

SUPPORTING INFORMATION

Dual pH and thermoresponsive alternating polyampholytes in alcohol/water solvent mixtures

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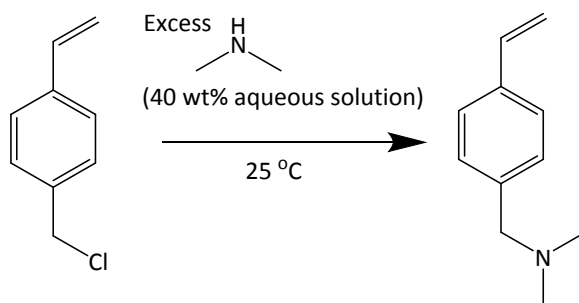
EXPERIMENTAL SECTION

Materials. Unless otherwise stated, all solvents and chemicals used in this work were analytical grade and used without further purification. The chemical reagents chloromethyl styrene (CMS, 90%), maleic anhydride (99%), *tert*-butanol (anhydrous, $\geq 99.5\%$), β -alanine (99%), *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 2,2'-azobis(isobutyronitrile) (AIBN) and HPLC grade solvents like *N,N*-dimethylacetamide (DMAc), dichloromethane and diethyl ether were purchased from Sigma Aldrich. AIBN was recrystallized twice from methanol before use. Dimethylamine (DMA, 40 wt% aqueous solution) was obtained from Fluka, Methanol (99.8%, extra dry, over molecular sieves, AcroSeal®) and 1, 4-dioxane (99.5%, extra dry, over molecular sieves, AcroSeal®) were obtained from Acros Organics. Trifluoroacetic acid (TFA) and 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC x HCl) were obtained from Iris Biotech, Germany. *N,N*-dimethylformamide (DMF) was obtained from Biosolve, n-hexane from Fischer Scientific and glacial acetic acid (100%) from Carl Roth, Germany. 2-(((butylthio)carbonothioyl)thio)propanoic acid (PABTC) was prepared as previously reported.¹

Characterization. ¹H NMR spectra of the polymers were performed on a Bruker FT-NMR (300 and 400 MHz) spectrometer using CDCl₃ as solvent. FTIR technique was used for the investigation of various functional groups present in the synthesized small molecules. Agilent Technologies

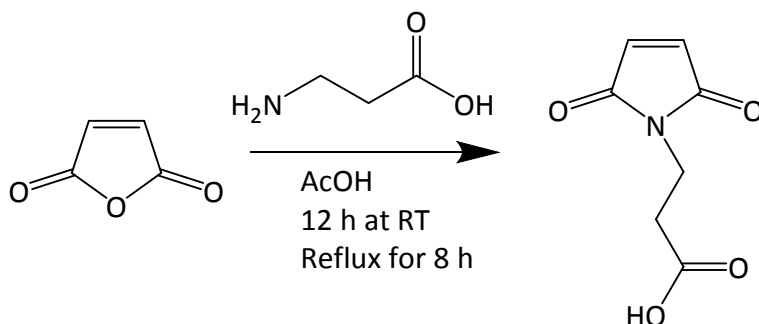
Carry 600 Series instrument was used for the FTIR analysis. KBr was used for the sample preparation and later compressed to form discs. Size-exclusion chromatography (SEC) was performed on a Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler (ALS), a thermostatted column compartment (TCC) at 50 °C equipped with two PLgel 5 μm mixed-D columns and a precolumn in series, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID) to determine the molecular weights and molecular weight distributions of the polymers. The used eluent was DMAc containing 50 mM of LiCl at a flow rate of 0.5 mL min⁻¹. The spectra were analysed using the Agilent Chemstation software with the GPC add on. Molar mass values and \bar{M} values were calculated against PMMA standards from PSS. Aqueous size-exclusion chromatography (SEC) was performed to determine the molecular weights and molecular weight distributions of the polyampholytes in a Waters 610 fluid unit and a Waters 600 control unit equipped with a Waters 410 RI detector (40 °C). The two Shodex SB806MHQ columns placed in series eluting 0.1 M phosphate buffer (pH 7) were kept at 80 °C using an external heating unit. Calibration was done using dextran standards. Samples were dissolved in 0.1 M phosphate buffer (pH 7) at a concentration of 1 mg mL⁻¹. Size exclusion chromatography measurements were also performed on a Waters instrument, equipped with Waters Styragel HR3, HR4, and HR5 serial columns (5 μm particle size) at 35 °C with a RI detector (2410 Waters), using PS standards for calibration, and CHCl₃ as an eluent at a flow rate of 1.0 mL min⁻¹. Molecular weights and dispersities were determined using the Breeze Millennium software. Dynamic light scattering (DLS) and Zeta potential measurements were executed on a Zetasizer Nano-ZS Malvern apparatus (Malvern Instruments Ltd) using disposable cuvettes. The excitation light source was a He–Ne laser at 633 nm and the intensity of the scattered light was measured at an angle of 173°. This method measures the rate of the intensity fluctuation and the size of the particles is determined through the Stokes–Einstein equation. Cloud point temperatures (T_{cp}) were determined via turbidimetry on a Crystal16™ parallel crystallizer (Avantium Technologies) which is connected to a recirculation cooler and dry compressed air. Aqueous polymer solutions (1 mg mL⁻¹) were heated from 2 to 60 °C with a heating rate of 5 °C min⁻¹ followed by cooling again to 5 °C at a cooling rate of 5 °C min⁻¹. The T_{cp} 's are reported as the 50% transmittance temperature in the second heating/cooling run for LCST/UCST polymers.

Synthesis of *N,N*-Dimethyl-1-(4-vinylphenyl)methanamine (DMAMSt) (1). *N,N*-Dimethyl-1-(4-vinylphenyl)methanamine was prepared from 4-vinylbenzyl chloride according to the method reported in the literature with additional modifications as described below.^{2,3} To a solution of chloromethyl styrene (CMSt) (20.0 g, 0.13 mol) in 160 mL diethyl ether was added a solution of 40 wt. % aqueous dimethylamine solution (40 mL) at room temperature. After stirring for 16 h at the room temperature, the resulting mixture was transferred in separatory funnel. The organic phase was separated and the aqueous phase was extracted with diethyl ether and the combined organic extracts were washed with brine. The solution was dried over sodium sulfate and concentrated. Finally light yellow compound was purified by SiO₂ column chromatography using hexane/ethyl acetate (1/1) as eluent and the pure *N,N*-dimethyl-1-(4-vinylphenyl)methanamine (**1**) was obtained as colorless liquid (Yield: 16 g, 76%). ¹H NMR of the DMAMSt is shown in **Fig. S1**. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.35 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.69 (dd, J = 11.0 and 17.7 Hz, 1H), 5.71 (dd, J = 1.0 and 17.6 Hz, 1H), 5.20 (dd, J = 1.0 and 11.0 Hz, 1H), 3.40 (s, 2H), 2.23 (s, 6H).



Synthesis of 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoic acid (CEMI) (2). 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoic acid was prepared from maleic anhydride according to the method reported in the literature.⁴ β-Alanine (37.5 g, 0.42 mol) and maleic anhydride (41.1 g, 0.42 mol) were dissolved in acetic acid (650 mL). The reaction mixture was stirred at room temperature for 12 h, under an argon atmosphere. The resulting suspension was then refluxed for a further 8 h to give a clear solution. The solvent was removed in vacuo and the residue was purified by flash column chromatography (CH₂Cl₂: glacial acetic acid = 95:5). Recrystallization from CH₂Cl₂/hexane afforded the title compound (Yield: 44 g, 62%) as a colorless solid. ¹H NMR

and FTIR of the CEMI are shown in **Figs. S2 and S3** respectively. ^1H NMR (300 MHz, CD_3OD , ppm): δ = 6.81 (s, 2H), 3.77 (t, J = 7.5 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H).



Synthesis of *tert*-butyl 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoate (*t*BuEMI) (**3**).

tert-Butyl 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoate (*t*BuEMI) was prepared from 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoic acid (CEMI) according to the method reported in the literature.⁴ CEMI (5.77 g, 0.034 mol) was dissolved in 70 mL dry 1,4-dioxane. *t*-Butanol (13.05 mL, 0.136 mol) and 4-dimethylaminopyridine (DMAP) (0.83 g, 0.007 mol) were added to the above solution. DCC (7.74 g, 0.0375 mol) was dissolved in 10 mL dry 1,4-dioxane and added dropwise to the above solution over 30 minutes. Then the reaction mixture was kept stirring for 12 h at room temperature. Then the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using EtOAc-hexane as eluents. (Yield: 4.1 g, 53 %). FTIR and ^1H NMR of the *t*BuEMI are shown in **Figs. S3 and S4** respectively. ^1H NMR (300 MHz, CD_3OD , ppm): δ = 6.82 (s, 2H), 3.74 (t, J = 7.5 Hz, 2H), 2.53 (t, J = 7.5 Hz, 2H), 1.42 (s, 9H).

