Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2024

Supporting information

Thermal Cleavage of Hydrogen Bonds-Induced LCST-type Phase Separation of PHEMA and Related Poly(hydroxyalkyl (meth)acrylate)s in Mixed Organic Solvents

Natsuki Inaba[1†], Koki, Takasu[2†], Keitaro Matsuoka[1,2,3*], and Kazuki Sada[1,2,3*]

[1] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan.

[2] Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan.

[3] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan.

Phone: +81-11-706-3473 / Fax: +081-11-706-3474

E-mail: sadatcm@sci.hokudai.ac.jp, ma2oka@sci.hokudai.ac.jp

[†]These authers equally contributed.

Contents.

1. General information

Poly(2-hydroxyethyl methacrylate) (PHEMA) (average M_v: 20,000) was purchased from Sigma-Aldrich (529265). All polymerization reactions were carried out in sealed vessels degassing under reduced pressure unless otherwise noted. Commercially available dimethylacetoamide (DMAc), (Wako Ltd., Super Dehydrated grade) was used without further manipulation as a reaction media for polymerization reactions. Commercially available 4-hydroxypropyl acrylate stabilized with 4-methoxyphenol was purified by silicagel column chromatography before use. 3-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, and 3-hydroxypropyl acrylate were prepared by the condensation reaction of the corresponding diol and methacrylic anhydride or acryloyl chloride. The NMR spectrum is consistent with the literature[1,2]. All other reagents were commercially available and used as received unless otherwise noted.

^{1}H NMR spectra were recorded on JEOL JNM-ECZ400 spectrometers. Chemical shifts were reported in the scale relative to $(CH_3)_2SO$ (2.50 ppm) and $(CH_3)_4Si$ (0.00 ppm) as an internal reference, respectively.

Size exclusion chromatography (SEC) Measurements were performed on a polystyrene gel column Shodex K-803L and K-805L connected to a SHIMADZU CTO-20A with LC-20AD gradient pump, SPD-20A UV detector, and RID-20A refractive detector. DMF was used as an eluent at 40 °C (flow rate of 1.0 mL/min). The calibrations were made against linear poly(ethylene oxide) standards. Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were determined by SEC Measurements.

Solubility test of poly(hydroxyalkyl (meth)acrylate)s in the mixtures of various hydrogen-bonding solvents and non-polar solvents was done by mixing the suitable amount of the solvent mixtures and poly(hydroxyalkyl (meth)acrylate)s at low temperature (0 °C), room temperature (ca. 25 °C) and elevated temperature (ca. 100 °C).

Transmittance Measurements at 800 nm were recorded on a Jasco V-750 spectrophotometer with a Jasco ETC-505T temperature controller, and the temperature scan rate was 1.5 °C/min. Cloud point (T_c) was determined by the Transmittance measurement using UV-vis as the temperature at which %Transmittance = 90 in the heating process for LCST-type phase separation or in the cooling process for LCST-type phase separation, respectively. Dynamic light scattering (DLS) data were collected on a Malvern Nano-S light scattering system with a 633 nm He/Ne laser at 20 °C.

Differential scanning calorimetry (DSC) was performed on a METTLER TOLEDO STAR^e System DSC 1 at a heating rate of 10 °C/min under a nitrogen flow of 60 mL/min.

2. Polymerization procedures and characterization of poly(hydroxyalkyl (meth)acrylate)s

Poly(3-hydroxypropyl methacrylate) (P3MA)

A solution of 3-hydroxypropyl methacrylate (3.12 g, 21.6 mmol), AIBN (6.82 mg, 0.04 mmol), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic Acid (84.1 mg, 0.21 mmol) in DMAc (5 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **P3MA** (3.12 g, 100% yield) as a yellow solid.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.45-4.66 (m, 1H), 3.85-4.08 (m, 2H), 3.42-3.62 (m, 2H), 1.56-2.03 (m, 4H), 0.53-1.06 (m, 3H).

SEC (DMF): M_n =8.21×10^3, PDI = 1.11.

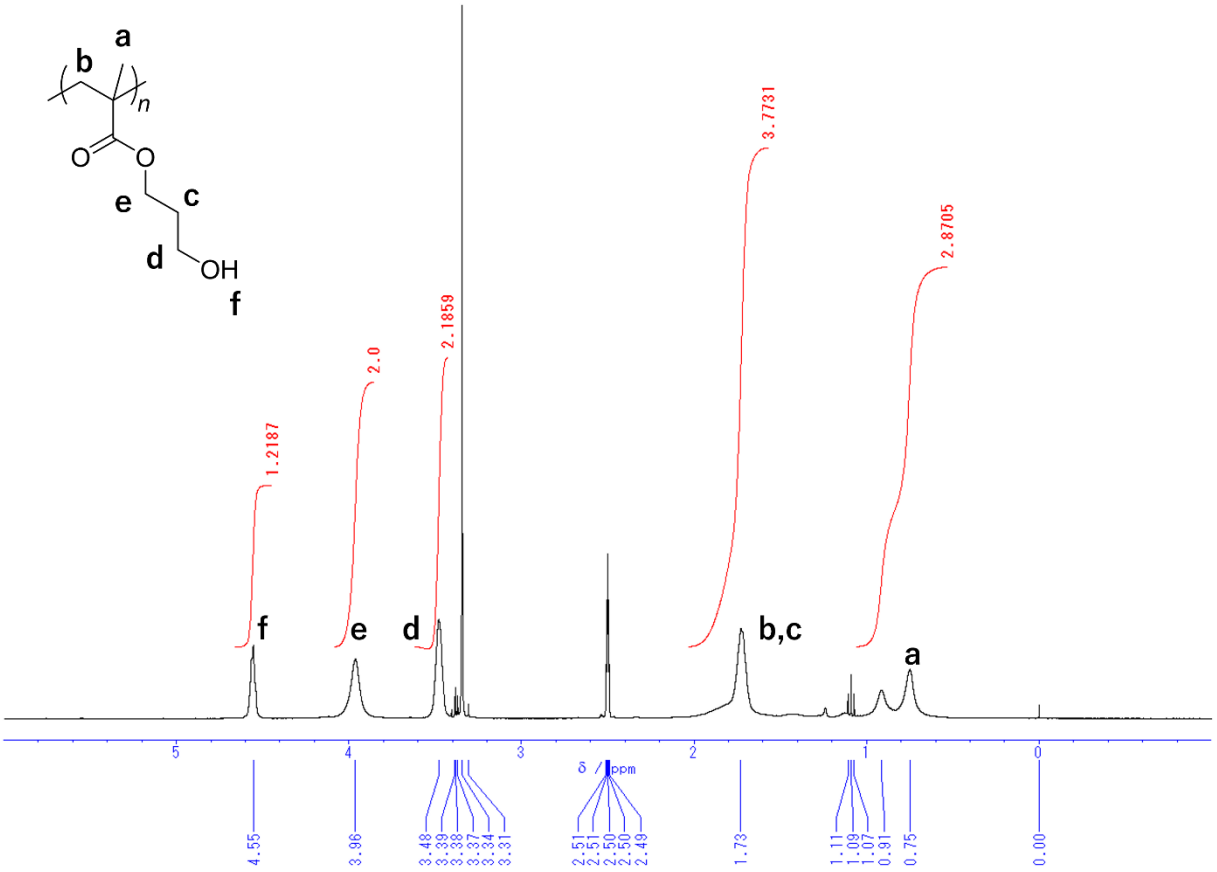


Figure S1a. ^{1}HNMR spectrum of **P3MA**

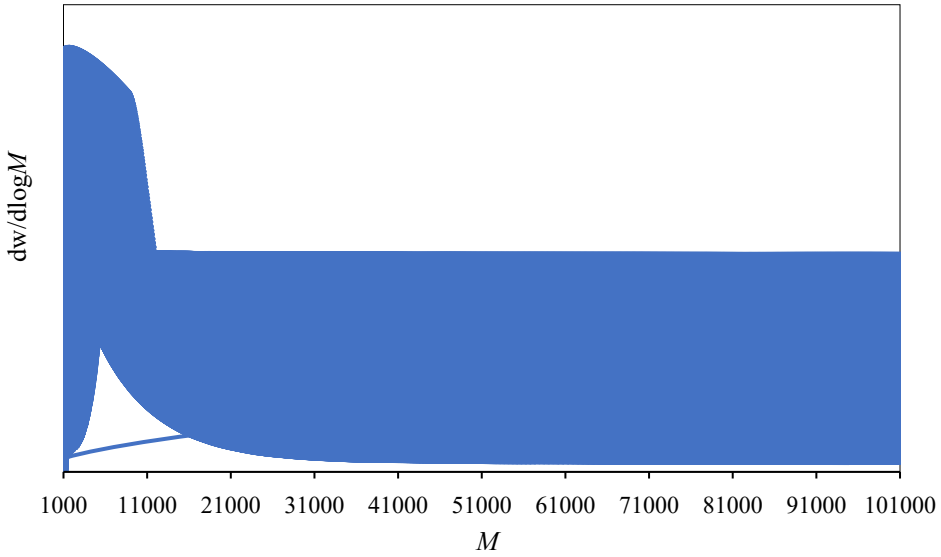


Figure S1b. SEC chromatogram of **P3MA.** The depressed peak with a molecular weight close to 1000 originates from residual solvent.

Poly(4-hydroxybutyl methacrylate) (P4MA)

A solution of 4-hydroxybutyl methacrylate (3.04 g, 19.2 mmol), AIBN (3.27 mg, 0.02 mmol), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic Acid (76.4 mg, 0.19 mmol) in DMAc (6 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **P4MA** (2.86 g, 94% yield) as a solid.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.41-4.56 (m, 1H), 3.76-4.02 (m, 2H), 3.37-3.49 (m, 2H), 1.35-1.93 (m, 6H), 0.50-1.05 (m, 3H).

SEC (DMF): M_n =8.76×10^3, PDI = 1.14.

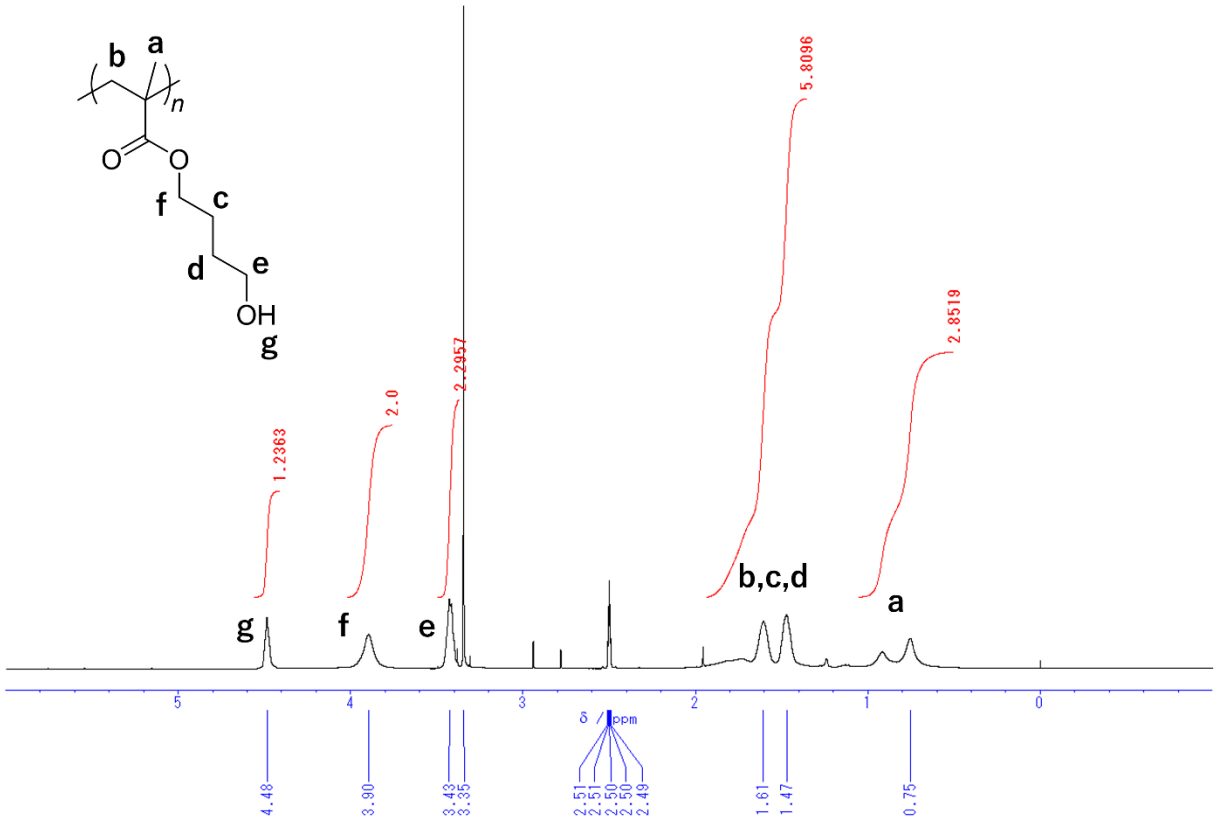


Figure S2a. ^{1}HNMR spectrum of **P4MA**

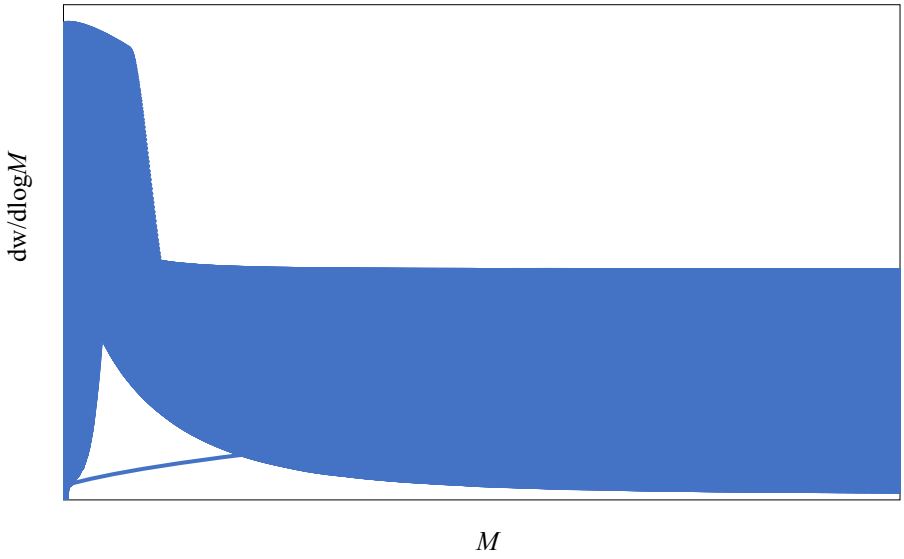


Figure S2b. SEC chromatogram of **P4MA.** The depressed peak with a molecular weight close to 1000 originates from residual solvent.

