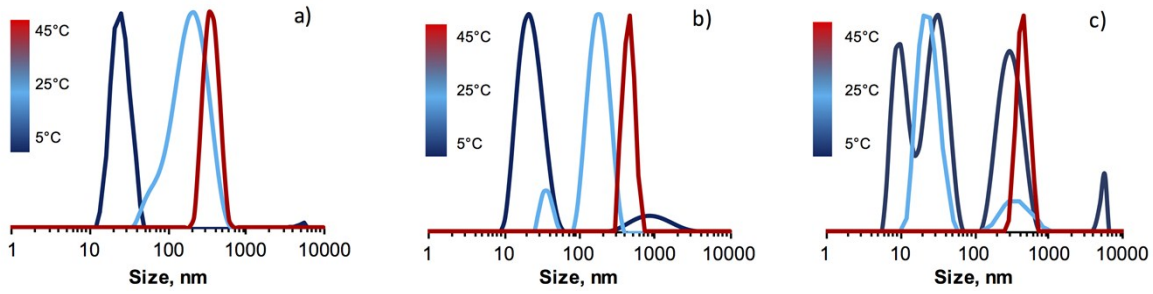

Figure S8. Hydrodynamic size distribution of a) $B_{30/70}$, a) $B_{40/60}$ and a) $B_{50/50}$ at the respective temperature.

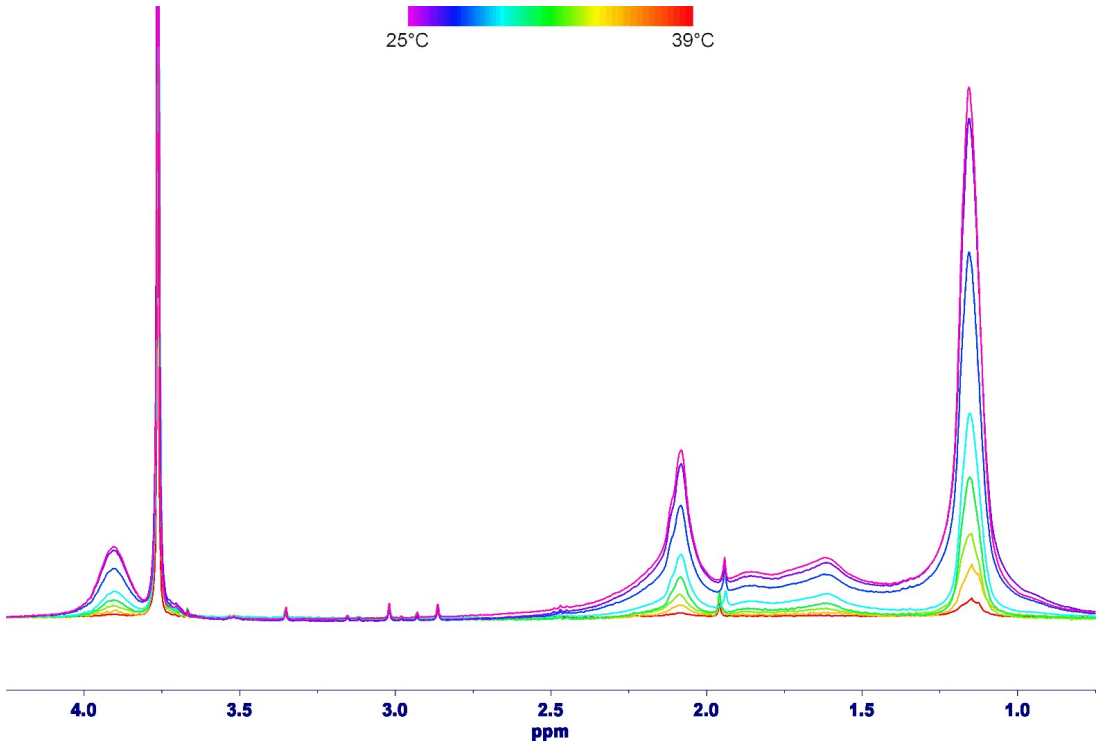

Figure S9. Evolution of ^{1}H NMR spectrum of $\mathbf{A}_{20/80}$ (10 mg mL^{-1} in D_2O)