Copolymerization of DMAMSt and CEMI using 2-(((butylthio)carbonothioyl)thio)propanoic acid (PABTC) as CTA. DMAMSt (750 mg, 4.65 mmol), CEMI (786 mg, 4.65 mmol), PABTC (22.17 mg, 0.093 mmol), AIBN (3.0 mg, 0.0186 mmol) with a ratio of [DMAMSt]:[CEMI]:[PABTC]:[AIBN] = [50]:[50]:[1]:[0.2] and DMF (3.1 mL) were placed in a dry Schleck tube with a magnetic stirring bar. The mixture was deoxygenated by purging with argon for 30 min by keeping the tube in cold water. After 12 h of polymerization, the reaction vessel was removed from the oil bath and opened to the air to stop the polymerization. The resulting polymer was precipitated by dropping the polymer solution into a large amount of

disinfectol (EtOH + 5% diethylether). Polymer was isolated via centrifugation (5 min, 5000 rpm). The resulting polymer was washed with disinfectol (2 times). Finally, powdery light brown polymer was dried overnight under vacuum at 50 °C. ¹H NMR spectrum of alternating (co)polymer P(DMAMSt-*alt*-CEMI) after purification is shown in **Fig. S5**. Water SEC was used to determine molecular weight and the dispersity (\bar{M}_w/\bar{M}_n) ($M_{n, SEC} = 3,600$ g/mol; $\bar{M}_w/\bar{M}_n = 1.78$) (**Fig. S6**).

Synthesis of methyl 2-(butylthiocarbonothioylthio)propanoate (MBTCTTP). Methyl 2-(butylthiocarbonothioylthio)propanoate (MBTCTTP) was prepared from 2-(((butylthio)carbonothioyl)thio)propanoic acid (PABTC) according to the method reported in the literature.⁵ PABTC (6.0 g, 0.025 mol) was dissolved in 100 mL dry DCM. CH₃OH (1.62 g, 0.05 mol) and DMAP (0.31 g, 0.0025 mol) were added to the above solution. EDC.HCl (5.32 g, 0.028 mol) was dissolved in 20 mL dry DCM and added dropwise to the above solution over 30 minutes while stirring in an ice bath for 2 h and subsequently at room temperature overnight. The crude product was transferred into a separating funnel and washed by H₂O (2 × 150 mL) and brine (150 mL). The organic layer was dried with MgSO₄, filtered and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with a mobile phase of EtOAc/hexane (1/10) (v/v) to afford MBTCTTP as a yellow liquid (5.0 g, 79 %). ¹H NMR of the MBTCTTP is shown in **Fig. S7**. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 0.93$ (t, J = 8.0 Hz, 3H), 1.39-1.46 (m, 2H), 1.60 (d, J = 8.0 Hz, 3H), 1.63-1.73 (m, 2H), 3.37 (t, J = 8.0 Hz, 2H), 3.74 (s, 3H), 4.84 (q, J = 8.0 Hz, 1H).

Kinetic investigation of the alternating copolymerization of DMAMSt and *t*BuEMI via RAFT (co)polymerization. DMAMSt (700 mg, 4.34 mmol), *t*BuEMI (1000 mg 4.34 mmol), MBTCTTP (21.9 mg, 0.087 mmol), AIBN (2.9 mg, 0.0174 mmol) with a ratio of [DMAMSt]:[*t*BuEMI]:[MBTCTTP]:[AIBN] = [50]:[50]:[1]:[0.2] and 1,4-Dioxane-*d*₈ (3.0 mL) were placed in a dry Schleck tube with a magnetic stirring bar. The mixture was deoxygenated by purging with argon for 50 min by keeping the tube in cold water. Later the stock reaction mixture was transferred in a glovebox and divided into individual clean and 2.0 mL dry microwave vials, which were crimped inside the glove box before placed in a preheated drysyn heating blocks at 70 °C. Kinetic investigations of alternating copolymerization were performed with an initial monomer concentration of 1.85 M. The monomer/CTA ratio was kept 100 in all runs. Samples were removed

periodically and cooled to 0 °C by ice to stop the reaction and later determined conversion via ¹H NMR (Fig. S8). SEC samples were prepared from the polymerization mixtures to determine the molecular weight (distribution) of the resulting polymers and the dispersity (Đ).

Alternating copolymerization of DMAMSt and *t*BuEMI via RAFT (co)polymerization. All copolymerizations of DMAMSt and *t*BuEMI monomers were carried out in Schleck tube with AIBN as a radical initiator via RAFT polymerization. A representative example is as follows: DMAMSt (500 mg, 3.10 mmol), *t*BuEMI (700 mg 3.10 mmol), MBTCTTP (15.7 mg, 0.062 mmol), AIBN (2.0 mg, 0.013 mmol) with a ratio of [DMAMSt]:[*t*BuEMI]:[MBTCTTP]:[AIBN] = [50]:[50]:[1]:[0.2] and 1,4-Dioxane (1.9 mL) were placed in a dry Schlenk tube with a magnetic stirring bar. The mixture was deoxygenated by purging with argon for 50 min by keeping the tube in cold water and then placed in a preheated oil bath at 70 °C. After reaction for a predetermined time, the reaction was stopped by quenching in ice water. The polymer was isolated through precipitation in a 20-fold excess volume of cold n-hexane and isolated by centrifugation (5000 rpm, 5 °C, 5 min) and decanting yielding the (co)polymer. This was repeated two times and finally dried in the vacuum oven at 50 °C for 4 h. ¹H-NMR in CD₂Cl₂ was used to know the degree of polymerization (DP) and SEC to determine the molecular weight and dispersity (Đ) (DP = 23; M_{n,NMR} = 8900 g mol⁻¹). ¹H NMR spectrum of alternating (co)polymer P(DMAMSt-*alt*-*t*BuEMI) after purification is shown in Fig. S9.

Synthesis of PNIPAM via RAFT polymerization. The RAFT polymerization of *N*-isopropyl acrylamide (NIPAM) was performed according to the method reported in the literature.⁶ NIPAM (2.0 g, 17.67 mmol), methyl 2-(butylthiocarbonothioylthio)propanoate (MBTCTTP) (44.61 mg, 0.18 mmol), 2,2'-azobisisobutyronitrile (AIBN) (14.51 mg, 0.09 mmol) and DMF (8.8 mL) were charged in the 25 mL Schlenk tube in the molar ratio of [NIPAM]:[MBTCTTP]:[AIBN] = [100]:[1]:[0.5]. Small residual O₂ was removed from the tube by bubbling argon over 40 minutes. Then the reaction mixture was placed in a preheated oil bath at 60 °C to initiate the polymerization. After 45 min of polymerization, the reaction vessel was removed from the oil bath and opened to the air to stop the polymerization. The resulting polymer was precipitated by dropping the polymer solution into a large amount of a 60:40 mixture of hexane and diethyl ether. After decantation of the solvent, the polymer was dissolved in tetrahydrofuran (THF) and precipitated again in diethyl

ether. This precipitation procedure was repeated three times. The resulting powdery light yellow polymer was dried overnight under vacuum at 50 °C. The conversion of the monomer was 31% measured by GC. The molecular weight of PNIPAM was calculated based on the ratio of monomer units to the terminal group in the ¹H-NMR spectra. ($M_{n,GC} = 3700 \text{ g mol}^{-1}$, $M_{n,NMR} = 3200 \text{ g mol}^{-1}$, $M_{nSEC, DMAc} = 3400 \text{ g mol}^{-1}$, $\bar{D} = 1.15$). ¹H NMR of the PNIPAM is shown in **Fig. S10**.

Synthesis of P(DMAMSt-*alt*-CEMI) from P(DMAMSt-*alt*-*t*BuEMI). A solution of poly(DMAMSt-*alt*-*t*BuEMI) ($M_{n,NMR} = 8900 \text{ g mol}^{-1}$) (16 mg, 0.0018 mmol) was treated with TFA (1 mL) and stirred for 2.5 h in ice cold water. The final polymer was isolated by precipitating into diethyl ether (20 fold excess). The resulting polymer was washed two times with diethyl ether and isolated by centrifugation finally dried in vacuum oven at 50 °C for 2 h.

Alternating copolymerization of DMAMSt and *t*BuEMI via RAFT (co)polymerization using PNIPAM as MacroCTA. A block copolymer PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) was synthesized using DMAMSt and *t*BuEMI monomers, AIBN as a radical initiator and PNIPAM as MacroCTA, via RAFT polymerization. In a typical reaction DMAMSt (390 mg, 2.42 mmol), *t*BuEMI (545 mg 2.42 mmol), MacroCTA (171 mg, 0.048 mmol), AIBN (1.6 mg, 0.0097 mmol) with a ratio of [DMAMSt]:[*t*BuEMI]:[MacroCTA]:[AIBN] = [50]:[50]:[1]:[0.2] and 1,4-dioxane (3.5 mL) were placed in a dry Schlenk tube with a magnetic stirring bar. The mixture was deoxygenated by purging with argon for 50 min by keeping the tube in cold water and then placed in a preheated oil bath at 70 °C. After reaction for a predetermined time, the reaction was stopped by quenching in ice water. The polymer was isolated through precipitation in a 20-fold excess volume of cold n-hexane and isolated by centrifugation (5000 rpm, 5 °C, 5 min) and decanting yielding the (co)polymer. This was repeated two times and finally dried in the vacuum oven at 50 °C for 4 h. ¹H NMR spectrum of alternating block (co)polymer PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) after purification is shown in **Fig. S11**. Molecular weight determination via NMR was difficult due to the overlapping signals of PNIPAM MacroCTA and block (co)polymer in the ¹H NMR spectrum. However, by considering NMR signal at 4.01 ppm we have calculated the DP and molecular weight of the block (co)polymer (DP = 18; $M_{n,NMR} = 10100 \text{ g mol}^{-1}$). SEC (DMAc) was used to determine the molecular weight and dispersity (\bar{D}). However, molecular weight could not

determine due to baseline drift of the SEC traces of the block (co)polymer PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) (Fig. S12).

