Supplementary Information

Natural Deep Eutectics: Expanding Green Solvents for Thermal-/Photo-Induced Polymerization of *N*-Isopropylacrylamide Toward Key Components for Sustainable Production of Semi-Natural Polymers

Shingo Yuki[†], *Reina, Shinohe*[†], *Yuta Tanaka* [†]*Hideharu Mori*[†*]

[†]Graduate School of Organic Materials Science, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan

EXPERIMENTAL SECTION

1. Materials

N-Isopropylacrylamide (NIPAM, Wako, > 98.0%) was purified by recrystallization from hexane. Thymol (Thy, TCI, >99.0 %), (±)-menthol (Men, TCI, >98.0 %), coumarin (Cou, Wako, >98.0 %), and 1-tetradecanol (Tdc, TCI, >98.0 %) were used without further purification. The melting points, as stated by the supplier, are 49.0–52.0 °C for Thy, 28 °C for Men, 68–72 °C for Cou, 38.0–41.0 °C for Tdc, and 63.0–67.0 °C for NIPAM. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97 %) was purified by recrystallization from methanol. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, TCI, >98.0%), 2-cyano-2-propyl dodecyl trithiocarbonate (97%, Sigma Aldrich), and other materials were used without further purification.

2. Preparation of natural deep eutectic solvents (NADESs) and polymerization in NADESs

2.1. Preparation of NADESs

NADESs were prepared by simple mixing two solids (e.g., Thy/Men, Thy/Cou, and Tdc/Men) at different feed ratios (1/2, 1/1, and 2/1), according to a reported method.[1] For instance, Thy (1.50g, 10.0 mmol) and Men (1.56 g, 10.0 mmol) were placed in a 10 mL glass vial equipped with a magnetic stirring bar and sealed with a plastic cap. The mixture was stirred under ambient conditions (approximately 25 °C in the air) for 3 h to afford Thy/Men (1/1) as a colorless liquid. The same simple method was used for the preparation of other NADESs. In all cases, mixing was performed under ambient conditions until a homogeneous solution was obtained (approximately 1 h for Thy/Men (1/2), 1.5 h for Tdc/Men (1/2), 2 h for Thy/Cou (1/1), and 1.5 h for Thy/Cou (2/1), respectively). The resulting NADESs were insoluble in water, and displayed a good miscibility in organic solvents, such as diethyl ether (Table S1). These hydrophobic NADESs, which were characterized by proton nuclear magnetic resonance (^{1}H NMR) measurement (Figure S1), were used directly for the polymerization.

2.2. Thermally-induced polymerization of NIPAM in NADES

A typical procedure for the thermally-induced free radical polymerization is as follows (Run 1 in Table 1): AIBN (1.64 mg, 0.01 mmol) and NIPAM (113 mg, 1.0 mmol) were dissolved in Thy/Men (1/1) NADES (339 mg, [M] = 25 wt. %) in a polymerization ampoule, and the mixture was degassed by three freeze-evacuate-thaw cycles. After sealing the ampoule, polymerization was performed at 60 °C for 24 h. Monomer conversion (>99%) was evaluated using ^{1}H NMR measurement of the crude product (Figure S3) by comparing the integration of the CH_2=C- resonance at 5.50 ppm with that of the -CH- main chain peak at 3.80 ppm. The mixture was purified by precipitation in diethyl ether, followed by filtration and then drying in vacuum to give PNIPAM (91.8 mg, yield = 81 %). The resulting PNIPAM was further characterized by ^{1}H NMR and size-exclusion chromatography (SEC) measurements (Figures S3 and S4).

For the thermally-induced RAFT polymerization (Run 2 in Table S3) using a trithiocarbonate-type chain transfer agent (CTA), AIBN (3.28 mg, 0.02 mmol), 2-cyano-2-propyl dodecyl trithiocarbonate (13.8 mg, 0.04 mmol), and NIPAM (453 mg, 4.0 mmol) were dissolved in Thy/Men (1/1) NADES (1.36 g, [M] = 25 wt. %). Thereafter, polymerization was performed in a sealed glass ampoule using the same procedure as that used for the thermally-induced free radical polymerization.

2.3. Photo-induced polymerization of NIPAM in NADES

A typical procedure for the photo-induced free radical polymerization of NIPAM is as follows (Run 3 in Table S7): DMPA (5.13mg, 0.02 mmol), NIPAM (226 mg, 2.0 mmol), and Thy/Men (1/1) NADES (0.528 g, [M] = 30 wt. %) were placed in a 5 mL glass vial. The mixture was stirred under air at room temperature for approximately 30 min with light shielding until a homogeneous solution was obtained. The mixture was irradiated with a mercury UV lamp (365 nm, 6.0 mW/cm^2, HLR100T-2 with HB100A) for 10 min under ambient conditions. The determination of the monomer conversion (94 %) by ^{1}H NMR, purification of the crude product by precipitation in diethyl ether (Yield = 77 %, 0.175 g), and characterization of resulting PNIPAM by ^{1}H NMR and SEC measurements were conducted using the same procedures as those used for the thermally-induced free radical polymerization.

For the photo-induced RAFT polymerization, DMPA (5.13mg, 0.02 mmol), NIPAM (226 mg, 2.0 mmol), and CTA (6.91 mg, 0.02 mmol) were dissolved in Thy/Men (1/1) NADES (0.528 g, [M] = 30 wt. %). Thereafter, polymerization was conducted by photolyzing with a 365 nm wavelength LED–UV light (HLV-24UV365-4WNRBT, CCS Inc., 6 cm away, LED = 330 mW/cm^2) under ambient conditions.

3. Synthesis and polymerization of NIPAM-based natural deep eutectic monomers (NADEMs)

3.1. Synthesis of NIPAM-based natural deep eutectic monomers (NADEMs)

All NADEMs were prepared by simple mixing of NIPAM with natural components (Thy, Men, Cou, and Tdc) under atmospheric conditions. As a representative example of NIPAM/Men (1/1), NIPAM (0.339 g, 3.0 mmol) and Men (0.469 g, 3.0 mmol) were placed in a 10 mL glass vial equipped with a magnetic stirring bar in air. The mixture was stirred on a hot plate at 30 °C for 30 min to afford NIPAM/Men as a colorless liquid.

3.2 Photo-induced polymerization of NIPAM-based NADEMs

The resulting NIPAM/Men (1/1) NADEM was used directly for the photo-induced polymerization. To the NIPAM/Men (1/1) NADEM (790 mg, 3.0 mmol) in the glass vial, DMPA (7.7 mg, 0.03 mmol) was added, and the mixture was stirred under air at room temperature for approximately 5 min with light shielding until a homogeneous solution was obtained. After the magnetic stirring bar was removed, photo-induced radical polymerization was conducted by photolyzing with a 365 nm wavelength LED–UV light (HLV-24UV365-4WNRBT, CCS Inc., 10 cm away, LED = 130 mW/cm^2) under ambient conditions. After the polymerization, the mixture was dissolved in a small amount of methanol, and purified by precipitation in diethyl ether, followed by filtration and drying under vacuum to give PNIPAM (270 g, yield = 79 %).

The same procedures were used for the preparation of other NADEMs and subsequent photo-induced polymerization. When the NADEM was prepared at higher polymerization temperatures (e.g., 50 °C for the preparation for NIPAM/Tdc (1/1)) NADEM was prepared by hating and stirring two solids using a

hot plate, and used directly for the photopolymerization. The ^{1}H NMR and digital photographs of the NIPAM-based NADEMs and corresponding NADEM-based polymers are shown in Table 2 and Figures S16-S19 (Supporting Information).

3. Instrumentation

^{1}H NMR (400 MHz) spectra were recorded with a JEOL JNM-ECX400. FT-IR spectra were obtained with a JASCO FT/IR-210 spectrometer. The dyad tacticity of PNIPAM was evaluated from the methylene proton peaks recorded in DMSO-d_6 at 150 °C. 2D NMR spectra were recorded on a JEOL ECZ-600 at a resonant frequency of 600 MHz. SEC measurement was conducted on a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column set was as follows: four consecutive hydrophilic vinyl polymer-based gel columns (TSK-GELs: α-M, α-4000, α-3000, α-2500) and a guard column (TSK-guardcolumn α]. The samples were run at a flow rate of 1.0 mL/min using DMF containing 10 mM LiBr as the eluent. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated relative to polystyrene standards (Tosoh) ranging from 1050 to 1090000. The UV–vis spectra were recorded on JASCO V-630BIO UV–vis spectrophotometer. The transmittance of the aqueous polymer solution was recorded on a JASCO V-630BIO UV-vis spectrophotometer equipped with a temperature controller (JASCO EHC-716 and EHC-717, respectively).[2]

Tensile tests were performed using a MX2-500N (IMADA Co., Ltd.) with a digital force gauge ZTA-500N machine (IMADA Co., Ltd.). For the preparation of the dog bone-shaped specimen (effective gauge dimensions: length = 12 mm, width = 2 mm, and thickness = 1.0 mm), NADEM and DMPA (0.01 mol % for NADEM) were introduced into a Teflon mold, followed by photolyzing with a 365 nm wavelength LED–UV light (LNSP-100UV3-365-FN, CCS Inc., 10 cm away, LED = 130 mW/cm^2) under ambient conditions for 1 min. The specimen was subjected to a tensile test.

Table S1. Miscibility of NADESs with common solvents and solubility of NIAPM in NADESs

Solvent /monomer	Thy/Men (1/1)	Thy/Men (1/2)	Tdc/Men (1/2)	Thy/Cou (1/1)	Thy/Cou (2/1)
H_2O	-	-	-	-	-
Acetone	+	+	+	+	+
Chloroform	+	+	+	+	+
Dichloromethane	+	+	+	+	+
Diethyl ether	+	+	+	+	+
Ethanol	+	+	+	+	+
Ethyl acetate	+	+	+	+	+
Methanol	+	+	+	+	+
n-Hexane	+	+	+	+	+
THF	+	+	+	+	+
DMF	+	+	+	+	+
NIPAM	++	++	++	++	++

+ : Miscible at room temperature. - : Immiscible at room temperature. ++ : Soluble at room temperature ([M] = 25 wt%).

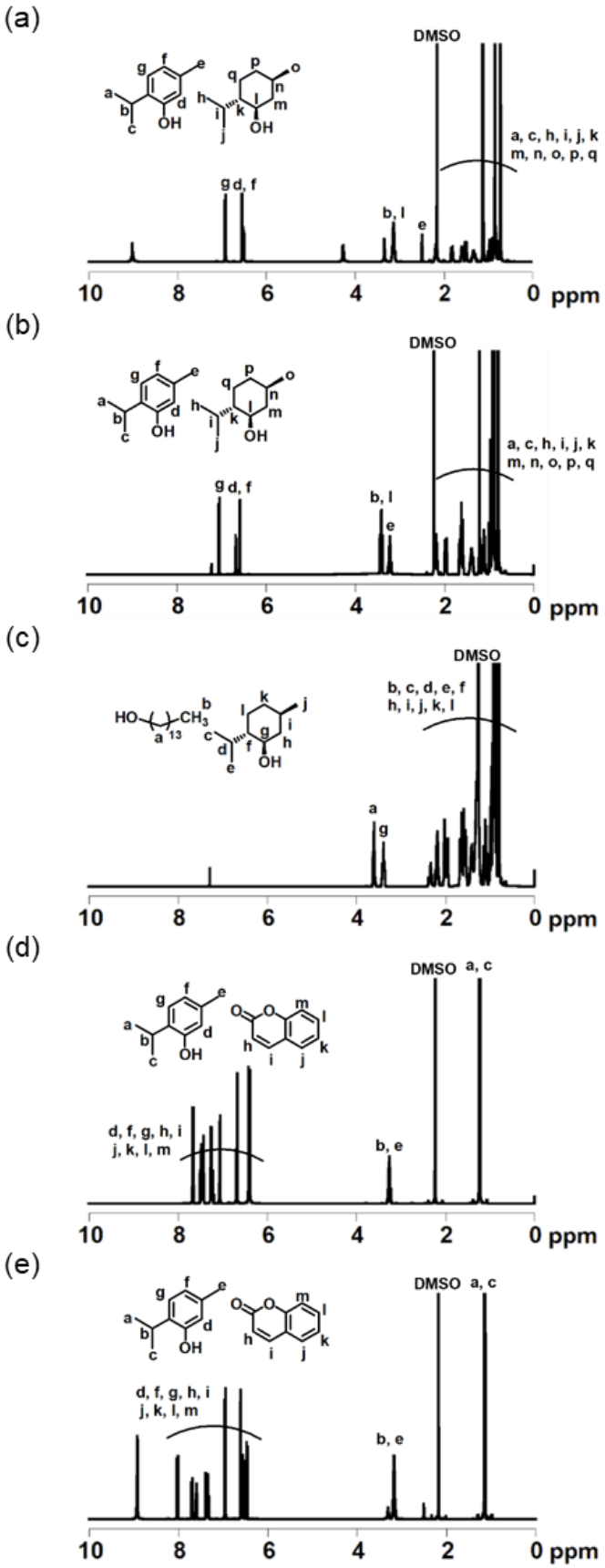


Figure S1. ^{1}H NMR spectra (DMSO-d_6) of NADESs: (a) Thy/Men (1/1), (b) Thy/Men (1/2), (c) Tdc/Men (1/2), Thy/Cou (1/1), and Thy/Cou (2/1).

