Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Precision Syntheses of Poly(NIPAM-*alt*-HEMA) and Effects of Alternating Sequence on Thermoresponsive Behaviors in Water

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Contents

General Information

Materials

For syntheses of monomers: 4-(Trifluoromethyl)salicylic acid (TCI, >98%), 2-Hydroxyethyl methacrylate (HEMA, TCI, >95%), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, TCI, >98%), 4-dimethylaminopyridine (DMAP, TCI, >99%), acryloyl chloride (Wako, >98%), acetyl chloride (TCI, >98%), triethylamine (Et_3N, TCI, >99%), sulfuric acid (Wako, >95%), methanol (MeOH, Nacalai Tesque, >99%), tetrahydrofuran (THF, super dehydrated, stabilizer free, Wako, >99.5%), dichloromethane (DCM, super dehydrated, Wako, >99.5%), sodium hydrogen carbonate ($NaHCO_3$, Wako, >99.5%), sodium chloride (NaCl, Wako, >99.5%), sodium sulfate (Na_2SO_4, Wako, >99%) were used as received. For purification with column chromatography, Wako gel C200 (Wako) and mixture solvents with *n*-hexane (Wako, >96%), ethyl acetate (AcOEt, Wako, >99.5%) were used.

For copolymerization of model monomers M_1 and M_2: 2,2'-azobis(isobutylonitrile) (AIBN, TCI, >98%), 1,2-Dimethoxyethane (Wako, >99%) was dried by Molecular sieves 4A (Wako) and bubbled with dry nitrogen for more than 15 min before use. 1,2,3,4-tetrahydronaphthalene (Tetralin, TCI, >98%, an internal standard for ^1H NMR analysis) was dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use.

For syntheses of alternating copolymers: Ethyl 2-Bromoisobutyrate (EMA-Br, TCI >98%), copper(I) bromide (CuBr, Wako, >95%), Tris[2-(dimethylamino)ethyl]amine (Me_6TREN, TCI, >98%), anhydrous dimethyl sulfoxide (DMSO super dehydrate, Wako, >99%), isopropylamine (*i*-$PrNH_2$, TCI, >99%) were used as received without further purification. For dialysis, MWCO1000 (Spectra/PorVR7, diameter 29 mm) and methanol (Wako, >99.5%) were used. For reprecipitation, diethyl ether (Wako, >99.5%) were used.

For syntheses of statistical copolymers and homopolymers: 2-Hydroxyethyl methacrylate (HEMA, TCI, >95%) was purified by passing through a column of inhibitor removers (Aldrich). N-isopropyl acrylamide (NIPAM, TCI, >98%) was purified by recrystallization in *n*-Hexane twice (Wako, >96%). Copper(I) chloride (CuCl, Wako, >95%), ultrapure water (Wako), anhydrous N,N-dimethylformamide (DMF, super dehydrated, Wako, >99.5%) were used as received. For dialysis, MWCO1000 (Spectra/PorVR7, diameter 29 mm) and methanol (Wako, >99.5%) were used. For reprecipitation, diethyl ether (Wako, >99.5%) were used.

Measurements

Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were measured by size exclusion chromatography (SEC) at 40℃ in THF or DMF (solution of 10 mM LiBr) as an eluent on three polystyrene-gel columns. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 800–2200000). For THF SEC experiment: Shodex LF-404; exclusion limit = 2×10^6; particle size = 6 μm; pore size = 3000 Å; 0.46 cm i.d. × 25 cm; flow rate, 0.35 mL min^{-1} connected to HLC-8320GPC (TOSOH). For DMF SEC experiment: Shodex KF-805L; exclusion limit = 4×10^6; particle size = 10 μm; pore size = 5000 Å; 0.8 cm i.d. × 30 cm; flow rate, 1.0 mL min^{-1} connected to a PU-2080 precision pump, a RI- 2031 refractive-index detector, and a UV-2075 UV/vis detector (all from JASCO).

NMR spectra were measured at room temperature on a JEOL JNM-ECA500 spectrometer operating at 500.16 MHz (^1H) or at 125.04 MHz (^{13}C).

Fourier transform infrared (FT-IR) measurements were performed on a Cary 630 FTIR spectrometer (Agilent). Samples were characterized in solid state.

MALDI-TOF-MS measurements were conducted at following conditions. Equipment Name： ultrafleXtreme, Manufacturer: Bruker Daltonics, Laser: 337 nm, Detection mode: reflector mode, Matrix: 2,5-Dihydroxybenzoic acid (2,5-DHB), Cationization agent: None.

Variable-temperature transmittance measurements were conducted on a V-750 spectrophotometer (Jasco, optical path length = 1.0 cm, λ = 670 nm). The polymer samples were dried in vacuum at 100˚C overnight and dissolved in ultrapure water (Wako) at 5 ˚C for 2 days before tests.

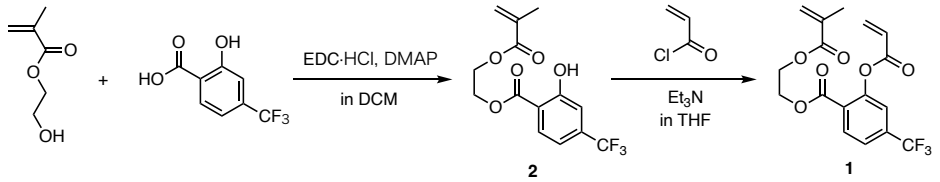
Dynamic light scattering (DLS) measurements were measured on a Zeta-potential & Particle size Analyzer ELSZ-2000 (Otsuka, wavelength: 638 nm). The measuring angle was 165˚ and the data was analyzed by cumulant method. The polymer solution samples were prepared by the same method for transmittance measurement.

Differential scanning calorimetry (DSC) measurements of polymers aqueous solutions were performed on a DSC Q200 calorimeter (TA instruments) equipped with an RCS 90 electric freezing machine under dry nitrogen flow at a heating or cooling rate of 2 ˚C/min. The polymer solution samples were prepared by the same method for transmittance measurement.

Experimental Section

Monomer Synthesis

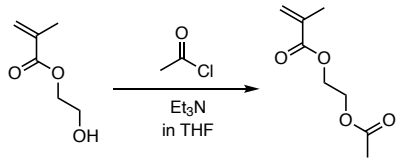
Synthesis of Divinyl Monomer 1



4-(trifluoromethyl)salicylic acid (10.31 g, 1.0 eq, 50.0 mmol), EDC·HCl (11.50 g, 1.2 eq, 60.0 mmol) and DMAP (1.53 g, 0.25 eq, 12.5 mmol) were placed in round-bottom-flask and dissolved in DCM (50 mL). The solution was stirred at 0 ˚C for 1.5 h. Then, 7.29 mL of HEMA (1.2 eq, 60 mmol) was added by syringe. The solution was stirred at 0 ˚C for 3 h, and at r.t. for another 16 h. The reaction was quenched with a few drops of MeOH, and the solution was filtered through a short plug of celite. The filtrate was washed with 10% NaCl aqueous solution three times, and then dried over Na_2SO_4, followed by purification with silica column chromatography (Hexane: AcOEt = 10:1 as eluent) to yield product **2** (6.42 g, 20.2 mmol, 40%) as colorless liquid. ^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 10.75 (s, 1H), 7.96 (d, 1H), 7.25 (s, 1H), 7.12 (d, 1H), 6.14 (s, 1H), 5.62-5.60 (m, 1H), 4.65-4.63 (m, 2H), 4.53-4.51 (m, 2H), 1.95 (s, 3H).

The product **2** (6.42 g, 1.0 eq, 20.2 mmol) was dissolved in 50 mL of anhydrous THF, and 3.1 mL of triethylamine (1.1 eq, 22.2 mmol) was added. The solution was cooled at 0 ˚C and 1.8 mL of acryloyl chloride (1.1 eq, 22.2 mmol) was added in drop while stirring. After being stirred at 0 ˚C for 3 h, the reaction was quenched with a few drops of MeOH. The precipitation was removed by filtration and the filtrate was concentrated under reduced pressure, followed by purification with silica column chromatography (Hexane: AcOEt = 10:1 as eluent) to yield divinyl monomer **1** (6.17 g, 16.6 mmol, 82%) as white solid. ^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 8.16 (d, 1H), 7.61 (d, 1H), 7.45 (s, 1H), 6.66 (d, 1H), 6.36 (dd, 1H), 6.14 (s, 1H), 6.08 (d, 1H), 5.62-5.60 (m, 1H), 4.55-4.53 (m, 2H), 4.43-4.41 (m, 2H),1.95 (t, 3H). ^{13}C NMR (126 MHz, chloroform-d): δ (ppm) 169.1, 167.1, 161.7, 137.4, 135.8, 130.9, 126.4, 124.3, 122.1, 115.7, 115.7, 115.2, 115.2, 114.9, 63.6, 62.0, 18.3.

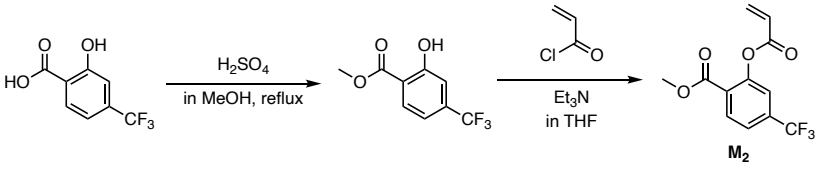
Synthesis of 2-acetoxyethyl methacrylate (M_1)



M_1

6.1 mL of HEMA (1.0 eq, 50.0 mmol) and 7.7 mL of triethylamine (1.1 eq, 55.0 mmol) were dissolved in 80 mL of anhydrous THF. The solution was cooled at 0 ˚C and 3.9 mL of acetyl chloride (1.1 eq, 55.0 mmol) was added in drop while stirring. After being stirred at 0 ˚C for 3 h, the reaction was quenched with drops of MeOH. The precipitation was removed by filtration and the filtrate was concentrated under reduced pressure, followed by purification with silica column chromatography (Hexane: AcOEt = 10:1 as eluent) to yield model monomer **M_1** (6.85 g, 39.8 mmol, 80%) as colorless liquid. ^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 6.14 (s, 1H), 5.60 (s, 1H), 4.37-4.32 (m, 4H), 2.08 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, chloroform-d): δ (ppm) 170.8, 167.1, 136.0, 126.0, 62.4, 62.1, 20.8, 18.3.