Synthesis of PNIPAM-*b*-P(DMAMSt-*alt*-CEMI) from PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI). A solution of PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) ($M_{n,NMR} = 10100 \text{ g mol}^{-1}$) (16 mg, 0.0016 mmol) was treated with TFA (1 mL) and stirred for 2.5 h in ice cold water. The final polymer was isolated by precipitating into diethyl ether (20 fold excess). The resulting polymer was washed two times with diethyl ether and isolated by centrifugation finally dried in vacuum oven at 50 °C for 2 h.

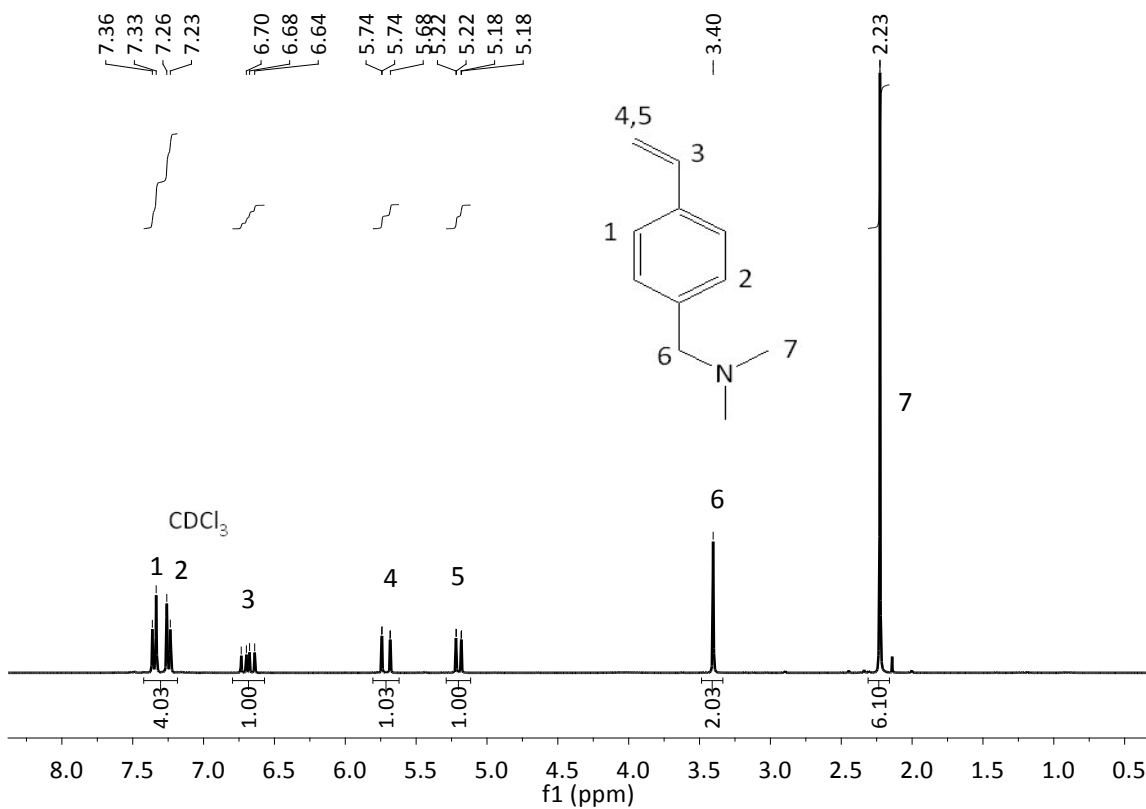


Fig. S1. ¹H NMR spectrum of *N,N*-dimethyl-1-(4-vinylphenyl)methanamine measured in CDCl₃.

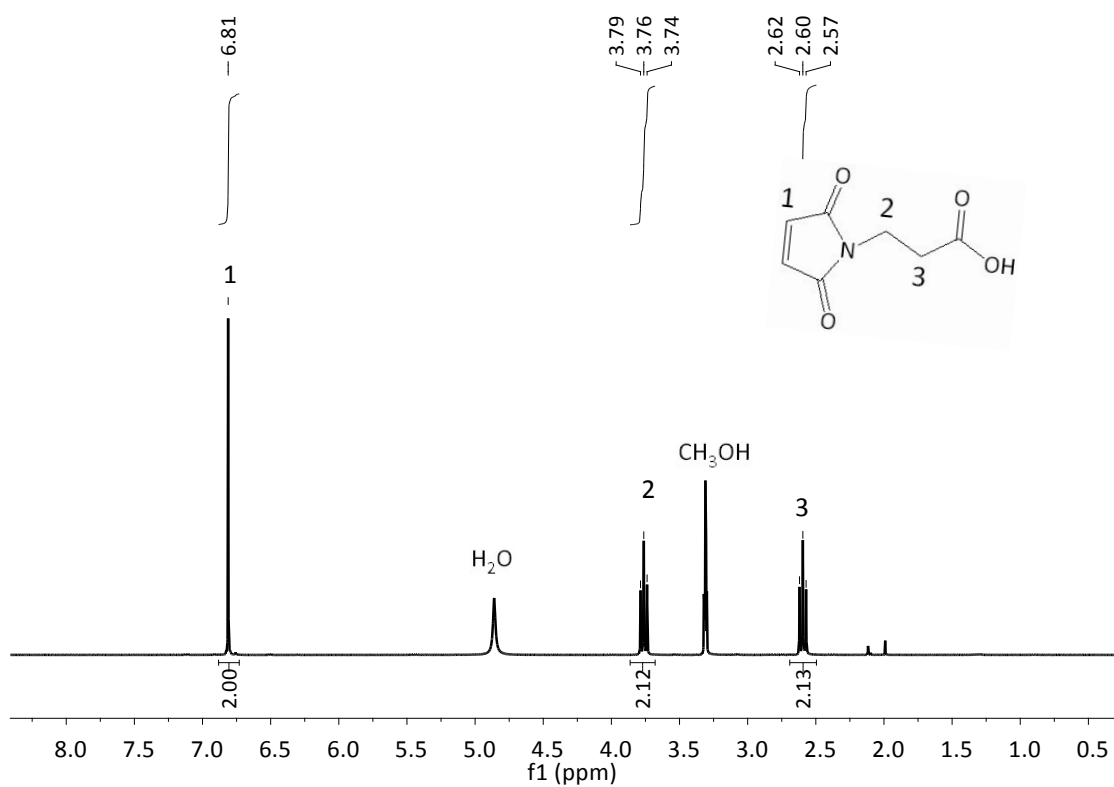


Fig. S2. ^1H NMR spectrum of 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoic acid measured in CD_3OD .

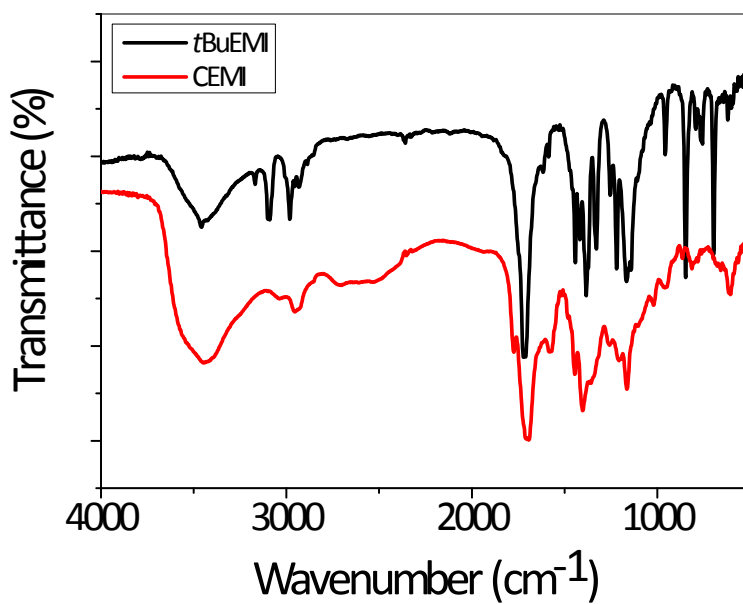


Fig. S3. FTIR spectra of CEMI and tBuEMI.