Poly(5-hydroxypentyl methacrylate) (P5MA)

A solution of 5-hydroxypentyl methacrylate (4.13 g, 24.0 mmol), AIBN (4.33 mg, 0.026 mmol), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic Acid (94.5 mg, 0.23 mmol) in DMAc (4.5 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **P5MA** (3.85 g, 93% yield) as a yellow solid.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.36-4.48 (m, 1H), 3.76-4.03 (m, 2H), 3.40-3.48 (m, 2H), 1.21-2.09 (m, 8H), 0.50-1.05 (m, 3H).

SEC (DMF): M_n =1.03×10^4, PDI = 1.35.

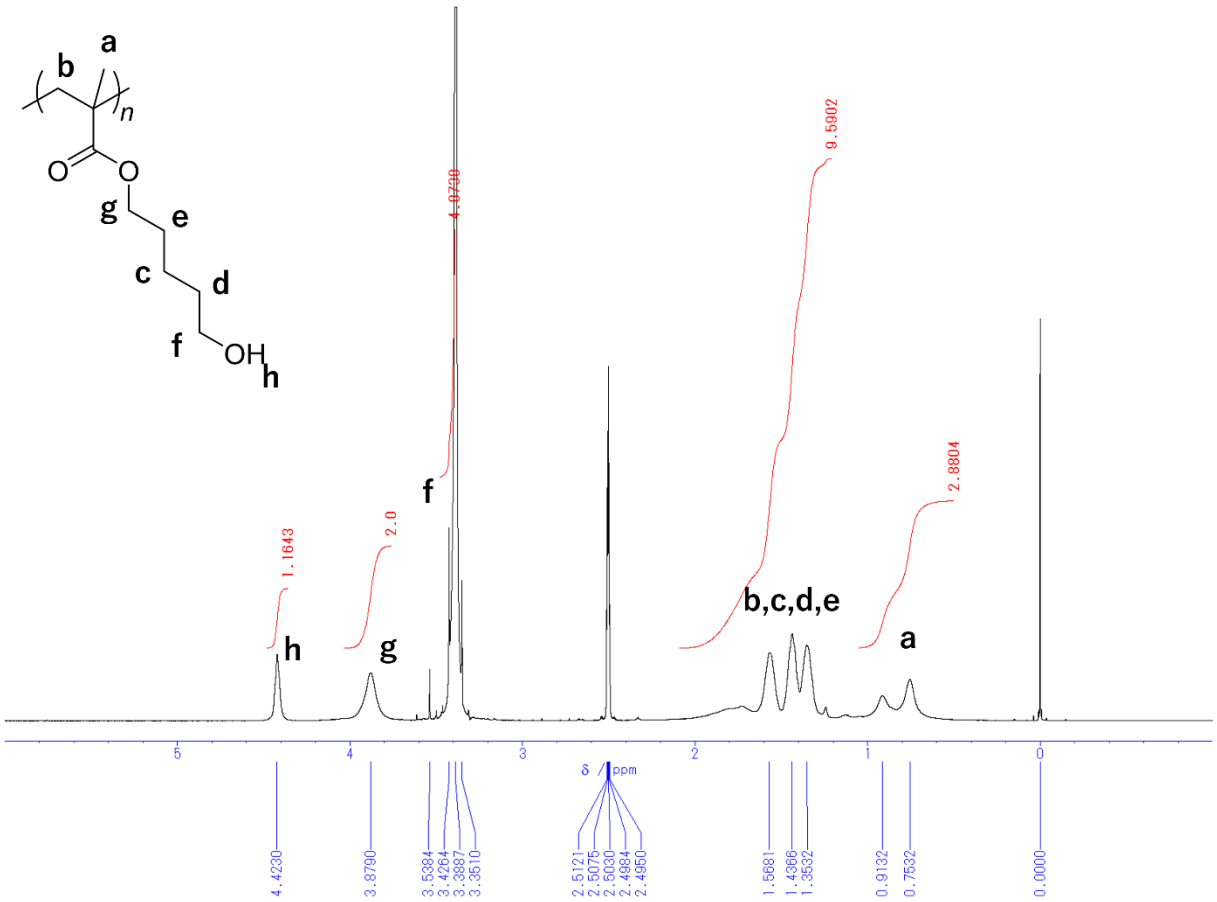


Figure S3a. ^{1}HNMR spectrum of **P5MA**

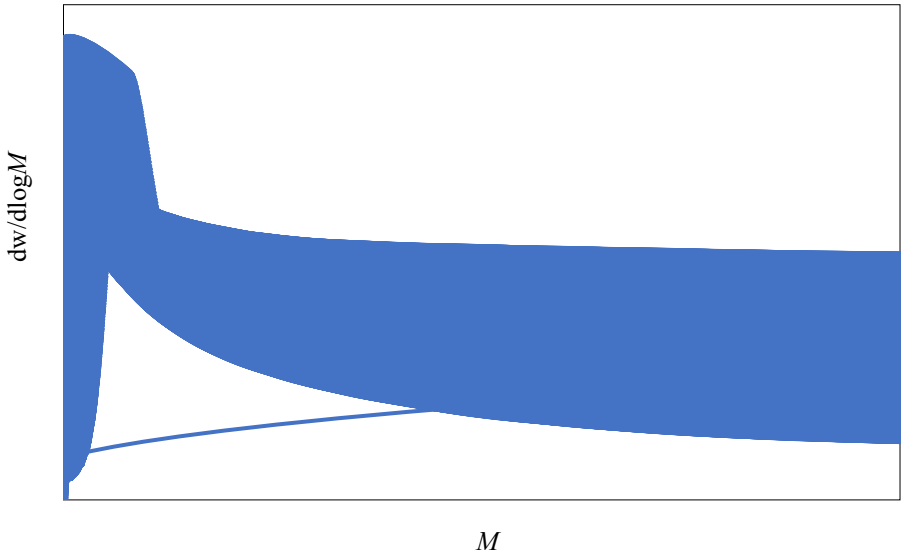


Figure S3b. SEC chromatogram of **P5MA.** The depressed peak with a molecular weight close to 1000 originates from residual solvent.

Poly(3-hydroxypropyl acrylate) (P3A)

A solution of 3-hydroxypropyl acrylate (3.08 g, 23.6 mmol), AIBN (3.80 mg, 0.023 mmol), 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic Acid (79.9 mg, 0.22 mmol) in DMAc (3 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **P3A** (2.83 g, 92% yield) as a solid.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.46-4.64 (m, 1H), 3.88-4.20 (m, 2H), 3.42-3.52 (m, 2H), 2.02-2.39 (m, 1H), 1.18-1.92 (m, 4H).

SEC (DMF): M_n =8.67×10^3, PDI = 1.04.

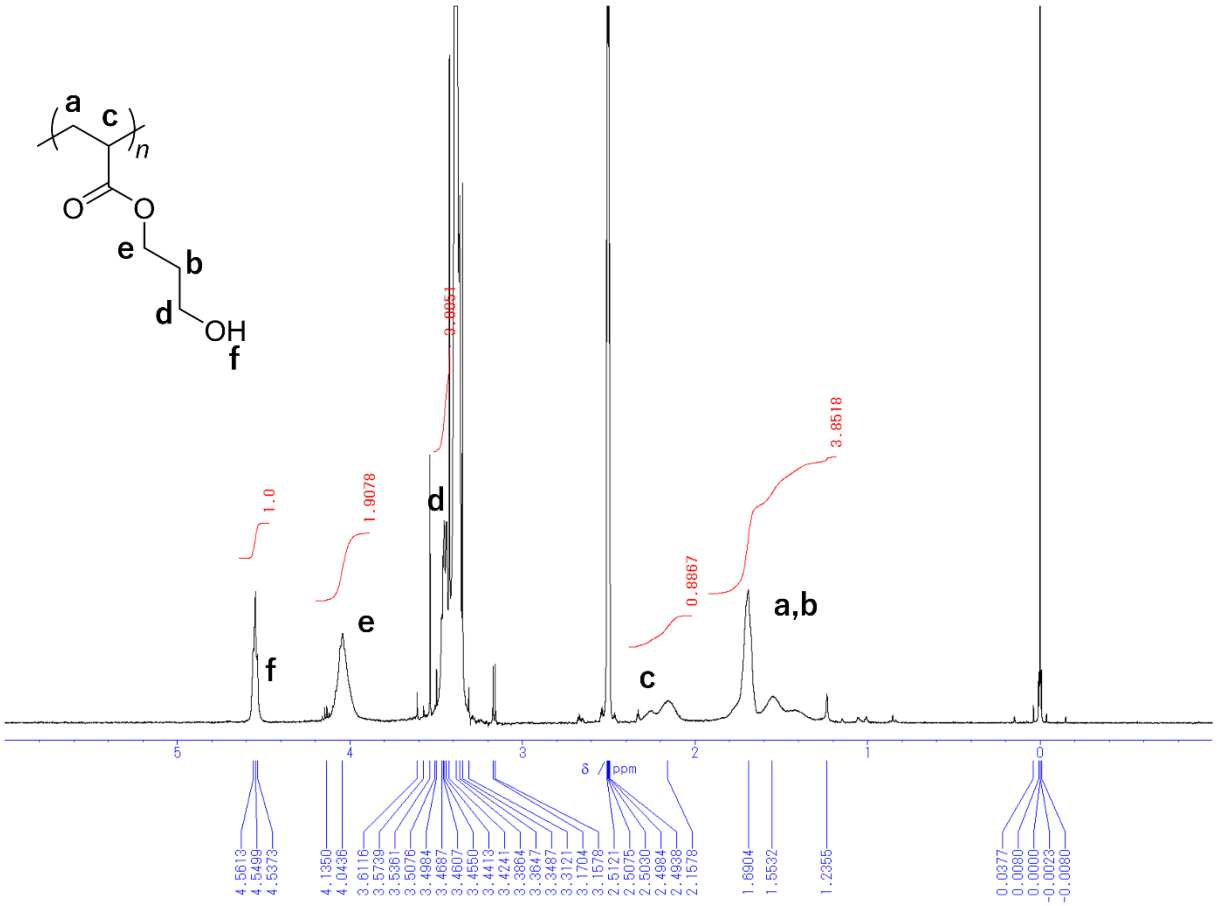


Figure S4a. ^{1}HNMR spectrum of **P3A**

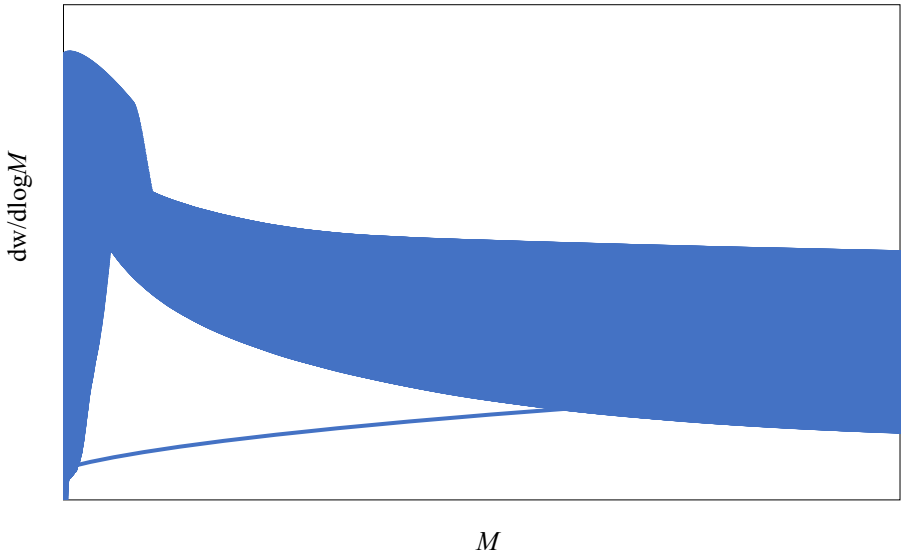


Figure S4b. SEC chromatogram of **P3A.** The depressed peak with a molecular weight close to 1000 originates from residual solvent.