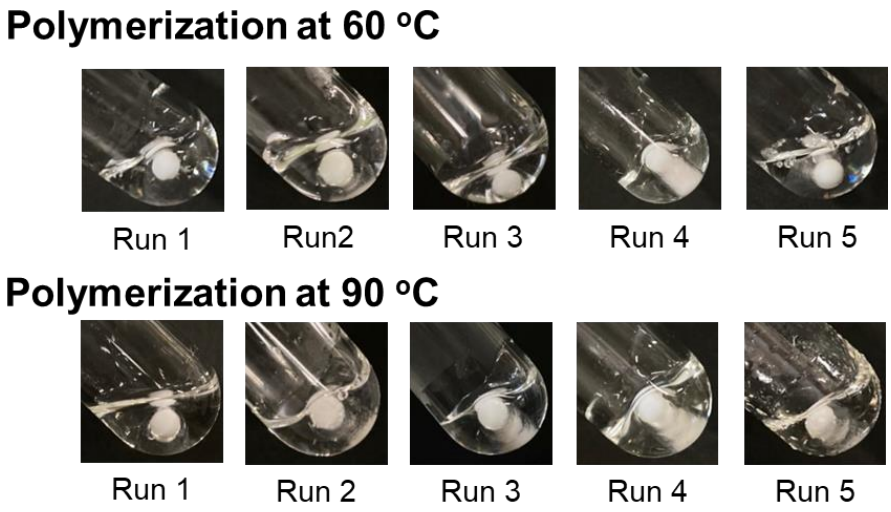


Figure S2. Appearance of polymerized products obtained by free radical polymerization of NIPAM in various NADESs (see Table 1 and Table S2 for detailed polymerization conditions).

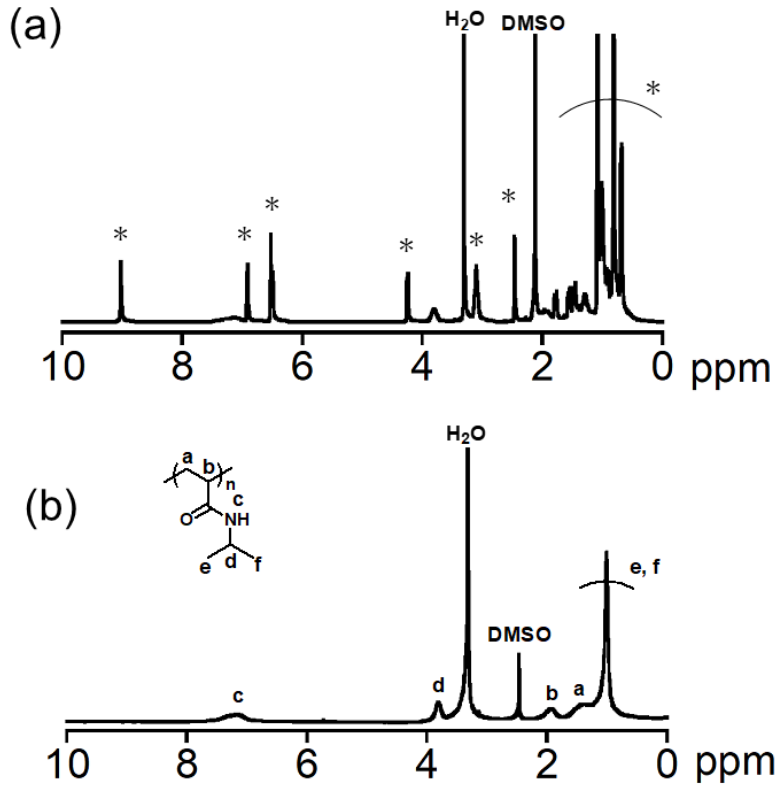


Figure S3. ^{1}H NMR spectra (DMSO-d_6) of (a) crude product prepared by the thermally-induced free radical polymerization of NIPAM in Thy/Men (1/1) (Run 1 in Table 1) and (b) PNIPAM purified by reprecipitation into diethyl ether and isolated by filtration. The asterisk corresponds to the peaks attributed to Thy/Men (1/1).

Table S2. Thermally-induced free radical polymerization of NIPAM in hydrophobic NADESs at 90 °C[a)]

Run	Solvent	Conv. [b)]/ Yield [c)] (%)	M_n [d)] (SEC)	M_w/M_n [d)] (SEC)
1	Thy/Men (1/1)	98/68	25000	1.89
2	Thy/Men (1/2)	98/76	33000	2.05
3	Tdc/Men (1/2)	＞99/86	67000	2.73
4	Thy/Cou (1/1)	-/81	26000	1.89
5	Thy/Cou (2/1)	78/69	13000	1.91

[a)] Polymerization with AIBN at 90 °C for 24 h. $[I]_0/[M]_0$ = 1/100. [M] = 25 wt%. [b)] Calculated using ^{1}H NMR spectroscopy in DMSO-d_6. [c)] Diethyl ether insoluble fraction. [d)] Measured by size-exclusion chromatography (SEC) using a polystyrene standard in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr).

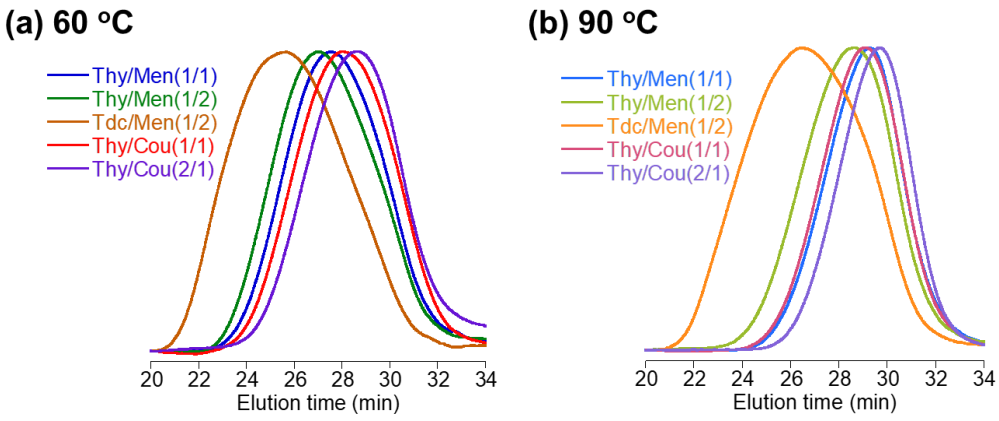
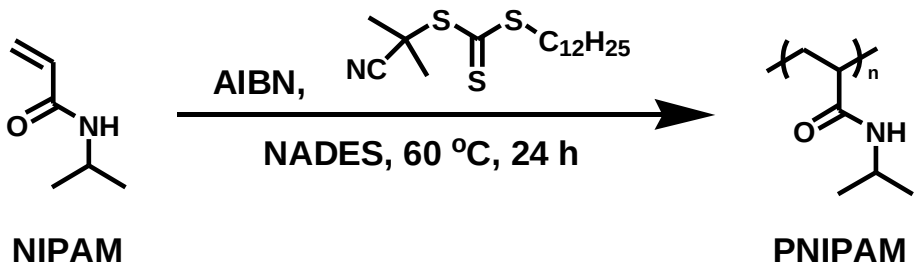


Figure S4. SEC curves (RI traces, DMF, LiBr) of PNIPAMs obtained by fee radical polymerization of NIPAM in various NADESs at (a) 60 °C and (b) 90 °C (see Table 1 and Table S2 for detailed polymerization conditions).



Scheme S1. Thermally-induced RAFT polymerization of NIPAM in NADES.

Table S3. Thermally-induced RAFT polymerization of NIPAM in NADES [a)]

Run	Solvent	$[I]_0/[CTA]_0/[M]_0$	Conv. [b)] /Yield [c)] (%)	M_n [b)] (theory)	M_n [d)] (SEC)	M_w/M_n [d)] (SEC)
1		1/2/100	99/40	6000	8000	1.21
2	Thy/Men	1/2/200	92/60	11000	17000	1.19
3	(1/1)	1/2/400	55/44	16000	21000	1.27
4		1/2/1000	28/24	14000	25000	1.35
5		1/2/100	＞99/31	5600	12000	1.18
6	Tdc/Men	1/2/200	＞99/83	11000	18000	1.21
7	(1/2)	1/2/400	＞99/94	22000	32000	1.28
8		1/2/1000	97/87	55000	52000	1.34

[a)] Polymerization with AIBN at 60 °C for 24 h. [M] = 25 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Diethyl ether-insoluble part. [d)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr).

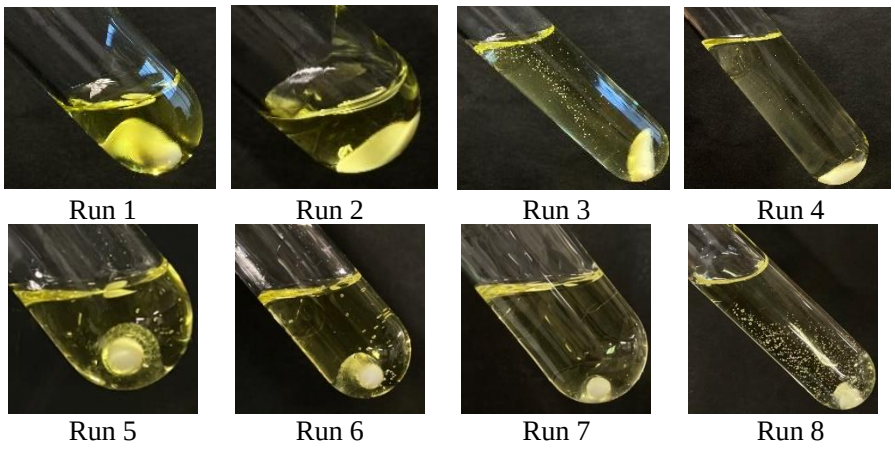


Figure S5. Appearance of polymerized products obtained by thermally-induced RAFT polymerization of NIPAM at different [M]/[CTA] ratios in NADESs (Run 1–Run 4 : Thy/Men (1/1), Run 5–Run 8 : Tdc/Men (1/2) in Table S3).

Table S4. Thermally-induced RAFT polymerization of NIPAM in NADESs [a)]

Run	Solvent	Time (h)	Conv. [b)] (%)	M_n [b)] (theo)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	Thy/Men (1/1)	1	0	-	-	-
2		2	10	1500	-	-
3		4	26	3300	-	-
4		8	75	9000	8200	1.15
5		24	99	12000	11000	1.17
6	Thy/Men (1/2)	1	0		-	-
7		2	2	600	-	-
8		4	64	7600	7400	1.17
9		8	85	10000	9000	1.18
10		24	99	12000	10000	1.20
11	Tdc/Men (1/2)	1	48	5800	-	-
12		2	92	11000	11000	1.15
13		4	99	12000	11000	1.14
14		8	99	12000	11000	1.13
15		24	99	12000	10000	1.14
16	Thy/Cou (1/1)	1	1	460	-	-
17		2	15	2000	-	-
18		4	71	8400	16000	1.21
19		8	76	8900	15000	1.21
20		24	90	11000	16000	1.24
21	Thy/Cou (2/1)	1	0	-	-	-
22		2	0	-	-	-
23		4	28	3500	-	-
24		8	59	7000	6400	1.19
25		24	78	9000	7600	1.23
26	DMF	3	82	10000	9100	1.18
27		6	94	11000	9600	1.22

[a)] Polymerization with AIBN at 60 ºC for 24 h. $[I]_0/[CTA]_0/[M]_0$ = 1/2/200. [M] = 25 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (10 mM LiBr).