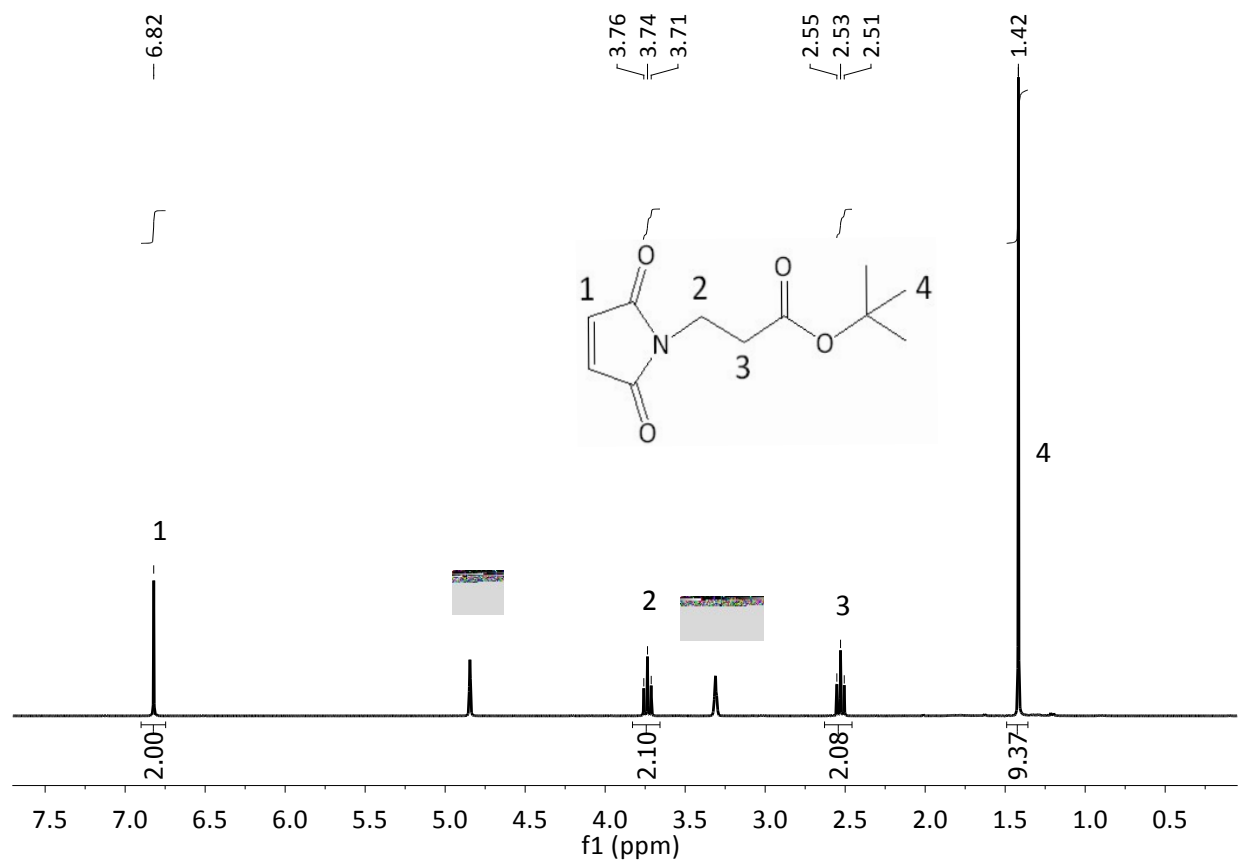


Fig. S4. ¹H NMR spectrum of tert-Butyl 3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propanoate (tBuEMI) measured in CD₃OD.

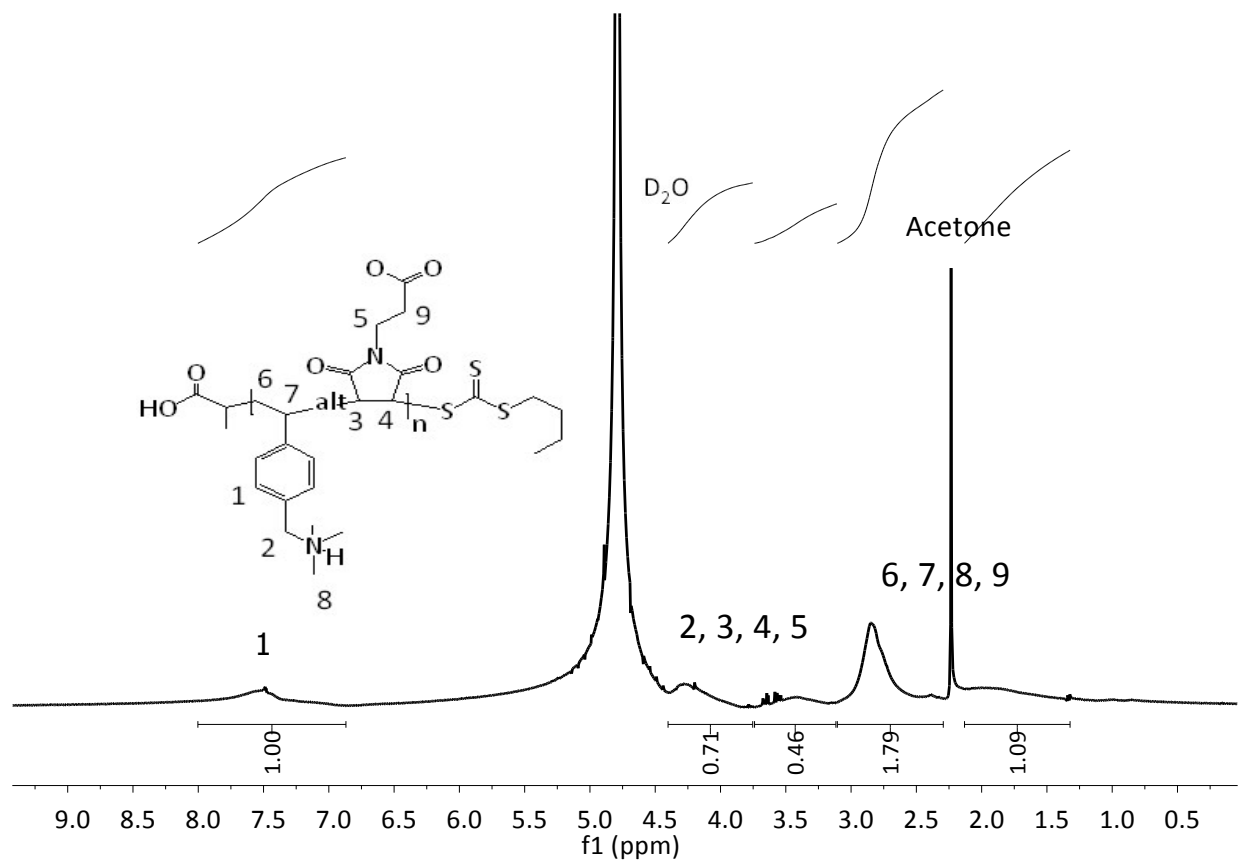


Fig. S5. ^1H NMR spectrum of P(DMAMSt-*alt*-CEMI) measured in D_2O .

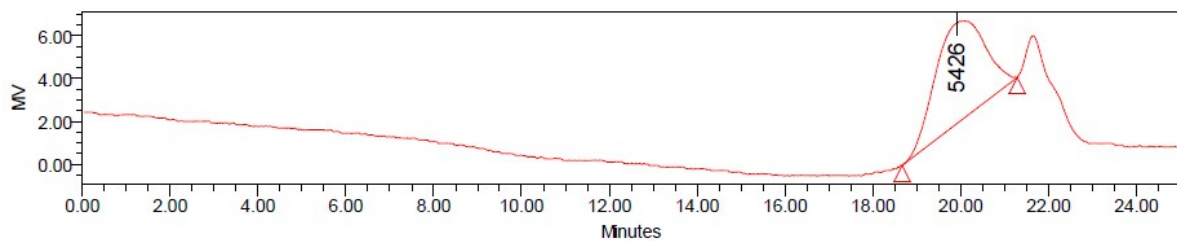


Fig. S6. SEC traces of P(DMAMSt-*alt*-CEMI) measured in 0.1 M phosphate buffer (pH 7) at 80 $^{\circ}\text{C}$. Calibration was done using dextran standards.