Poly(4-hydroxybutyl acrylate) (P4A)

A solution of 4-hydroxybutyl acrylate (5.20 g, 36.1 mmol), AIBN (10.9 mg, 0.067 mmol), 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic Acid (130 mg, 0.34 mmol) in DMAc (5 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **P4A** (4.66 g, 90% yield) as a yellow solid.

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.34-4.51 (m, 1H), 3.81-4.08 (m, 2H), 3.37-3.46 (m, 2H), 2.01-2.40 (m, 1H), 1.29-1.87 (m, 6H).

SEC (DMF): M_n =7.05×10^3, PDI = 1.25.

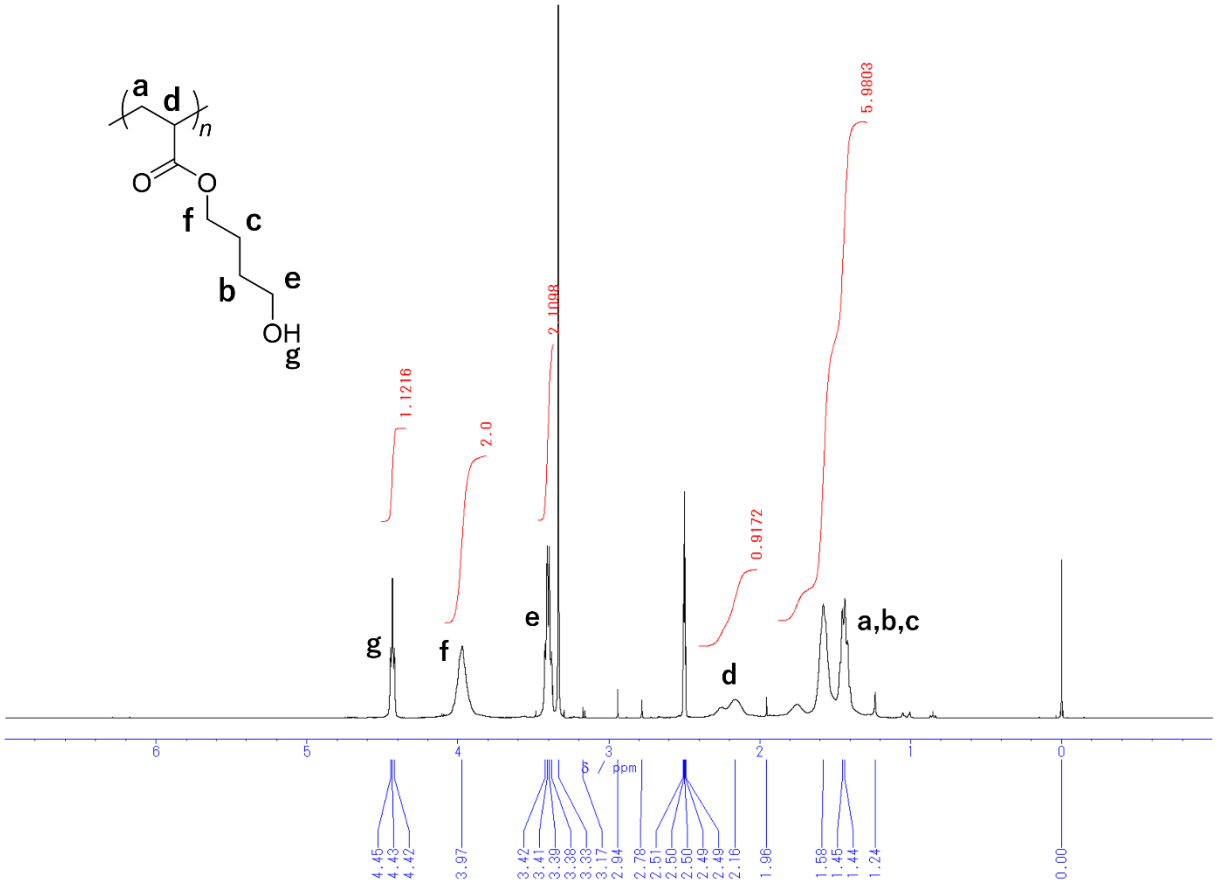


Figure S5a. ^{1}HNMR spectrum of **P4A**

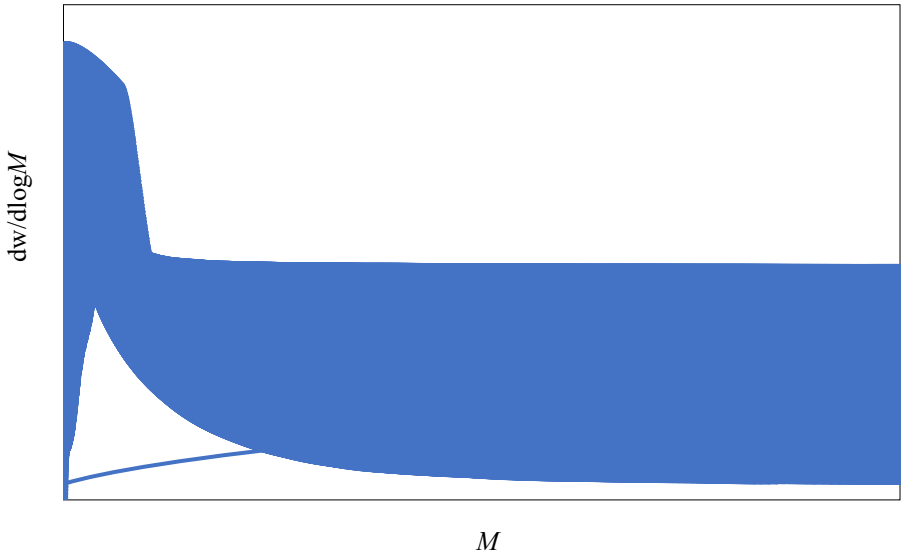


Figure S5b. SEC chromatogram of **P4A.** The depressed peak with a molecular weight close to 1000 originates from residual solvent.

3. Solubility and Thermo-responsiveness of PHEMA

S: soluble, I: insoluble, P: partially soluble, F: freeze of solvent, cool: ca. 0°C, heat: ca. 100°C

Table S1. Solubility of **PHEMA**

polymer	solvent	volume	solubility		
			cool	r.t.	heat
2.15 mg	DMSO	85 µL	F	S	S
3.31 mg	acetonitrile	130 µL	I	I	I
2.26 mg	DMF	90 µL	S	S	S
4.22 mg	methanol	170 µL	S	S	S
2.62 mg	ethanol	105 µL	S	S	S
2.27 mg	1-propanol	90 µL	I	S	S
2.38 mg	2-butanone	95 µL	I	I	I
2.10 mg	1-octanol	100 µL	I	I	I
2.55 mg	THF	100 µL	I	I	I
2.49 mg	acetic acid	100 µL	S	S	S
2.78 mg	ethyl acetate	110 µL	I	I	I
2.42 mg	1,4-dioxane	100 µL	I	I	S
2.34 mg	toluene	95 µL	I	I	I
2.47 mg	DCE	100 µL	I	I	I
2.48 mg	cyclohexane	100 µL	F	I	I

Table S2. Thermo-responsiveness of **PHEMA** in pure solvent

polymer	solvent	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.30 mg	1-butanol	92 μL	I	I	S	UCST
2.50 mg		250 μL	I	I	S	UCST
2.23 mg		446 μL	I	I	S	UCST
2.39 mg	2-butanol	96 μL	I	S	S	UCST
3.02 mg		302 μL	I	S	S	UCST
2.83 mg		566 μL	P	S	S	
2.25 mg	2-methyl-1-propanol	90 μL	I	I	S	UCST
3.41 mg		341 μL	I	I	S	UCST
2.86 mg		572 μL	I	I	S	UCST
3.20 mg	ethylene glycol	88 μL	S	S	S	
3.13 mg		313 μL	S	S	S	
3.10 mg		620 μL	S	S	S	
2.45 mg	glycerol	98 μL	F	I	S	UCST
2.30 mg		230 μL	F	I	S	UCST
2.43 mg	1-hexanol	99 μL	I	I	I	

Table S3. Thermo-responsiveness of **PHEMA** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.37 mg	DMF : DCE = 3.0 : 7.0	95 μL	S	S	S	
2.73 mg	DMF : DCE = 2.5 : 7.5	110 μL	S	S	S	
3.09 mg	DMF : DCE = 2.2 : 7.8	120 μL	S	S	S	
2.85 mg	DMF : DCE = 2.1 : 7.9	115 μL	S	S	S	
2.97 mg	DMF : DCE = 2.0 : 8.0	120 μL	S	I	I	LCST
2.96 mg	DMF : DCE = 1.0 : 9.0	120 μL	I	I	I	
3.10 mg	methanol : DCE = 5.0 : 5.0	125 μL	S	S	S	
2.44 mg	methanol : DCE = 4.0 : 6.0	100 μL	S	S	I	LCST
3.32 mg	methanol : DCE = 3.5 : 6.5	130 μL	S	S	I	LCST
3.97 mg	methanol : DCE = 3.0 : 7.0	160 μL	S	I	I	LCST
3.72 mg	ethanol : DCE = 4.0 : 6.0	150 μL	S	S	S	
3.02 mg	ethanol : DCE = 3.0 : 7.0	120 μL	S	S	I	LCST
4.03 mg	ethanol : DCE = 2.0 : 8.0	160 μL	I	I	I	

3.38 mg	1-propanol : DCE = 4.0 : 6.0	135 µL	S	S	S	
25.51mg	1-propanol : DCE = 3.0 : 7.0	1000 µL	S	S	I	LCST (67 °C)
21.13mg	1-propanol : DCE = 2.8 : 7.6	845 µL	S	S	I	LCST (52 °C)
20.30mg	1-propanol : DCE = 2.6 : 7.4	810 µL	S	S	I	LCST (33 °C)
20.52mg	1-propanol : DCE = 2.5 : 7.5	820 µL	S	S	I	LCST (26 °C)
20.72mg	1-propanol : DCE = 2.4 : 7.6	830 µL	I	I	I	
4.89 mg	1-propanol : DCE = 2.0 : 8.0	195 µL	I	I	I	
5.03 mg	morpholine : DCE = 5.0 : 5.0	200 µL	S	S	S	
2.51 mg	morpholine : DCE = 4.0 : 6.0	100 µL	S	S	S	
2.79 mg	morpholine : DCE = 3.0 : 7.0	110 µL	S	S	S	
3.60 mg	morpholine : DCE = 2.0 : 8.0	145 µL	S	S	I	LCST
3.45 mg	morpholine : DCE = 1.0 : 9.0	140 µL	I	I	I	
3.94 mg	benzylamine : DCE = 5.0 : 5.0	155 µL	S	S	S	
4.11 mg	benzylamine : DCE = 4.0 : 6.0	165 µL	S	S	S	
2.34 mg	benzylamine : DCE = 3.0 : 7.0	95 µL	S	S	S	
2.32 mg	benzylamine : DCE = 2.0 : 8.0	95 µL	S	S	I	LCST
2.90 mg	benzylamine : DCE = 1.0 : 9.0	115 µL	I	I	I	
2.74 mg	acetic acid : DCE = 9.0 : 1.0	110 µL	S	S	S	
2.61 mg	acetic acid : DCE = 8.0 : 2.0	105 µL	S	S	S	
3.08 mg	acetic acid : DCE = 7.0 : 3.0	120 µL	I	S	S	UCST
2.43 mg	acetic acid : DCE = 6.0 : 4.0	100 µL	I	I	S	UCST
2.51 mg	1-butanol : DCE = 3.5 : 6.5	100 µL	S	S	S	
2.10 mg	1-butanol : DCE = 3.0 : 7.0	84 µL	S	S	I	LCST
2.35 mg	1-butanol : DCE = 2.5 : 7.5	94 µL	S	S	I	LCST
2.48 mg	1-butanol : DCE = 2.0 : 8.0	99 µL	P	P	I	
2.51 mg	1-butanol : DCE = 1.5 : 8.5	100 µL	I	I	I	
2.23 mg	2-butanol : DCE = 3.5 : 6.5	89 µL	S	S	S	
1.90 mg	2-butanol : DCE = 3.0 : 7.0	76 µL	S	S	I	LCST
2.45 mg	2-butanol : DCE = 2.5 : 7.5	98 µL	S	S	I	LCST
2.53 mg	2-butanol : DCE = 2.0 : 8.0	101 µL	S	P	I	LCST
2.58 mg	2-butanol : DCE = 1.5 : 8.5	103 µL	I	I	I	
2.47 mg	2 methyl-1-propanol : DCE = 3.5 : 6.5	99 µL	S	S	S	
2.33 mg	2 methyl-1-propanol : DCE = 3.0 : 7.0	93 µL	S	S	I	LCST
2.14 mg	2 methyl-1-propanol : DCE = 2.5 : 7.5	86 µL	S	S	I	LCST
2.34 mg	2 methyl-1-propanol : DCE =	94 µL	P	P	I	

2.56 mg	2.0 : 8.0 2 methyl-1-propanol : DCE = 1.5 : 8.5	102 µL	I	I	I

Table S4. Composition of solution.

polymer	solvent	volume	concentration
23.14 mg	1-propanol	930 µL	24.9 mg/mL

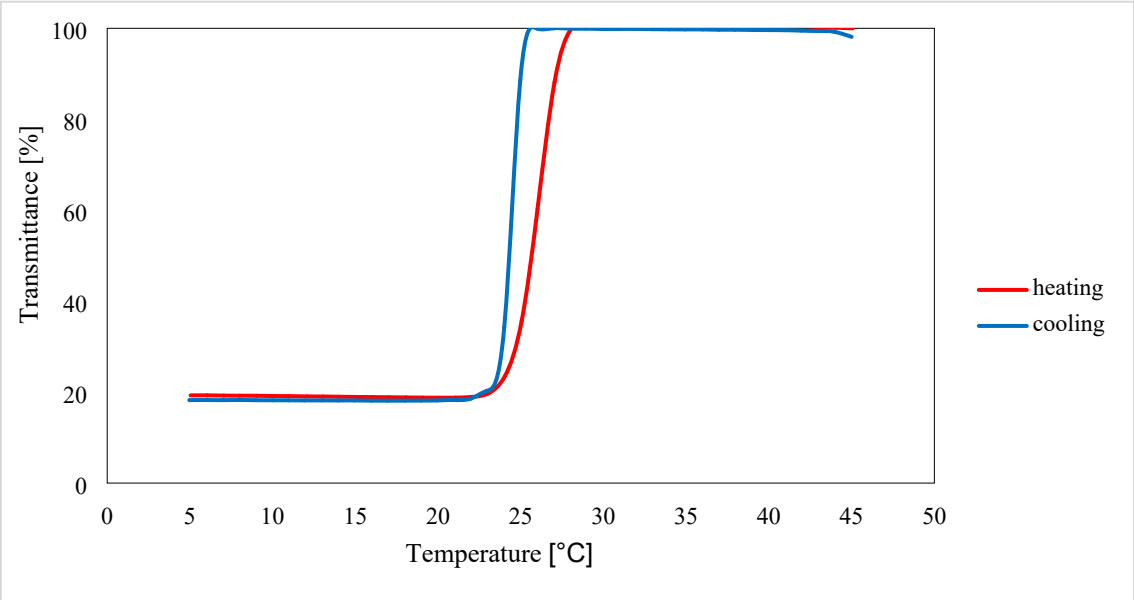


Figure S6. Transmittance change of **PHEMA** in 1-propanol at 800 nm.

