Supporting information

Design of LCST-type Phase Separation of Poly(4-hydroxystyrene)

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Contents:

S-1 Table S1 Thermal behaviors of **PHS** in the mixed organic solvents of some hydrogen-bonding solvents with toluene and hexane[a,b].

Hydrogen-bonding solvent	Non-solvent	Mol. ratio	Phase Separation (cloud point)
acetonitrile	toluene	6.8 : 3.2	UCST & LCST
benzonitrile	toluene	9.0 : 1.0	UCST (39 °C)
methanol	toluene	5.5 : 4.5	LCST
ethanol	toluene	4.2 : 5.8	LCST (40 °C)
tetramethylurea	toluene	4.0 : 6.0	UCST (40 °C)
1-propanol	toluene	3.5 : 6.5	LCST (65 °C)
propionitrile	toluene	6.8 : 3.2	UCST & LCST
2-butanone	toluene	6.0 : 4.0	LCST (63 °C)
pyridine	toluene	5.9 : 4.1	UCST (15 °C)
THF	toluene	6.5 : 3.5	LCST (65 °C)
acetic acid	toluene	8.5 : 1.5	UCST (60 °C)
ethyl acetate	toluene	6.5 : 3.5	LCST (49 °C)
1,4-dioxane	toluene	6.0 : 4.0	LCST (59 °C)
1-propanol	hexane	6.5 : 3.5	LCST (61 °C)
2-butanone	hexane	8.5 : 1.5	LCST (62 °C)
THF	hexane	9.0 : 1.0	UCST (22 °C) & LCST (41 °C)
ethyl acetate	hexane	8.8 : 1.2	LCST (50 °C)

[a] The conditions: **PHS** (ca. 25 mg) in the mixed organic solvents (1.0 mL) from ca. 20 °C to ca. 100 °C.

[b] Cloud point was determined by a transmittance change (90% of transmission) at 800 nm light.

S-2 Experimental Detail

Poly(4-hydroxystyrene) (**PHS**) (average Mw: ~25,000) was purchased from Sigma-Aldrich. All other reagents were obtained from commercial sources and used without further purification. Solubility test of **PHS** in the mixtures of various hydrogen-bonding solvents and non-polar solvents was done by mixing the suitable amount of the solvent mixtures and **PHS**. Transmittance measurements 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. 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.

S-2-1. DMF and DCE

Table S-2-1 Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.58 mg	DMF : DCE = 2.0 : 8.0	100 μL	+	+	+	
2.46 mg	DMF : DCE = 1.6 : 8.4	100 μL	+	+	–	LCST
2.51 mg	DMF : DCE = 1.5 : 8.5	100 μL	+	–	–	LCST
2.58 mg	DMF : DCE = 1.0 : 9.0	100 μL	–	–	–	

+: soluble, —: insoluble

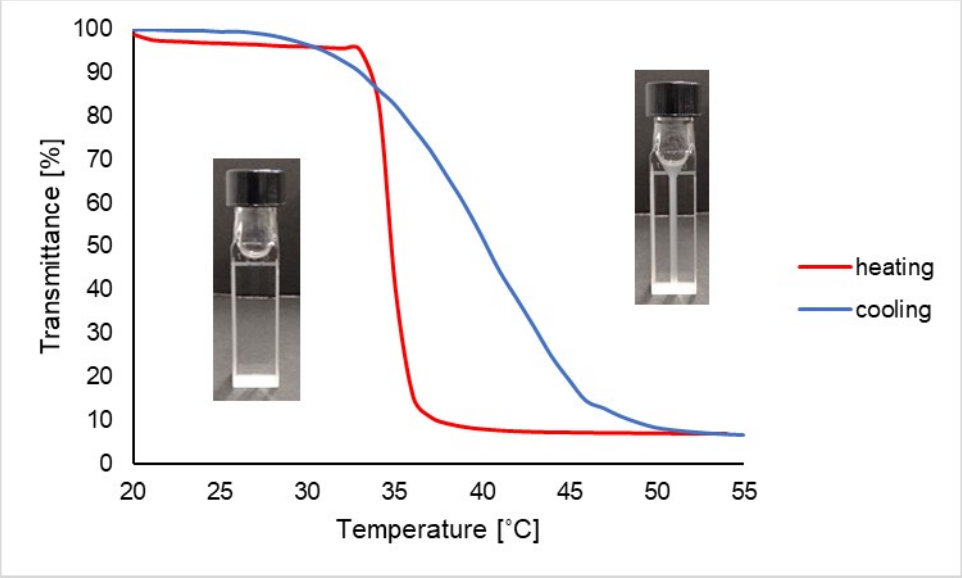

Figure S-2-1 Transmittance change of **PHS** in DMF and DCE at 800 nm

S-2-2. benzonitrile and DCE

Table S-2-2. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.50 mg	benzonitrile : DCE = 9.0 : 1.0	100 μL	–	–	+	UCST
2.52 mg	benzonitrile : DCE = 8.0 : 2.0	100 μL	–	–	–	

+: soluble, —: insoluble

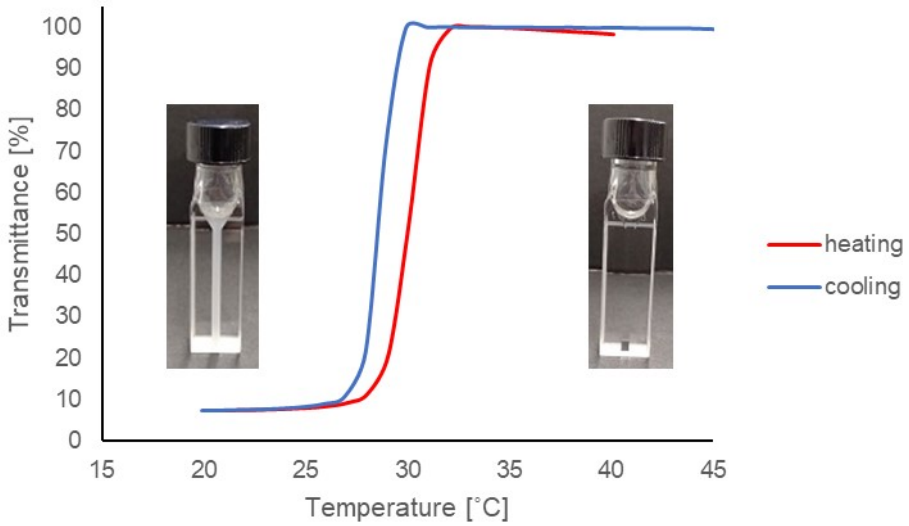

Figure S-2-2 Transmittance change of **PHS** in benzonitrile and DCE at 800 nm

S-2-3. methanol and DCE

Table S-2-3. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.40 mg	methanol : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.48 mg	methanol : DCE = 4.0 : 6.0	100 μL	+	+	−	LCST
2.61 mg	methanol : DCE = 3.9 : 6.1	100 μL	+	+	−	LCST
2.49 mg	methanol : DCE = 3.8 : 6.2	100 μL	+	+	−	LCST
2.50 mg	methanol : DCE = 3.7 : 6.3	100 μL	+	+	−	LCST
2.41 mg	methanol : DCE = 3.5 : 6.5	100 μL	−	−	−	