Synthesis of methyl acryloyl-4-(trifluoromethyl)salicylate (M_2)



M_2

4-(Trifluoromethyl)salicylic acid (10.4 g, 50.0 mmol) was placed in round-bottom-flask and dissolved in 50 mL of methanol. To the resultant solution, 3.0 mL of sulfuric acid was added dropwise. After being stirred at r.t. for 5 min, the solution was refluxed at 85 ˚C for 24 h. After the reaction, 100 mL of distilled water was added. The aqueous solution was then extracted three times with DCM. The three DCM fraction was combined and washed with saturated $NaHCO_3$ and brine, and then dried over Na_2SO_4. The organic solvent was evaporated to yield product (9.62 g, 43.7 mmol, 87%) as colorless liquid. ^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 10.89 (s, 1H), 7.95 (d, 1H), 7.25 (d, 1H), 7.12 (dd, 1H), 3.99 (s, 3H).

To a solution of methyl 4-(trifluoromethyl)salicylate (9.62 g, 1.0 eq, 43.7 mmol) in 80 mL of anhydrous THF was added triethylamine (6.7 mL, 1.1 eq, 47.8 mmol) and acryloyl chloride (3.9 mL, 1.1 eq, 47.8 mmol) at 0 ˚C in order. After 3 h stirring, the reaction was quenched with MeOH, and filtered. The filtrate was concentrated under reduced pressure, followed by purification with silica column chromatography (Hexane: AcOEt = 10:1 as eluent) to yield **M_2** (5.72 g, 20.8 mmol, 48%) as white solid. ^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 8.14 (d, 1H), 7.59 (d, 1H), 7.45 (s, 1H), 6.67

(dd, 1H), 6.38 (dd, 1H), 6.10 (dd, 1H), 3.87 (s, 3H).

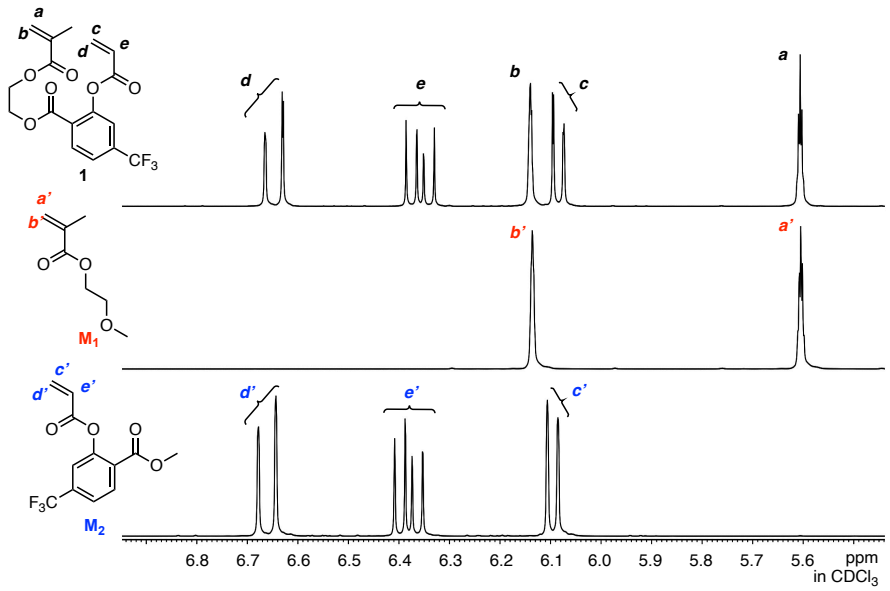
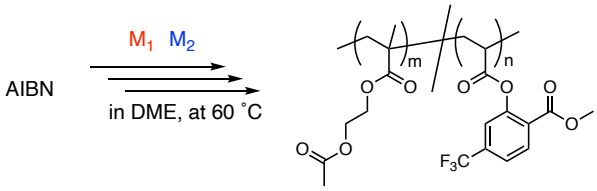


Figure S1. ^{1}H NMR spectra of divinyl monomer **1**, model monomer M_1 and M_2.

Procedures to Determine Monomer Reactivity Ratio



Copolymerizations of M_1 and M_2 were performed with AIBN by changing the feed ratios f_1 (f_1 = $[M_1]_0/([M_1]_0+[M_2]_0)$ = 0.84, 0.71, 0.47, 0.30, and 0.14). Typical procedure is as follows. In a Schlenk tube, M_1 (1.35 mL of 1200 mM degassed stock solution in DME), M_2 (1.35 mL of 1200 mM degassed stock solution in DME), AIBN (0.30 mL of 100 mM degassed stock solution in DME) and degassed tetralin (0.03 mL, internal standard) were added at room temperature under dry argon (5:5 injection condition). For immediately after mixing, the flask was placed in an oil bath kept at 60℃ for 10 min. The reaction was terminated by cooling down to -78˚C. The composition ratio F_1 was determined from the conversion: $F_1 = [M_1]_0 \times conv._{M1}/([M_1]_0 \times conv._{M1}+[M_2]_0 \times conv._{M2})$. The actual monomer feed ratio f_1 and conversion rates were determined by ^{1}H NMR. The monomer reactivity ratios were then calculated via Fineman-Ross method[1] and non-linear curve fitting method (Table S1 and Figure S2).

Table S1. Conditions of radical copolymerization for determination of monomer reactivity ratio[a]

Entry	$[M_1]_0$, mM	$[M_2]_0$, mM	f_1[b]	Time, min	Conv.$_{M1}$, %	Conv.$_{M2}$, %	F_1[c]	H[d]	G[e]
1	840	160	0.84		4.7	3.1	0.89	3.46	4.57
2	720	290	0.71		4.0	2.4	0.80	1.49	1.82
3	470	530	0.47	10	5.4	2.3	0.67	0.38	0.45
4	300	700	0.30		4.4	2.4	0.43	0.23	-0.13
5	140	860	0.14		7.0	2.9	0.28	0.07	-0.26

[a] The copolymerizations were conducted under following conditions: $([M_1]_0+[M_2]_0)/[AIBN]_0$ = 1000/10 mM, in DME, at 60 °C. [b] The value of f_1 was determined from $[M_1]_0/([M_1]_0+[M_2]_0)$. [c] The value of F_1 was determined from $[M_1]_0\times$conv.$_{M1}/([M_1]_0\times$conv.$_{M1}+[M_2]_0\times$conv.$_{M2})$. [d] The value of H was determined from $f_1^2(1-F_1)/(1-f_1)^2F_1$. [e] The value of G was determined from $f_1(2F_1-1)/(1-f_1)F_1$.

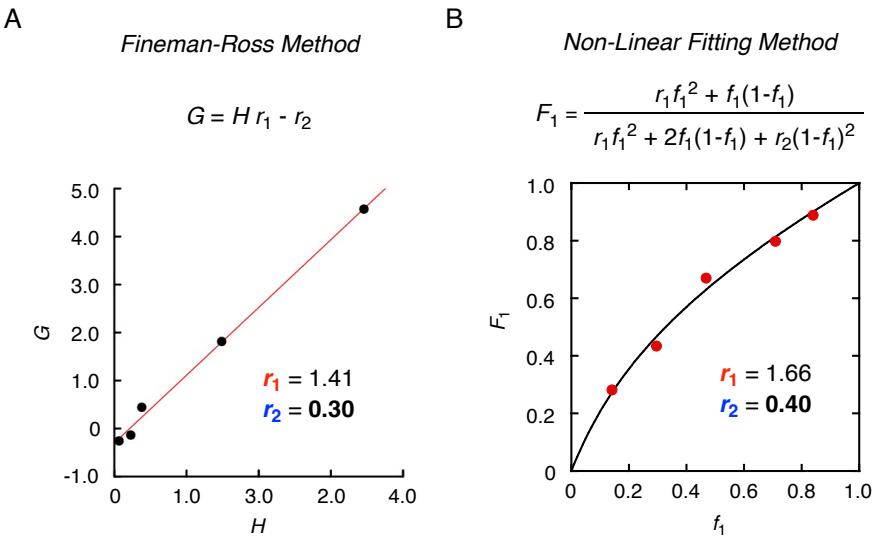
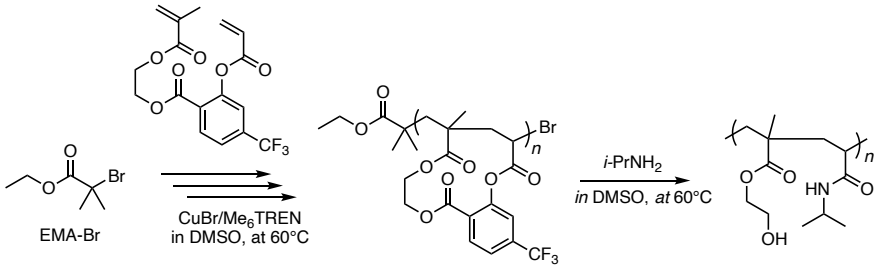


Figure S2. Determination of monomer reactivity ratios (r_1 and r_2) of M_1 and M_2. (A) Fineman-Ross method. The value of r_1 was determined from the slope and that of r_2 was from the y-intercept. (B) Non-linear fitting method. Nonlinear least squares analysis was used to determine the values of r_1 and r_2 that provided the best fit curve for the experimental values of f_1 and F_1. The analysis was performed by using the Solver Function in Microsoft Office Excel 2019.