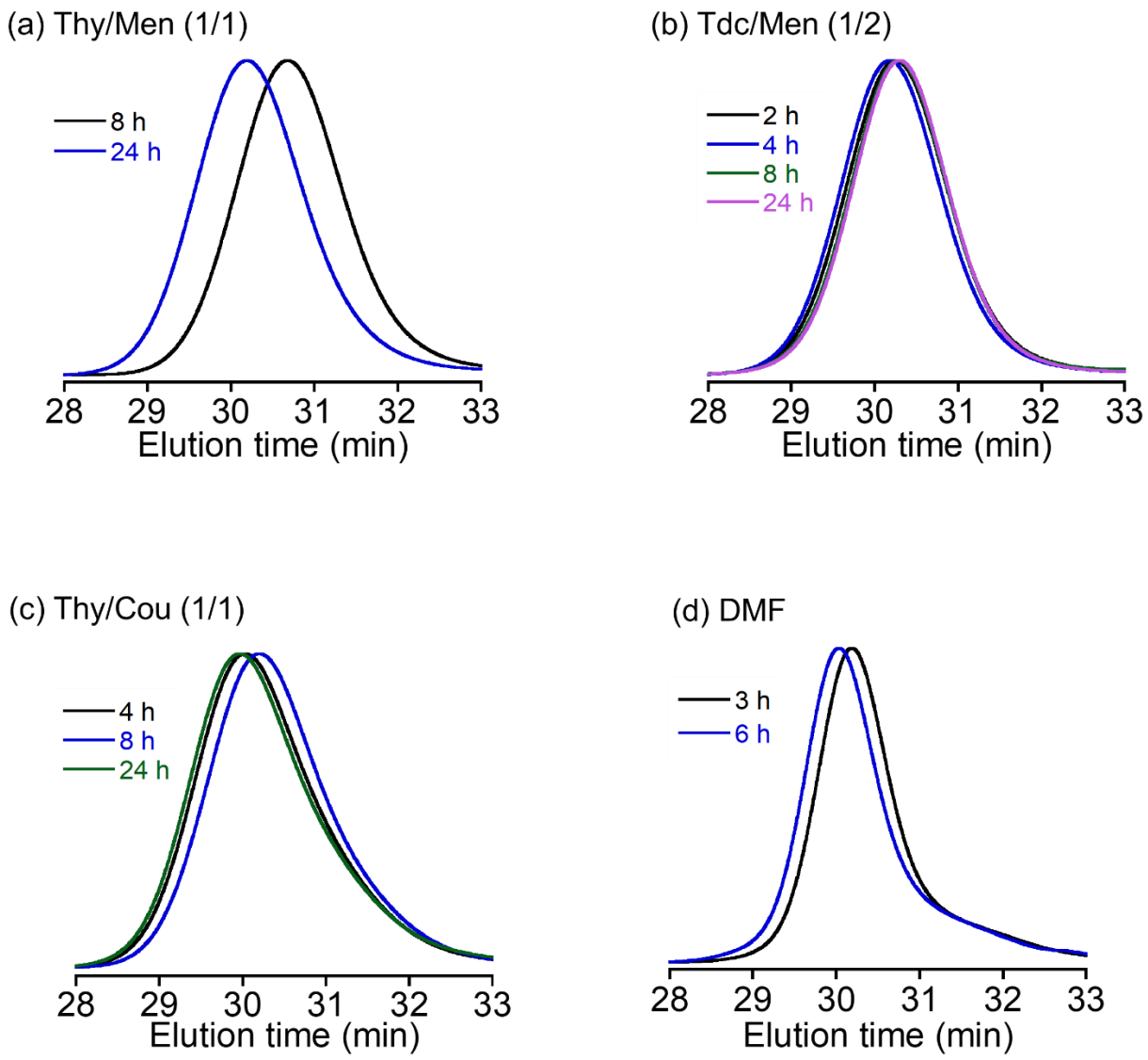


Figure S6. SEC curves (RI traces, DMF, LiBr) of PNIPAMs obtained by thermally-induced RAFT polymerization of NIPAM in (a-c) NADESs and (d) DMF (Table S4).

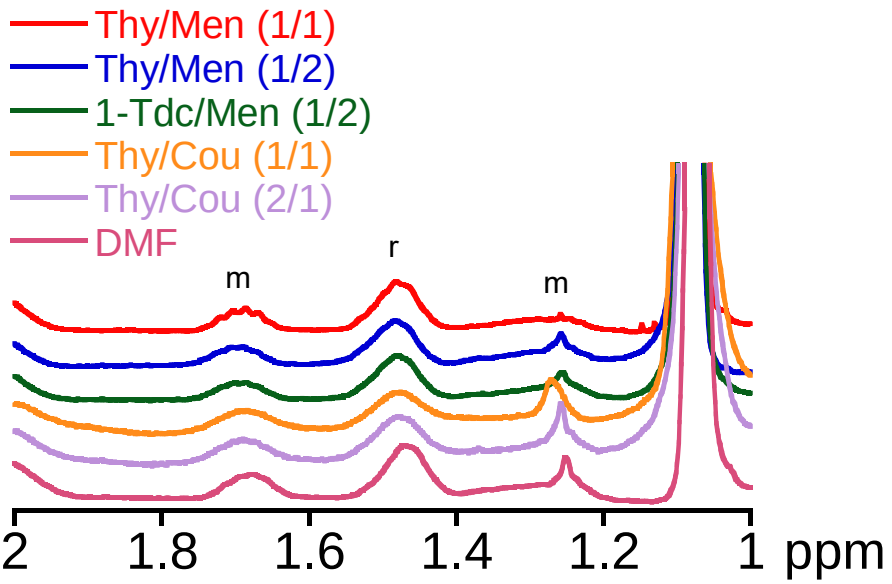


Figure S7. ^{1}H NMR spectra (DMSO-d_6, 150 ^{o}C) of PNIPAMs obtained by thermally-induced RAFT polymerization of NIPAM in hydrophobic NADESs (Runs 5, 10, 15, 20, 25, 27 in Table S4).

Table S5. Summary of tacticity of PNIPAMs prepared in different NADESs

Solvent	meso (m)	racemo (r)
Thy/Men (1/1)	48	52
Thy/Men (1/2)	51	49
Tdc/Men (1/2)	49	51
Thy/Cou (1/1)	54	46
Thy/Cou (2/1)	54	46
DMF	54	46

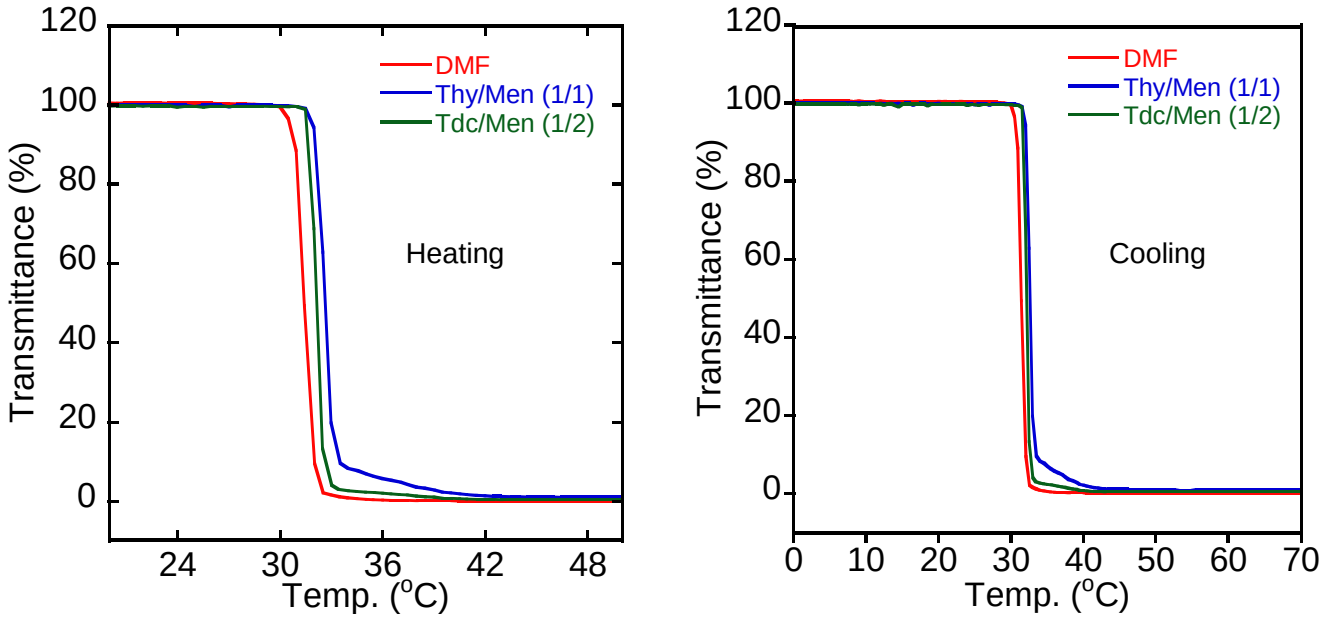


Figure 8. Temperature dependence of the transmittance at 500 nm of aqueous solutions of PNIPAMs prepared in NADESs, Thy/Men (1/1) and Tdc/Men (1/2), and DMF.

Table S6. Photo-induced free radical polymerization of NIPAM under UV light (Hg lamp) in various NADESs [a)]

Run	Solvent	Conv. [b)] (%)	Yield [c)] (%)	M_n [d)] (SEC)	M_w/M_n [d)] (SEC)
1	Thy/Men (1/1)	96	30	83000	1.61
2	Thy/Men (1/2)	99	63	68000	2.03
3	Tdc/Men (1/2)	99	60	190000	2.06
4	Thy/Cou (1/1)	<1	-	-	-
5	Thy/Cou (2/1)	<1	-	-	-

[a)] Polymerization with DMPA at room temperature for 90 min under air. $[I]_0/[M]_0$ = 1/100. [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Diethyl ether-insoluble part. [d)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (10 mM LiBr).

Figure S9. Appearance of polymerized products obtained by photo-induced free radical polymerization of NIPAM in various NADESs (see Table S6).