+: soluble, −: insoluble

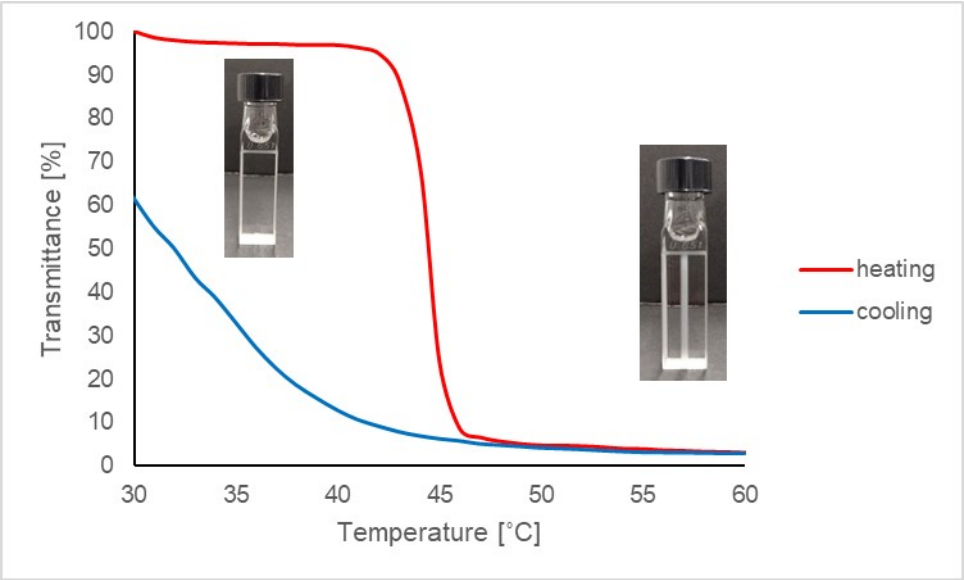

Figure S-2-3. Transmittance change of **PHS** in methanol and DCE at 800 nm

S-2-4. ethanol and DCE

Table S-2-4. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.52 mg	ethanol : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.52 mg	ethanol : DCE = 4.0 : 6.0	100 μL	+	+	+	
2.67 mg	ethanol : DCE = 3.0 : 7.0	100 μL	+	+	−	LCST
2.50 mg	ethanol : DCE = 2.9 : 7.1	100 μL	+	+	−	LCST

+: soluble, −: insoluble

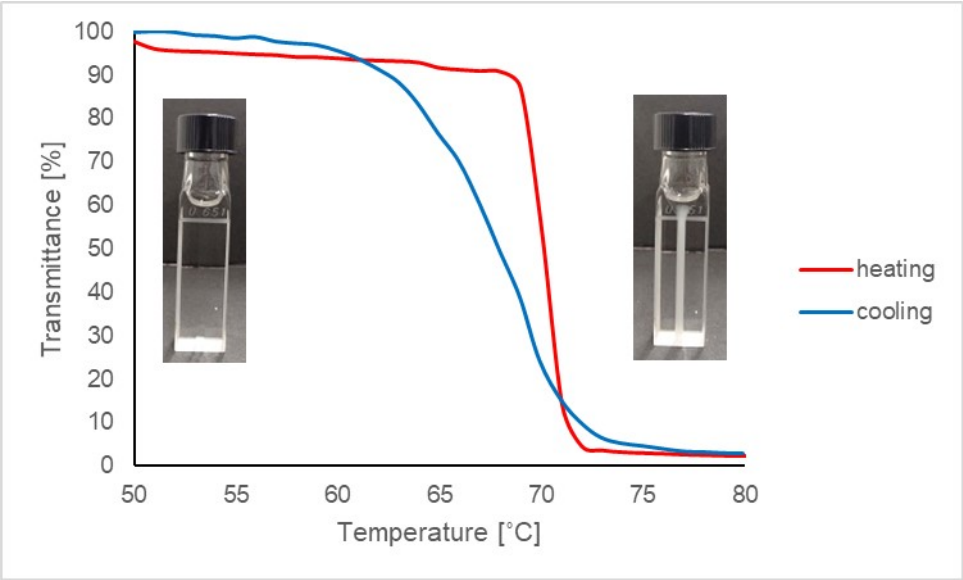

Figure S-2-4. Transmittance change of **PHS** in ethanol and DCE at 800 nm

S-2-5. 1-propanol and DCE

Table S-2-5. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.57 mg	1-propanol : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.62 mg	1-propanol : DCE = 4.0 : 6.0	100 μL	+	+	+	
2.59 mg	1-propanol : DCE = 3.0 : 7.0	100 μL	+	+	+	
2.57 mg	1-propanol : DCE = 2.5 : 7.5	100 μL	+	+	−	LCST
2.38 mg	1-propanol : DCE = 2.4 : 7.6	100 μL	+	+	−	LCST
2.44 mg	1-propanol : DCE = 2.0 : 8.0	100 μL	−	−	−	

+: soluble, −: insoluble

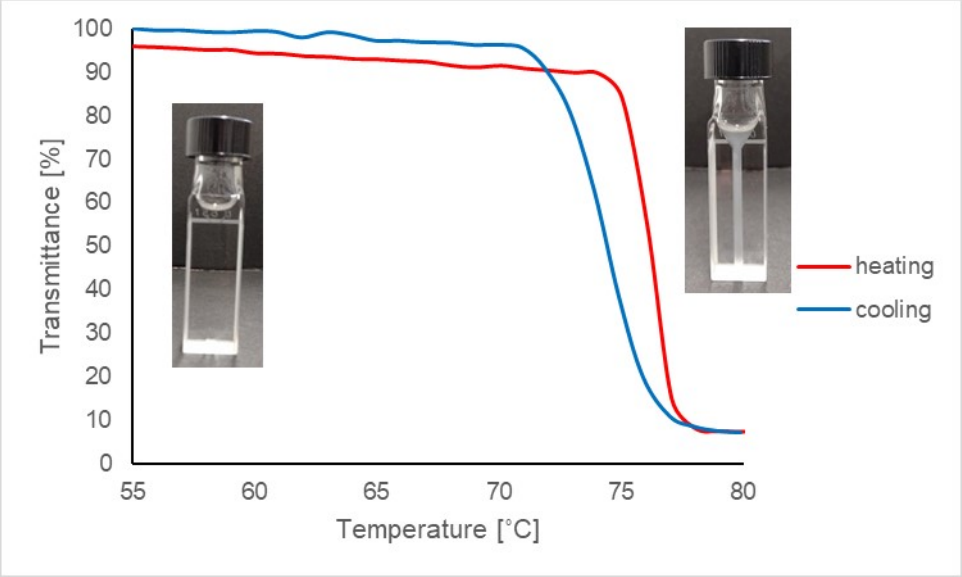

Figure S-2-5. Transmittance change of **PHS** in 1-propanol and DCE at 800 nm

S-2-6. 1-butanol and DCE

Table S-2-6. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.57 mg	1-butanol : DCE = 2.0 : 8.0	100 μL	+	+	–	LCST
2.60 mg	1-butanol : DCE = 1.0 : 9.0	100 μL	–	–	–	

+: soluble, —: insoluble

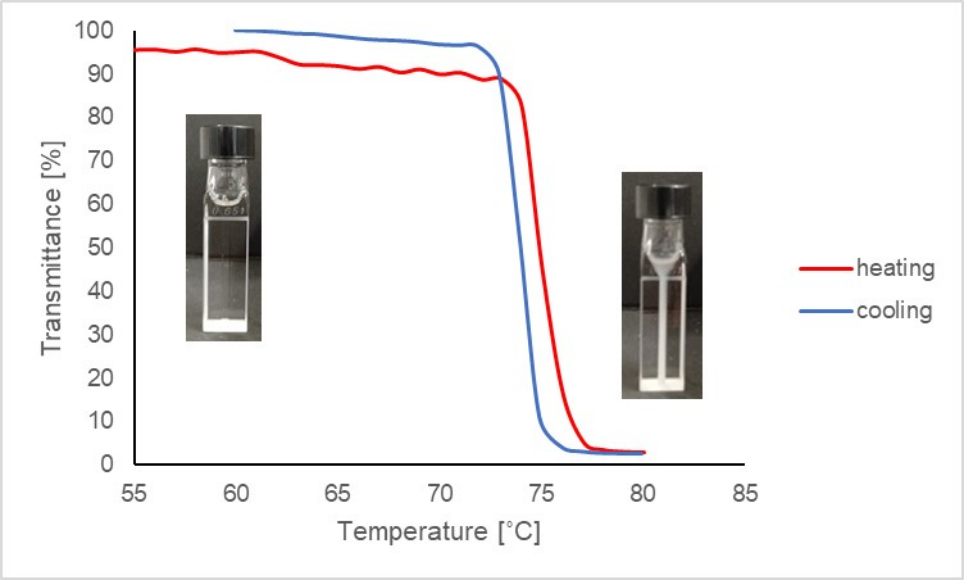

Figure S-2-6. Transmittance change of **PHS** in 1-butanol and DCE at 800 nm

S-2-7. 2-butanone and DCE

Table S-2-7. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.48 mg	2-butanone : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.62 mg	2-butanone : DCE = 4.5 : 5.5	100 μL	+	+	−	LCST
2.61 mg	2-butanone : DCE = 4.3 : 5.7	100 μL	+	+	−	LCST
2.54 mg	2-butanone : DCE = 4.0 : 6.0	100 μL	−	−	−	