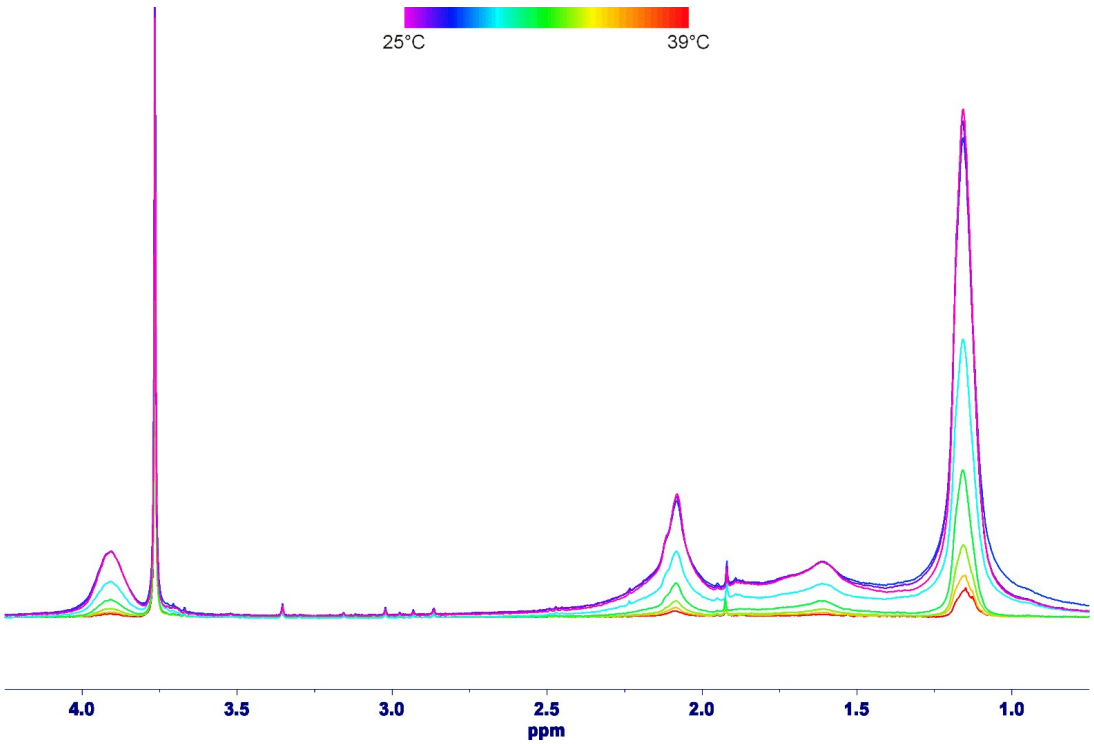

Figure S10. Evolution of ^{1}H NMR spectrum of $\mathbf{A}_{30/70}$ (10 mg mL^{-1} in D_2O)

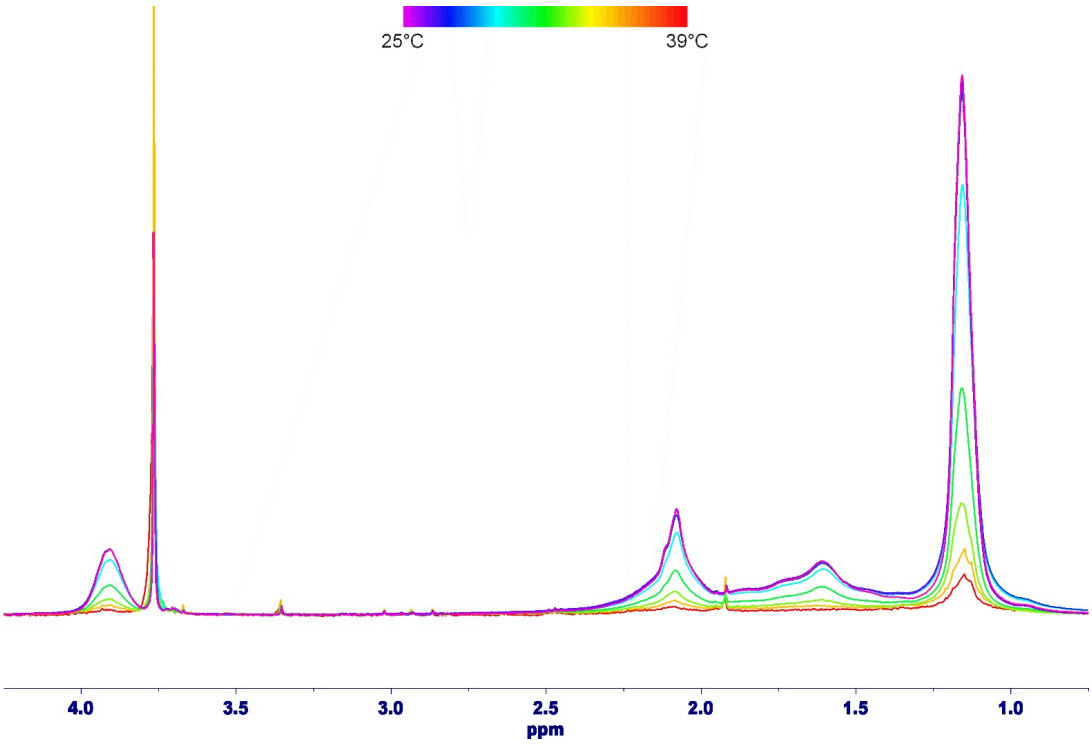

Figure S11. Evolution of ^{1}H NMR spectrum of $\mathbf{A}_{40/60}$ (10 mg mL^{-1} in D_2O)