Polymer Synthesis

Syntheses of Poly(NIPAM-*alt*-HEMA)s



10 mL of anhydrous DMSO was preciously degassed with N_2 before polymerization. 744.6 mg of divinyl monomer **1** (2.0 mmol), 15.0 μL of EMA-Br (0.1 mmol) and 50 μL of tetralin (internal standard) were dissolved in 8.4 mL of anhydrous DMSO in a Schlenk tube equipped with a three-way stopcock and degassed with N_2 for 30 min. To another Schlenk tube was placed 2.9 mg of CuBr (0.02 mmol) and 32.0 μL of Me_6TREN (0.12 mmol). 3.0 mL of degassed anhydrous DMSO was added under N_2. After being dissolved properly, 1.5 mL of Cu(I) complex solution (0.01 mmol of CuBr and 0.06 mmol of Me_6TREN) was transferred into the solution of divinyl monomer under N_2 via syringe. Then, the combined solution was bubbled with N_2 flow at r.t. for 15 min. Afterwards, the solution was heated up to 60 ˚C. Aliquots were taken periodically under N_2 for ^{1}H NMR analysis and passed through a short column of neutral alumina to remove dissolved copper salts prior to SEC analysis. The polymerization was terminated by cooling down to -78 ˚C and opened to the air. A part of the polymer was purified by reprecipitation with diethyl ether for NMR analysis.

To 5 mL of polymerization solution (monomer unit: 1.0 mmol) was directly added 0.82 mL of *i*-$PrNH_2$ (10.0 mmol). The reaction mixture was stirred at 60 ˚C for 24 hours. Then, the reaction mixture was dialyzed with MeOH (more than 3 hours stirring; 3 times replacement of the solvent) to remove low molecular weight compounds for purification of poly(NIPAM-*alt*-HEMA).

Cyclopolymers with different molecular weights were synthesized by changing the feed ratio of divinyl monomer **1** to initiator EMA-Br, as shown in **Table S2**. The cyclopolymers were subject to aminolysis with *i*-$PrNH_2$ for syntheses of poly(NIPAM-*alt*-HEMA)s with different molecular weights. **Figure S3** shows the SEC curves before and after aminolysis.

Table S2. Syntheses of cyclopolymers with different molecular weights.

Entry	$[\mathbf{1}]_0$:[EMA-Br]$_0$:[CuBr]$_0$:[Me$_6$TREN]$_0$	t, h	Conv.$_M$/Conv.$_A$, %	M_n, kg/mol	M_w/M_n
1	200 : 2.0 : 0.20 : 1.2	1	35/35	15.6	1.57
		3	82/81	27.4	1.84
		6	90/91	29.7	2.04
2	100 : 4.0 : 0.40 : 2.4	0.5	31/31	10.1	1.64
		1	63/63	13.2	1.76
		3	90/90	18.5	1.79
		5	97/96	19.4	1.87
3	200 : 10 : 1.0 : 6.0	1	83/84	8.0	1.48
		3	97/96	9.5	1.51
4	100 : 10 : 1.0 : 6.0	1	38/38	3.8	1.51
		3	100/100	5.0	1.50

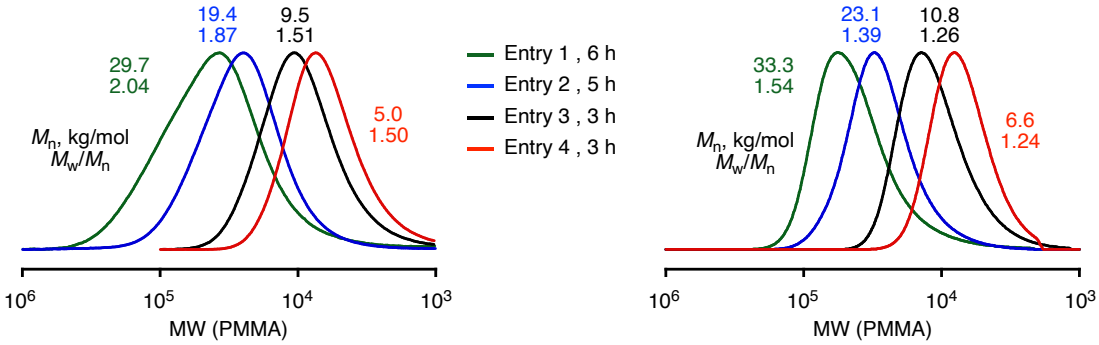
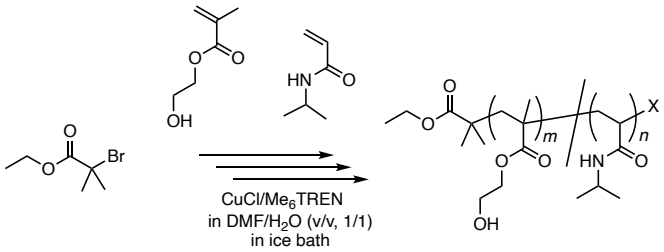


Figure S3. SEC curves of cyclopolymers (before aminolysis) and poly(NIPAM-*alt*-HEMA)s (after aminolysis).

Syntheses of Poly(NIPAM-*sta*-HEMA)s and Homopolymers

Synthesis of Poly(NIPAM-*sta*-HEMA)s



The procedure of copolymerization was modified from the report by D. M. Haddleton et al.[2] 9.9 mg of CuCl (0.1 mmol), 27.2 μL of Me_6TREN (0.1 mmol) and a magnetic stir bar were placed in a Schlenk tube equipped with a three-way stopcock under N_2. 5 mL of degassed ultrapure water was added under N_2 flow. The mixture was allowed to stirred at r.t. for 30 min for full disproportionation of Cu(I) complex. In another Schlenk tube, 7 mL of DMF solution containing HEMA (1200 mM), NIPAM (2800 mM) and EMA-Br (20 mM) was prepared. After being degassed with N_2 for 30 min, 5 mL of monomer solution was transferred to the disproportionated copper mixture at 0 ˚C (polymerization condition: $[HEMA]_0/[NIPAM]_0/[EMA\text{-}Br]_0/[CuCl]_0/[Me_6TREN]_0$ = 600/1400/10/10/10 mM, DMF/H_2O = 1/1, v/v). The polymerization started immediately and was terminated in 2 h by direct dialysis with MeOH (more than 3 h stirring; 3 times replacement of the solvent) to afforded purified poly(NIPAM-s*ta*-HEMA).

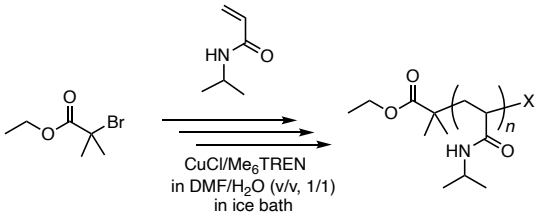
Statistical copolymers with different composition were synthesized in the same procedure by changing the feed ratio of HEMA and NIPAM. The details are as follows.

Table S3. Syntheses of poly(NIPAM-*sta*-HEMA) with different composition.

Entry	$[HEMA]_0$:$[NIPAM]_0$	t, h	$Conv._{HEMA}/Conv._{NIPAM}$	*m*:*n*[a]	M_n, kg/mol	M_w/M_n
1	500:500	8	92%/33%	74:26	29.1	1.66
2	700:1300	1	95%/38%	64:36	37.8	1.27
3	600:1400	2	99%/45%	51:49	39.8	1.33
4	500:1500	3	93%/35%	46:54	35.2	1.54
5	600:1400	3	98%/80%	38:62	55.0	1.25

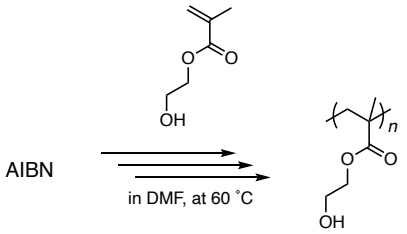
a. Calculated by integrals of ^1H NMR spectra of polymers in CD_3OD. *m*: $DP_{n,NIPAM}$, *n*: $DP_{n,HEMA}$

Synthesis of poly(NIPAM)



The procedure of polymerization was modified from the report by D. M. Haddleton et al.[2] 3.0 mg of CuCl (0.03 mmol), 8.1 μL of Me_6TREN (0.03 mmol) and a magnetic stir bar were placed in a Schlenk tube equipped with a three-way stopcock under N_2. 5 mL of degassed ultrapure water was added under N_2 flow. The mixture was allowed to stirred at r.t. for 30 min for full disproportionation of Cu(I) complex. In another Schlenk tube, 7 mL of DMF solution containing NIPAM (2400 mM) and EMA-Br (12 mM) was prepared. After being degassed with N_2 for 30 min, 5 mL of monomer solution was transferred to the disproportionated copper mixture at 0 ˚C (polymerization condition: $[NIPAM]_0/[EMA\text{-}Br]_0/[CuCl]_0/[Me_6TREN]_0$ = 1200/6/3/3 mM, DMF/H_2O = 1/1, v/v). The polymerization started immediately and was terminated in 2 h by direct dialysis with MeOH (more than 3 h stirring; 3 times replacement of the solvent) to afforded purified poly(NIPAM).

Synthesis of poly(HEMA)



To a Schlenk tube equipped with a three-way stopcock was added 0.61 mL of HEMA (5 mmol), 8.2 mg of AIBN (0.05 mmol) and 4.39 mL of DMF. The solution was bubbled with N_2 flow in ice bath. Afterwards, the solution was heated up to 60 ˚C to start the polymerization (polymerization condition: $[HEMA]_0/[AIBN]_0$ = 1000/10 mM). The polymerization was terminated in 2 h by cooling down to -78 ˚C and poly(HEMA) was purified by precipitation in hexane twice.