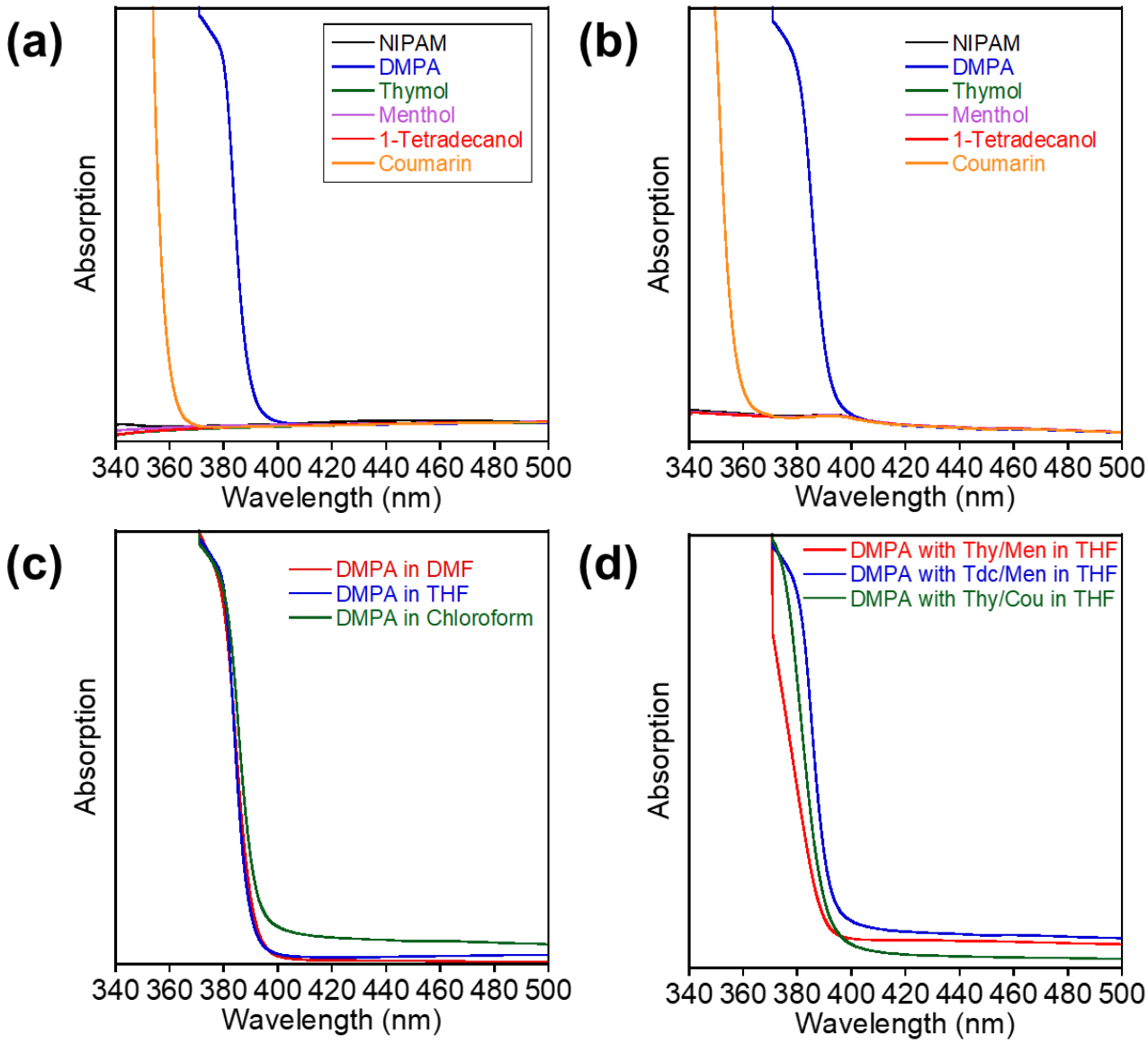


Figure S10. UV-vis spectra of (a,b) NADES components, monomer (NIPAM), and photoinitiator (DMPA) in (a) $CHCl_3$ and (b) THF. UV-vis spectra of (c) DMPA in different solvents and (d) DMPA with NADESs in THF.

Table S7. Photo-induced free radical and RAFT polymerization of NIPAM in Thy/Men (1/1) NADES using different lights [a)]

Run	$[I]_0/[CTA]_0/[M]_0$ (light)	Time (min)	Conv. [b)] (%)	M_n [b)] (theo)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	1/0/100 (Hg lamp, 6.0 mW/cm^2)	1	0	-	-	-
2		5	81	-	32000	2.64
3		10	94	-	34000	2.20
4	1/0/100 (LED-UV light, 330 mW/cm^2)	1	99	-	24000	2.33
5		2	99	-	24000	2.13
6		3	99	-	25000	2.32
7	1/1/100 (LED-UV light, 330 mW/cm^2)	1	0	-	-	-
8		2	12	1700	-	-
9		3	70	8000	14000	1.29
10		5	86	10000	16000	1.34
11		10	92	11000	16000	1.38
12		30	93	11000	16000	1.43

[a)] Polymerization with DMPA at room temperature under air. [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Diethyl ether-insoluble part. [d)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr).

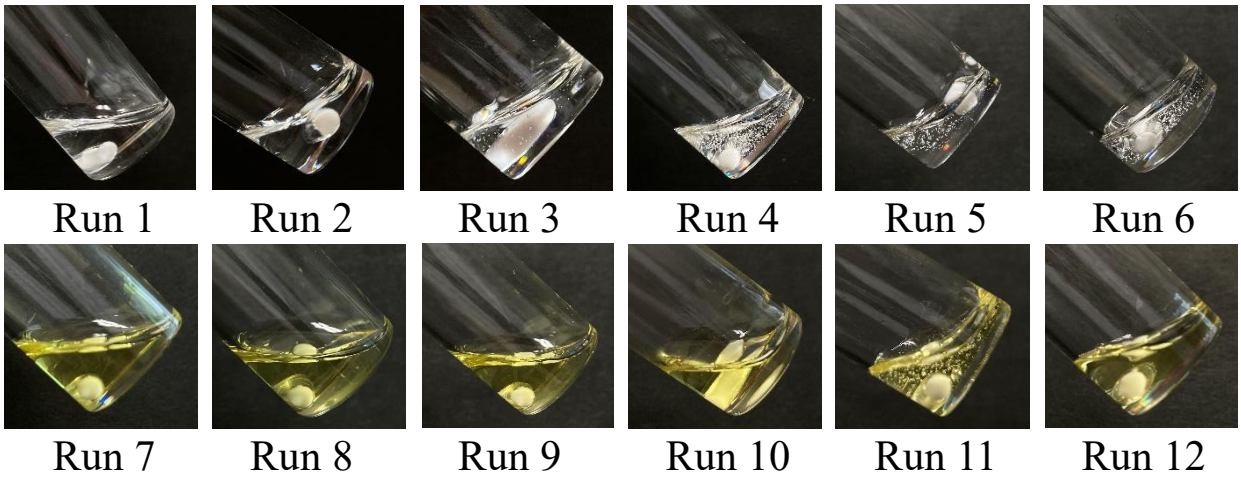


Figure S11. Appearance of polymerized products obtained by free radical and RAFT polymerizations of NIPAM in Thy/Men (1/1) NADES (Table S7).

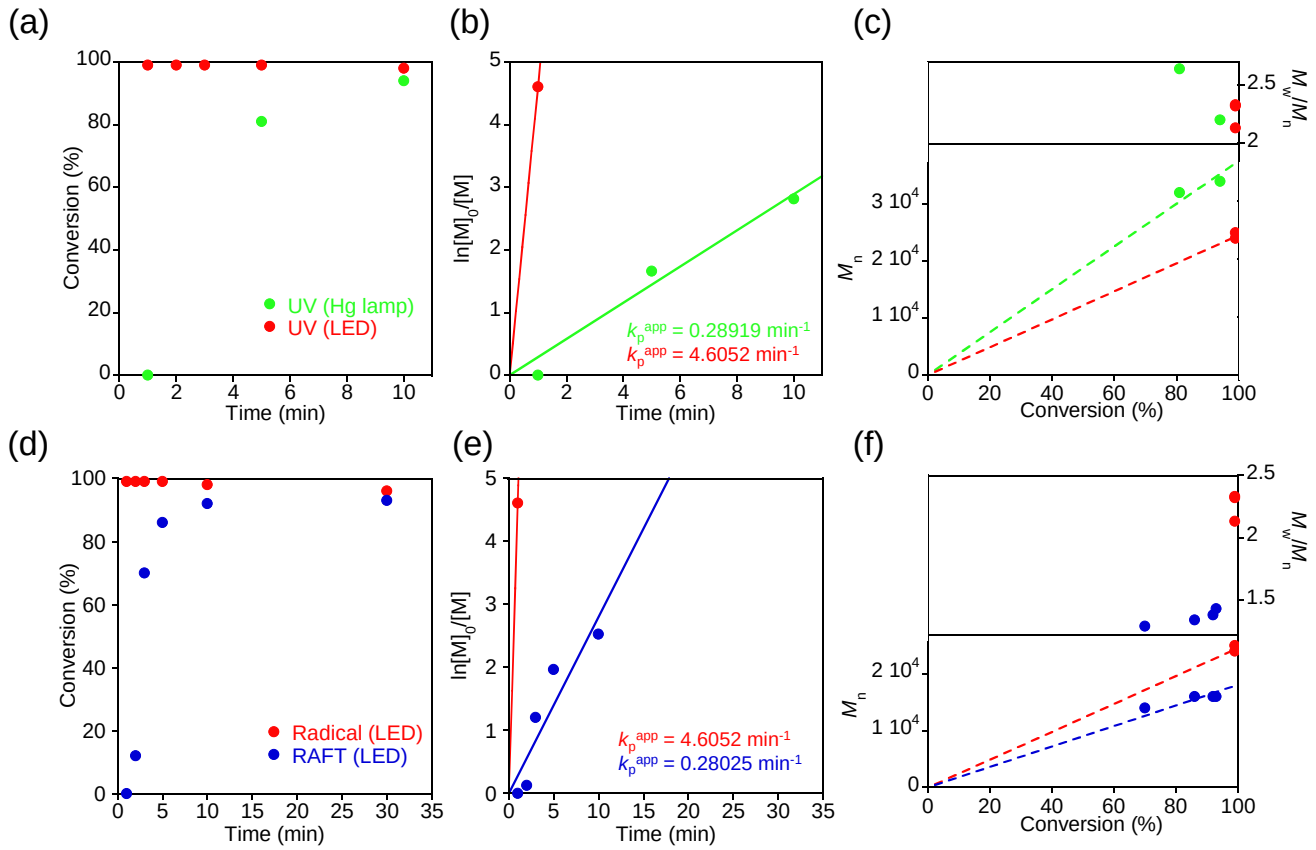


Figure S12. (a) Time-conversion and (b) first-order kinetic plots for the photo-induced free radical polymerization of NIPAM in Thy/Men (1/1) NADES under different UV lights (Hg lump and LED). (c) Number-average molecular weight and polydispersity as a function of conversion. (d) Time-conversion and (e) first-order kinetic plots for the photo-induced free radical and RAFT polymerizations of NIPAM in Thy/Men (1/1) NADES under LED-UV light. (f) Number-average molecular weight and polydispersity as a function of conversion.

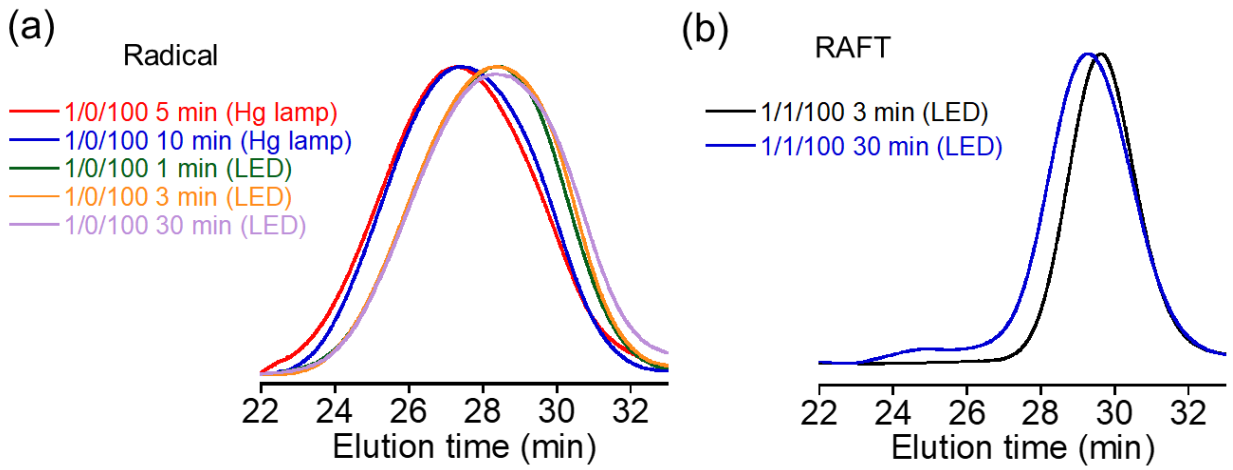


Figure S13. SEC curves (RI traces, DMF, LiBr) of PNIPAMs obtained by photo-induced (a) free radical and (b) RAFT polymerizations under air in Thy/Men (1/1) NADES (see Table S7 for detailed conditions).

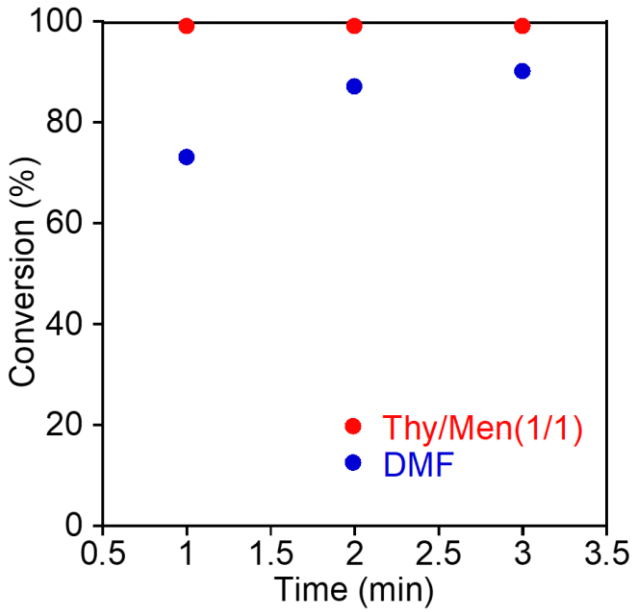


Figure S14. Time-conversion plots of photo-induced free radical polymerization of NIPAM under LED-UV light in Thy/Men (1/1) NADES and DMF.