4. Temperature-dependent particle size change of PHEMA

Table S5. Composition of solution.

polymer	solvent (mol. ratio)		concentration
24.39 mg	1-propanol : DCE = 3.0 : 7.0	980 μL	25 mg/mL

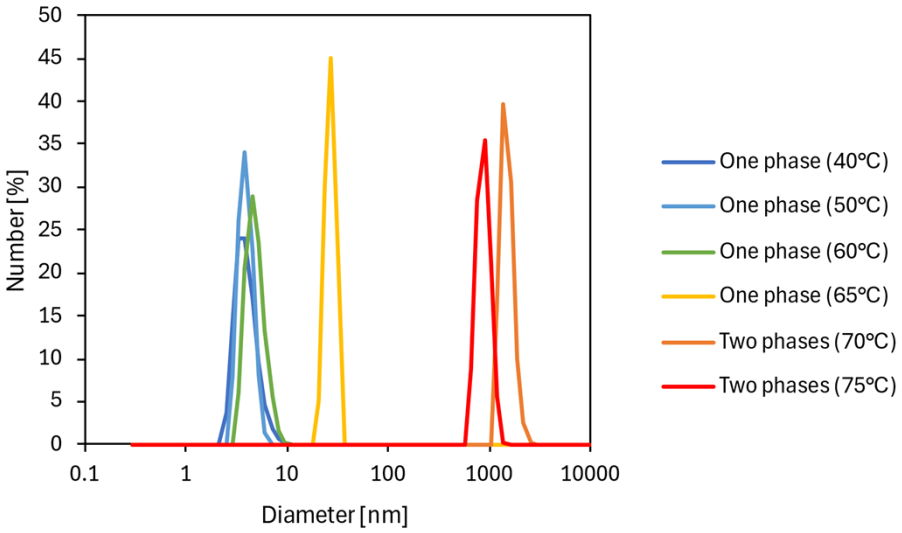


Figure S7. Size distribution by number of **PHEMA** in 1-propanol and DCE.

5. Polymer concentration dependence on Thermo-responsiveness of poly(hydroxyalkyl (meth)acrylate)s

Table S6. Measurement conditions: 1-propanol:DCE = 2.8:7.2.

PHEMA	solvent	Conc.	solubility			Thermo-responsiveness
			cool	r.t.	heat	
10.58 mg	1060 µL	10 mg/mL	S	S	I	LCST
21.13 mg	845 µL	25 mg/mL	S	S	I	LCST
41.7 mg	835 µL	50 mg/mL	S	S	I	LCST
61.0 mg	815 µL	75 mg/mL	S	S	I	LCST
82.0 mg	820 µL	100 mg/mL	I	I	I	insoluble

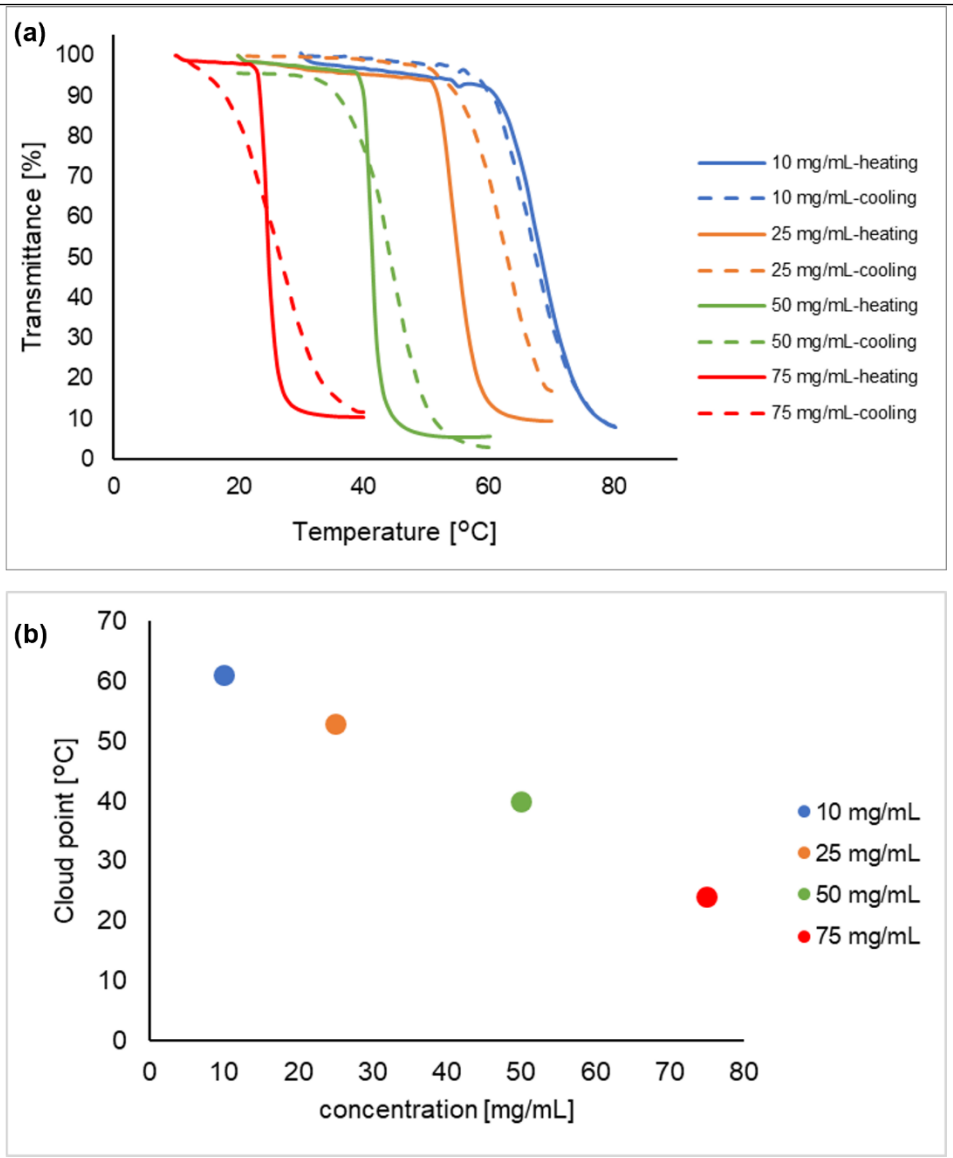


Figure S8. (a) Transmittance change at 800 nm of PHEMA in 1-propanol:DCE (mol. ratio: 2.8:7.2) with the increased polymer concentration from 10 mg/mL to 75 mg/mL. (b) The effects of polymer concentration on the change of the cloud point in the heating process (90% of transmission).

6. The effect of molecular weight on the thermo-responsiveness of PHEMA

6-1. Preparation of lower molecular weight of Poly(2-hydroxyethyl methacrylate) (sPHEMA)

A solution of 2-hydroxyethyl methacrylate (3.0 g, 23.3 mmol), AIBN (3.47 mg, 0.021 mmol), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic Acid (92.2 mg, 0.23 mmol) in DMAc (6 mL) was prepared in an ampule. The ampule was degassed with three freeze-evacuate-thaw cycles and sealed. The reaction mixture was stirred at 80 °C for 24 h. After the ampule was cooled, the mixture was diluted with MeOH and reprecipitated with diethyl ether. Filtration and drying in vaquo afforded **sPHEMA** (3.10 g, quant).

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 4.70-4.94 (m, 1H), 3.73-4.26 (m, 2H), 3.47-3.73 (m, 2H), 1.37-2.24 (m, 2H), 0.48-1.07 (m, 3H).

SEC (DMF): M_n = 8.22×10^3, M_w = 7.07×10^3, PDI = 1.13.