Thermoresponsive Behaviors: Transmittance Measurements

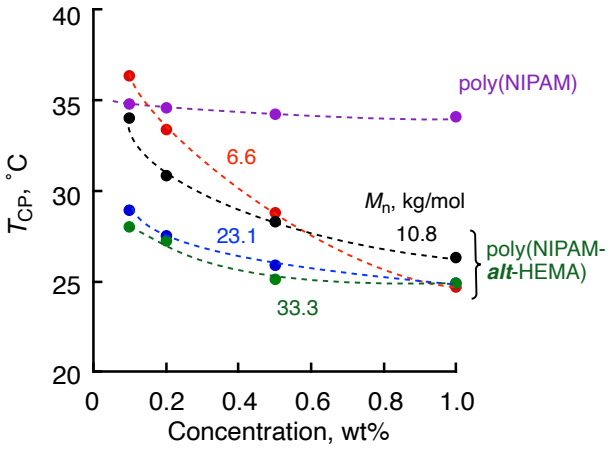


Figure S4. Concentration effects of poly(NIPAM-*alt*-HEMA)s with different molecular weights on T_{CP}s in comparison with poly(NIPAM).

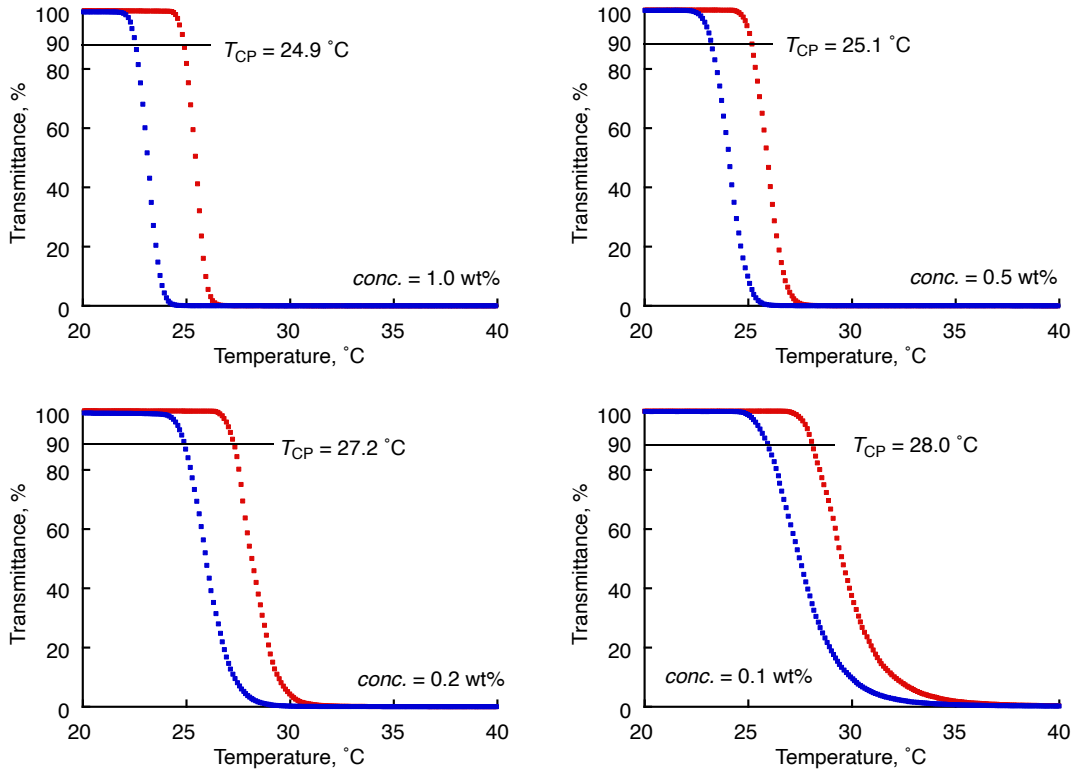


Figure S5. Transmittance (λ = 670 nm) versus temperature plots of poly(NIPAM-*alt*-HEMA*)* (M_n = 33.3 kg/mol) aqueous solutions (1.0, 0.5, 0.2, and 0.1 wt% in water) on heating (red) at 1˚C/min and cooling (blue) at 1˚C/min.

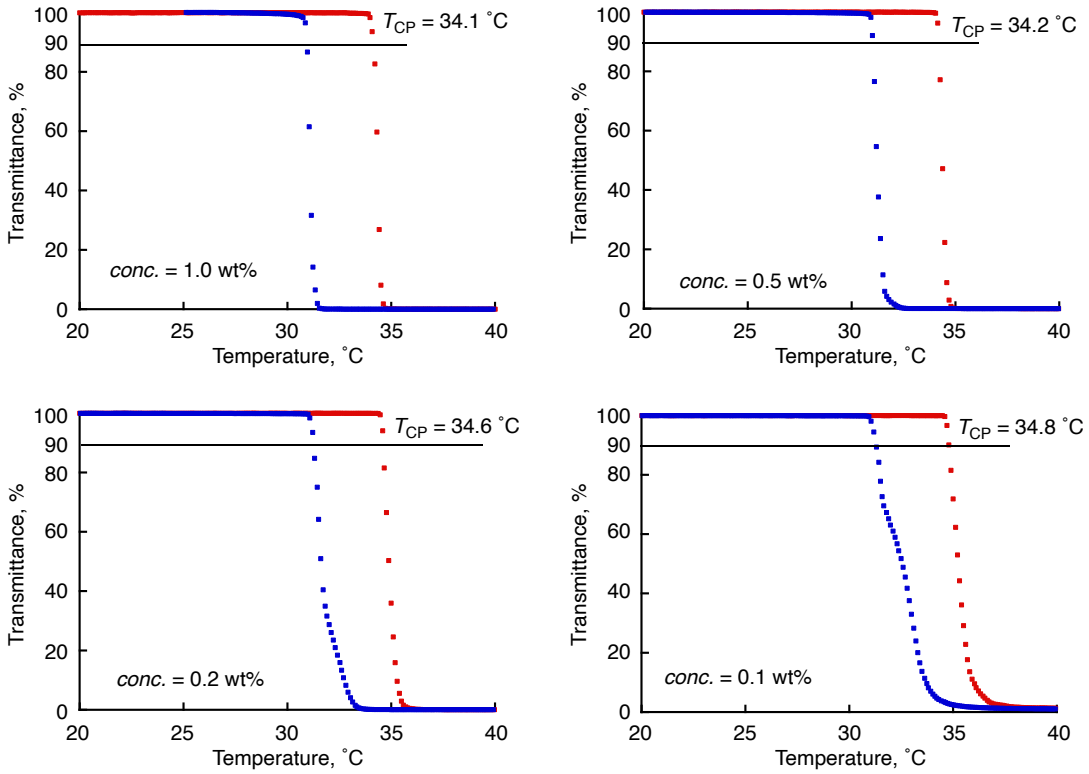


Figure S6. Transmittance (λ = 670 nm) versus temperature plots of poly(NIPAM) (M_n = 36.8 kg/mol) aqueous solutions (1.0, 0.5, 0.2, and 0.1 wt% in water) on heating (red) at 1˚C/min and cooling (blue) at 1˚C/min.

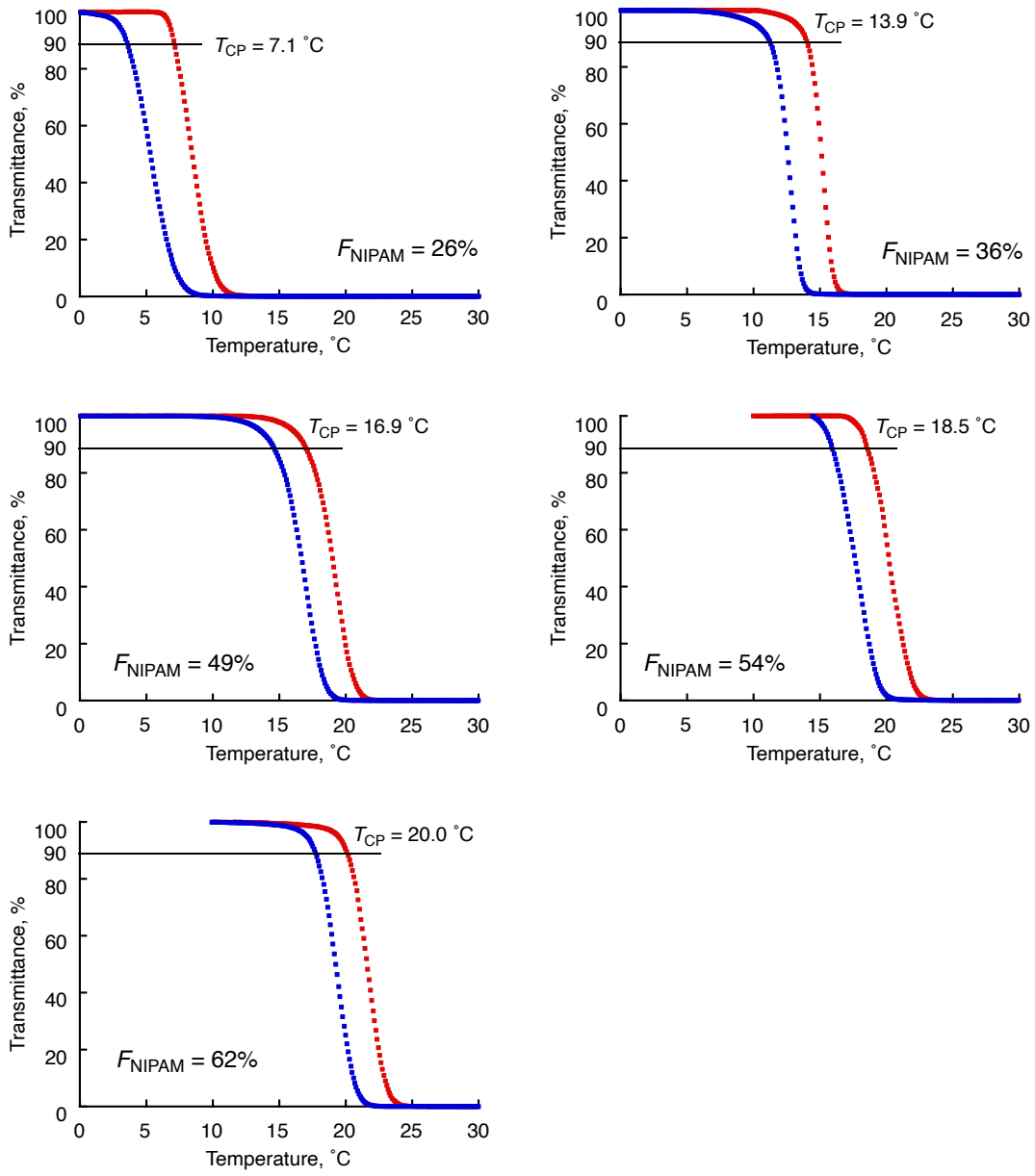


Figure S7. Transmittance (λ = 670 nm) versus temperature plots of 1.0 wt% poly(NIPAM-*sta*-HEMA) aqueous solutions with different mole fraction of NIPAM (F_{NIPAM}) on heating (red) at 1˚C/min and cooling (blue) at 1˚C/min, $F_{NIPAM} = DP_{n,\,NIPAM} / (DP_{n,\,NIPAM} + DP_{n,\,HEMA})$.