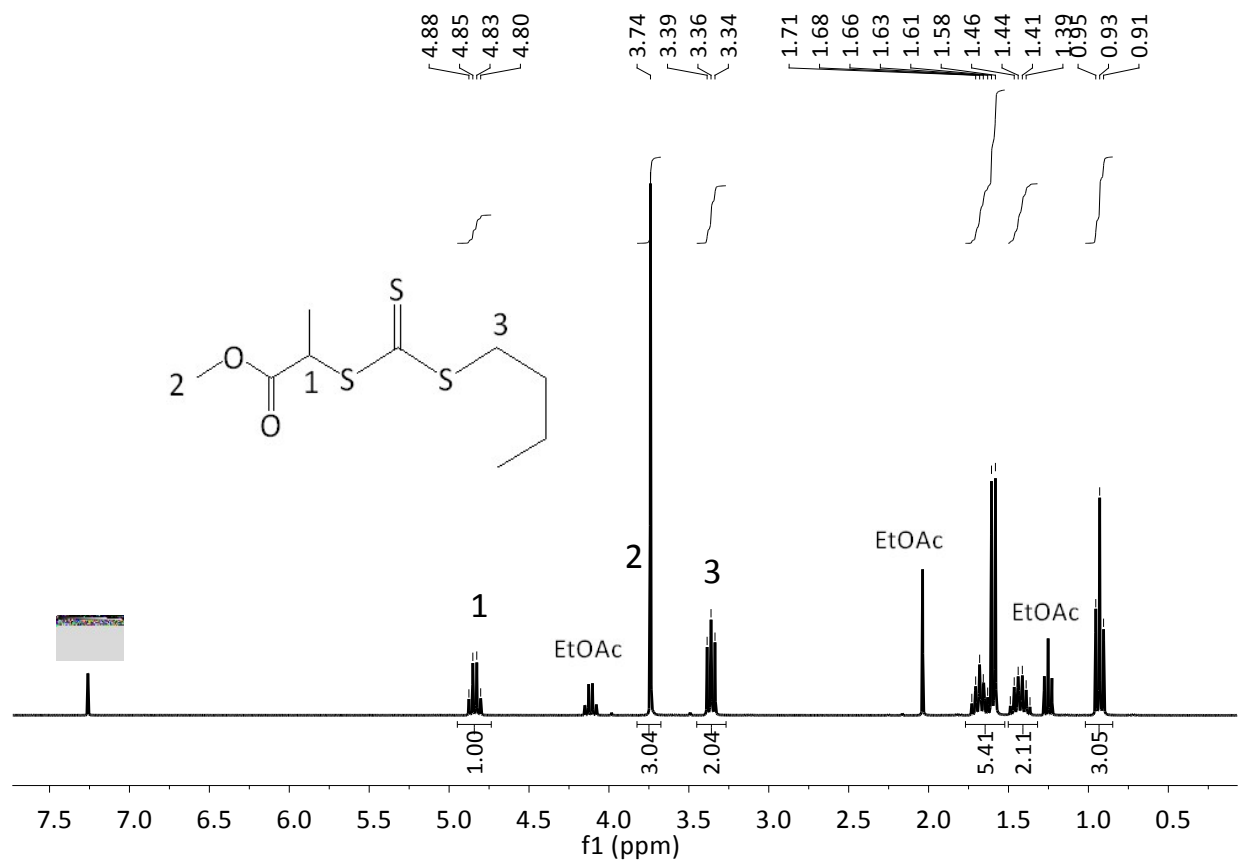


Fig. S7. ¹H NMR spectrum of MBTCTTP (RAFT-OMe).

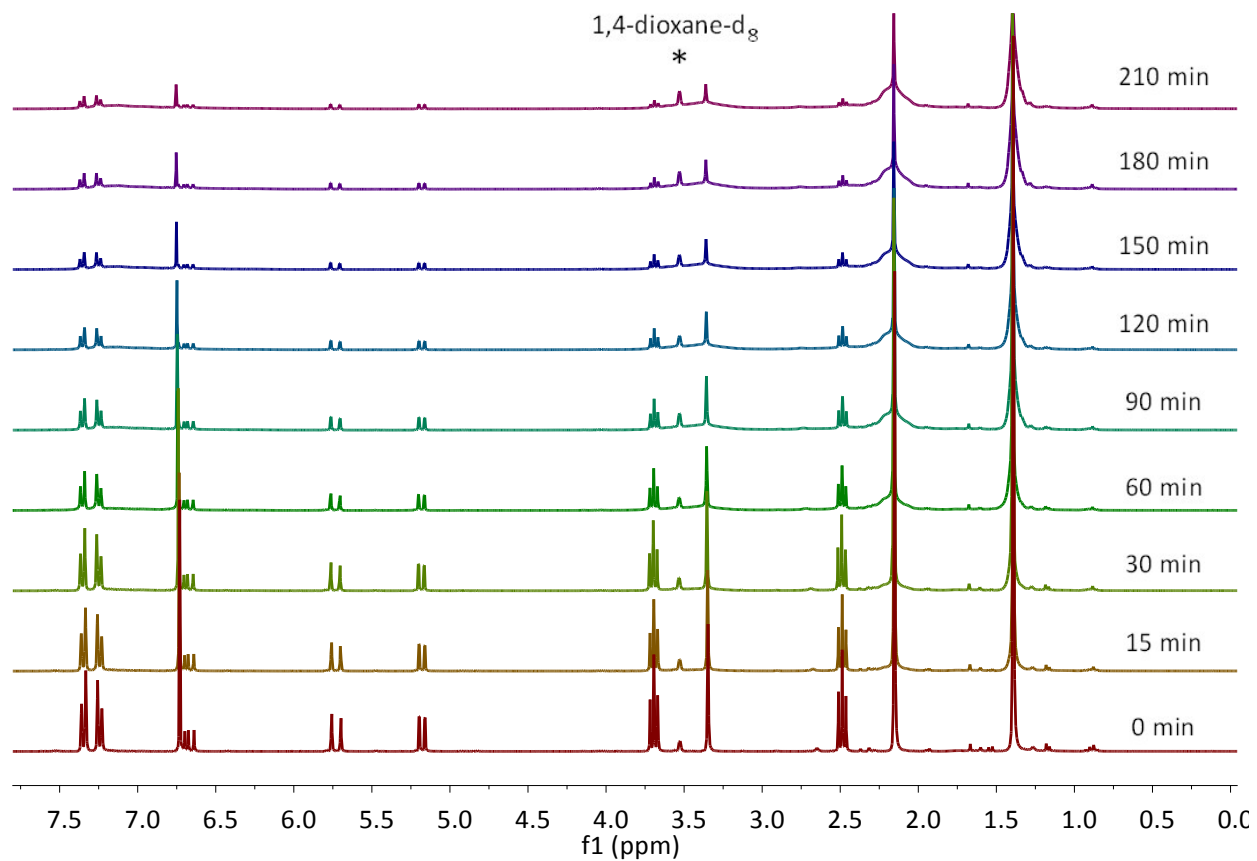


Fig. S8. ^1H NMR spectra was recorded in 1,4 dioxane d_8 which was used as polymerization solvent during the RAFT copolymerization of DMAMSt and *t*BuEMI at 70 °C. Conditions: [DMAMSt]/[*t*BuEMI] feed molar ratio = 1.0; [CTA]/[AIBN] molar ratio = 5.

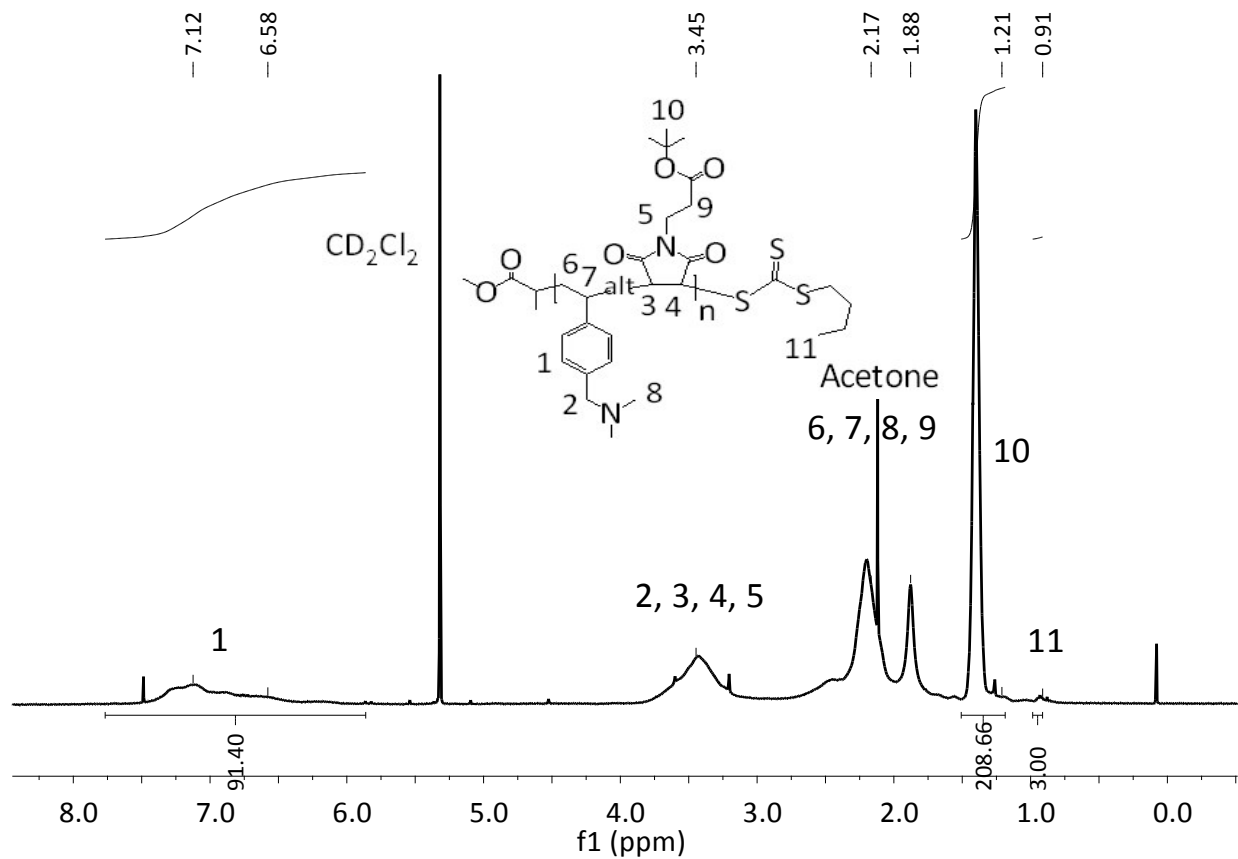


Fig. S9. ¹H NMR spectrum of alternating polymer P(DMAMSt-*alt*-*t*BuEMI) after purification measured in CD₂Cl₂, Acetone present as impurity.