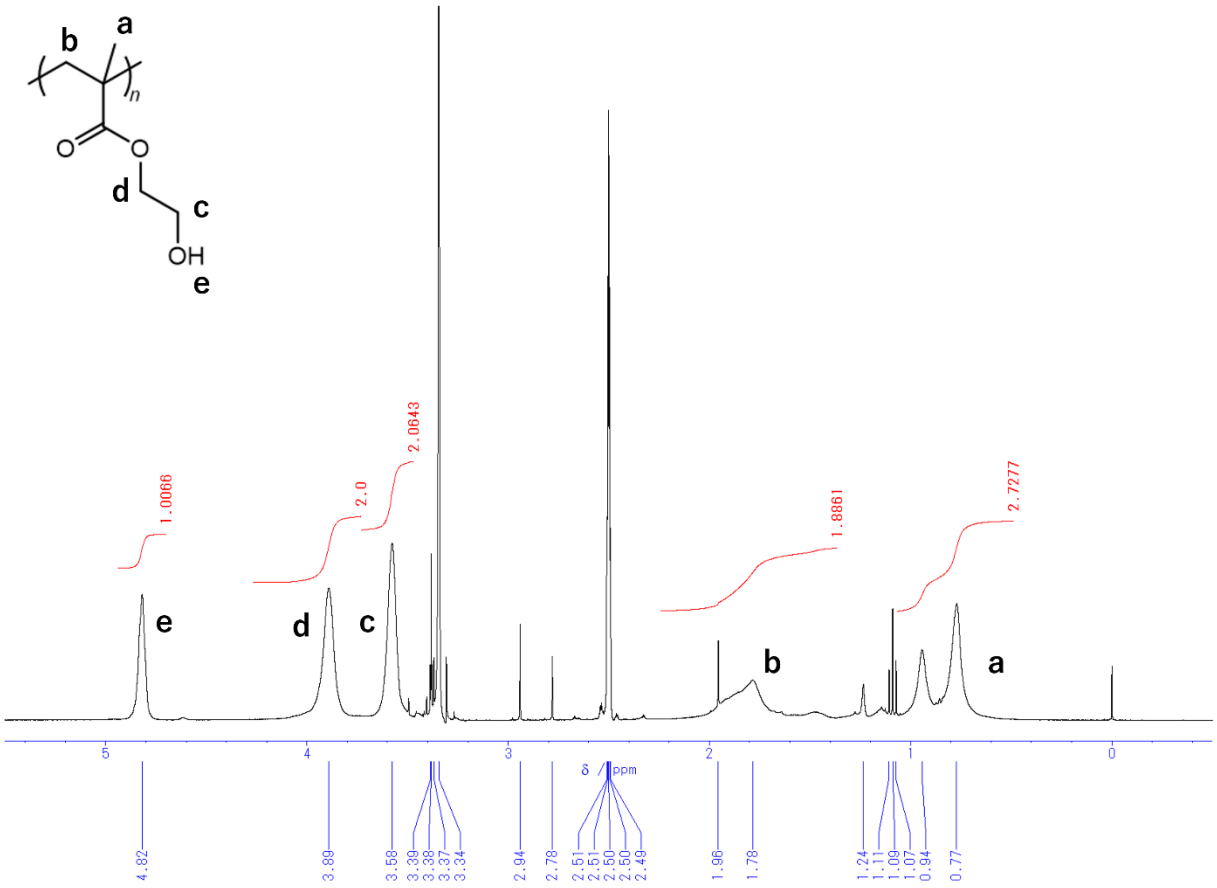


Figure S9a. ^{1}HNMR spectrum of s**PHEMA**

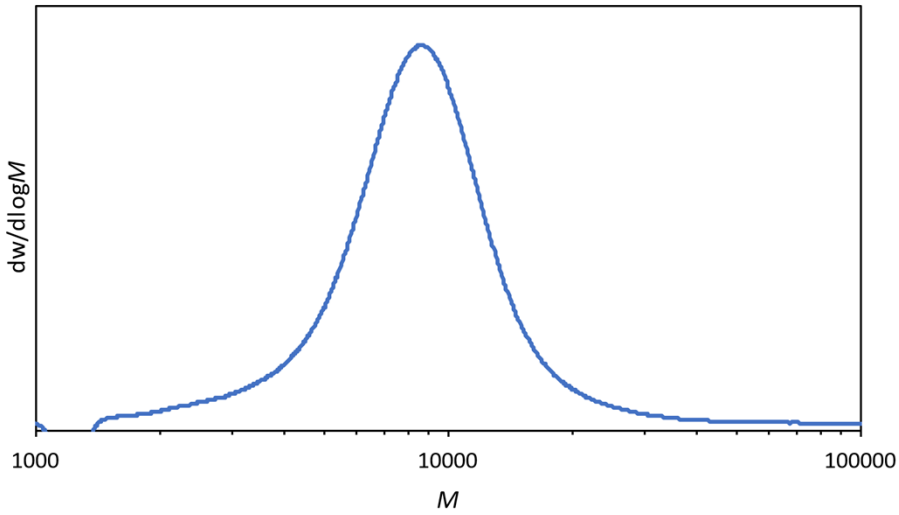


Figure S9b. SEC chromatogram of s**PHEMA**

6-2. Thermo-responsiveness of sPHEMA

Table S7. Thermo-responsiveness of **sPHEMA** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
4.80 mg	methanol : DCE = 5.0 : 5.0	95 µL	S	S	S	
4.99 mg	methanol : DCE = 4.0 : 6.0	100 µL	S	S	I	LCST
4.79 mg	methanol : DCE = 3.0 : 7.0	95 µL	I	I	I	
4.76 mg	ethanol : DCE = 4.0 : 6.0	95 µL	S	S	S	
4.84 mg	ethanol : DCE = 3.0 : 7.0	95 µL	S	S	I	LCST
5.73 mg	ethanol : DCE = 2.0 : 8.0	115 µL	I	I	I	
5.05 mg	1-propanol : DCE = 4.0 : 6.0	100 µL	S	S	S	
4.85 mg	1-propanol : DCE = 3.0 : 7.0	95 µL	S	S	S	
5.11 mg	1-propanol : DCE = 2.5 : 7.5	100 µL	S	S	I	LCST
5.65 mg	1-propanol : DCE = 2.0 : 8.0	115 µL	I	I	I	

Table S8. Composition of solution.

polymer	solvent (mol. ratio)		concentration
41.6 mg	1-propanol : DCE = 2.5 : 7.5	815 µL	51 mg/mL

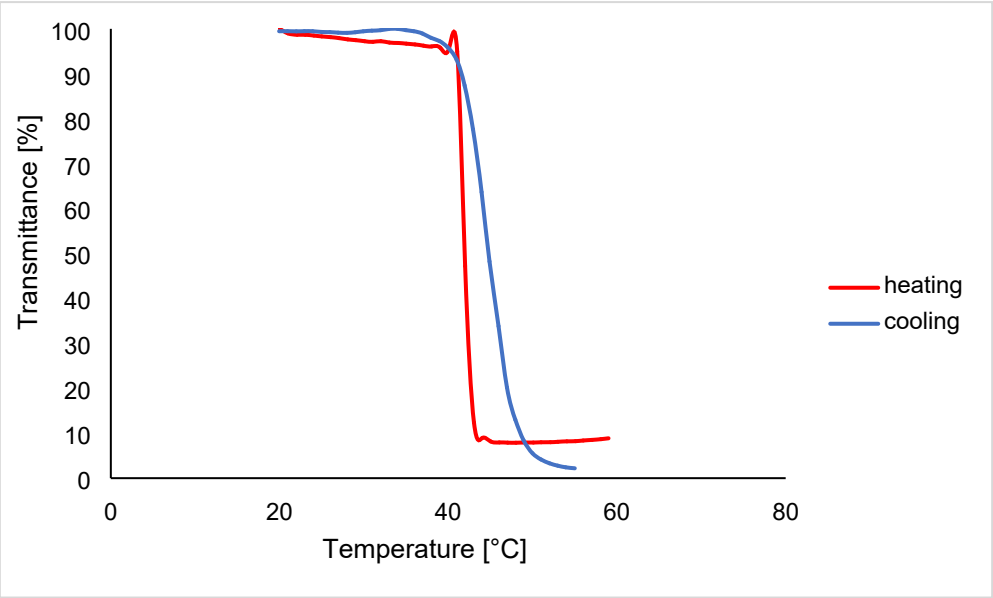
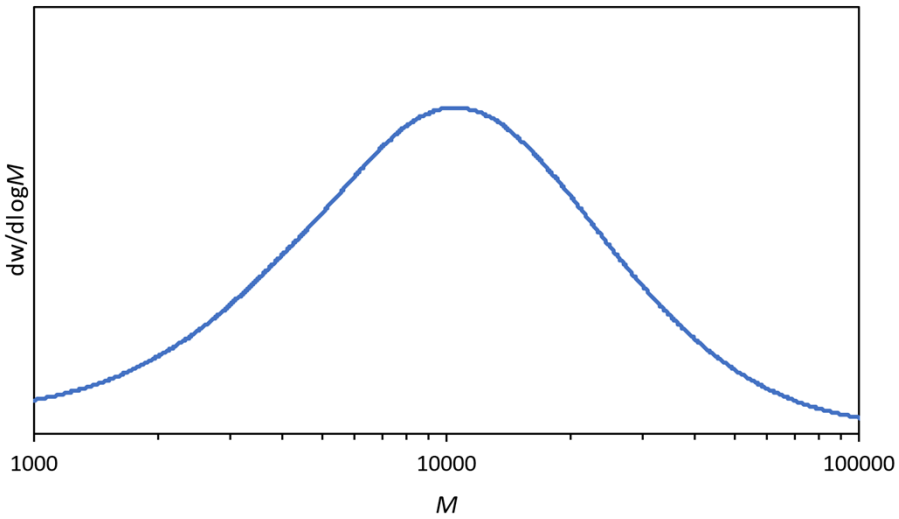


Figure S10. Transmittance change of **sPHEMA** in 1-propanol and DCE at 800 nm.

6-3. Comparison of PHEMA and sPHEMA on their thermo-responsiveness

Since only M_v was listed on the website for commercially available **PHEMA** concerning their molecular weight, we conducted SEC measurement of **PHEMA** and calculated M_n, M_w, and PDI.



SEC (DMF): $M_n = 7.63\times10^3$, $M_w = 1.53\times10^4$, PDI = 2.00.

Figure S11. SEC chromatogram of commercially available **PHEMA**

Table S9. The effect of molecular weight on the thermo-responsiveness.[a]

Polymer	M_w ($\times 10^3$)	Solvent (mol. ratio)	Thermo-responsiveness
PHEMA	15.3	1-propanol : DCE = 2.8 : 7.2	LCST (40 °C)
sPHEMA	8.22	1-propanol : DCE = 2.5 : 7.5	LCST (42 °C)

[a] Concentration: 50-51 mg/mL, 800 nm, scan rate: 1.5 °C

As shown in **Table S9**, both **PHEMA** and **sPHEMA** exhibited LCST-type phase separation in 1-propanol/DCE binary solvent at almost the same cloud point (ca. 40 °C). Because of its lower molecular weight, **sPHEMA** had a higher solubility in 1-propanol/DCE and a lower molar ratio of 1-propanol on the LCST-type phase separation than **PHEMA**.

7. Solubility and Thermo-responsiveness of poly(hydroxyalkyl (meth)acrylate)s

7-1. Summary of solubility of poly(hydroxyalkyl (meth)acrylate)s in a series of primary aliphatic alcohols

Table S10. Solubility of poly(hydroxyalkyl methacrylate)s (25 mg/mL, rt).

	PHEMA	**P3MA**	**P4MA**	**P5MA**
methanol	S	S	S	S
ethanol	S	S	S	S
1-propanol	S	S	S	S
1-butanol	I	S	S	S
1-hexanol	I	I	S	S
1-octanol	I	I	I	S

Table S11. Solubility of poly(hydroxyalkyl acrylate)s (25 mg/mL, rt).

	P3A	**P4A**
methanol	S	S
ethanol	S	S
1-propanol	S	S
1-butanol	S	S
1-hexanol	I	S
1-octanol	I	I

7-2. Thermo-responsiveness of P3MA

Table S12. Thermo-responsiveness of **P3MA** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
5.19 mg	methanol : DCE = 5.0 : 5.0	105 μL	S	S	S	
5.63 mg	methanol: DCE = 4.0 : 6.0	115 μL	S	S	I	LCST
6.05 mg	methanol: DCE = 3.0 : 7.0	120 μL	I	I	I	
4.90 mg	ethanol : DCE = 4.0 : 6.0	100 μL	S	S	S	
4.84 mg	ethanol: DCE = 3.7 : 6.3	95 μL	S	S	I	LCST
4.86 mg	ethanol: DCE = 3.5 : 6.5	95 μL	S	I	I	LCST
5.05 mg	ethanol: DCE = 3.0 : 7.0	100 μL	I	I	I	
5.18 mg	ethanol: DCE = 2.0 : 8.0	105 μL	I	I	I	
4.77 mg	1-propanol : DCE = 4.0 : 6.0	95 μL	S	S	S	
5.30 mg	1-propanol: DCE = 3.5 : 6.5	105 μL	S	S	I	LCST
5.32 mg	1-propanol: DCE = 3.3 : 6.7	105 μL	S	S	I	LCST
5.07 mg	1-propanol: DCE = 3.0 : 7.0	100 μL	I	I	I	
5.47 mg	1-butanol: DCE = 4.0 : 6.0	110 μL	S	S	S	
5.12 mg	1-butanol: DCE = 3.0 : 7.0	100 μL	S	S	I	LCST
4.83 mg	ethanol : toluene = 7.0 : 3.0	95 μL	S	S	S	
7.00 mg	ethanol : toluene = 6.0 : 4.0	140 μL	S	S	I	LCST
5.39 mg	ethanol : toluene = 5.8 : 4.2	110 μL	I	I	I	
5.23 mg	ethanol : toluene = 5.0 : 5.0	105 μL	I	I	I	
4.64 mg	1-propanol : toluene = 7.0 : 3.0	95 μL	S	S	S	
7.49 mg	1-propanol : toluene = 6.0 : 4.0	150 μL	S	S	I	LCST
5.14 mg	1-propanol : toluene = 5.9 : 4.1	100 μL	S	S	I	LCST
5.67 mg	1-propanol : toluene = 5.8 : 4.2	115 μL	S	S	I	LCST
5.67 mg	1-propanol : toluene = 5.0 : 5.0	115 μL	I	I	I	
5.84 mg	1-butanol : toluene = 7.0 : 3.0	115 μL	S	S	S	
9.51 mg	1-butanol : toluene = 6.0 : 4.0	190 μL	S	S	I	LCST
5.76 mg	1-butanol : toluene = 5.8 : 4.2	115 μL	I	I	I	
4.69 mg	1-butanol : toluene = 5.0 : 5.0	95 μL	I	I	I	

Table S13. Composition of solution.

polymer	solvent (mol. ratio)	volume	concentration
149.1 mg	1-propanol : DCE = 3.5 : 6.5	2920 μL	51 mg/mL

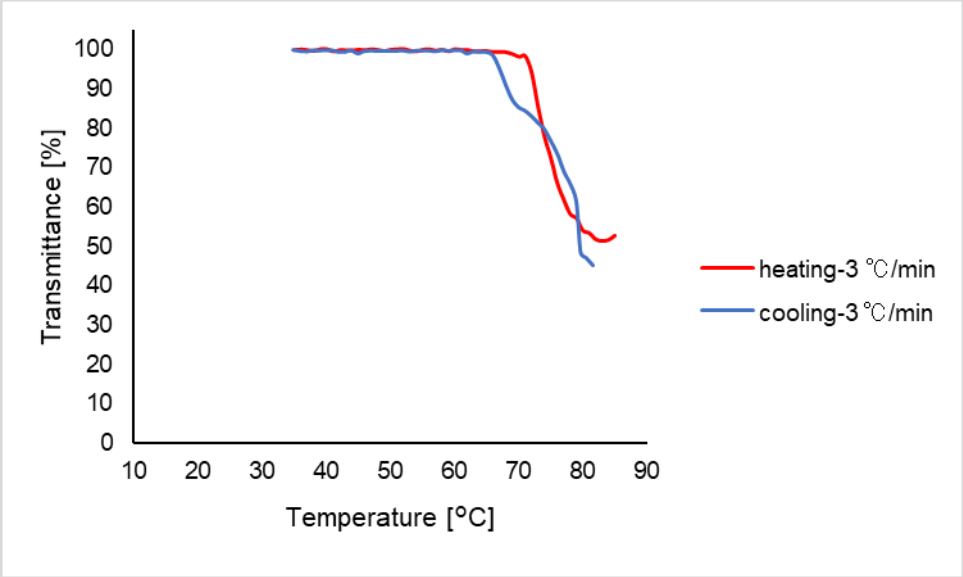


Figure S12. Transmittance change of **P3MA** in 1-propanol and DCE at 800 nm. (3 °C/min)

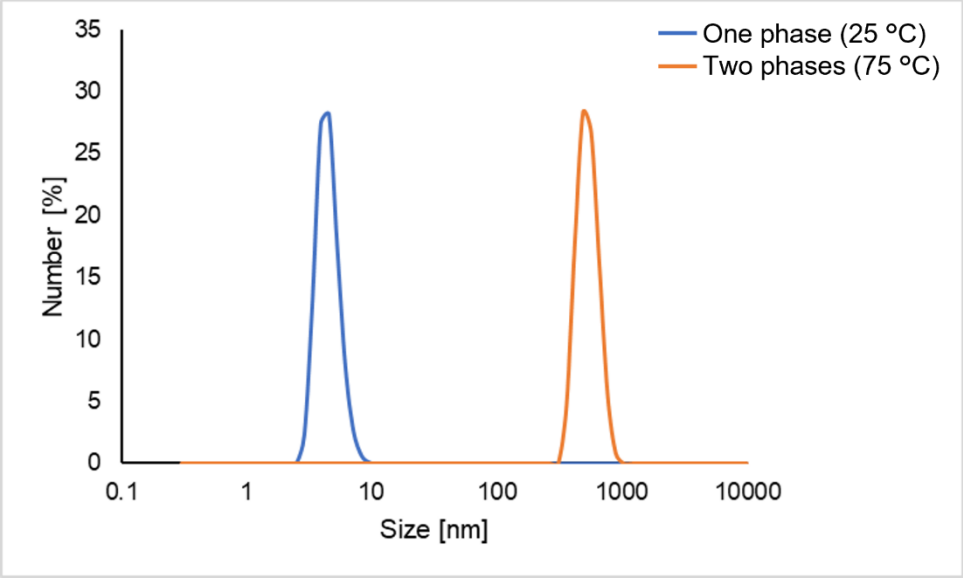


Figure S13. Size distribution by number of **P3MA** in 1-propanol and DCE.