+: soluble, −: insoluble

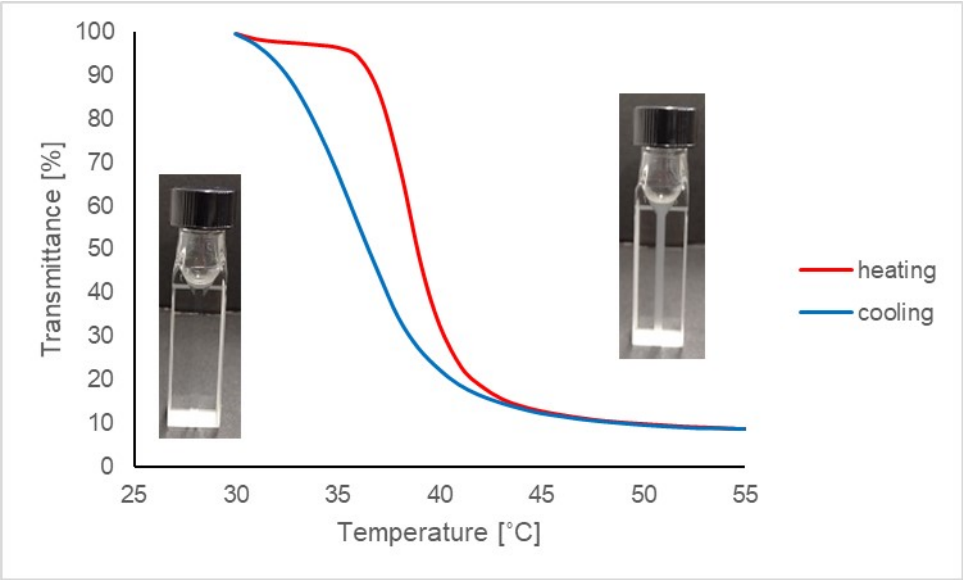

Figure S-2-7. Transmittance change of **PHS** in 2-butanone and DCE at 800 nm

S-2-8. pyridine and DCE

Table S-2-8. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.56 mg	pyridine : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.48 mg	pyridine : DCE = 4.0 : 6.0	100 μL	+	+	+	
2.44 mg	pyridine : DCE = 3.0 : 7.0	100 μL	+	+	+	
2.55 mg	pyridine : DCE = 2.0 : 8.0	100 μL	+	+	−	LCST

+: soluble, −: insoluble

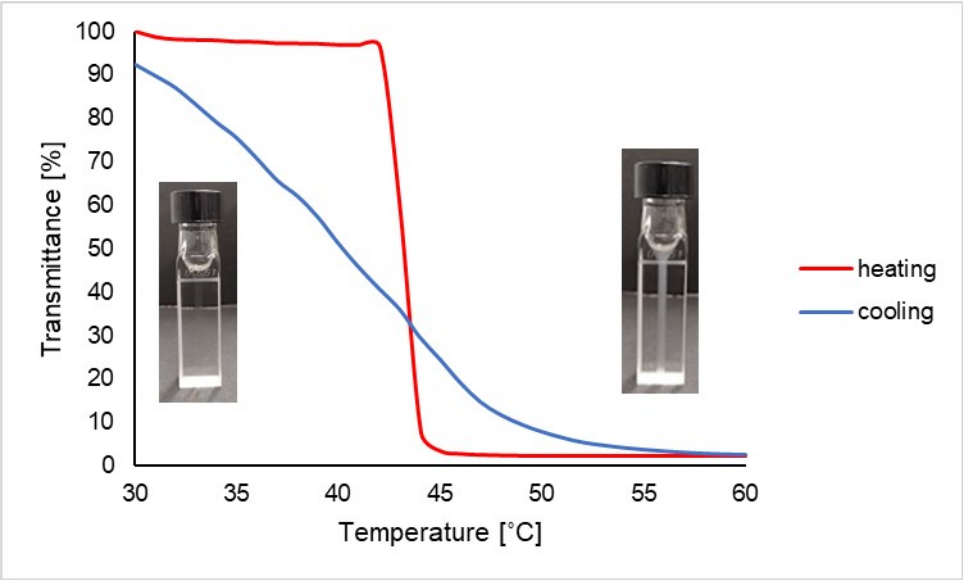

Figure S-2-8. Transmittance change of **PHS** in pyridine and DCE at 800 nm

S-2-9. 1-hexanol and DCE

Table S-2-9. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.51 mg	1-hexanol : DCE = 2.0 : 8.0	100 μL	+	+	+	
2.48 mg	1-hexanol : DCE = 1.5 : 8.5	100 μL	+	+	–	LCST
2.49 mg	1-hexanol : DCE = 1.0 : 9.0	100 μL	–	–	–	

+: soluble, —: insoluble

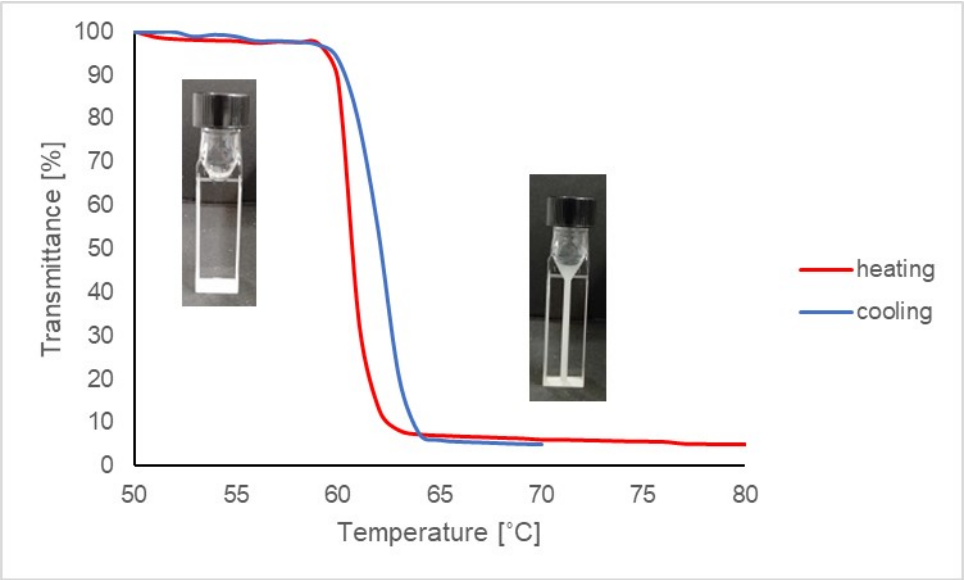

Figure S-2-9. Transmittance change of **PHS** in 1-hexanol and DCE at 800 nm

S-2-10. THF and DCE

Table S-2-10. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.61 mg	THF : DCE = 9.0 : 1.0	100 μL	+	+	+	
2.54 mg	THF : DCE = 8.0 : 2.0	100 μL	+	+	+	
2.46 mg	THF : DCE = 7.0 : 3.0	100 μL	+	+	+	
2.48 mg	THF : DCE = 6.0 : 4.0	100 μL	+	+	+	
2.57 mg	THF : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.42 mg	THF : DCE = 4.0 : 6.0	100 μL	+	+	+	
2.46 mg	THF : DCE = 3.0 : 7.0	100 μL	+	+	−	LCST
2.35 mg	THF : DCE = 2.0 : 8.0	100 μL	−	−	−	