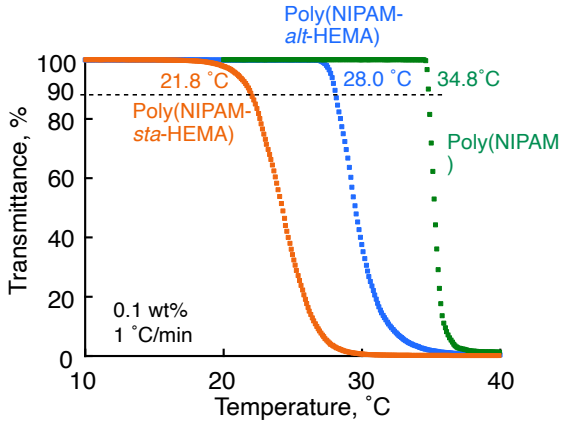


Figure S8. Transmittance versus temperature plots of 0.1 wt% aqueous solutions of poly(NIPAM-*alt*-HEMA) (M_n = 33.3 kg/mol), poly(NIPAM-*sta*-HEMA)s with equal fractions of NIPAM and HEMA units (M_n = 55.0 kg/mol) and poly(NIPAM) (M_n = 36.8 kg/mol) in aqueous solutions on heating process at 1 ˚C/min.

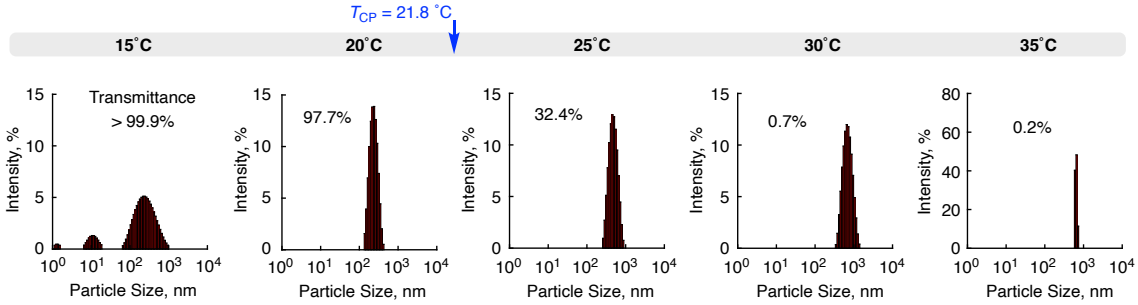


Figure S9. DLS measurements of 0.1 wt% aqueous solution of poly(NIPAM-*sta*-HEMA) with equal fractions of NIPAM and HEMA units at different temperatures.

Thermoresponsive Behaviors: DSC Measurements

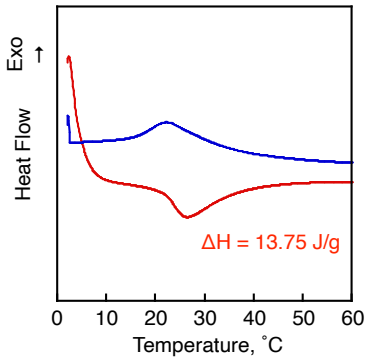


Figure S10. DSC curves of 10.0 wt% poly(NIPAM-*alt*-HEMA) aqueous solutions, M_n = 33.3 kg/mol (red: heating curves; blue: cooling curves; heating & cooling rate 2 ˚C/min).

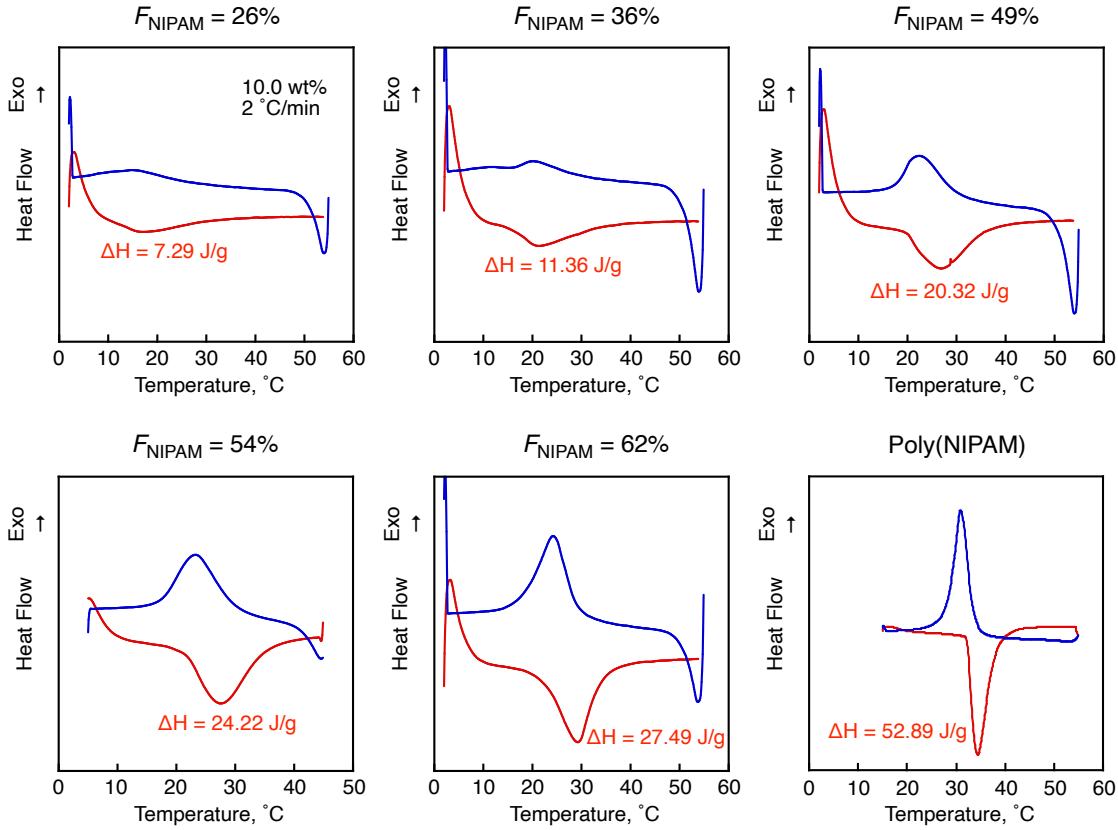


Figure S11. DSC curves of 10.0 wt% poly(NIPAM-*sta*-HEMA) and poly(NIPAM) aqueous solutions, $F_{NIPAM} = DP_{n,\,NIPAM} / (DP_{n,\,NIPAM} + DP_{n,\,HEMA})$ (Red: heating curves; blue: cooling curves; heating & cooling rate 2 ˚C/min).

^{1}H NMR and ^{13}C NMR Spectra of Monomer Syntheses

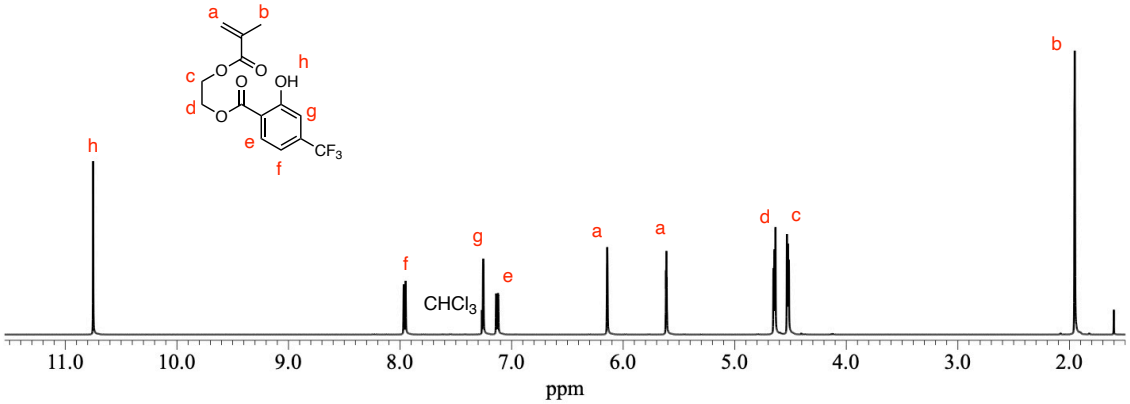


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of 2-(methacryloyloxy)ethyl 2-hydroxy-4-(trifluoromethyl)benzoate.