7-3. Thermo-responsiveness of P4MA

Table S14. Thermo-responsiveness of **P4MA** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
5.15 mg	methanol : DCE = 6.0 : 4.0	105 μL	S	S	S	
5.12 mg	methanol : DCE = 5.0 : 5.0	100 μL	S	S	S	
5.42 mg	methanol : DCE = 4.0 : 6.0	110 μL	S	S	S	
5.09 mg	methanol : DCE = 3.0 : 7.0	100 μL	S	S	I	LCST
4.96 mg	methanol : DCE = 2.0 : 8.0	100 μL	I	I	I	
5.47 mg	ethanol : DCE = 4.0 : 6.0	110 μL	S	S	S	
4.83 mg	ethanol : DCE = 3.0 : 7.0	95 μL	S	S	I	LCST
5.70 mg	ethanol : DCE = 2.7 : 7.3	115 μL	S	S	I	LCST
4.74 mg	ethanol : DCE = 2.5 : 7.5	95 μL	I	I	I	
4.77 mg	ethanol : DCE = 2.0 : 8.0	95 μL	I	I	I	
4.94 mg	1-propanol : DCE = 4.0 : 6.0	100 μL	S	S	S	
4.77 mg	1-propanol : DCE = 3.0 : 7.0	95 μL	S	S	S	
5.15 mg	1-propanol : DCE = 2.5 : 7.5	105 μL	S	S	I	LCST
5.17 mg	1-propanol : DCE = 2.0 : 8.0	105 μL	I	I	I	
5.08 mg	1-butanol : DCE = 3.0 : 7.0	100 μL	S	S	S	
5.31 mg	1-butanol : DCE = 2.5 : 7.5	105 μL	S	S	I	LCST
5.42 mg	1-butanol : DCE = 2.3 : 7.7	110 μL	S	I	I	LCST
4.73 mg	1-butanol : DCE = 2.0 : 8.0	95 μL	I	I	I	
4.84 mg	1-hexanol : DCE = 3.0 : 7.0	95 μL	S	S	S	
5.49 mg	1-hexanol : DCE = 2.0 : 8.0	110 μL	S	S	I	LCST
5.70 mg	ethanol : toluene = 6.0 : 4.0	115 μL	S	S	S	
5.98 mg	ethanol : toluene = 5.0 : 5.0	120 μL	S	S	I	LCST
6.08 mg	ethanol : toluene = 4.5 : 5.5	120 μL	S	S	I	LCST
6.37 mg	ethanol : toluene = 4.0 : 6.0	125 μL	I	I	I	
5.46 mg	1-propanol : toluene = 6.0 : 4.0	110 μL	S	S	S	
4.75 mg	1-propanol : toluene = 5.0 : 5.0	95 μL	S	S	S	
5.91 mg	1-propanol : toluene = 4.0 : 6.0	120 μL	S	I	I	LCST
5.19 mg	1-butanol : toluene = 5.0 : 5.0	105 μL	S	S	S	
5.85 mg	1-butanol : toluene = 4.0 : 6.0	115 μL	S	S	I	LCST
5.43 mg	1-butanol : toluene = 3.0 : 7.0	110 μL	I	I	I	

5.76 mg	1-hexanol : toluene = 5.0 : 5.0	115 μL	S	S	S	
5.80 mg	1-hexanol : toluene = 4.5 : 5.5	115 μL	S	S	I	LCST
5.39 mg	1-hexanol : toluene = 4.0 : 6.0	110 μL	I	I	I	
6.28 mg	1-hexanol : toluene = 3.0 : 7.0	125 μL	I	I	I	

Table S15. Composition of solution.

polymer	solvent (mol. ratio)		concentration
154.2 mg	1-propanol : toluene = 4.2 : 5.8	3020 μL	51 mg/mL

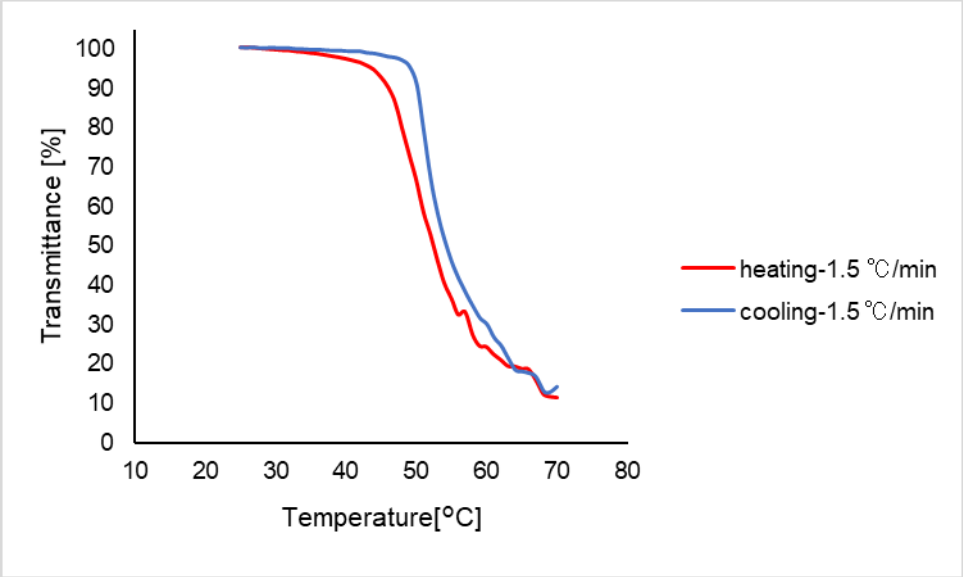


Figure S14. Transmittance change of **P4MA** in 1-propanol and toluene at 800 nm.

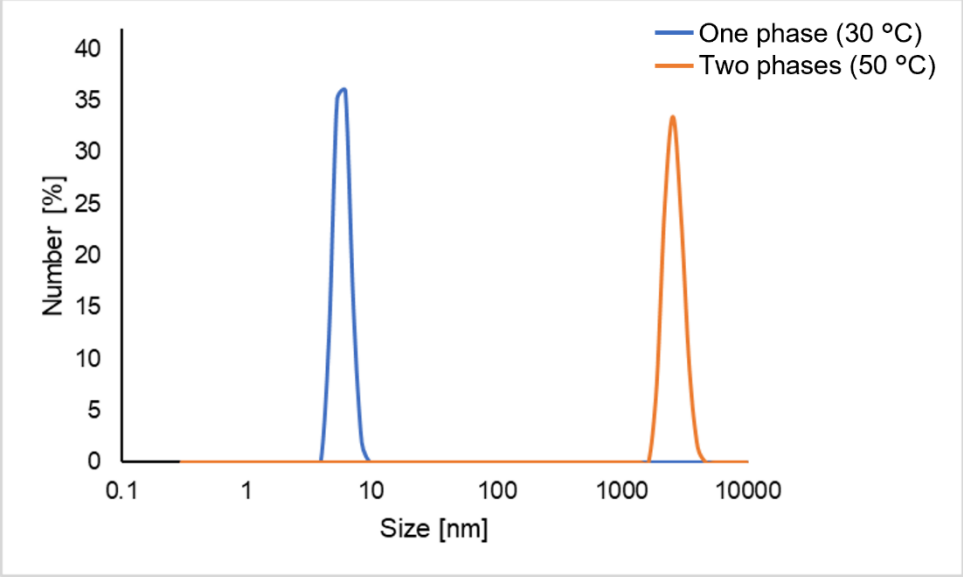


Figure S15. Size distribution by number of **P4MA** in 1-propanol and toluene.

7-4. Thermo-responsiveness of P5MA

Table S16. Thermo-responsiveness of **P5MA** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.75 mg	methanol : DCE = 4.0 : 6.0	55 μL	S	S	S	
5.53 mg	methanol : DCE = 3.0 : 7.0	110 μL	S	S	S	
5.09 mg	methanol : DCE = 2.8 : 7.2	100 μL	S	S	I	LCST
5.15 mg	methanol : DCE = 2.0 : 8.0	105 μL	I	I	I	
6.05 mg	ethanol : DCE = 4.0 : 6.0	120 μL	S	S	S	
4.84 mg	ethanol : DCE = 3.0 : 7.0	95 μL	S	S	S	
5.67 mg	ethanol : DCE = 2.7 : 7.3	115 μL	S	S	S	
5.39 mg	ethanol : DCE = 2.6 : 7.4	110 μL	S	S	S	
4.69 mg	ethanol : DCE = 2.5 : 7.5	95 μL	I	I	I	
6.20 mg	ethanol : DCE = 2.0 : 8.0	125 μL	I	I	I	
4.90 mg	1-propanol : DCE = 4.0 : 6.0	100 μL	S	S	S	
7.28 mg	1-propanol : DCE = 3.0 : 7.0	145 μL	S	S	S	
5.23 mg	1-propanol : DCE = 2.5 : 7.5	105 μL	S	S	S	
6.84 mg	1-propanol : DCE = 2.4 : 7.6	135 μL	S	S	S	
5.34 mg	1-propanol : DCE = 2.3 : 7.7	105 μL	S	S	S	
5.83 mg	1-propanol : DCE = 2.0 : 8.0	115 μL	I	I	I	
6.42 mg	1-butanol : DCE = 3.0 : 7.0	130 μL	S	S	S	
5.00 mg	1-butanol : DCE = 2.2 : 7.8	100 μL	S	S	S	
6.73 mg	1-butanol : DCE = 2.1 : 7.9	135 μL	S	S	S	
7.44 mg	1-butanol : DCE = 2.0 : 8.0	150 μL	I	I	I	
5.06 mg	1-hexanol : DCE = 3.0 : 7.0	100 μL	S	S	S	
5.24 mg	1-hexanol : DCE = 2.0 : 8.0	105 μL	S	S	S	
5.68 mg	1-hexanol : DCE = 1.8 : 8.2	115 μL	I	I	I	
5.34 mg	1-hexanol : DCE = 1.5 : 8.5	105 μL	I	I	I	
5.12 mg	1-octanol : DCE = 2.0 : 8.0	100 μL	S	S	S	
5.00 mg	1-octanol : DCE = 1.7 : 8.3	100 μL	I	I	I	
5.31 mg	1-octanol : DCE = 1.5 : 8.5	105 μL	I	I	I	
6.34 mg	1-octanol : DCE = 1.0 : 9.0	125 μL	I	I	I	
8.10 mg	ethanol : toluene = 6.0 : 4.0	160 μL	S	S	S	
6.46 mg	ethanol : toluene = 5.0 : 5.0	130 μL	I	I	I	
7.42 mg	ethanol : toluene = 4.5 : 5.5	150 μL	S	S	S	
7.72 mg	ethanol : toluene = 4.3 : 5.7	155 μL	S	S	I	LCST
5.15 mg	ethanol : toluene = 4.0 : 6.0	105 μL	I	I	I	

6.05 mg	1-propanol : toluene = 6.0 : 4.0	120 μL	S	S	S	
6.05 mg	1-propanol : toluene = 5.0 : 5.0	110 μL	S	S	S	
4.86 mg	1-propanol : toluene = 4.0 : 6.0	95 μL	S	S	I	LCST
5.82 mg	1-propanol : toluene = 3.8 : 6.2	115 μL	S	S	I	LCST
6.77 mg	1-butanol : toluene = 6.0 : 4.0	135 μL	S	S	S	
5.49 mg	1-butanol : toluene = 5.0 : 5.0	110 μL	S	S	S	
5.41 mg	1-butanol : toluene = 4.0 : 6.0	110 μL	S	S	S	
5.60 mg	1-butanol : toluene = 3.5 : 6.5	110 μL	S	S	I	LCST
6.09 mg	1-butanol : toluene = 3.0 : 7.0	120 μL	I	I	I	
5.35 mg	1-hexanol : toluene = 5.0 : 5.0	105 μL	S	S	S	
6.86 mg	1-hexanol : toluene = 4.0 : 6.0	135 μL	S	S	S	
6.14 mg	1-hexanol : toluene = 3.5 : 6.5	125 μL	S	S	I	LCST
5.10 mg	1-hexanol : toluene = 3.0 : 7.0	100 μL	I	I	I	
6.78 mg	1-octanol : toluene = 5.0 : 5.0	135 μL	S	S	S	
5.46 mg	1-octanol : toluene = 4.0 : 6.0	110 μL	I	I	S→I	LCST & UCST
4.80 mg	1-octanol : toluene = 3.5 : 6.5	95 μL	I	I	I	
5.02 mg	1-octanol : toluene = 3.0 : 7.0	100 μL	I	I	I	