+: soluble, −: insoluble

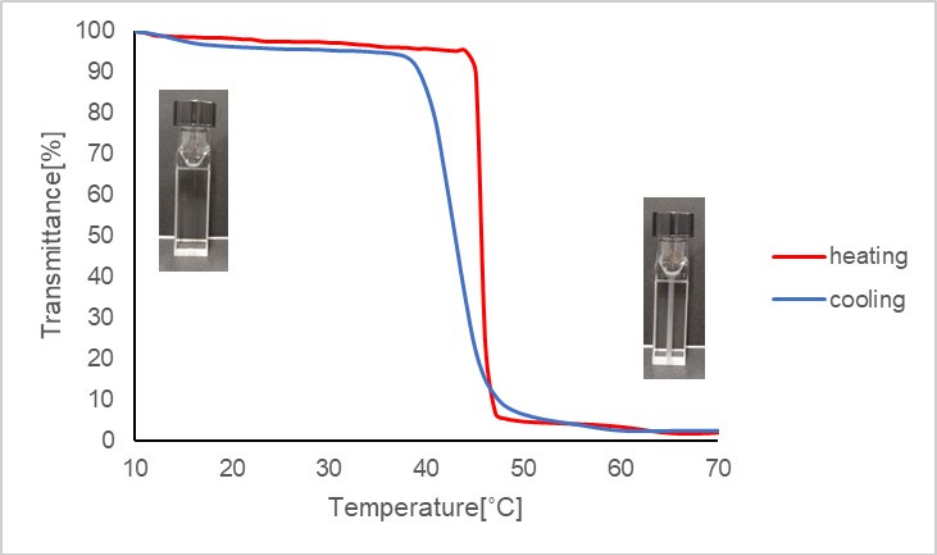

Figure S-2-10. Transmittance change of **PHS** in THF and DCE at 800 nm

S-2-11. acetic acid and DCE

Table S-2-11. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.54 mg	acetic acid : DCE = 9.0 : 1.0	100 μL	+	+	+	
2.40 mg	acetic acid : DCE = 8.0 : 2.0	100 μL	−	+	+	UCST
2.51 mg	acetic acid : DCE = 7.0 : 3.0	100 μL	−	−	−	

+: soluble, −: insoluble

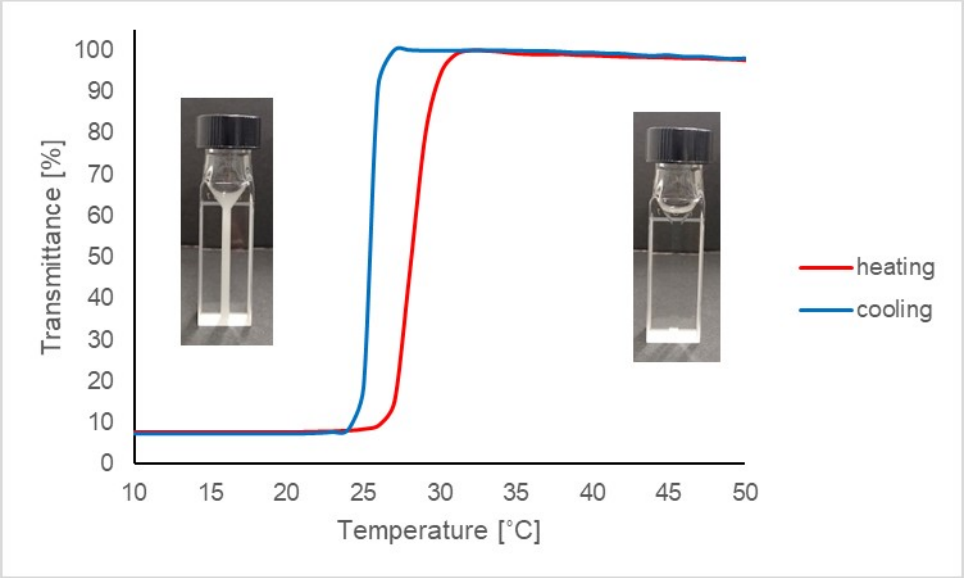

Figure S-2-11 Transmittance change of **PHS** in acetic acid and DCE at 800 nm

S-2-12. ethyl acetate and DCE

Table S-2-12. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.41 mg	ethyl acetate : DCE = 5.0 : 5.0	100 μL	+	+	−	LCST
2.50 mg	ethyl acetate : DCE = 4.9 : 5.1	100 μL	+	+	−	LCST
2.41 mg	ethyl acetate : DCE = 4.8 : 5.2	100 μL	+	+	−	LCST
2.50 mg	ethyl acetate : DCE = 4.7 : 5.3	100 μL	+	+	−	LCST
2.55 mg	ethyl acetate : DCE = 4.5 : 5.5	100 μL	−	−	−	

+: soluble, −: insoluble

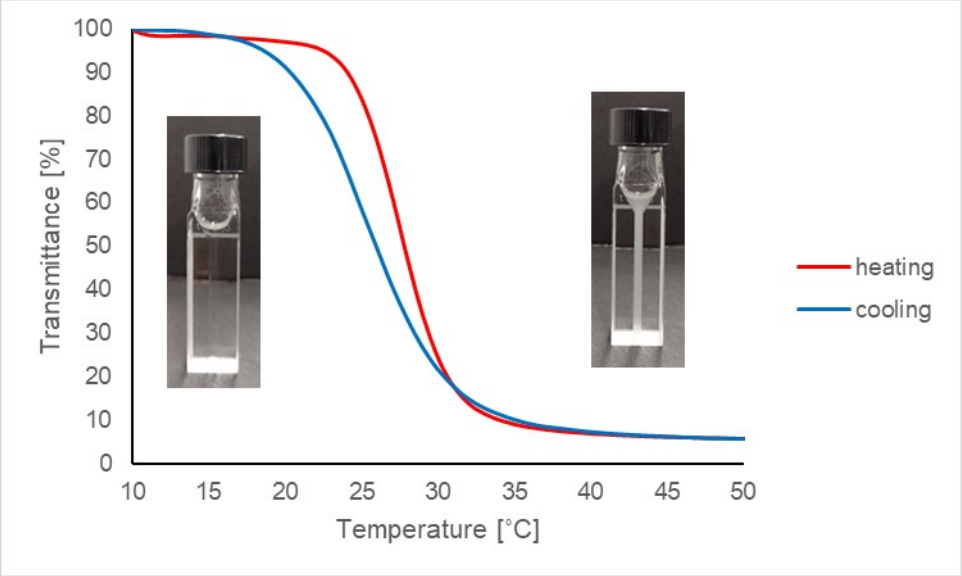

Figure S-2-12. Transmittance change of **PHS** in ethyl acetate and DCE at 800 nm

S-2-13. 1,4-dioxane and DCE

Table S-2-13. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.56 mg	1,4-dioxane : DCE = 5.0 : 5.0	100 μL	+	+	+	
2.43 mg	1,4-dioxane : DCE = 4.0 : 6.0	100 μL	+	+	–	LCST
2.50 mg	1,4-dioxane : DCE = 3.0 : 7.0	100 μL	–	–	–	

+: soluble, —: insoluble

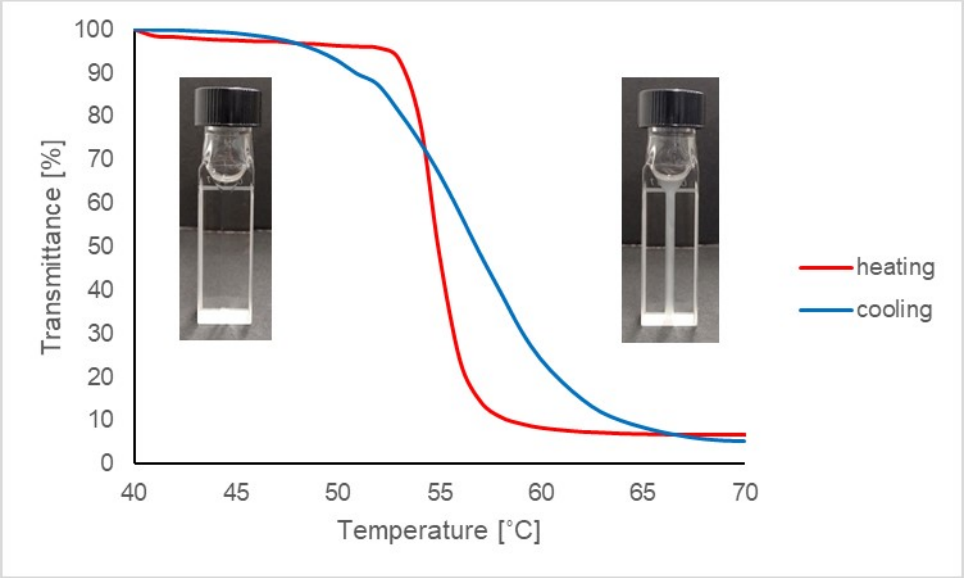

Figure S-2-13. Transmittance change of **PHS** in 1,4-dioxane and DCE at 800 nm

S-2-14. benzonitrile and toluene

Table S-2-14. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.61 mg	benzonitrile : toluene = 9.0 : 1.0	100 μL	−	−	+	UCST
2.54 mg	benzonitrile : toluene = 8.0 : 2.0	100 μL	−	−	−	