Table S8. Photo-induced RAFT polymerization of NIPAM under UV light (LED-UV) in Tdc/Men (1/2) NADES [a)]

Run	Time (min)	Conv. [b)] (%)	M_n [b)] (theo)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	1	0	-	-	-
2	2	67	8000	19000	1.38
3	3	88	10000	21000	1.51
4	5	95	11000	21000	1.58
5	10	99	12000	19000	1.61
6	30	98	11000	17000	1.51

[a)] Polymerization with DMPA at room temperature under air. $[I]_0/[CTA]_0/[M]_0 = 1/1/100$. [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (10 mM LiBr).

Table S9. Photo-induced RAFT polymerization of NIPAM under UV light (LED light) in hydrophobic NADESs [a)]

Run	Solvent	$[I]_0/[CTA]_0/[M]_0$	Conv. [b)] /Yield [c)] (%)	M_n [b)] (theory)	M_n [d)] (SEC)	M_w/M_n [d)] (SEC)
1		1/1/100	＞99/88	11000	26000	1.39
2		1/1/200	＞99/91	22000	28000	1.36
	Thy/Men (1/1)					
3		1/1/500	＞99/86	56000	44000	1.54
4		1/1/1000	＞99/75	110000	69000	1.76
5		1/1/100	95/72	11000	22000	1.36
6		1/1/200	>99/79	22000	30000	1.34
	Tdc/Men (1/2)					
7		1/1/500	>99/82	57000	50000	1.56
8		1/1/1000	96/89	110000	60000	1.94

[a)] Polymerization with DMPA at room temperature for 30 min under air. [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Diethyl ether-insoluble part. [d)] Measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr).

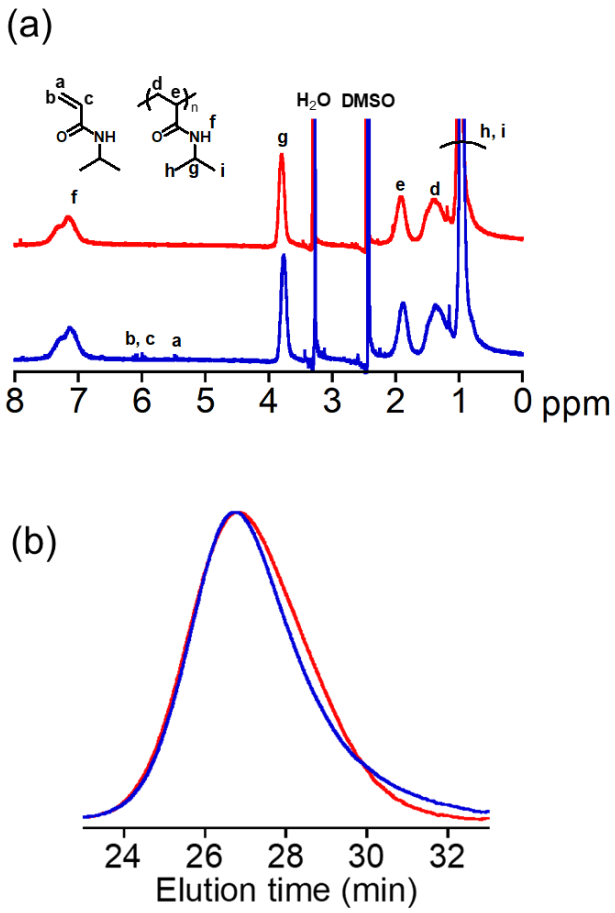


Figure S15. (a) ^{1}H NMR spectra and (b) SEC curves (RI detector, DMF, LiBr) of PNIPAMs obtained by photo-induced RAFT polymerization under air in Tdc/Men (1/2) NADES, which was purified by reprecipitation into diethyl ether, followed by filtration (red line) and by mixing with a distilled water by ultrasonicated (40 kHz) at 30 °C for 5 min, followed by filtration (blue line).

Table S10. Characteristics of PNIPAMs obtained by different purification processes [a)]

Run	Conv. [b)] (%)	Yield (%)	M_n [b)] (theo)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	99	82 [d)]	56000	47000	1.64
2	99	57 [e)]	56000	43000	1.80

[a)] Polymerization with DMPA at room temperature for 10 min under LED-UV light (365 nm, 330 mW/cm^2) in Tdc/Men (1/2). [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [d)] Diethyl ether-insoluble part. [e)] Water-soluble part.

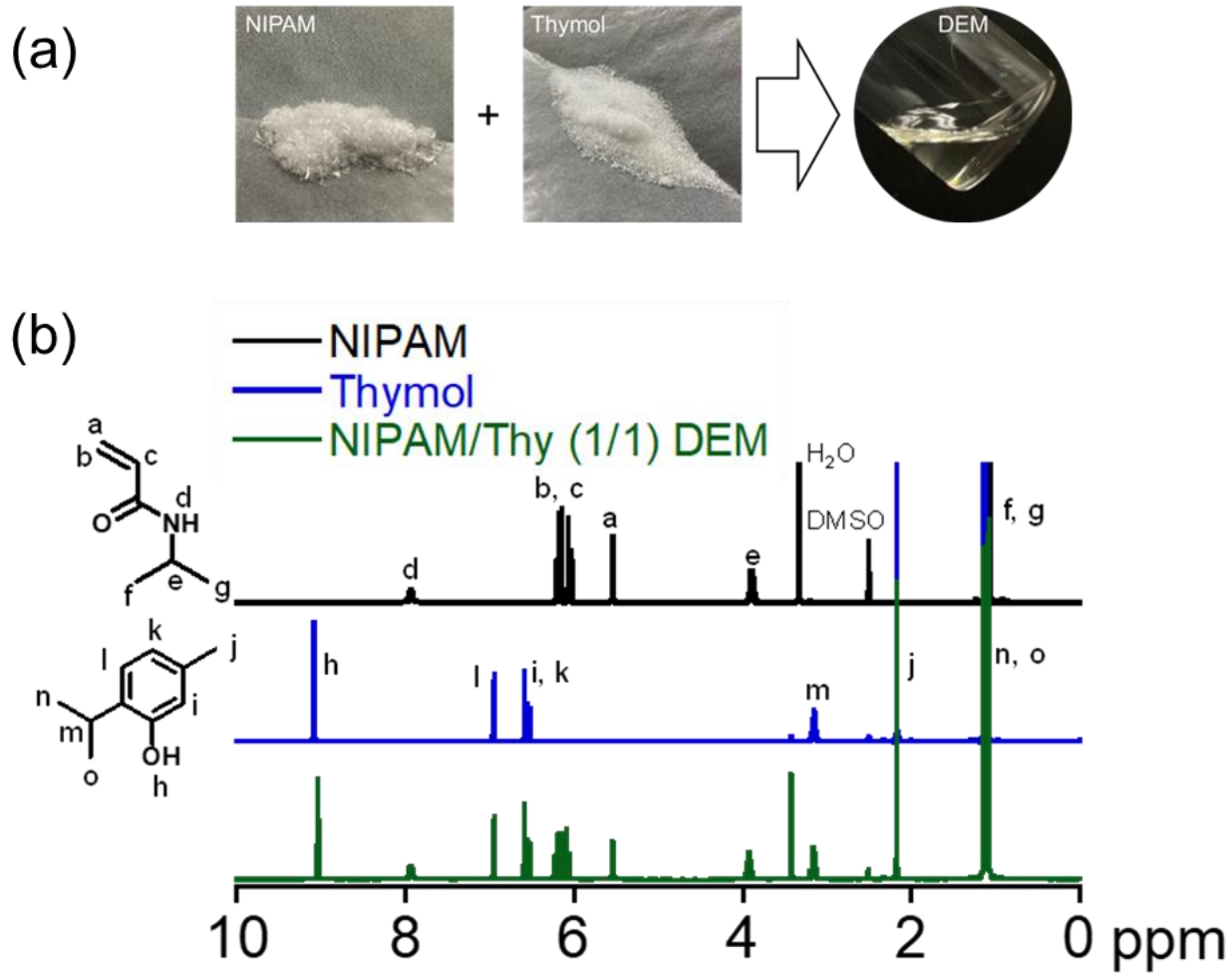


Figure S16. (a) Appearance of NIPAM (solid), thymol (solid), and NIPAM/Thy NADEM (liquid), and (b) ^{1}H NMR spectra of NIPAM, thymol and NIPAM/Thy (1/1) NADEM in DMSO-d_6.

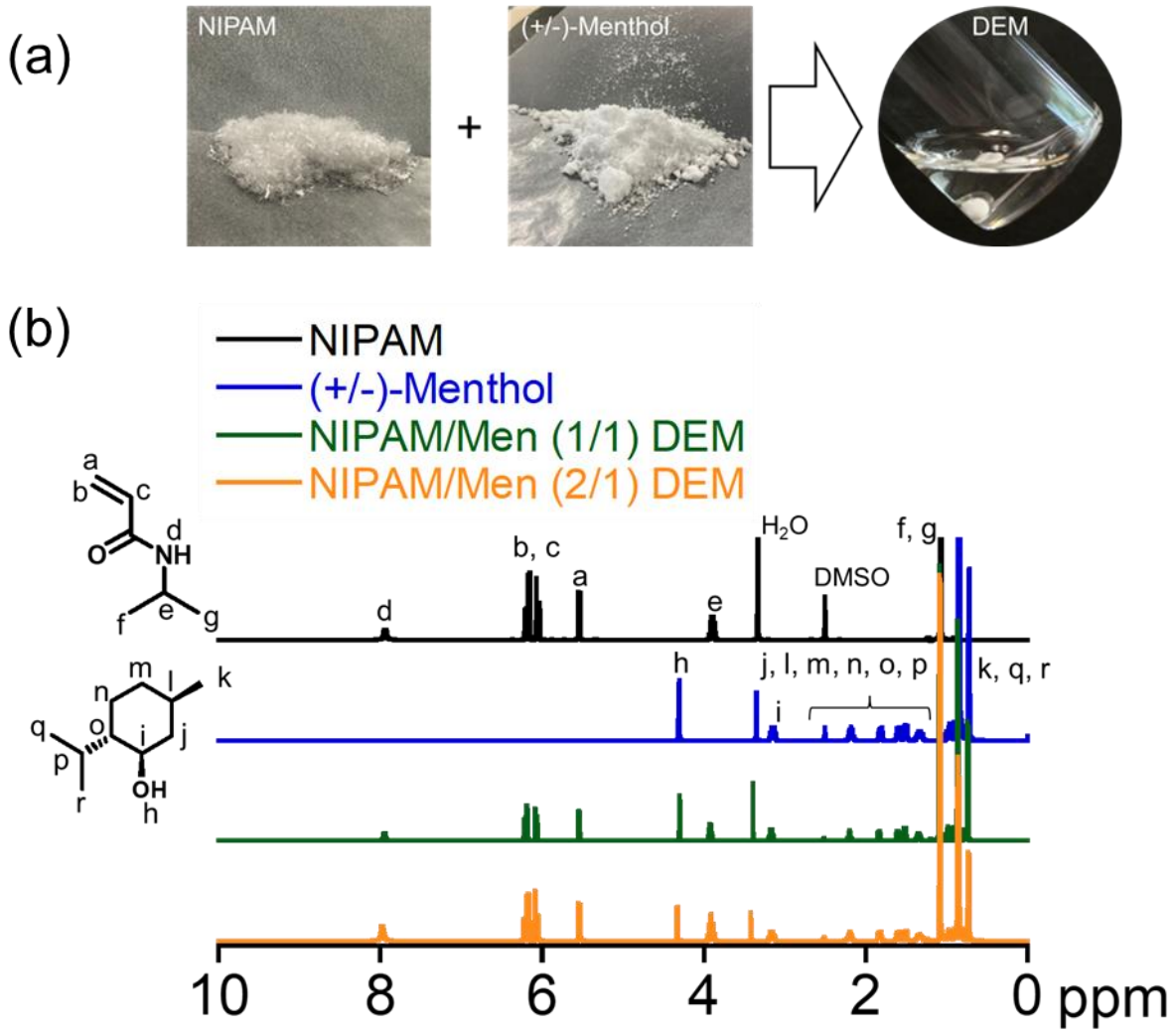


Figure S17. (a) Appearance of NIPAM (solid), (±)-menthol (solid), and NIPAM/Men (1/1) NADEM (liquid), and (b) ^{1}H NMR spectra of NIPAM, (±)-menthol, and NIPAM/Men (1/1 and 2/1) NADEMs in DMSO-d_6.