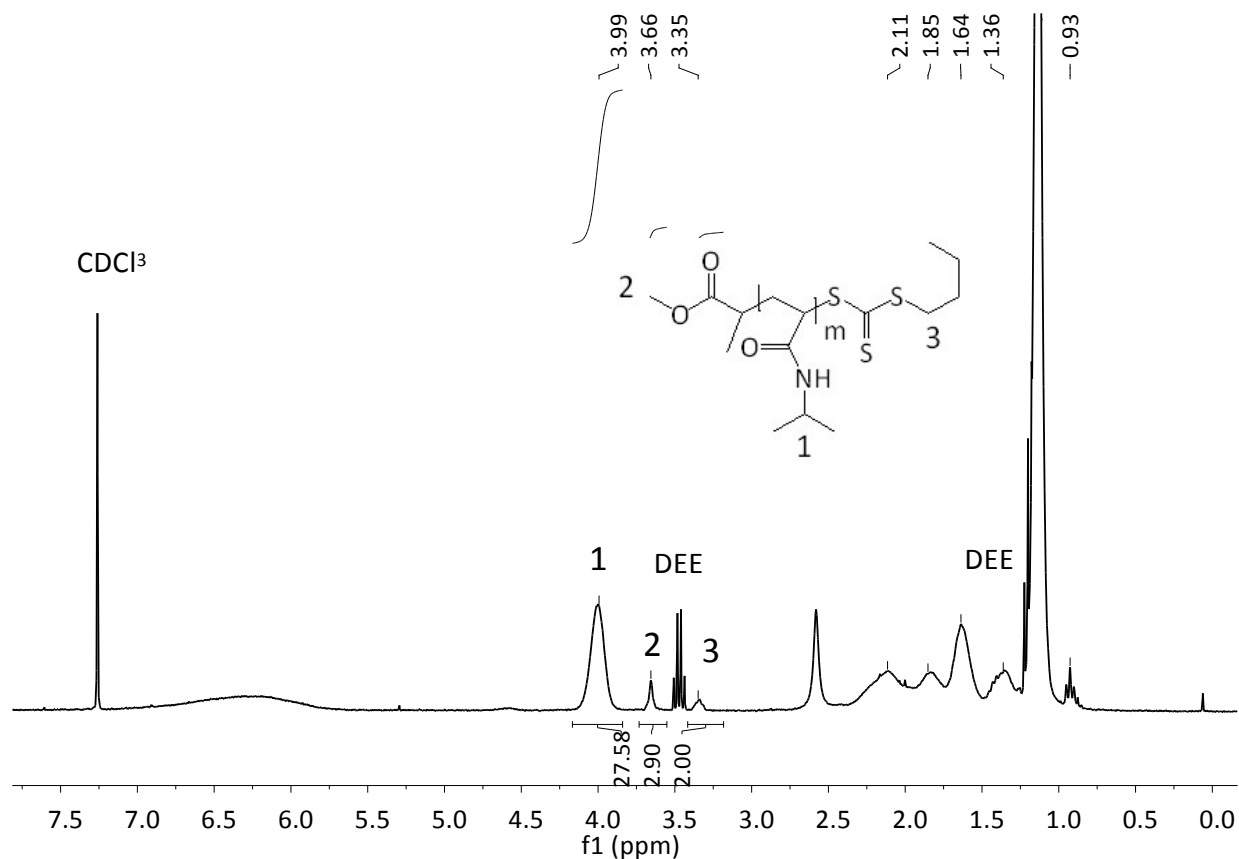


Fig. S10. ^1H NMR spectrum of PNIPAM-OMe measured in CDCl_3 .

Table S1. Characterization data for polymers synthesized via RAFT polymerization in DMF/1, 4 dioxane at 70 °C using AIBN initiator.

Entry no.	$[\text{M}_1]:[\text{M}_2]:[\text{CTA}]:[\text{AIBN}]$	Solvent	Reaction time (min)	Conversion (%)	M_n (theo.) (g mol $^{-1}$)	M_n (NMR) (g mol $^{-1}$)	M_n (SEC) (g mol $^{-1}$)	\bar{D}
1.	[NIPAM]:[MBTCTTP]:[AIBN] [100]:[1]:[0.5]	DMF	45	31	3,700	3,200	3,400 [§]	1.15
2.	[DMAMSt]:[CEMI]:[PABTC]:[AIBN] [50]:[50]:[1]:[0.2]	DMF	720	-	-	-	3,600 [#]	1.78
3.	[DMAMSt]:[tBuEMI]:[MBTCTTP]:[AIBN] [50]:[50]:[1]:[0.2]	1,4-dioxane	240	77	7,700	8,900	6100 [*]	1.54
4.	[DMAMSt]:[tBuEMI]:[Macro-CTA]:[AIBN] [50]:[50]:[1]:[0.2]	1,4-dioxane	135	ND [□]	-	10,100	-	-

[§]Measured in DMF GPC; [#]Measured in H_2O GPC; ^{*}Measured in CHCl_3 GPC; [□]ND: not determined.

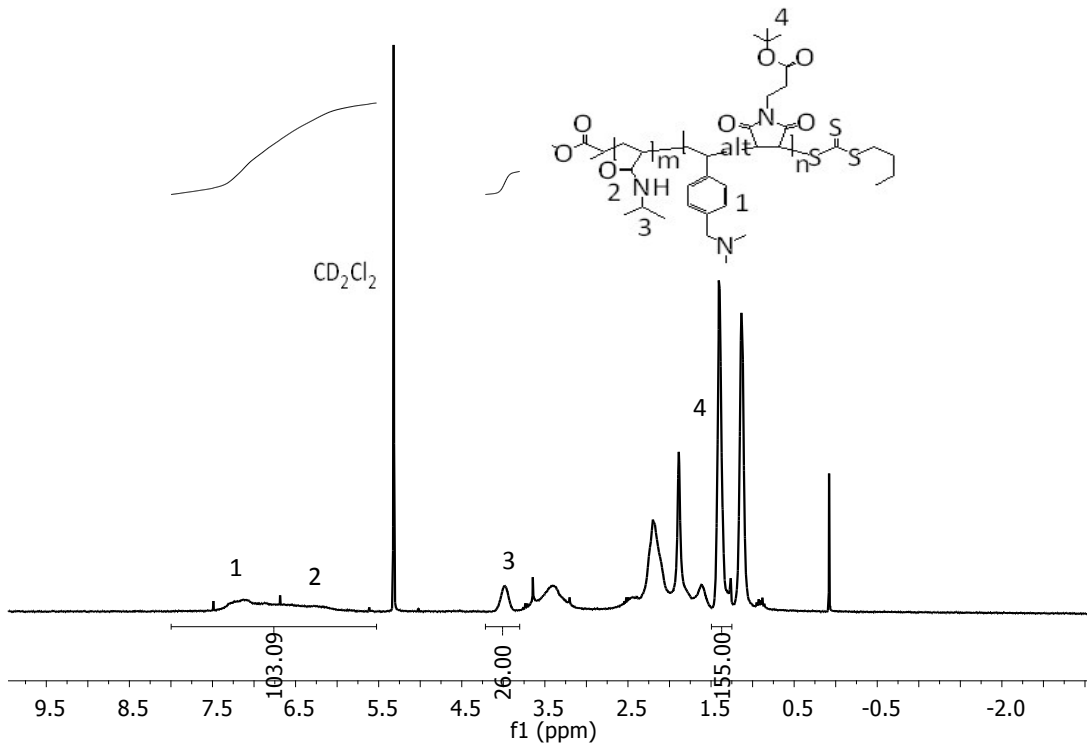
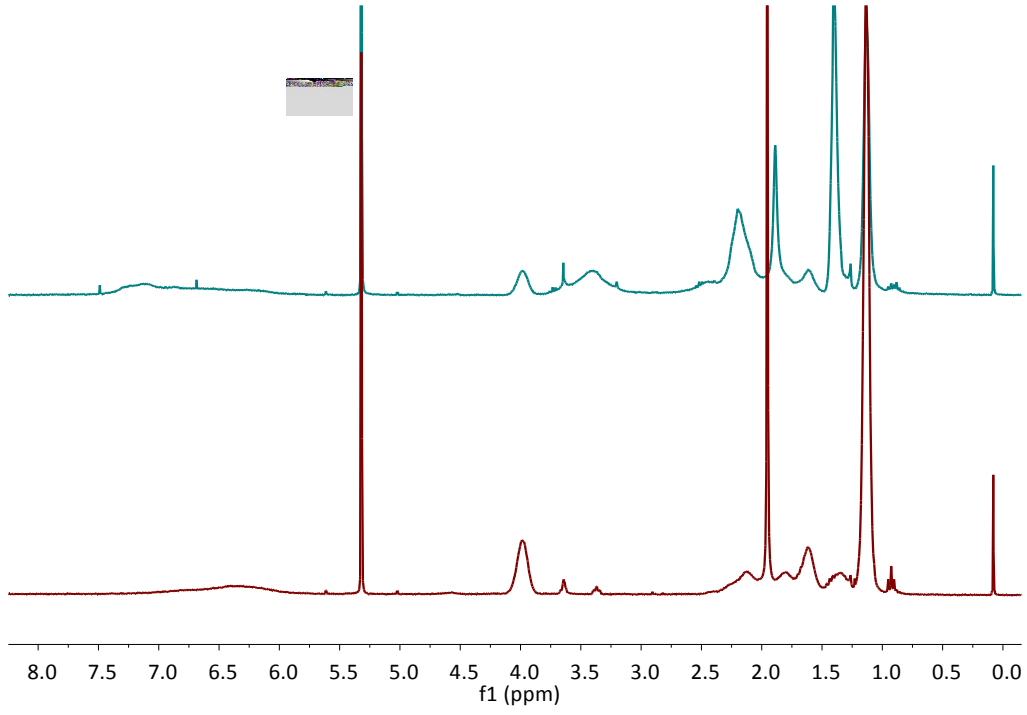