+: soluble, −: insoluble

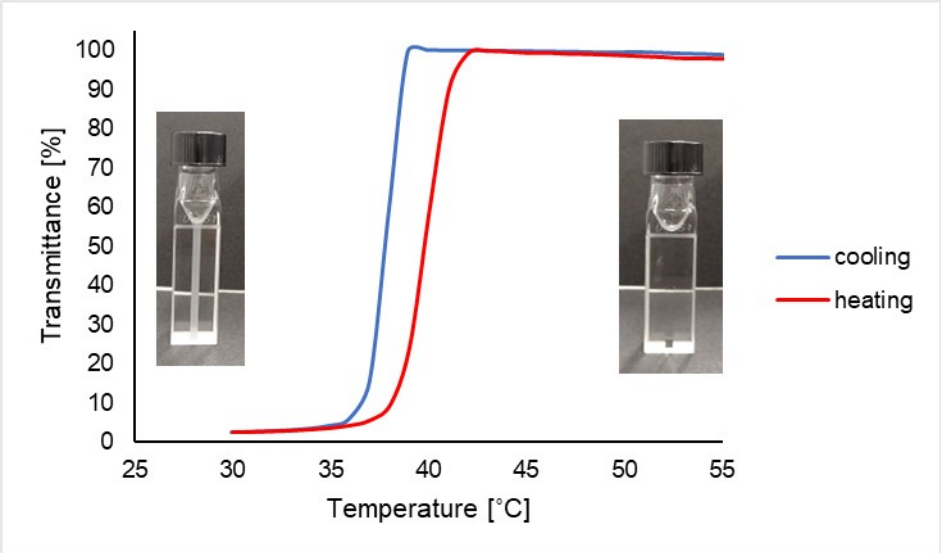

Figure S-2-14. Transmittance change of **PHS** in benzonitrile and toluene at 800 nm

S-2-15. ethanol and toluene

Table S-2-15. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.54 mg	ethanol : toluene = 5.0 : 5.0	100 μL	+	+	+	
2.58 mg	ethanol : toluene = 4.5 : 5.5	100 μL	+	+	+	
2.38 mg	ethanol : toluene = 4.2 : 5.8	100 μL	+	+	−	LCST
2.46 mg	ethanol : toluene = 4.1 : 5.9	100 μL	+	−	−	LCST
2.64 mg	ethanol : toluene = 4.0 : 6.0	100 μL	−	−	−	

+: soluble, −: insoluble

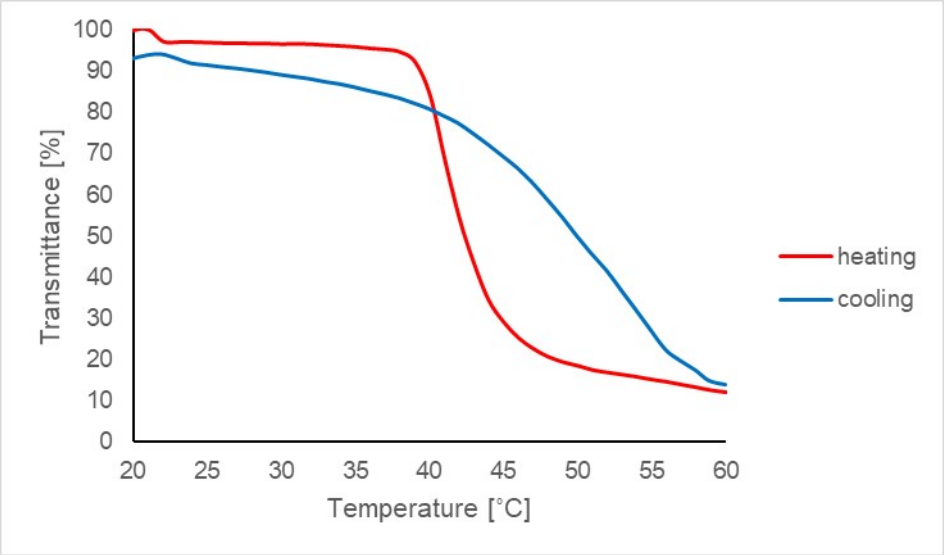

Figure S-2-15. Transmittance change of **PHS** in ethanol and toluene at 800 nm

S-2-16. 1-propanol and toluene

Table S-2-16. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.47 mg	1-propanol : toluene = 5.0 : 5.0	100 μL	+	+	+	
2.44 mg	1-propanol : toluene = 4.0 : 6.0	100 μL	+	+	+	
2.37 mg	1-propanol : toluene = 3.5 : 6.5	100 μL	+	+	−	LCST
2.47 mg	1-propanol : toluene = 3.0 : 7.0	100 μL	−	−	−	

+: soluble, −: insoluble

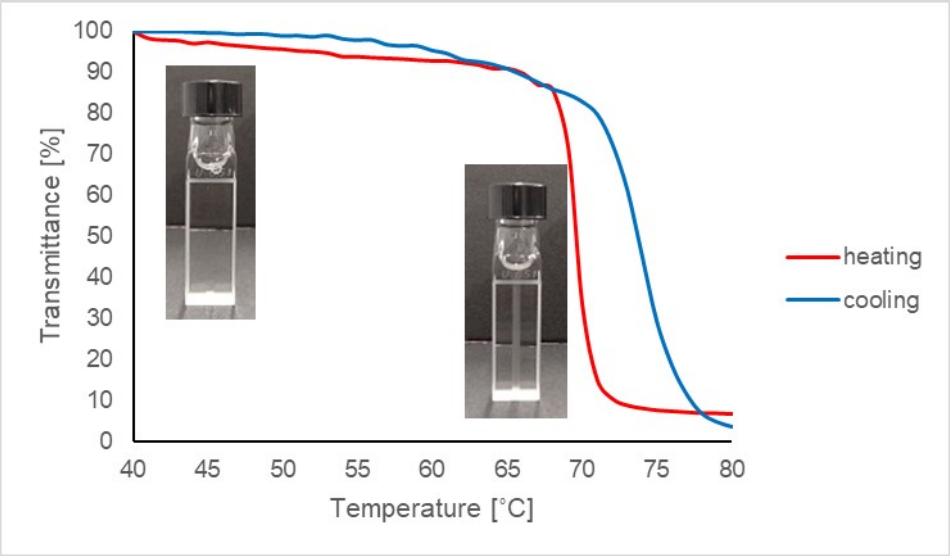

Figure S-3-16. Transmittance change of **PHS** in 1-propanol and toluene at 800 nm

S-2-17. 2-butanone and toluene

Table S-2-17. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.50 mg	2-butanone : toluene = 6.0 : 4.0	100 μL	+	+	–	LCST
2.43 mg	2-butanone : toluene = 5.0 : 5.0	100 μL	–	–	–	