Table S17. Composition of solution.

polymer	solvent (mol. ratio)		concentration
152.6 mg	1-propanol : toluene = 3.8 : 4.2	3000 μL	51 mg/mL

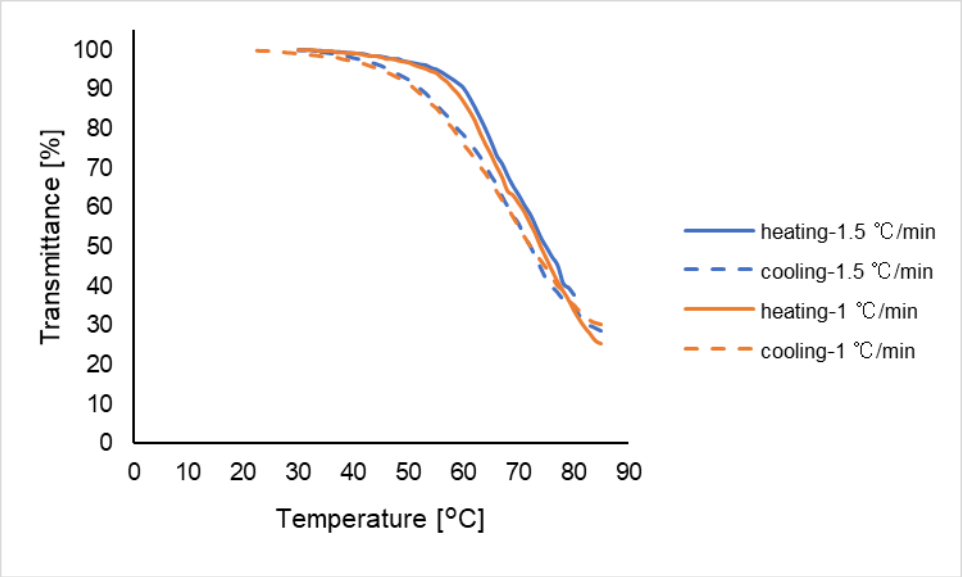


Figure S16. Transmittance change of **P5MA** in 1-propanol and toluene at 800 nm.

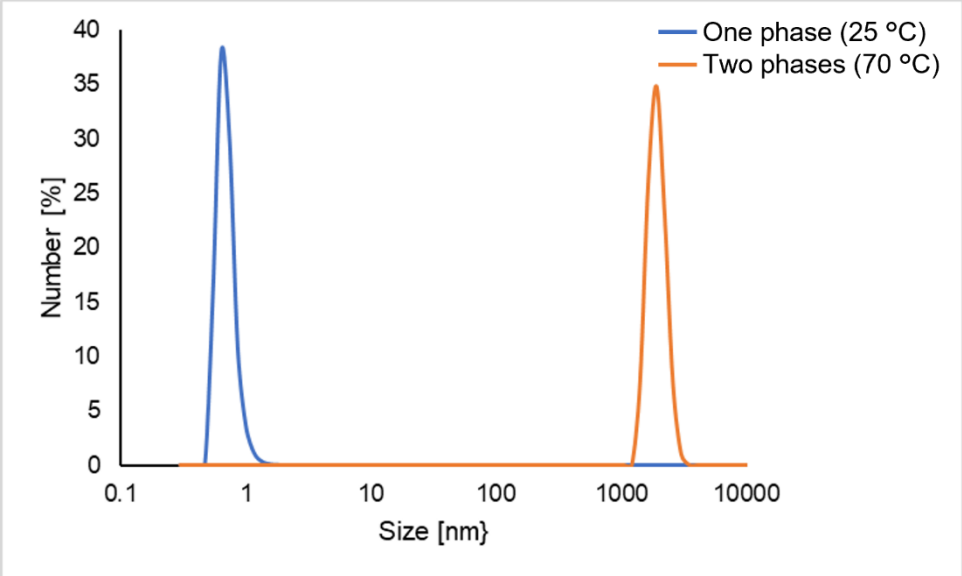


Figure S17. Size distribution by number of **P5MA** in 1-propanol and toluene.

7-5. Thermo-responsiveness of P3A

Table S18. Thermo-responsiveness of **P3A** in the mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
4.62 mg	methanol : DCE = 5.0 : 5.0	90 μL	S	S	S	
4.71 mg	methanol : DCE = 4.0 : 6.0	95 μL	S	S	I	LCST
4.79 mg	methanol : DCE = 3.0 : 7.0	95 μL	I	I	I	
5.79 mg	ethanol : DCE = 5.0 : 5.0	115 μL	S	S	S	
5.09 mg	ethanol : DCE = 4.0 : 6.0	100 μL	S	S	S	
6.26 mg	ethanol : DCE = 3.0 : 7.0	125 μL	S	I	I	LCST
5.18 mg	1-propanol : DCE = 4.0 : 6.0	105 μL	S	S	S	
5.79 mg	1-propanol : DCE = 3.0 : 7.0	115 μL	S	S	I	LCST
5.26 mg	1-butanol : DCE = 4.0 : 6.0	105 μL	S	S	S	
5.57 mg	1-butanol : DCE = 3.0 : 7.0	110 μL	S	S	I	LCST
6.07 mg	1-butanol : DCE = 2.0 : 8.0	120 μL	I	I	I	

Table S19. Composition of solution.

polymer	solvent (mol. ratio)		concentration
154.8 mg	1-propanol : DCE = 3.0 : 7.0	3000 μL	52 mg/mL

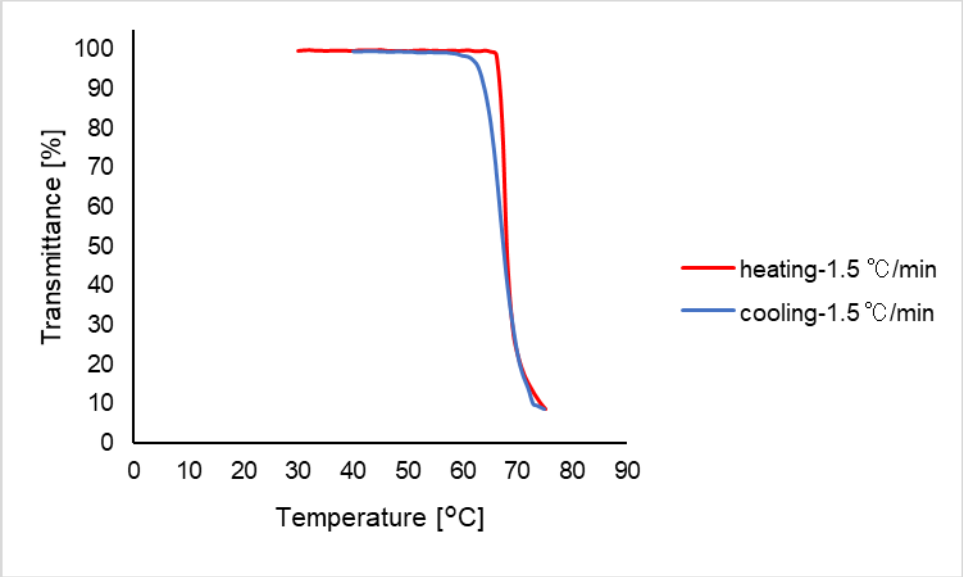


Figure S18. Transmittance change of **P3A** in 1-propanol and DCE at 800 nm.

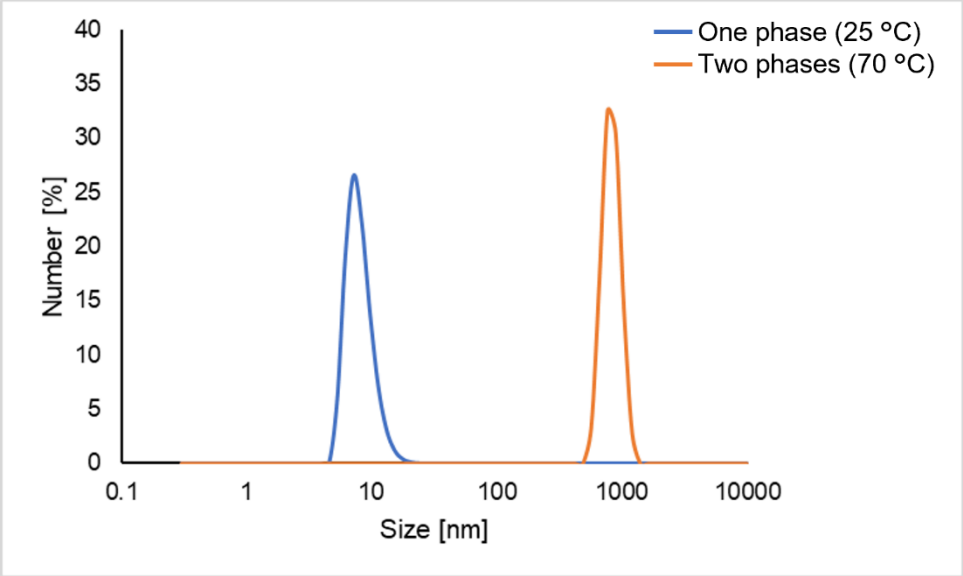


Figure S19. Size distribution by number of **P3A** in 1-propanol and DCE.

7-6. Thermo-responsiveness of P4A

Table S20. Thermo-responsiveness of **P4A** in mixed solvent.

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
6.56 mg	methanol : DCE = 4.0 : 6.0	130 μL	S	S	S	
4.96 mg	methanol : DCE = 3.5 : 6.5	100 μL	S	S	S	
4.53 mg	methanol : DCE = 3.3 : 6.7	90 μL	S	S	I	LCST
5.16 mg	methanol : DCE = 3.2 : 6.8	105 μL	S	S	I	LCST
4.83 mg	methanol : DCE = 3.0 : 7.0	95 μL	I	I	I	
5.24 mg	methanol : DCE = 2.0 : 8.0	105 μL	I	I	I	
5.06 mg	ethanol : DCE = 4.0 : 6.0	100 μL	S	S	S	
5.56 mg	ethanol : DCE = 3.0 : 7.0	110 μL	S	S	S	
6.91 mg	ethanol : DCE = 2.9 : 7.1	140 μL	S	S	S	
5.91 mg	ethanol : DCE = 2.8 : 7.2	120 μL	S	S	I	LCST
6.33 mg	ethanol : DCE = 2.7 : 7.3	125 μL	I	I	I	
4.68 mg	ethanol : DCE = 2.5 : 7.5	95 μL	I	I	I	
5.94 mg	ethanol : DCE = 2.0 : 8.0	120 μL	I	I	I	
4.84 mg	1-propanol : DCE = 4.0 : 6.0	95 μL	S	S	S	
4.69 mg	1-propanol : DCE = 3.0 : 7.0	95 μL	S	S	S	
5.85 mg	1-propanol : DCE = 2.5 : 7.5	115 μL	S	S	S	
6.61 mg	1-propanol : DCE = 2.4 : 7.6	130 μL	S	S	I	LCST
5.09 mg	1-propanol : DCE = 2.3 : 7.7	100 μL	I	I	I	
4.98 mg	1-propanol : DCE = 2.0 : 8.0	100 μL	I	I	I	
4.88 mg	1-butanol : DCE = 3.0 : 7.0	95 μL	S	S	S	
4.75 mg	1-butanol : DCE = 2.5 : 7.5	95 μL	S	S	S	
5.55 mg	1-butanol : DCE = 2.3 : 7.7	110 μL	S	S	S	
5.40 mg	1-butanol : DCE = 2.2 : 7.8	110 μL	S	S	I	LCST
6.53 mg	1-butanol : DCE = 2.1 : 7.9	130 μL	I	I	I	
4.67 mg	1-butanol : DCE = 2.0 : 8.0	95 μL	I	I	I	
5.09 mg	1-butanol : DCE = 1.0 : 9.0	100 μL	I	I	I	
4.98 mg	1-hexanol : DCE = 3.0 : 7.0	100 μL	S	S	S	
7.14 mg	1-hexanol : DCE = 2.0 : 8.0	145 μL	S	S	I	LCST

Table S21. Composition of solution.

polymer	solvent (mol. ratio)		concentration
159.6 mg	1-propanol : DCE = 2.4 : 7.6	3290 μL	49 mg/mL

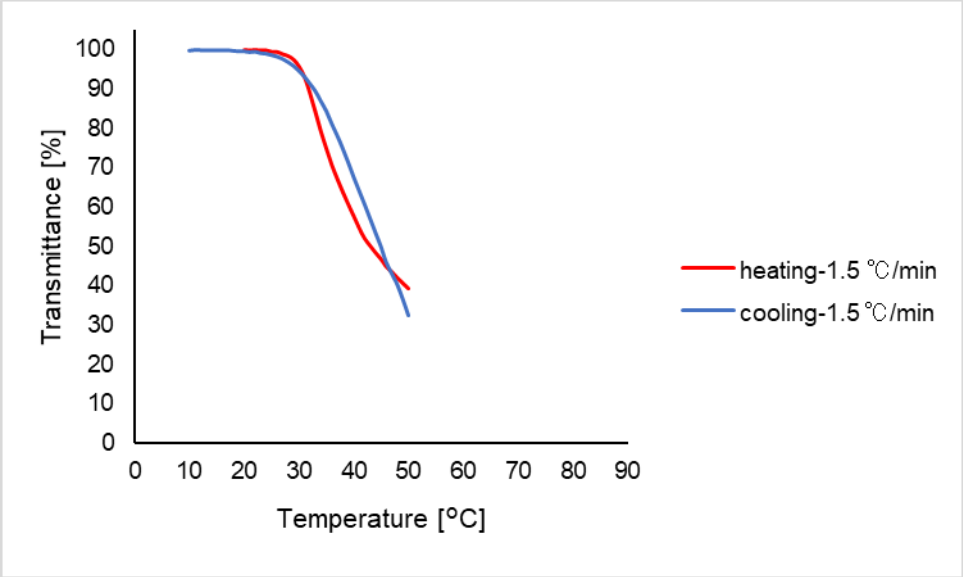


Figure S20. Transmittance change of **P4A** in 1-propanol and DCE at 800 nm.