Fig. S11. (Top) Overlapping of ^1H NMR spectrum of PNIPAM and PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) after purification (measured in CD_2Cl_2); (Bottom) ^1H NMR spectrum of PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI).

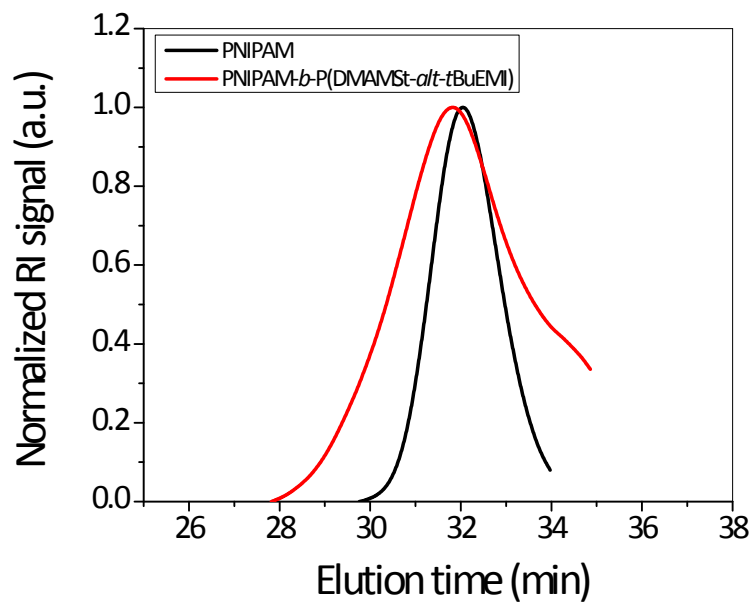


Fig. S12. SEC (DMAc) traces of the PNIPAM and PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI).

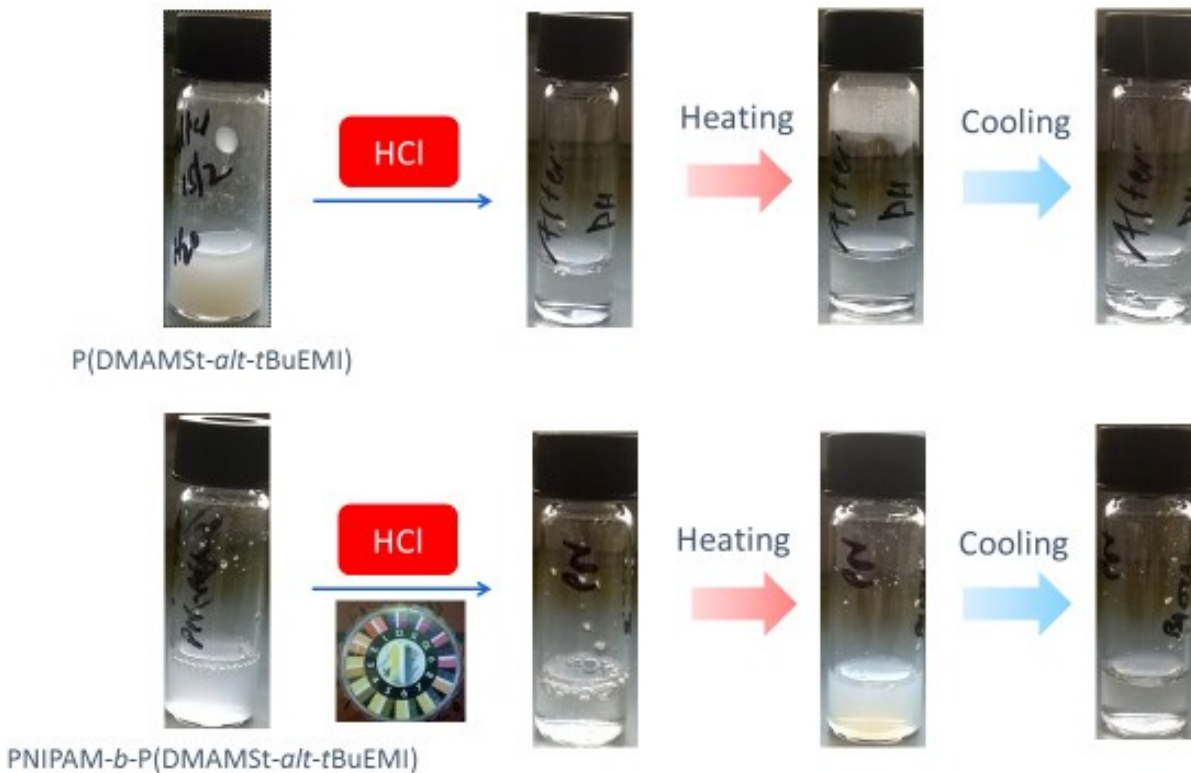


Fig. S13. Stimuli responsive behavior of alternating copolymers.

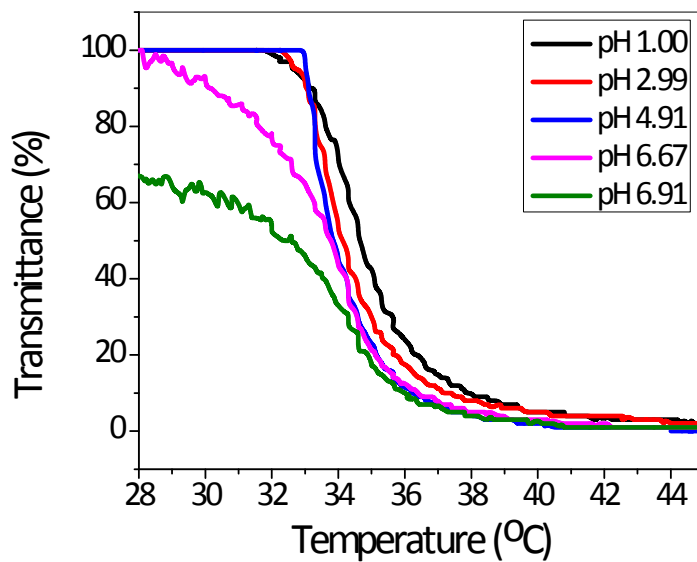


Fig. S14. Transmittance versus temperature plot of the aqueous PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) at different pH.