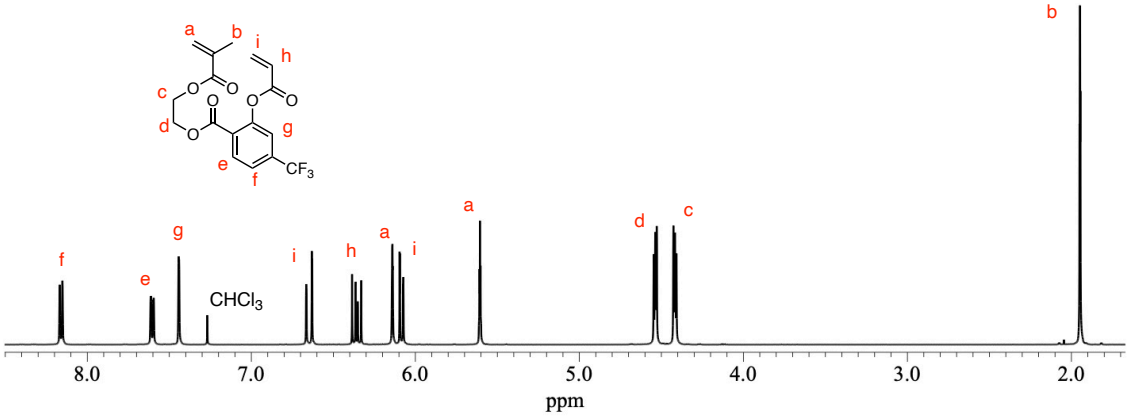


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of divinyl monomer **1**.

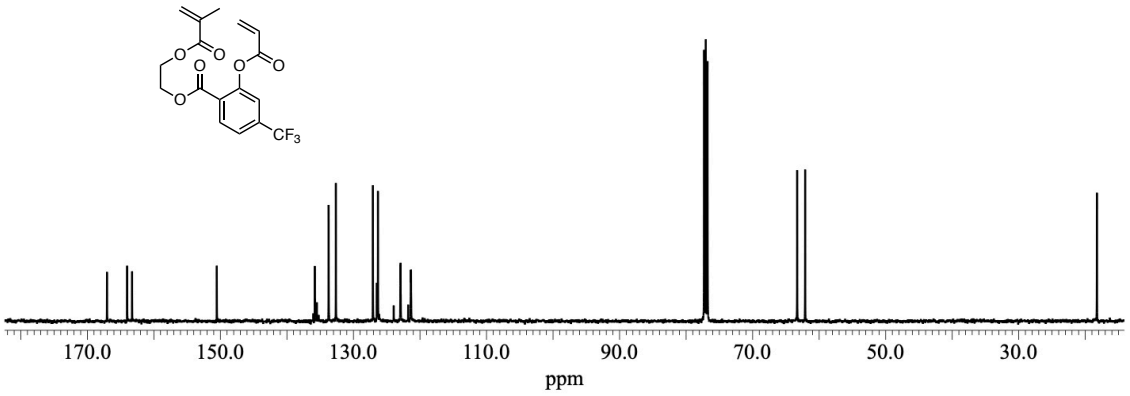


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, r.t.) of divinyl monomer **1**.

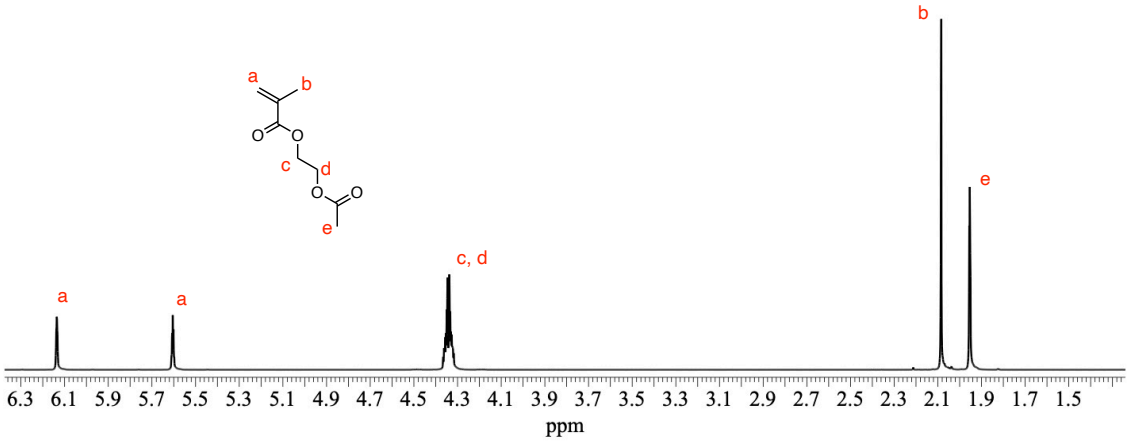


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of model monomer M_1.

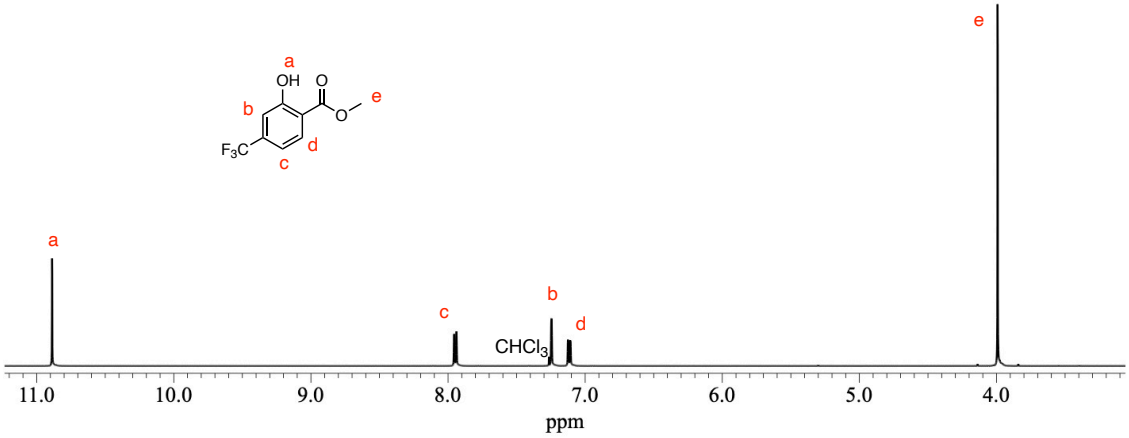


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of methyl 4-(trifluoromethyl)salicylate.

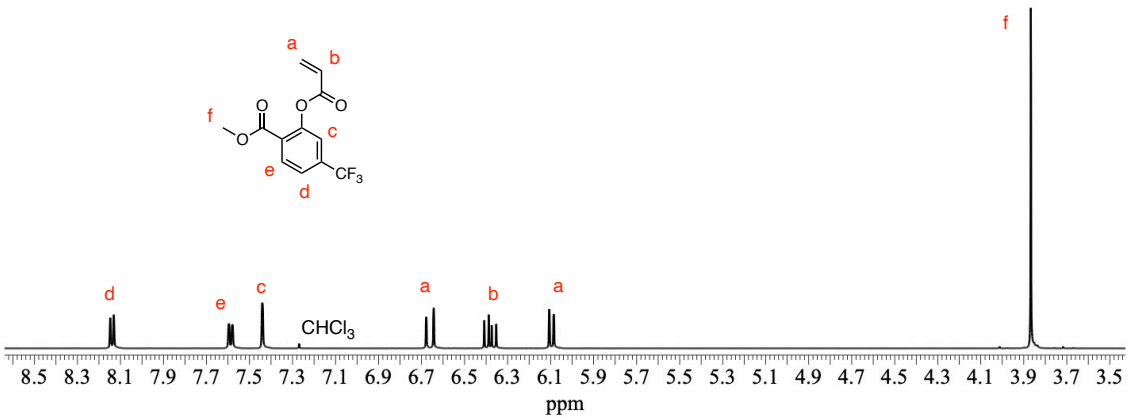


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of model monomer M_2.

^{1}H NMR Spectra of Alternating Copolymer Syntheses

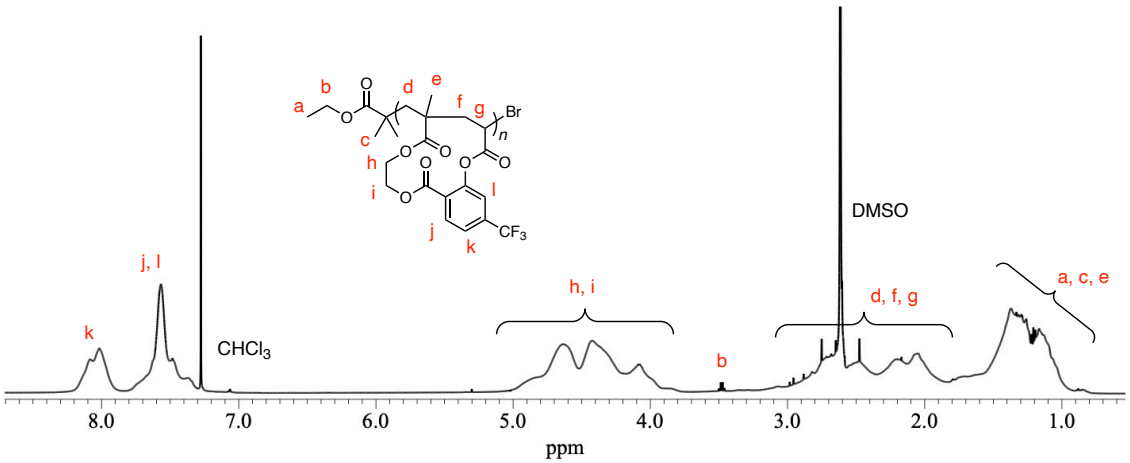


Figure S18. ^{1}H NMR spectrum ($CDCl_3$, r.t.) of cyclopolymer (**Table S2**, **Entry 4**).