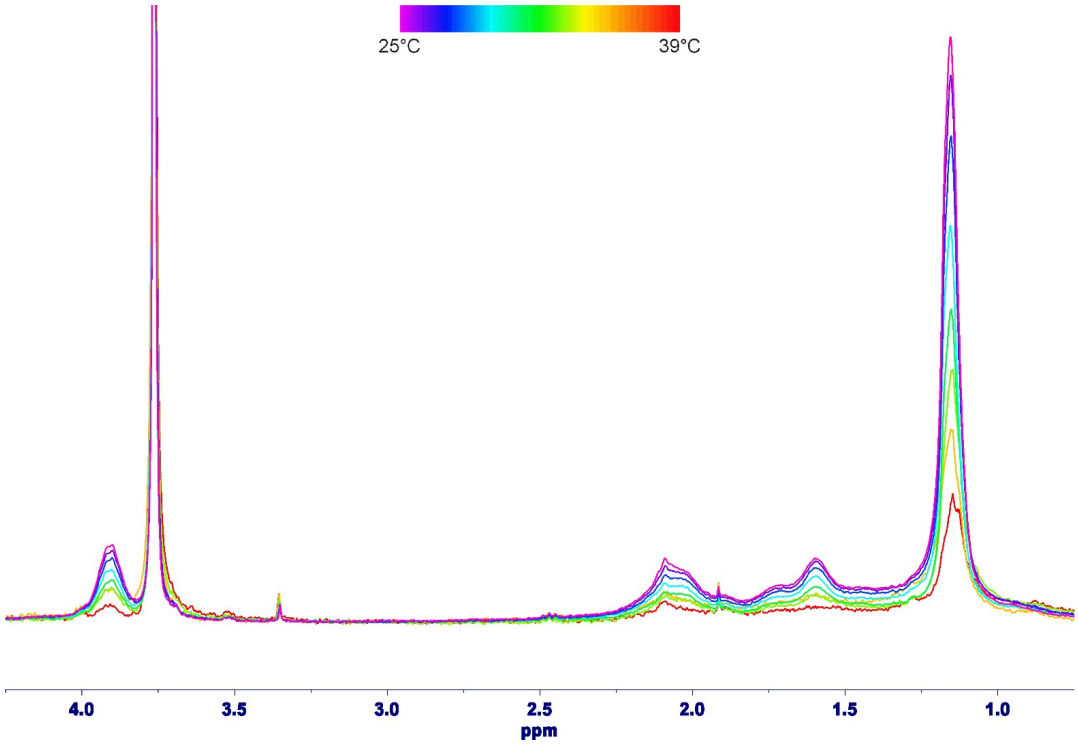

Figure S12. Evolution of ^{1}H NMR spectrum of **A'**$_{20/80}$ (10 mg mL^{-1} in D_2O)