+: soluble, —: insoluble

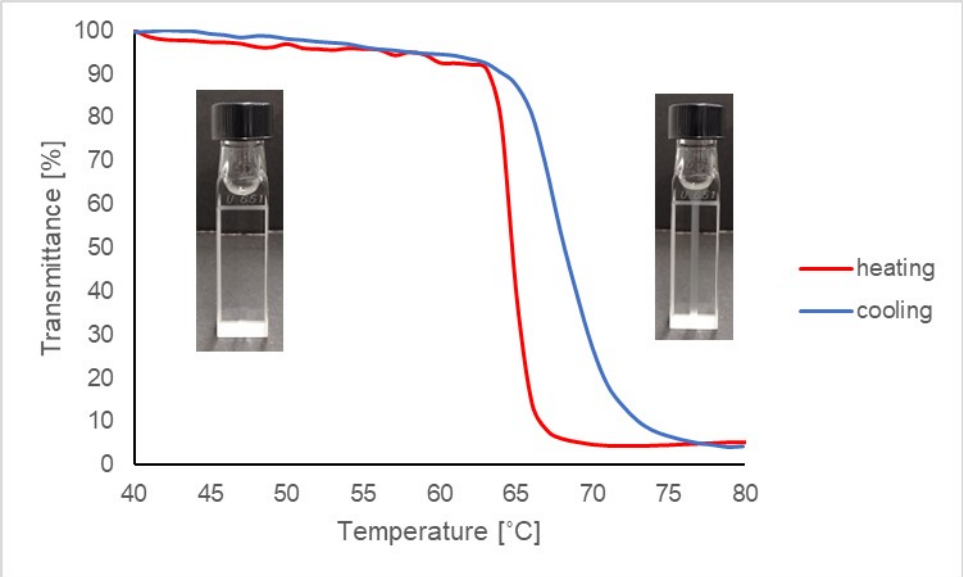

Figure S-2-17. Transmittance change of **PHS** in 2-butanone and toluene at 800 nm

S-2-18. THF and toluene

Table S-2-18. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.79 mg	THF : toluene = 9.0 : 1.0	100 μL	+	+	+	
2.68 mg	THF : toluene = 8.0 : 2.0	100 μL	+	+	+	
2.40 mg	THF : toluene = 7.0 : 3.0	100 μL	+	+	+	
2.43 mg	THF : toluene = 6.5 : 3.5	100 μL	+	+	−	LCST
2.68 mg	THF : toluene = 6.0 : 4.0	100 μL	−	−	−	

+: soluble, −: insoluble

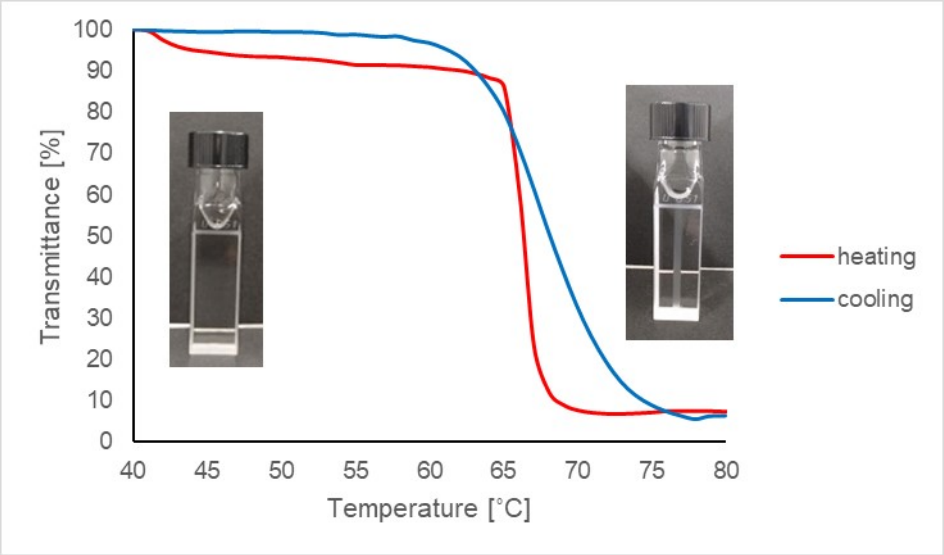

Figure S-2-18. Transmittance change of **PHS** in THF and toluene at 800 nm

S-2-19. acetic acid and toluene

Table S-2-19. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.56 mg	acetic acid : toluene = 9.0 : 1.0	100 μL	−	+	+	UCST
2.27 mg	acetic acid : toluene = 8.5 : 1.5	100 μL	−	−	+	UCST
2.53 mg	acetic acid : toluene = 8.0 : 2.0	100 μL	−	−	−	

+: soluble, −: insoluble

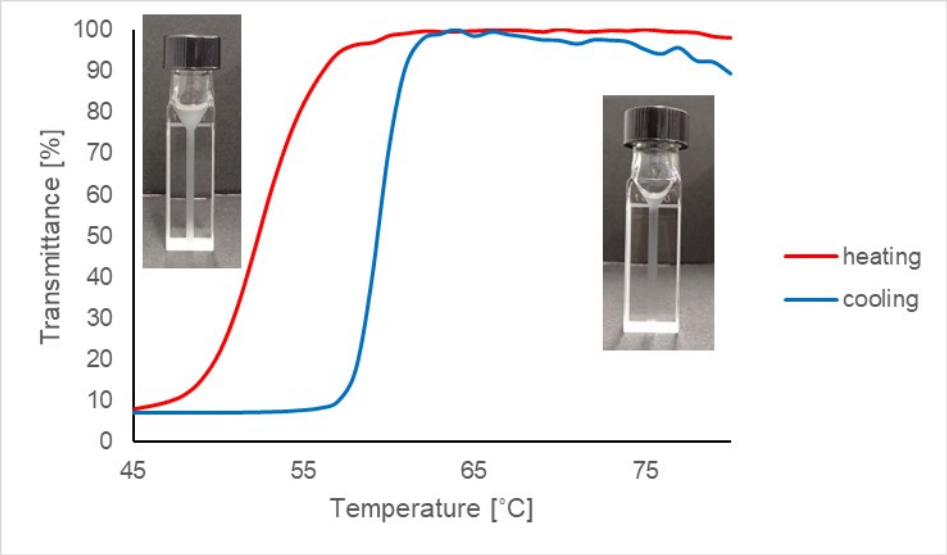

Figure S-2-19. Transmittance change of **PHS** in acetic acid and toluene at 800 nm

S-2-20. ethyl acetate and toluene

Table S-2-20. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.56 mg	ethyl acetate : toluene = 9.0 : 1.0	100 μL	+	+	+	
2.27 mg	ethyl acetate : toluene = 8.0 : 2.0	100 μL	+	+	+	
2.53 mg	ethyl acetate : toluene = 7.0 : 3.0	100 μL	+	+	+	
2.56 mg	ethyl acetate : toluene = 6.5 : 3.5	100 μL	+	+	−	LCST
2.38 mg	ethyl acetate : toluene = 6.0 : 4.0	100 μL	−	−	−	

+: soluble, −: insoluble

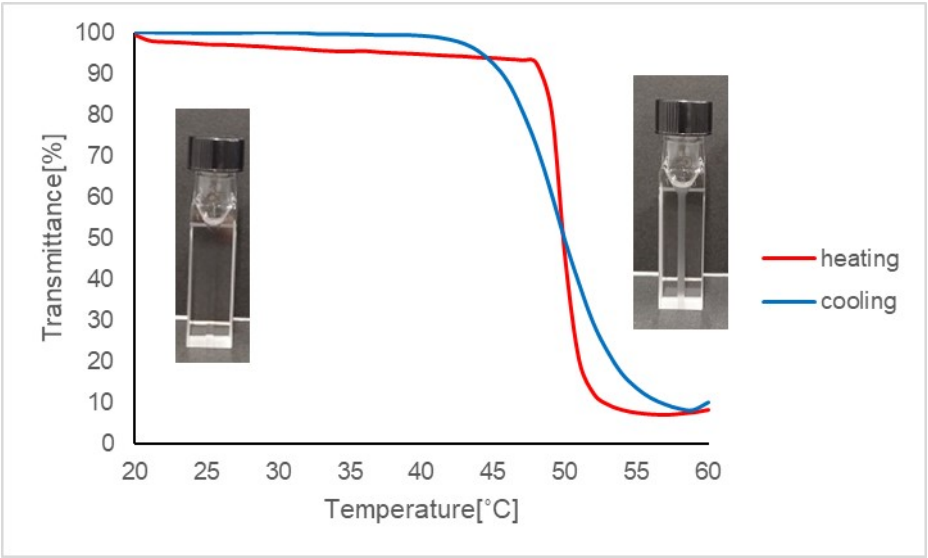

Figure S-2-20. Transmittance change of **PHS** in ethyl acetate and toluene at 800 nm