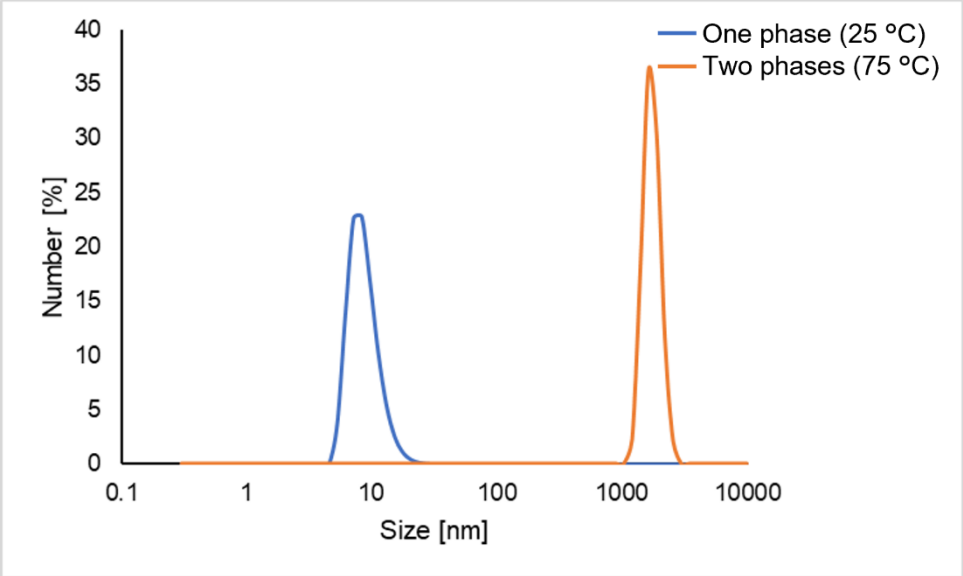


Figure S21. Size distribution by number of **P4A** in 1-propanol and DCE.

8. Thermal properties of poly(hydroxyalkyl (meth)acrylate)s analyzed by DSC

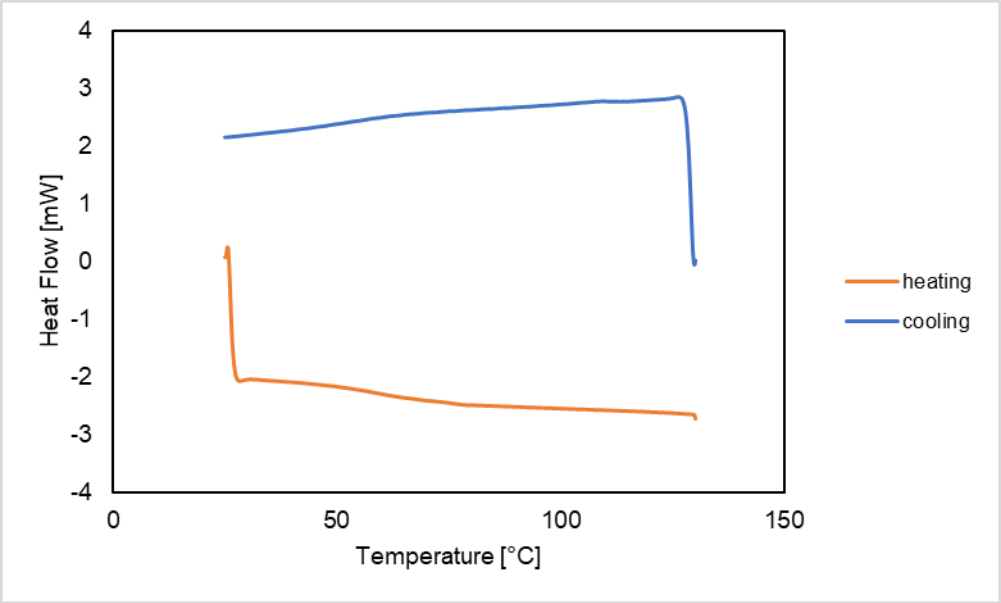


Figure S22. DSC thermographs of **P3MA** (T_g = 70 °C).

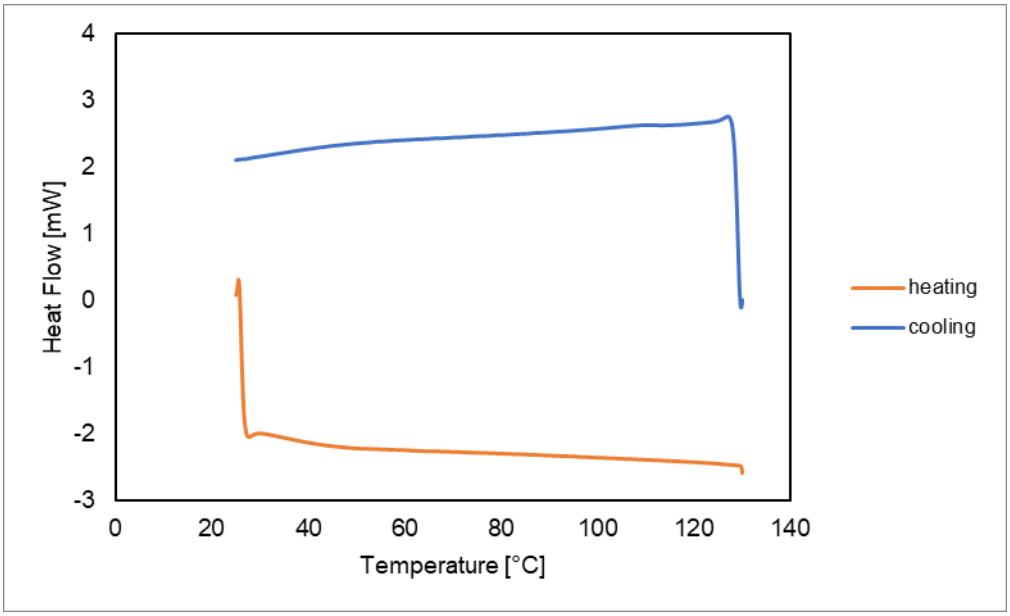


Figure S23. DSC thermographs of **P4MA** (T_g = 49 °C).

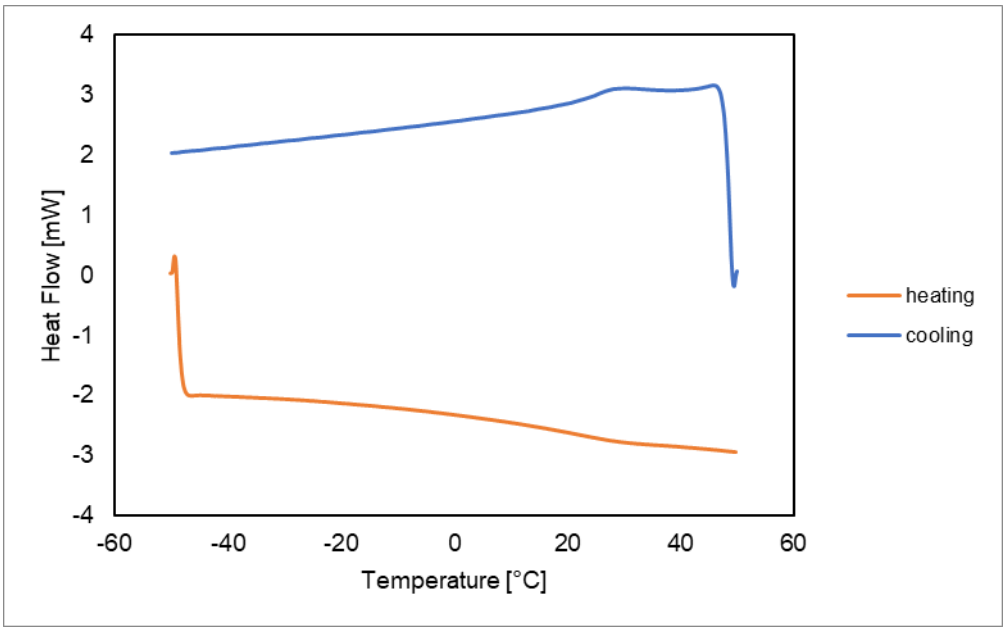


Figure S24. DSC thermographs of **P5MA** (T_g = 33 °C).

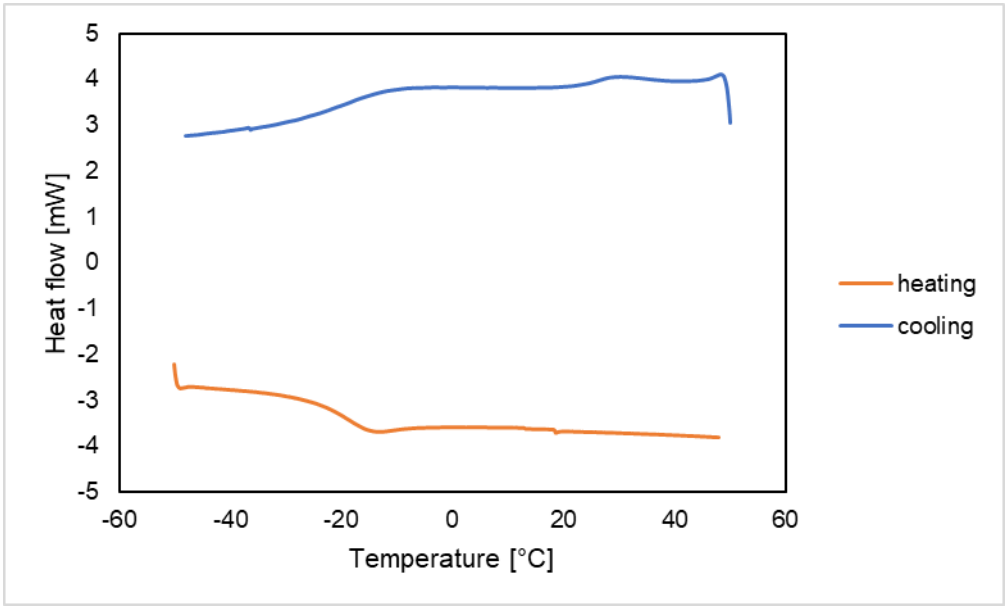


Figure S25. DSC thermographs of **P3A** (T_g = –11 °C).

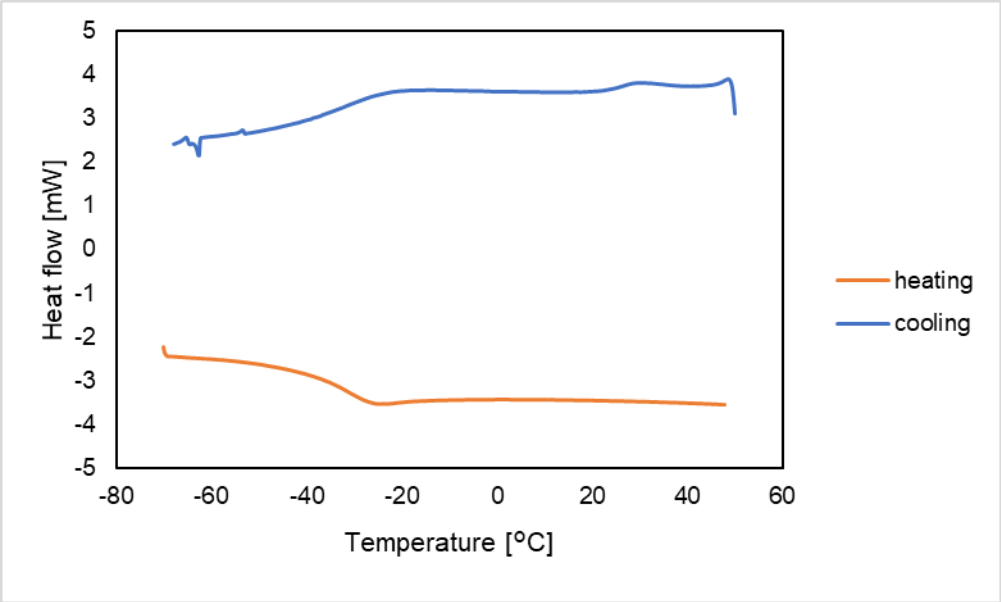


Figure S26. DSC thermographs of **P4A** (T_g = –23 °C).

9. Supplementary references

(1) D. Popescu, R. Hoogenboom, H. Keul and M. Moeller, *J. Mol. Catal. B-Enzym.*, 2010, **62**, 80.

(2) T. Kato, S. Akebi, H. Nagae, K. Yonehara, T. Oku and K. Mashima, *Catal. Sci. Technol.* 2021, **11**, 6975.