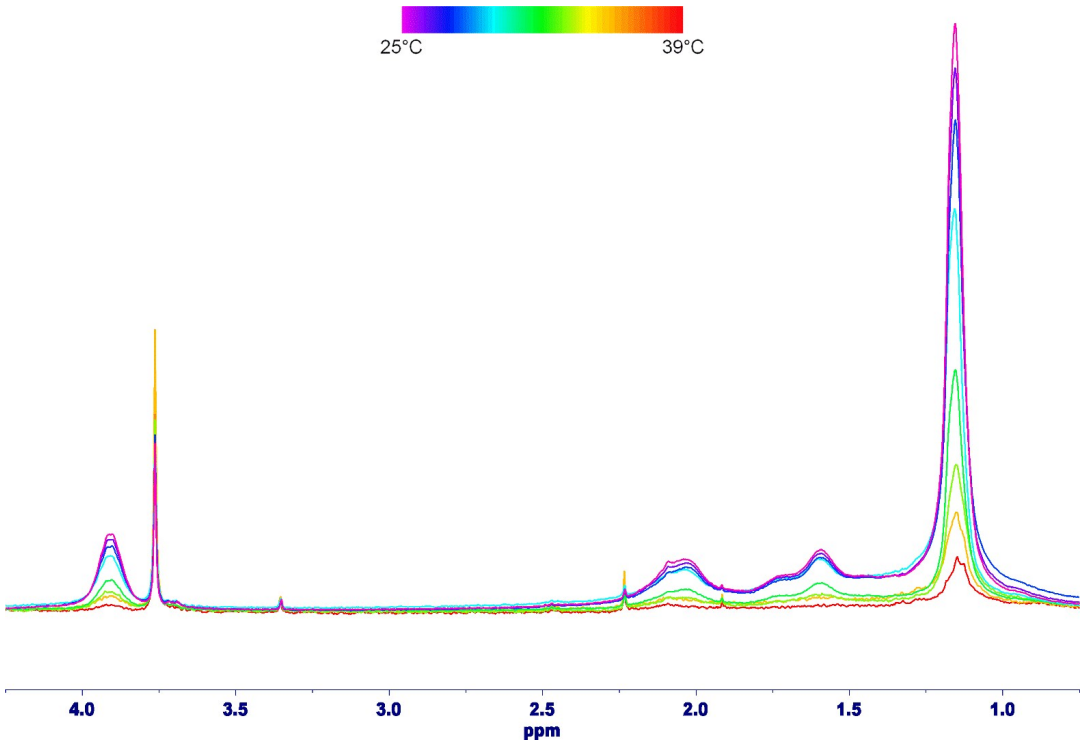

Figure S13. Evolution of ^{1}H NMR spectrum of **A'**$_{30/70}$ (10 mg mL^{-1} in D_2O)

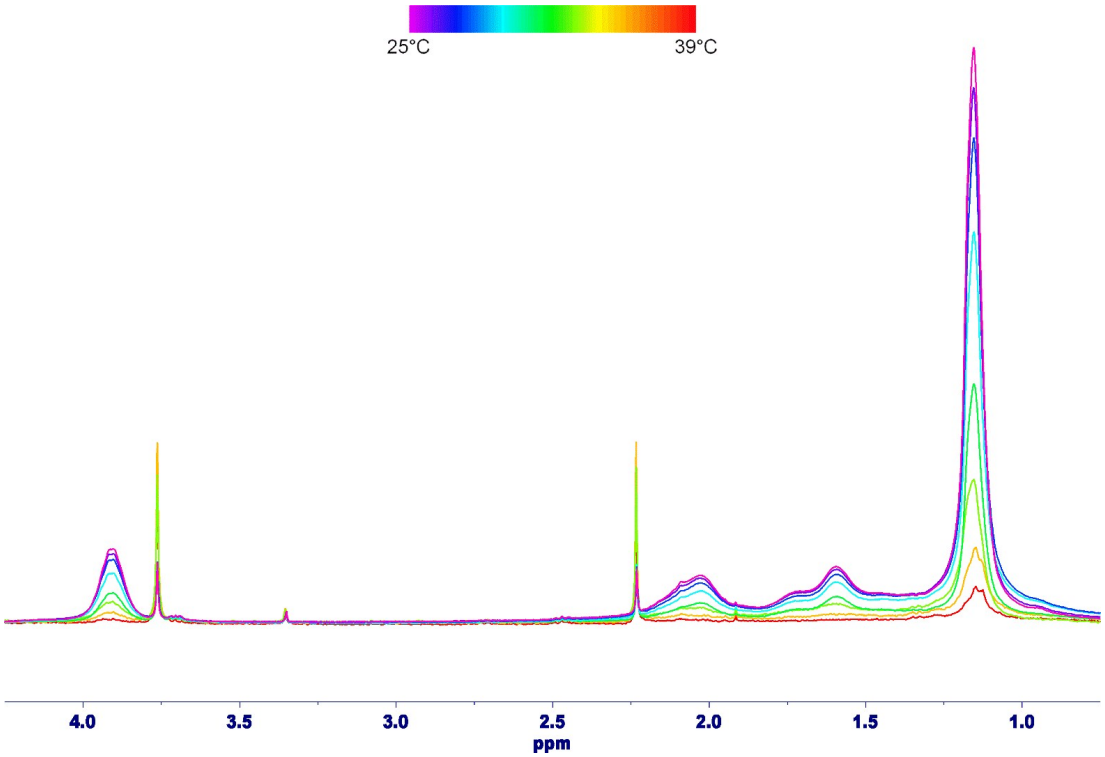

Figure S14. Evolution of ^{1}H NMR spectrum of **A'**$_{40/60}$ (10 mg mL^{-1} in D_2O)