S-2-21. 1,4-dioxane and toluene

Table S-2-21. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.40 mg	1,4-dioxane : toluene = 7.0 : 3.0	100 μL	+	+	+	
2.52 mg	1,4-dioxane : toluene = 6.0 : 4.0	100 μL	+	+	–	LCST
2.61 mg	1,4-dioxane : toluene = 5.0 : 5.0	100 μL	–	–	–	

+: soluble, —: insoluble

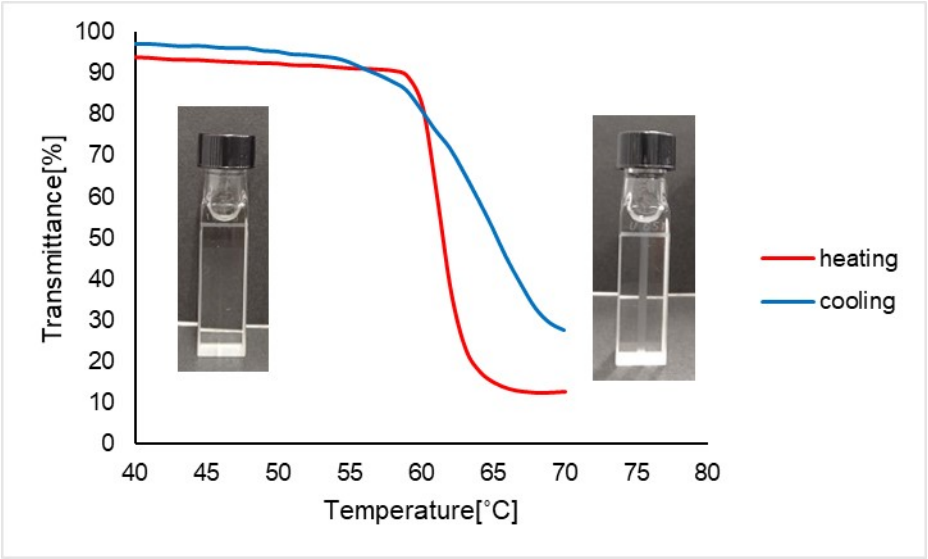

Figure S-2-21. Transmittance change of **PHS** in 1,4-dioxane and toluene at 800 nm

S-2-22. pyrrolidine and toluene

Table S-2-22. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.61 mg	pyrrolidine : toluene = 7.0 : 3.0	100 μL	+	+	−	LCST
2.46 mg	pyrrolidine : toluene = 6.0 : 4.0	100 μL	–	−	−	

+: soluble, −: insoluble

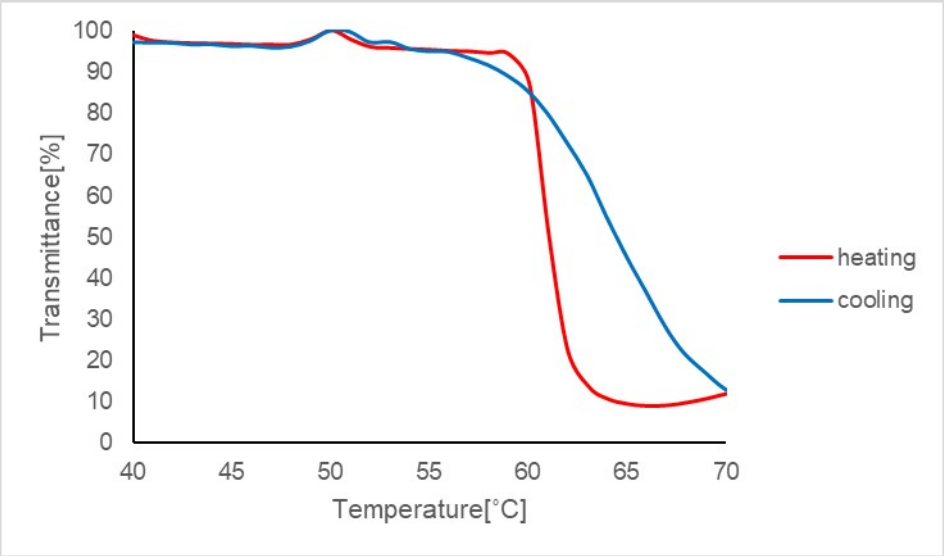

Figure S-2-22. Transmittance change of **PHS** in pyrrolidine and toluene at 800 nm

S-2-23. tetramethylurea and toluene

Table S-2-23. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.61 mg	tetramethylurea : toluene = 9.0 : 1.0	100 μL	+	+	+	
2.63 mg	tetramethylurea : toluene = 8.0 : 2.0	100 μL	+	+	+	
2.36 mg	tetramethylurea : toluene = 7.0 : 3.0	100 μL	+	+	+	
2.47 mg	tetramethylurea : toluene = 6.0 : 4.0	100 μL	+	+	+	
2.42 mg	tetramethylurea : toluene = 5.0 : 5.0	100 μL	+	+	+	
2.45 mg	tetramethylurea : toluene = 4.0 : 6.0	100 μL	−	−	+	UCST
2.52 mg	tetramethylurea : toluene = 3.5 : 6.5	100 μL	−	−	−	

+: soluble, −: insoluble

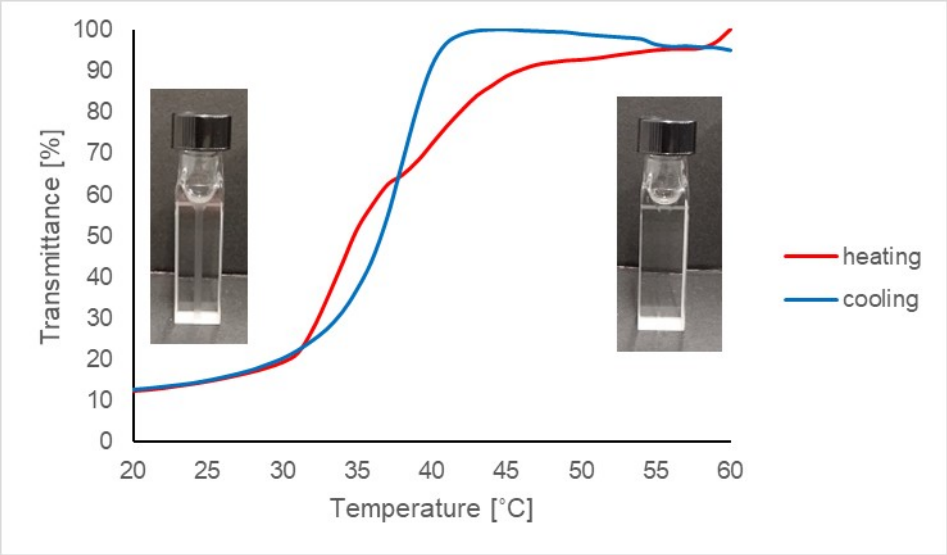

Figure S-2-23. Transmittance change of **PHS** in tetramethylurea and toluene at 800 nm

S-2-24. 1-propanol and hexane

Table S-2-24. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.57 mg	1-propanol : hexane = 9.0 : 1.0	100 μL	+	+	+	
2.62 mg	1-propanol : hexane = 8.0 : 2.0	100 μL	+	+	+	
2.59 mg	1-propanol : hexane = 7.0 : 3.0	100 μL	+	+	+	
2.57 mg	1-propanol : hexane = 6.5 : 3.5	100 μL	+	+	−	LCST
2.38 mg	1-propanol : hexane = 6.0 : 4.0	100 μL	−	−	−	