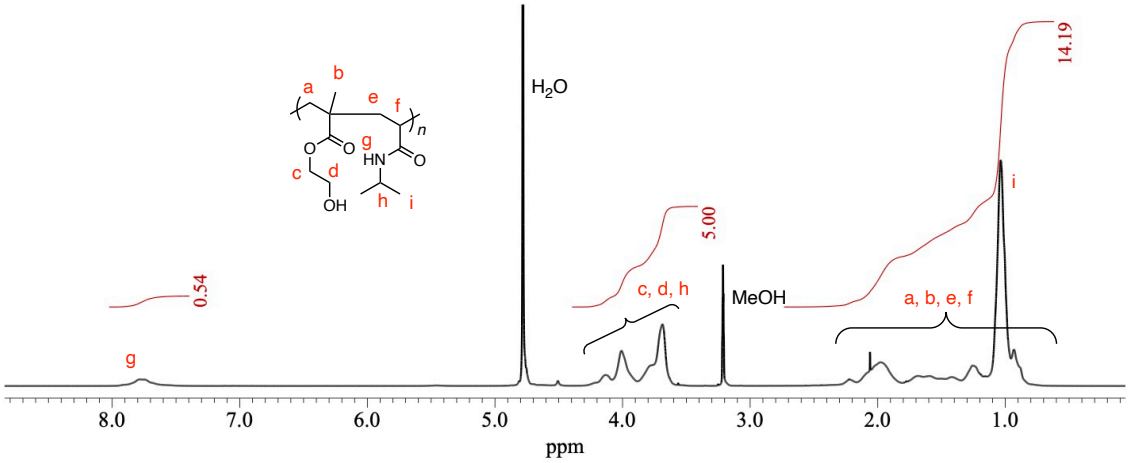


Figure S19. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*alt*-HEMA) (M_n = 33.3 kg/mol).

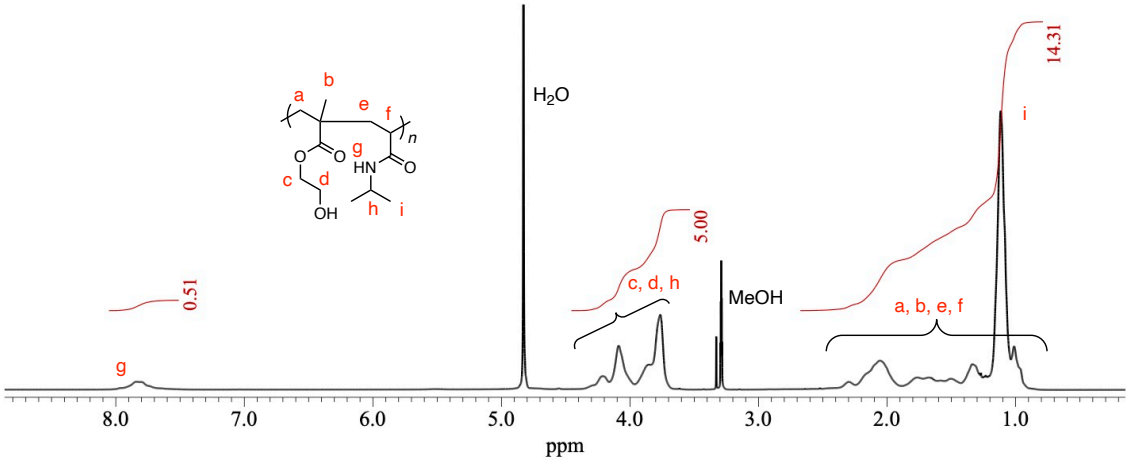


Figure S20. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*alt*-HEMA) (M_n = 23.1 kg/mol).

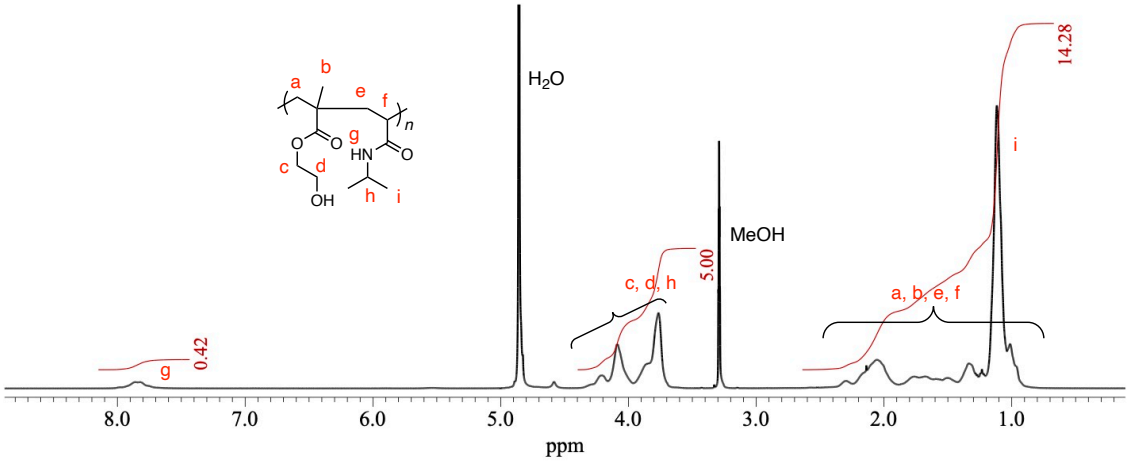


Figure S21. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*alt*-HEMA) (M_n = 10.8 kg/mol).

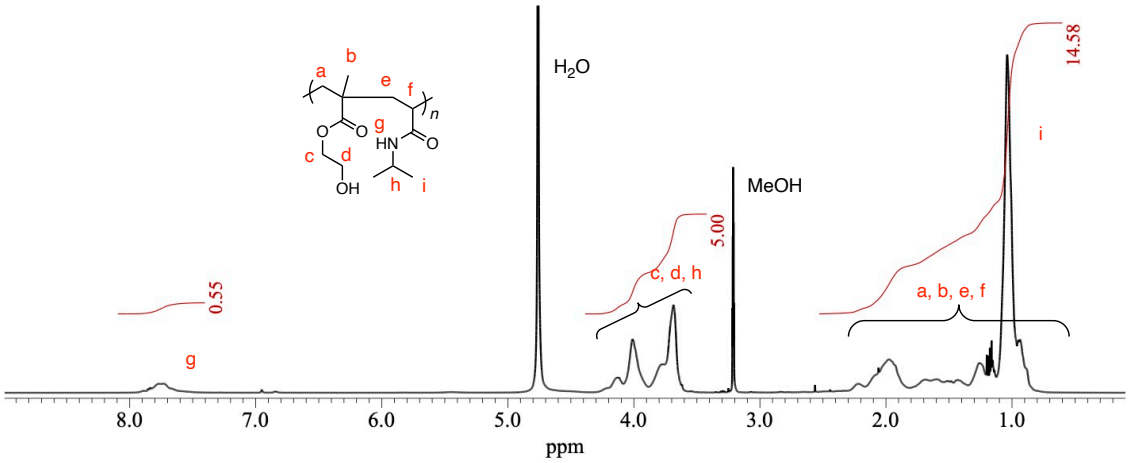


Figure S22. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*alt*-HEMA) (M_n = 6.6 kg/mol).

^{1}H NMR Spectra of Statistical Copolymer Syntheses

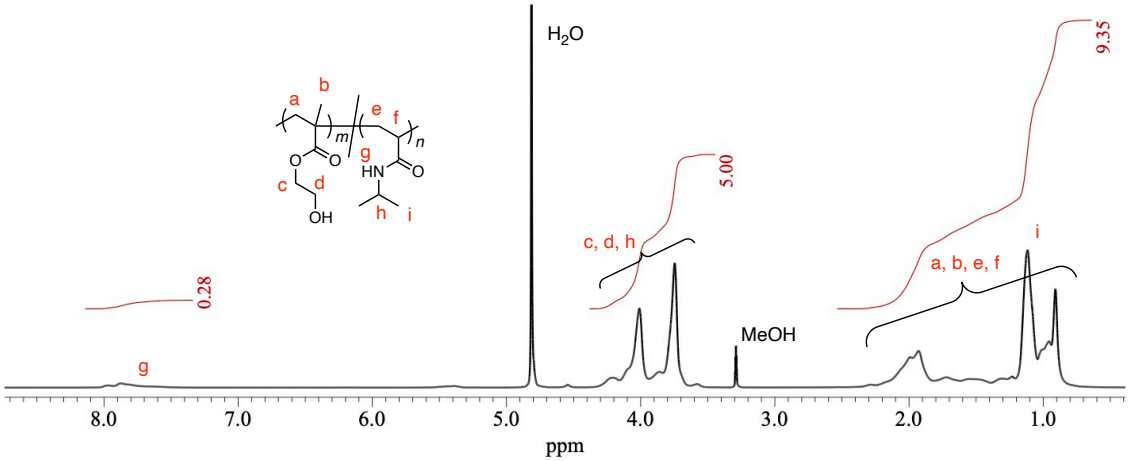


Figure S23. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*sta*-HEMA) (**Table S3**, **Entry 1**, m:n = 74:26).

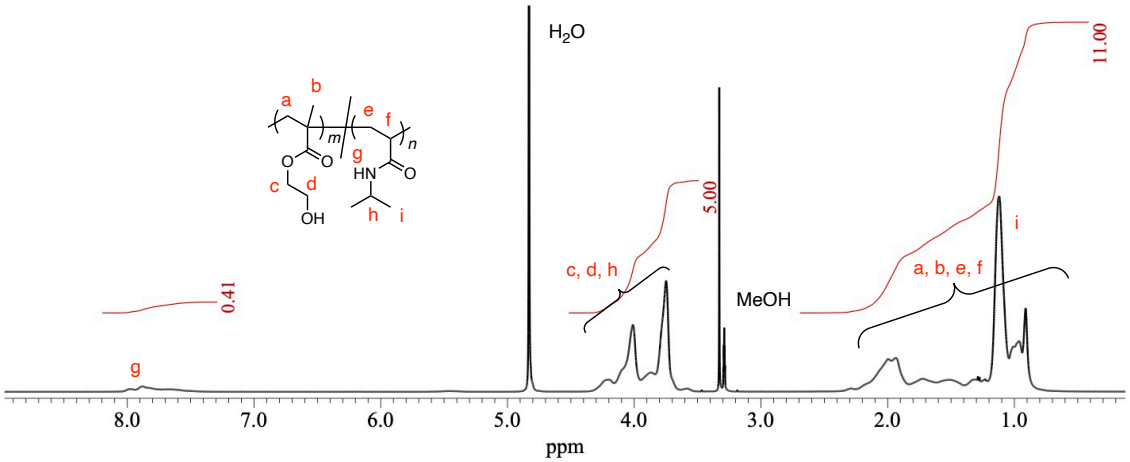


Figure S24. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*sta*-HEMA) (**Table S3**, **Entry 2**, m:n = 64:36).