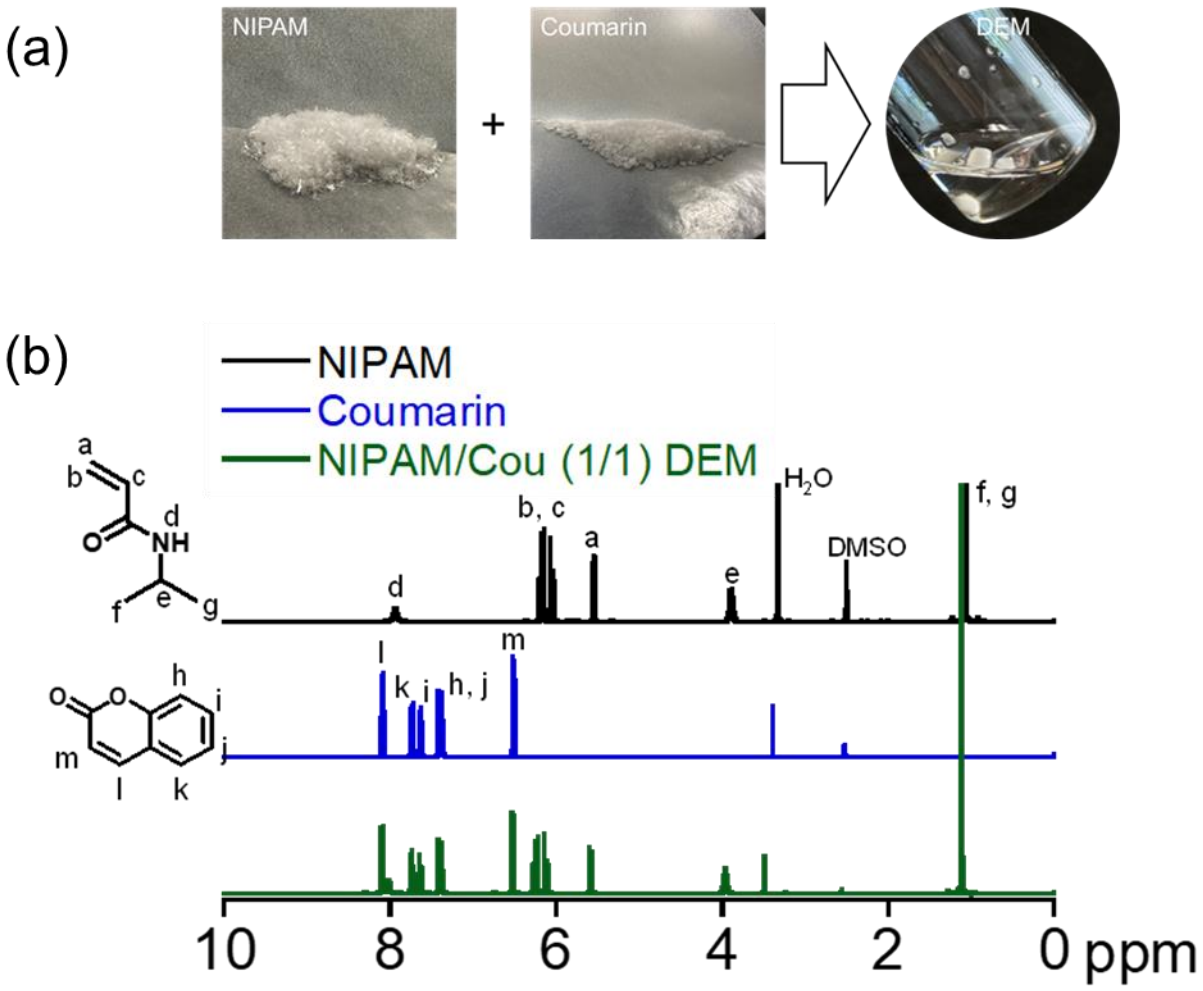


Figure S18. (a) Appearance of NIPAM (solid), coumarin (solid), and NIPAM/Cou (1/1) NADEM (liquid), and (b) ^{1}H NMR spectra of NIPAM, coumarin, and NIPAM/Cou (1/1) NADEM in DMSO-d_6.

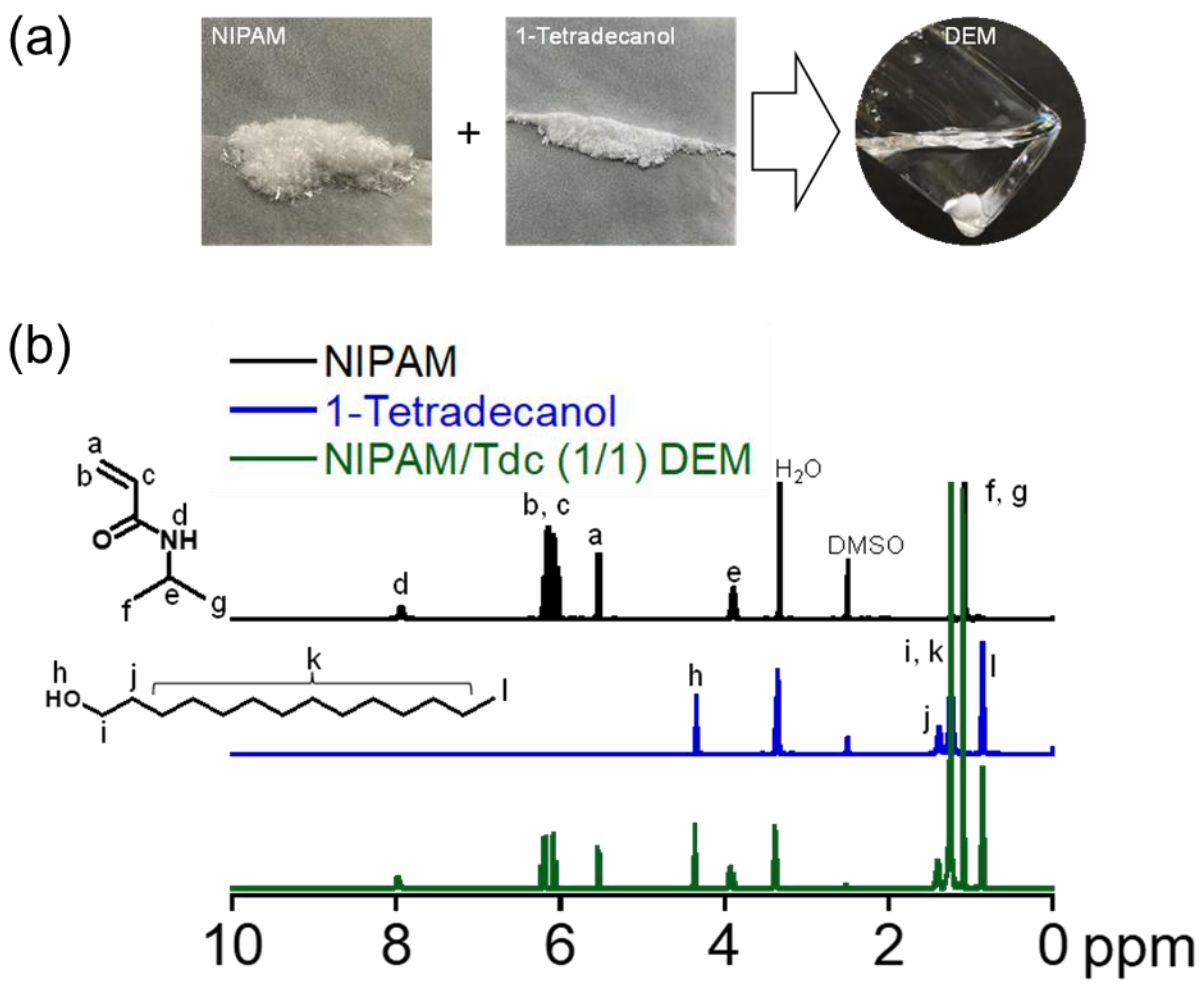
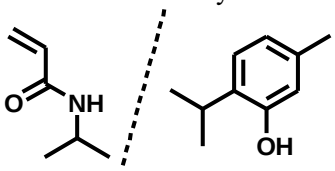
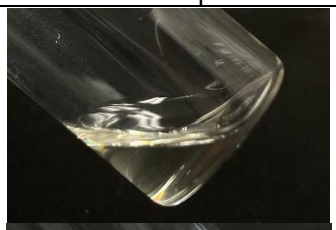
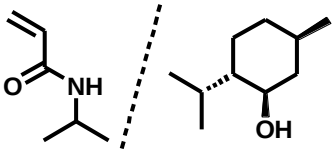
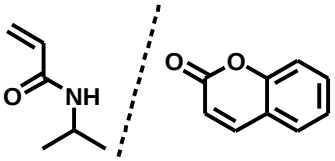
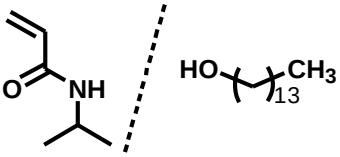


Figure S19. (a) Appearance of NIPAM (solid), 1-tatradecanol (solid), and NIPAM/Tdc (1/1) NADEM (liquid), and (b) ^{1}H NMR spectra of NIPAM, 1-tetradecanol, and NIPAM/Tdc (1/1) NADEM in DMSO-d_6.

Table S11. Synthesis of NIPAM-based NADEMs and their appearances

Run	Molar ratio	Appearance	
		Reaction temperature	1 day later [d]
NIPAM/Thy [a] 	1/1		
NIPAM/Men [b] 	1/1		
NIPAM/Cou [c] 	1/1		
NIPAM/Tdc [c] 	1/1		

[a] Mixing at 25 °C for 10 min. [b] Mixing at 30 °C for 30 min. [c] Mixing at 50 °C for 30 min. [d] At room temperature.

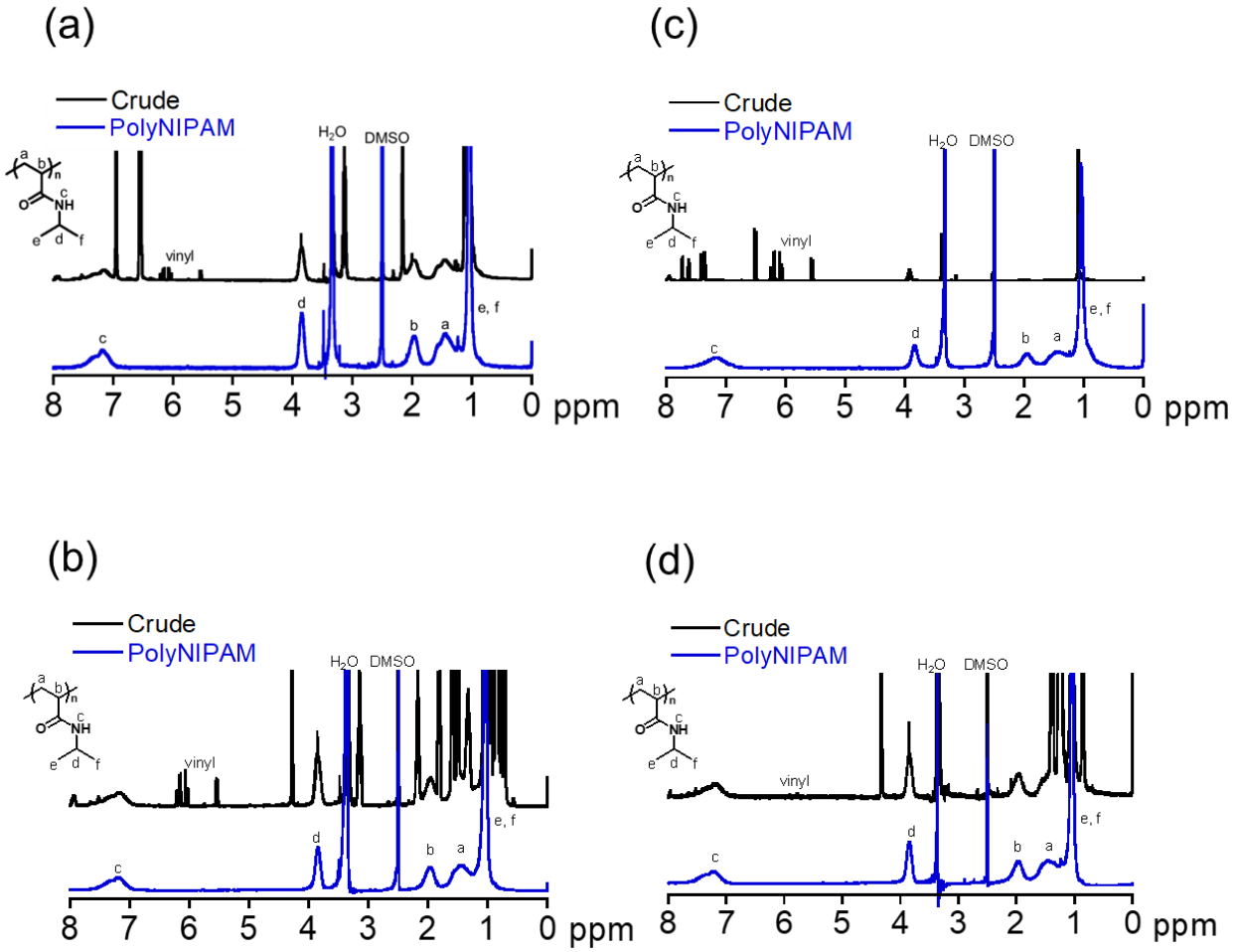


Figure S20. ^{1}H NMR spectra (DMSO-d_6) of crude products (black line) obtained by photoinduced radical polymerization of (a) NIPAM/Thy (1/1), (b) NIPAM/Men (1/1), (c) NIPAM/Cou (1/1), and (d) NIPAM/Tdc (1/1), and their purified product, PNIPAM, by reprecipitation into diethyl ether.