+: soluble, −: insoluble

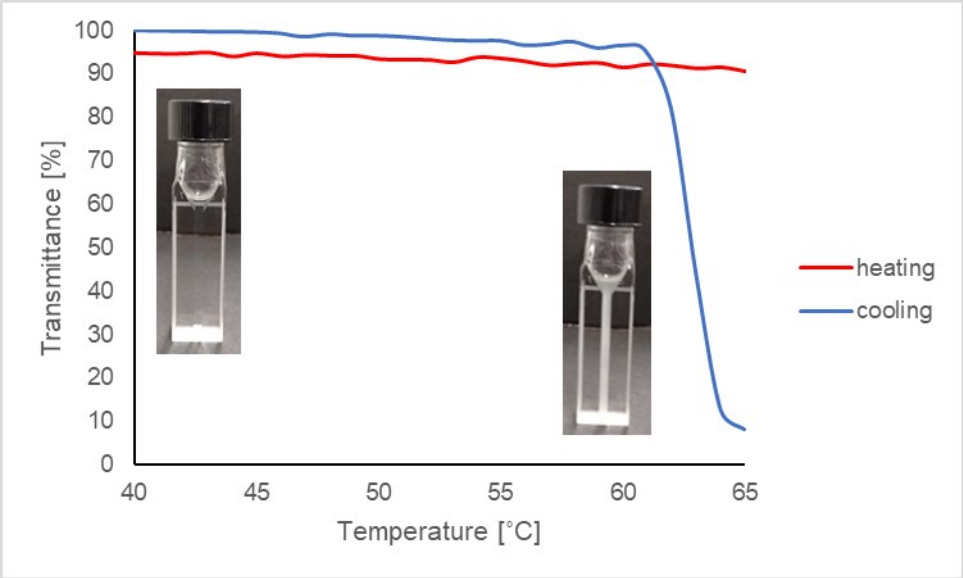

Figure S-2-24. Transmittance change of **PHS** in 1-propanol and hexane at 800 nm

S-2-25. 2-butanone and hexane

Table S-2-25. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.47 mg	2-butanone : hexane = 9.0 : 1.0	100 μL	+	+	+	
2.47 mg	2-butanone : hexane = 8.5 : 1.5	100 μL	+	+	–	LCST
2.46 mg	2-butanone : hexane = 8.0 : 2.0	100 μL	–	–	–	

+: soluble, —: insoluble

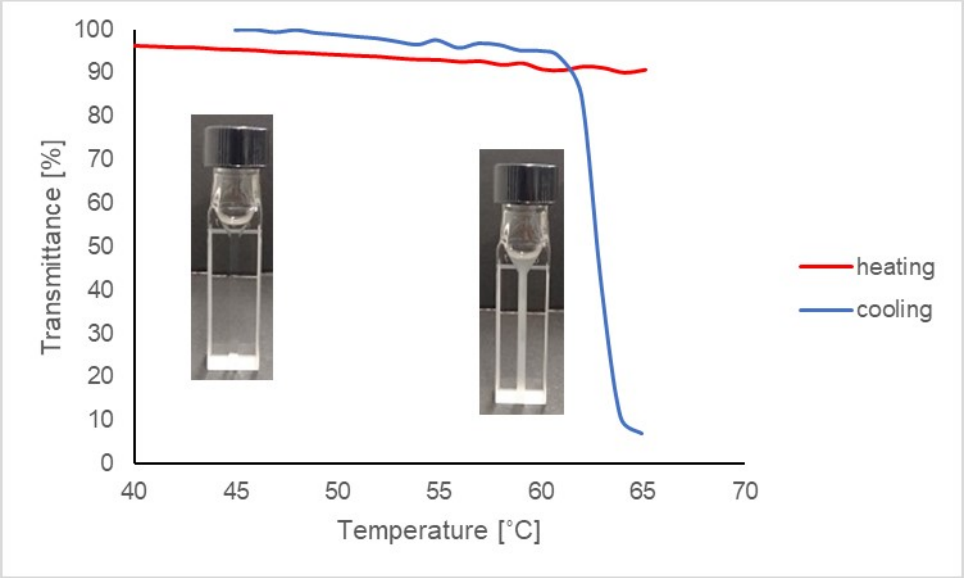

Figure S-2-25. Transmittance change of **PHS** in 2-butanone and hexane at 800 nm

S-2-26. THF and hexane

Table S-2-26. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.49 mg	THF : hexane = 9.0 : 1.0	100 μL	−	+	−	UCST & LCST
2.29 mg	THF : hexane = 8.9 : 1.1	100 μL	−	−	−	

+: soluble, −: insoluble

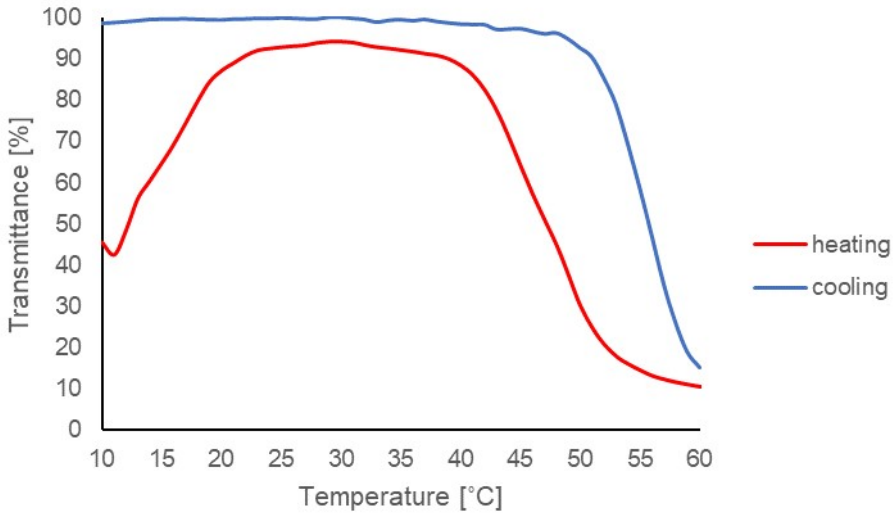

Figure S-2-26. Transmittance change of **PHS** in THF and hexane at 800 nm

S-2-27. ethyl acetate and hexane

Table S-2-27. Solubility test

polymer	solvent (mol. ratio)	volume	solubility			Thermo-responsiveness
			cool	rt	heat	
2.64 mg	ethyl acetate : hexane = 9.0 : 1.0	100 μL	+	+	+	
2.47 mg	ethyl acetate : hexane = 8.9 : 1.1	100 μL	+	+	+	
2.50 mg	ethyl acetate : hexane = 8.8 : 1.2	100 μL	+	+	−	LCST
2.59 mg	ethyl acetate : hexane = 8.5 : 1.5	100 μL	−	−	−	

+: soluble, −: insoluble

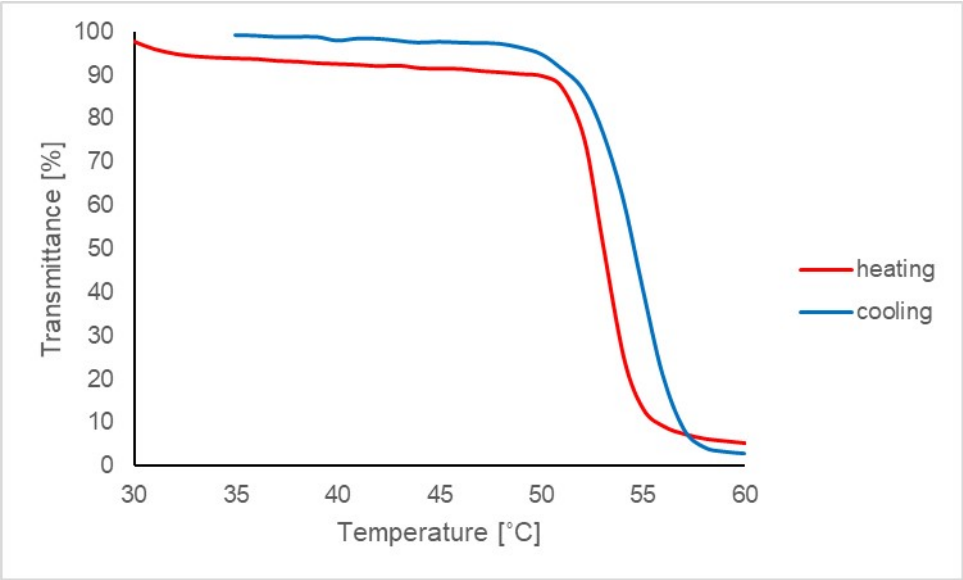

Figure S-2-27. Transmittance change of **PHS** in ethyl acetate and hexane at 800 nm