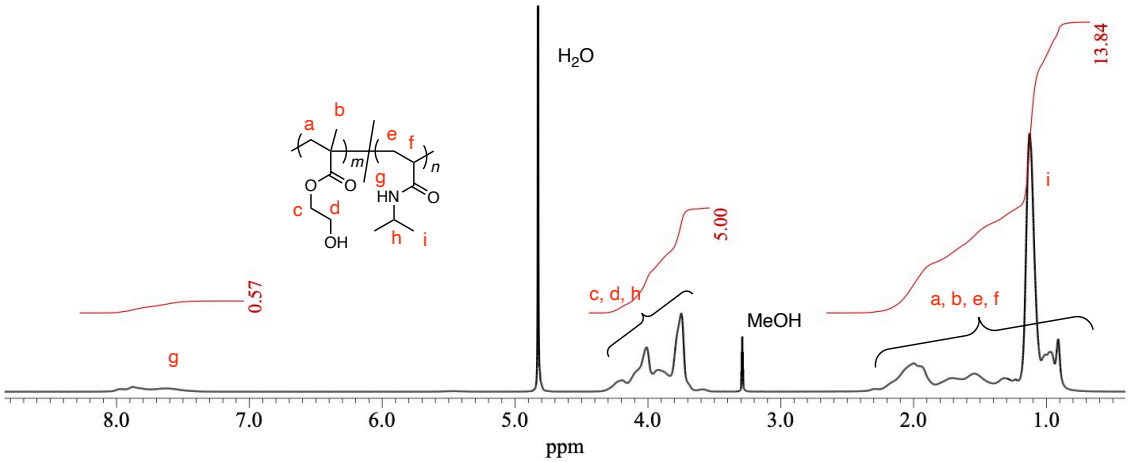


Figure S25. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*sta*-HEMA) (**Table S3**, **Entry 3**, m:n = 51:49).

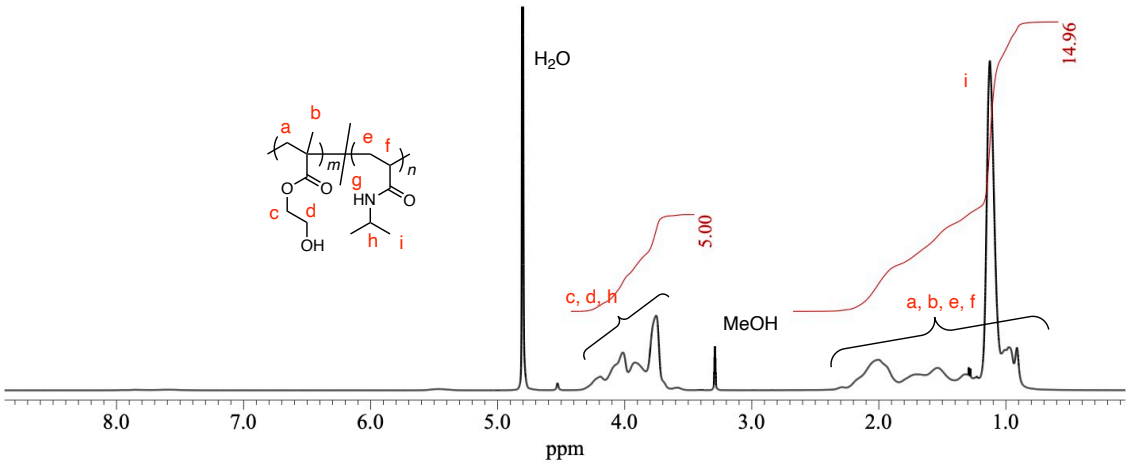


Figure S26. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*sta*-HEMA) (**Table S3**, **Entry 4**, m:n = 46:54).

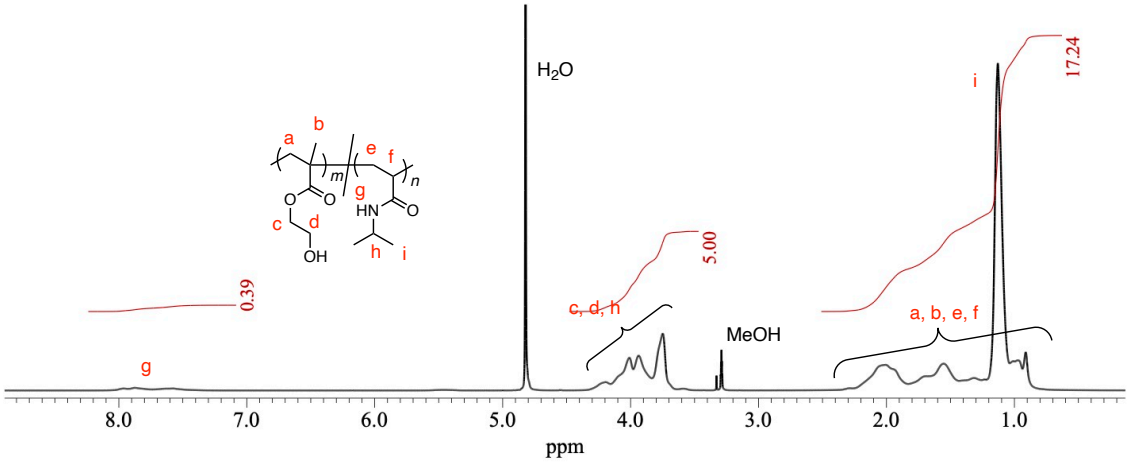


Figure S27. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(NIPAM-*sta*-HEMA) (**Table S3**, **Entry 5**, m:n = 38:62).

^{1}H NMR and ^{13}C NMR Spectra of Homopolymer Syntheses

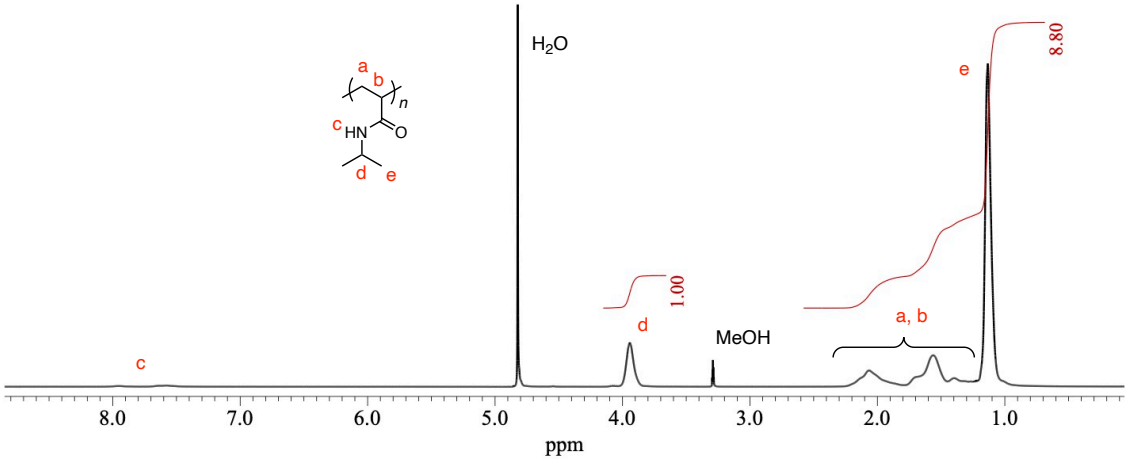


Figure S28. ^{1}H NMR (CD_3OD, r.t.) spectrum of poly(NIPAM).

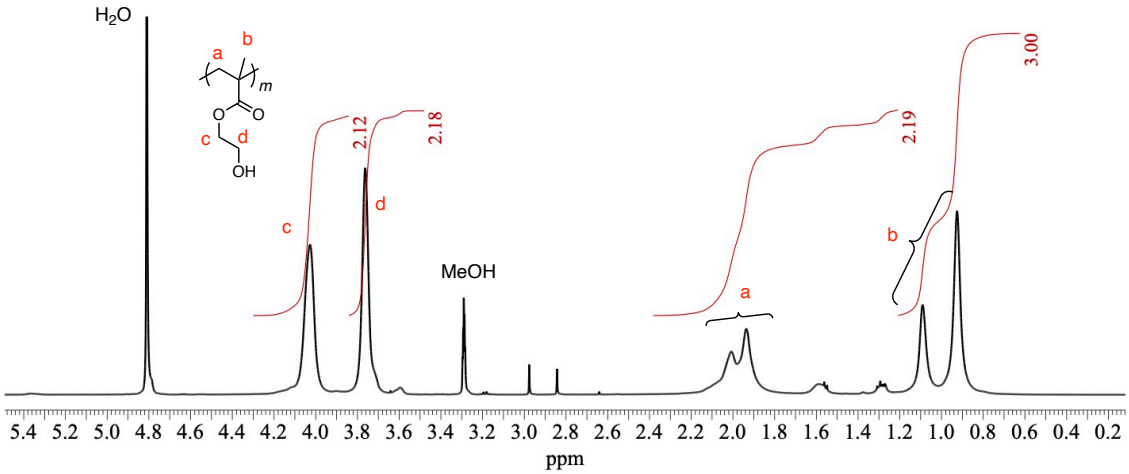


Figure S29. ^{1}H NMR spectrum (CD_3OD, r.t.) of poly(HEMA).

Reference

1 M. Fineman and S. D. Ross, *Journal of Polymer Science*, 1950, **5**, 259–262.

2 Q. Zhang, P. Wilson, Z. Li, R. McHale, J. Godfrey, A. Anastasaki, C. Waldron and D. M. Haddleton, *J. Am. Chem. Soc.*, 2013, **135**, 7355–7363.