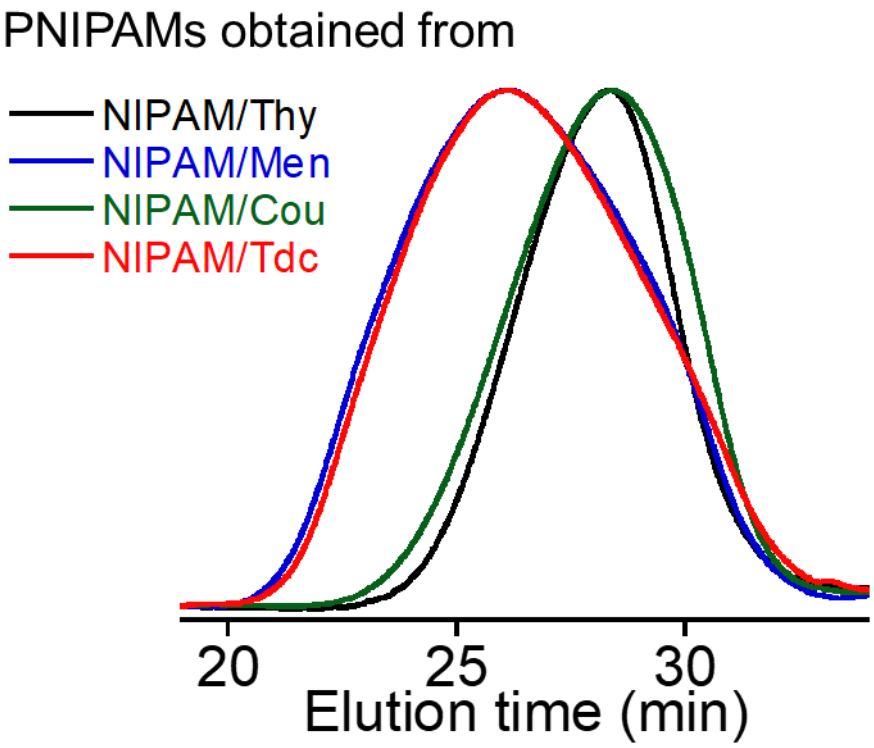


Figure S21. SEC curves (RI traces, DMF, LiBr) of PNIPAMs obtained by photo-induced polymerization of NIPAM-based NADEMs (see Table 2 for detailed polymerization conditions).

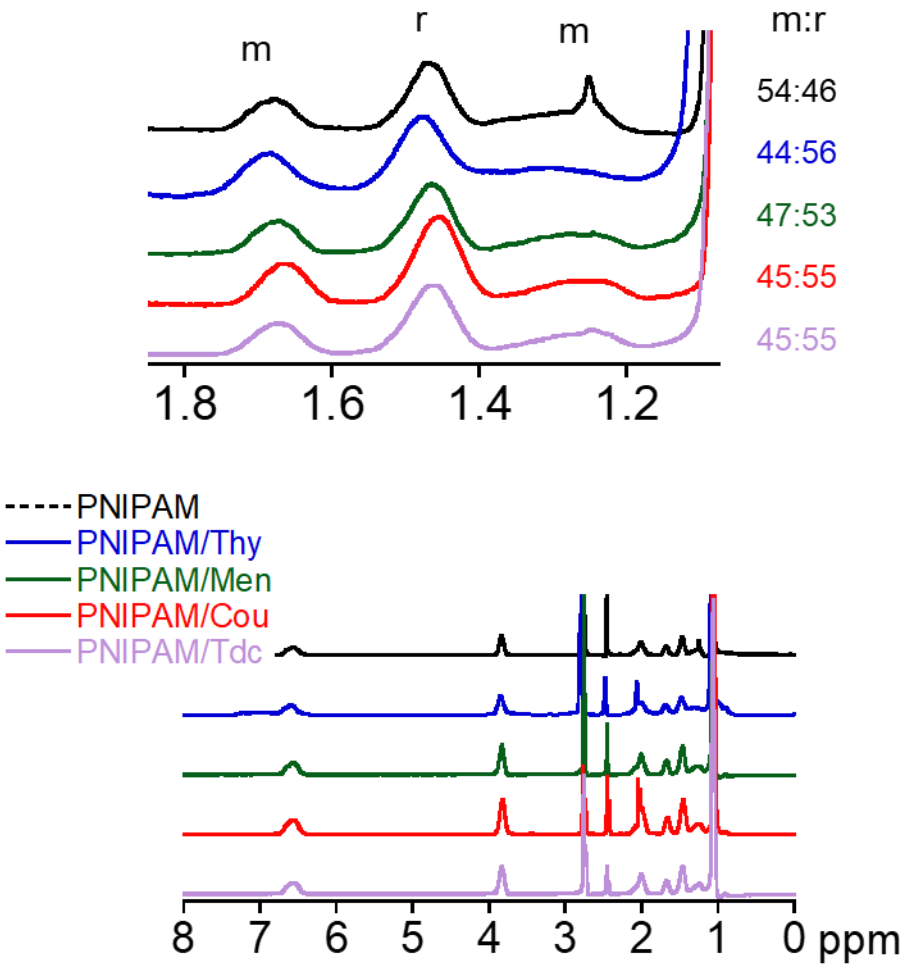


Figure S22. ^{1}H NMR spectra (DMSO-d_6, 150 ^{o}C) of PNIPAMs obtained by photo-induced polymerization of NIPAM-based NADEMs (see Table 2 for detailed polymerization conditions).

Table S12. Photo-induced free radical polymerization of NADEMs under UV light (LED-UV) [a)]

Run	NADEM	Time (s)	Conv. [b)] (%)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	NIPAM/Men (1/1)	1	24	59000	3.47
2		2	36	64000	3.06
3		3	42	52000	3.34
4		4	43	46000	3.16
5		5	55	54000	3.09
6		10	91	53000	3.48
7	NIPAM/Tdc (1/1) [d)]	1	29	49000	2.67
8		2	28	48000	2.90
9		3	45	45000	2.90
10		4	63	41000	3.36
11		5	73	41000	3.17
12		10	99	64000	2.87

[a)] Polymerization with DMPA at room temperature under air. $[I]_0/[M]_0 = 1/100$. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Measured by size-exclusion chromatography (SEC) using polystyrene standard in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [d)] Polymerization at approximately 50 °C.

Table S13. Photo-induced RAFT polymerization of NADEMs under UV light (LED-UV) [a)]

Run	NADEM	Time (min)	Conv. [b)] (%)	M_n [b)] (theo)	M_n [c)] (SEC)	M_w/M_n [c)] (SEC)
1	NIPAM/Men (1/1)	1	33	4100	13000	1.39
2		2	61	7200	16000	1.41
3		5	68	8000	17000	1.40
4		10	87	10000	16000	1.43
5		20	94	11000	15000	1.53
6	NIPAM/Tdc (1/1) [d)]	1	77	9000	12000	1.41
7		2	95	11000	12000	1.39
8		5	99	12000	15000	1.39
9		10	99	12000	14000	1.49
10		20	99	12000	15000	1.44

[a)] Polymerization with DMPA at room temperature under air. $[I]_0/[CTA]_0/[M]_0 = 1/1/100$. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [d)] Polymerization at approximately 50 °C.

Table S14. Photo-induced RAFT polymerization of NADEMs under UV light (LED-UV) [a)]

Run	NADEM	$[I]_0/[CTA]_0/[M]_0$	Conv. [b)] /Yield [c)] (%)	M_n [b)] (theory)	M_n [d)] (SEC)	M_w/M_n [d)] (SEC)
1	NIPAM/Men (1/1)	1/1/100	>99/83	11000	17000	1.40
2		1/1/200	>99/80	22000	28000	1.57
3		1/1/500	>99/91	55000	43000	1.71
4		1/1/1000	98/88	110000	52000	2.20
5	NIPAM/Tdc (1/1) [e)]	1/1/100	94/68	11000	15000	1.43
6		1/1/200	94/74	21000	22000	1.69
7		1/1/500	92/86	52000	37000	1.78
8		1/1/1000	94/78	11000	56000	1.87

[a)] Polymerization with DMPA at room temperature for 2 min under air. [M] = 30 wt%. [b)] Calculated by ^{1}H NMR in DMSO-d_6. [c)] Diethyl ether-insoluble part. [d)] Measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [e)] Polymerization at approximately 50 °C.

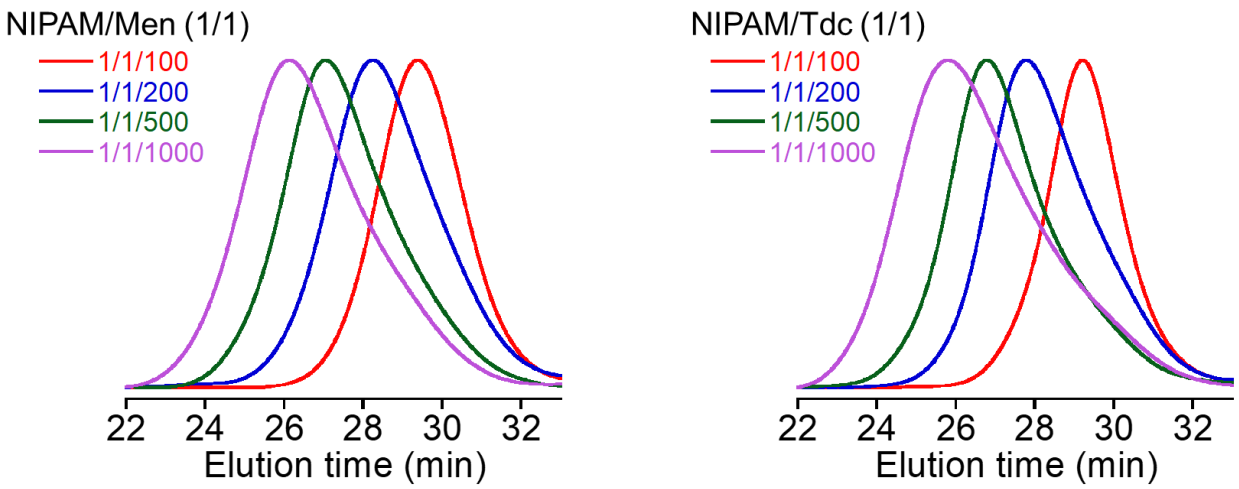


Figure S23. SEC curves (RI detector, DMF, LiBr) of PNIPAMs obtained by photo-induced RAFT polymerization of NIPAM-based NADEMs at different $[DMPA]_0/[CTA]_0/[NADEM]_0$ ratios.

.

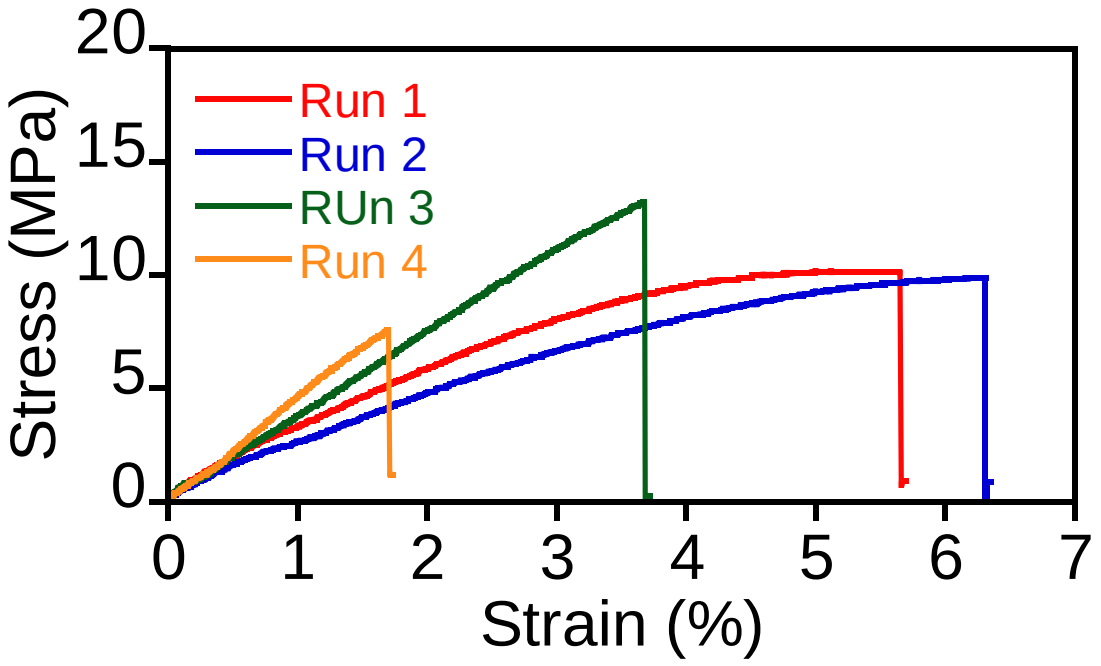


Figure S24. Stress–strain curves of polymerized products prepared from NIPAM/Men (3/2).

Table S15. Mechanical properties of the polymerized products prepared from NIPAM/Men (3/2) [a)]

Run	Young`s modulus [b)] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness [c)] (MJ/m^3)
1	399	10.10	5.65	0.39
2	295	9.88	6.30	0.40
3	256	13.20	3.68	0.25
4	370	7.57	1.70	0.07
Average	330	10.19	4.33	0.28

[a)] The sample was prepared independently by photopolymerization of NIPAM/Men (3/2), which was prepared by mixing at 40 °C, with DMPA under LED-UV light (365 nm, 130 mW/cm^2). $[I]_0/[M]_0$ = 1/100. [b)] Calculated from stress at small strain (0.05-0.25). [c)] Estimated by the area under the stress-strain curve until fracture point.

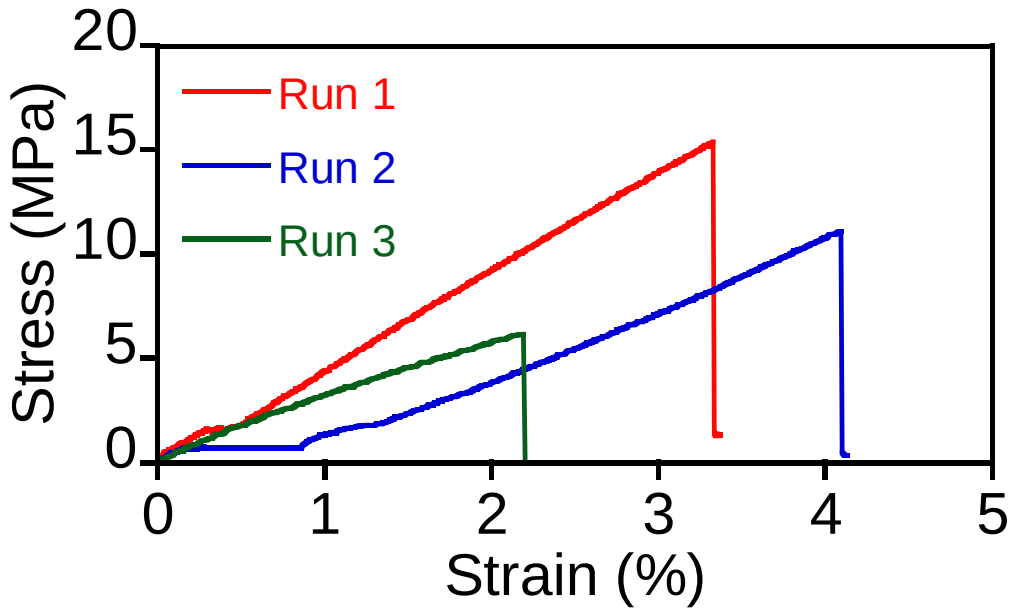


Figure S25. Stress–strain curves of polymerized products prepared from NIPAM/Men (2/1).

Table S16. Mechanical properties of the polymerized products prepared from NIPAM/Men (2/1) [a)]

Run	Young`s modulus [b)] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness [c)] (MJ/m^3)
1	457	15.36	3.36	0.25
2	169	11.06	4.09	0.19
3	366	6.17	2.19	0.07
Average	331	10.86	3.21	0.17

[a)] The sample was prepared independently by photopolymerization of NIPAM/Men (2/1), which was prepared by mixing at 50 °C, with DMPA under LED-UV light (365 nm, 130 mW/cm^2). $[I]_0/[M]_0$ = 1/100. [b)] Calculated from stress at small strain (0.05-0.25). [c)] Estimated by the area under the stress-strain curve until fracture point.

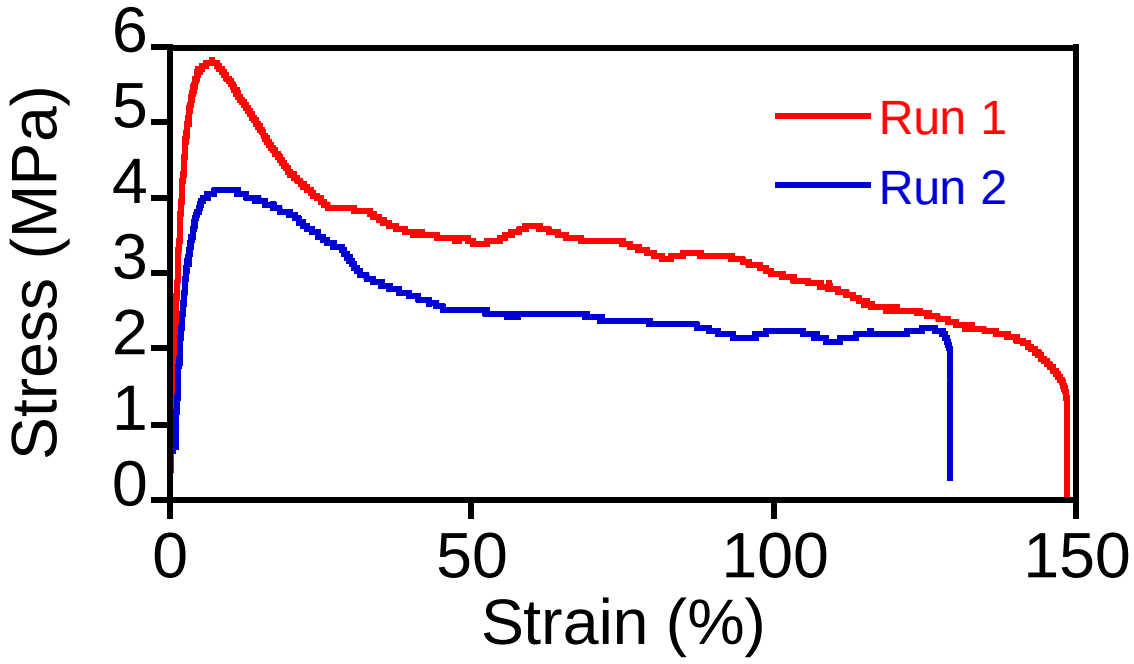


Figure S26. Stress–strain curves of polymerized products prepared from NIPAM/Thy (3/2).

Table S17. Mechanical properties of the polymerized products prepared from NIPAM/Thy (3/2) [a)]

Run	Young`s modulus [b)] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness [c)] (MJ/m^3)
1	20.0	5.82	148.70	4.95
2	212	4.05	129.24	3.43
Average	116	4.94	138.97	4.19

[a)] The sample was prepared independently by photopolymerization of NIPAM/Thy (3/2) with DMPA at room temperature under LED-UV light (365 nm, 130 mW/cm^2). $[I]_0/[M]_0$ = 1/100. [b)] Calculated from stress at small strain (0.05-0.25). [c)] Estimated by the area under the stress-strain curve until fracture point.

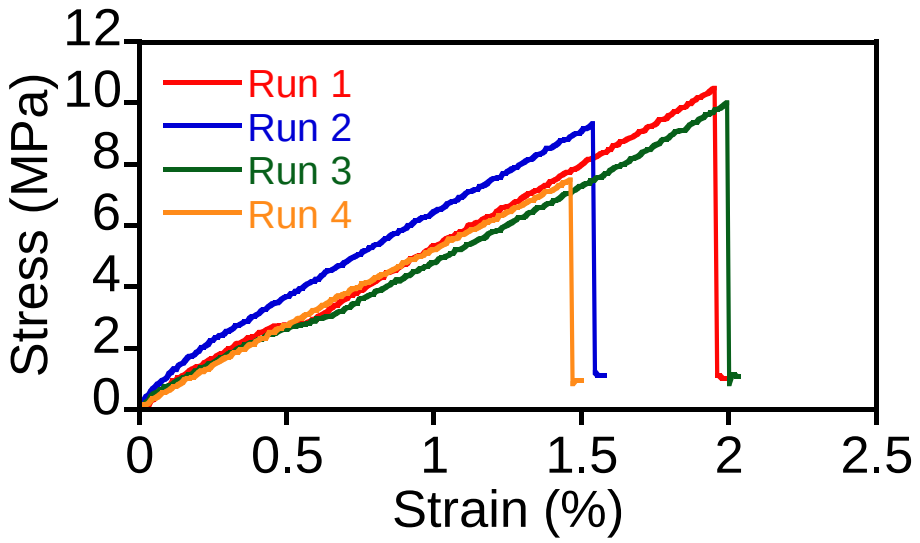


Figure S27. Stress–strain curves of polymerized products prepared from NIPAM/Thy (2/1).

Table S18. Mechanical properties of the polymerized products prepared from NIPAM/Thy (2/1) [a)]

Run	Young`s modulus [b)] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness [c)] (MJ/m^3)
1	627	10.47	1.95	0.10
2	781	9.31	1.54	0.08
3	501	9.98	1.99	0.10
4	533	7.47	1.46	0.06
Average	611	9.31	1.74	0.09

[a)] The sample was prepared independently by photopolymerization of NIPAM/Thy (2/1) with DMPA at room temperature under LED-UV light (365 nm, 130 mW/cm^2). $[I]_0/[M]_0$ = 1/100. [b)] Calculated from stress at small strain (0.05-0.25). [c)] Estimated by the area under the stress-strain curve until fracture point.

NIPAM/Men (1/1)

NIPAM/Thy (1/1)

Figure S28. Photographs of the samples prepared by photo-induced free radical polymerization of NIPAM/Men (1/1) and NIPAM/Thy (1/1).

References

(1) van Osch, D. J. G. P.; Dietz, C. H. J. T.; van Spronsen, J.; Kroon, M. C.; Gallucci, F.; Annaland, M. v. S.; Tuinier, R.: A Search for Natural Hydrophobic Deep Eutectic Solvents Based on Natural Components. *ACS Sustainable Chemistry & Enginnering* **2019**, *7*, 2933-2942.

(2) Kanto, R.; Qiao, Y.; Masuko, K.; Furusawa, H.; Yano, S.; Nakabayashi, K.; Mori, H.: Synthesis, Assembled Structures, and DNA Complexation of Thermoresponsive Lysine-Based Zwitterionic and Cationic Block Copolymers. *Langmuir* **2019**, *35*, 4646–4659.