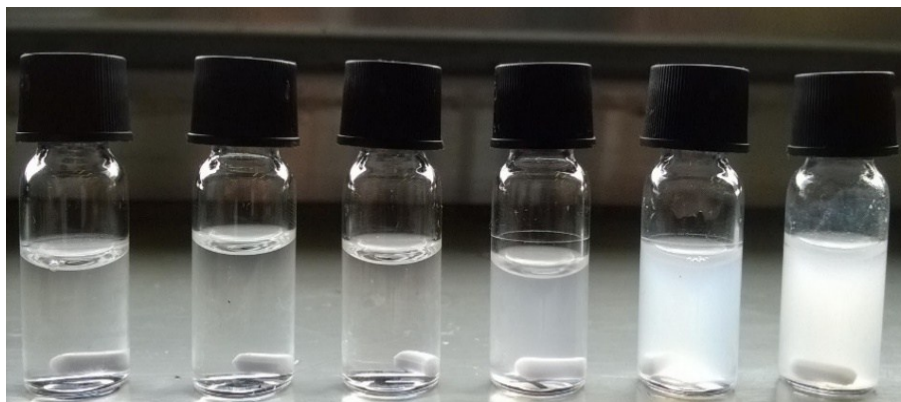


Fig. S15. Photographs of PNIPAM-*b*-P(DMAMSt-*alt*-*t*BuEMI) in different pH at RT. pH left to right: (1.00, 2.99, 4.91, 6.67, 6.91 and 7.15)

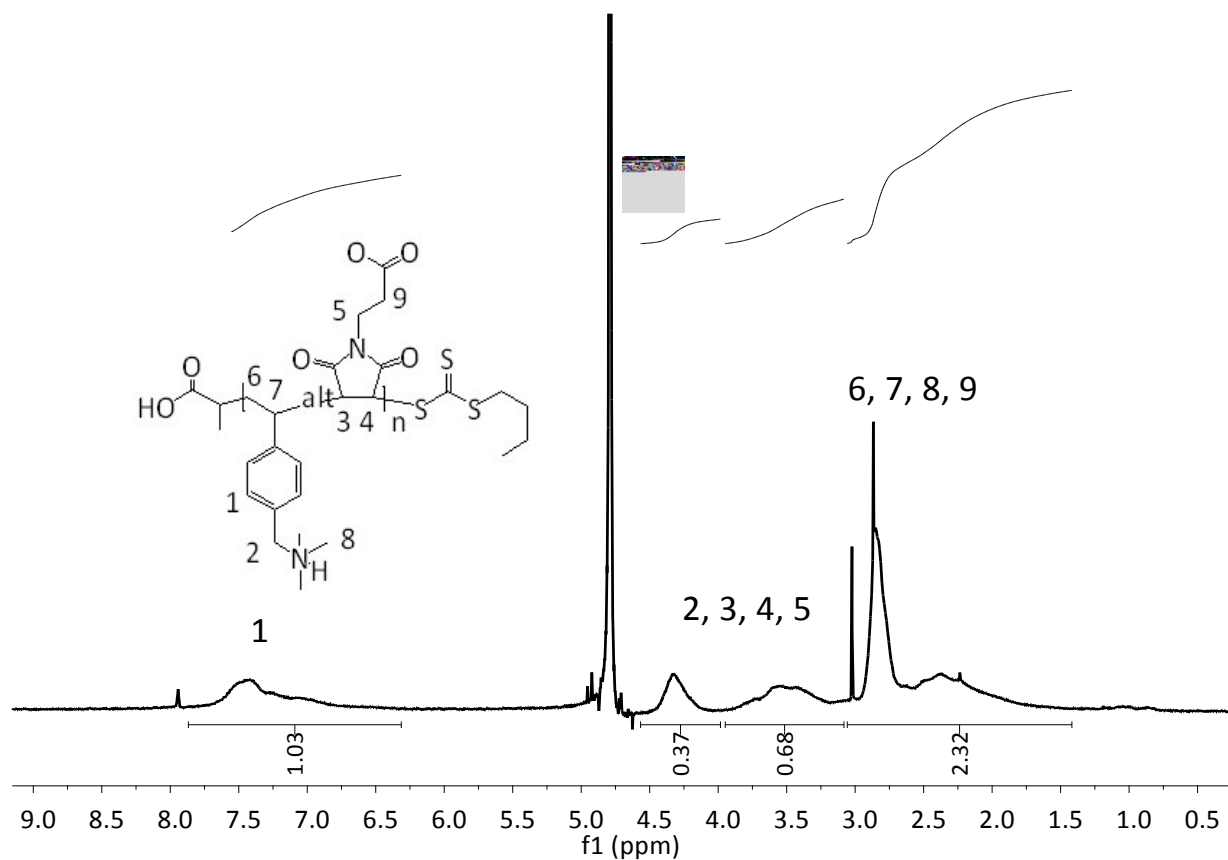


Fig. S16. ¹H NMR spectrum of P(DMAMSt-*alt*-*t*BuEMI) after deprotection measured in D₂O.

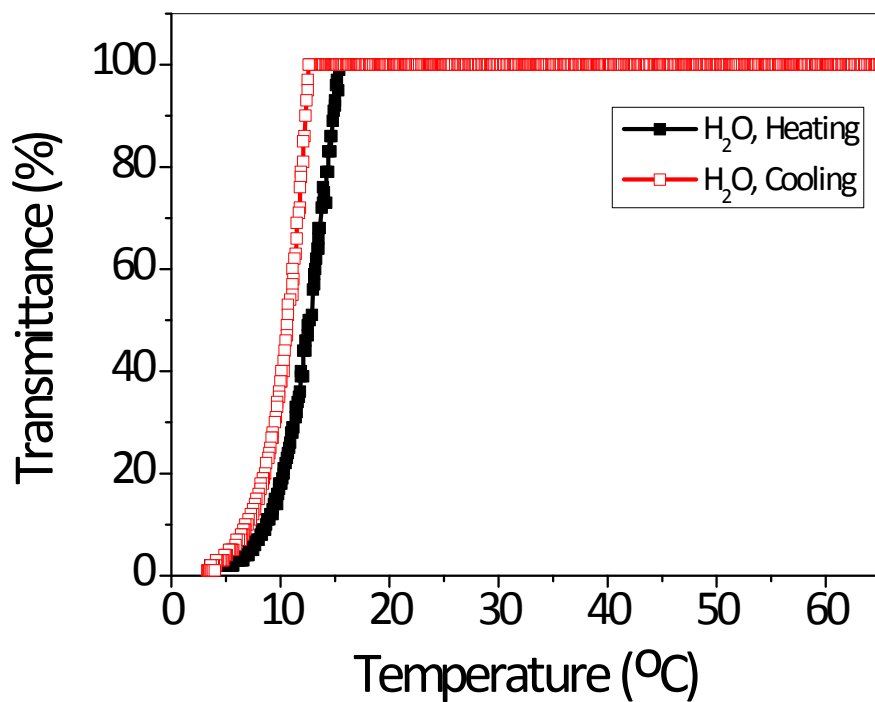


Fig. S17. UCST thermoresponsive behavior of P(DMAMSt-*alt*-CEMI) in H₂O (Concentration: 5 mg mL⁻¹; Heating and Cooling Rate: 1°C min⁻¹)

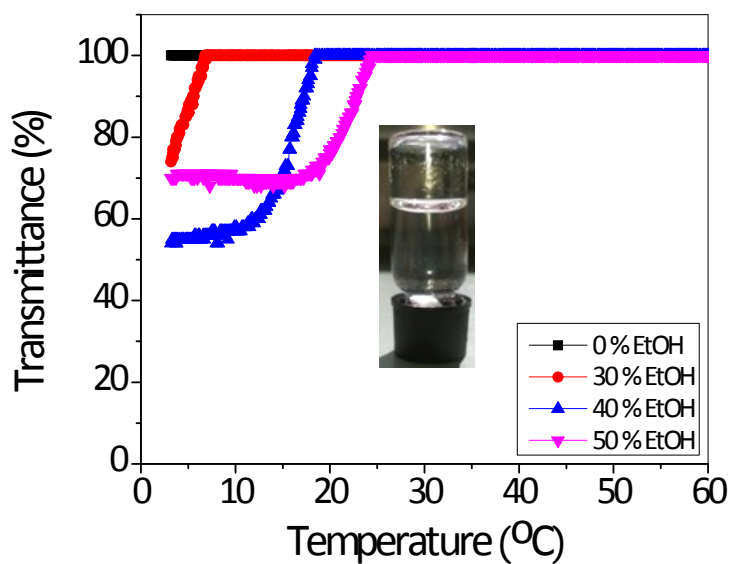


Fig. S18. UCST behavior of P(DMAMSt-*alt*-CEMI) in EtOH/H₂O mixtures (Concentration: 1 mg mL⁻¹; Cooling Rate: 1°C min⁻¹).

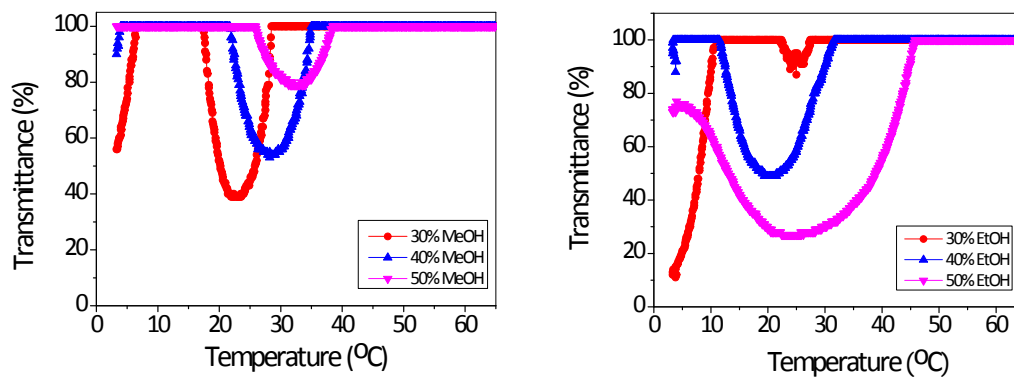


Fig. S19. UCST behavior of P(DMAMSt-*alt*-CEMI) in left) MeOH/H₂O and right) EtOH/H₂O mixtures (Concentration: 5 mg mL⁻¹; Cooling Rate: 1°C min⁻¹)

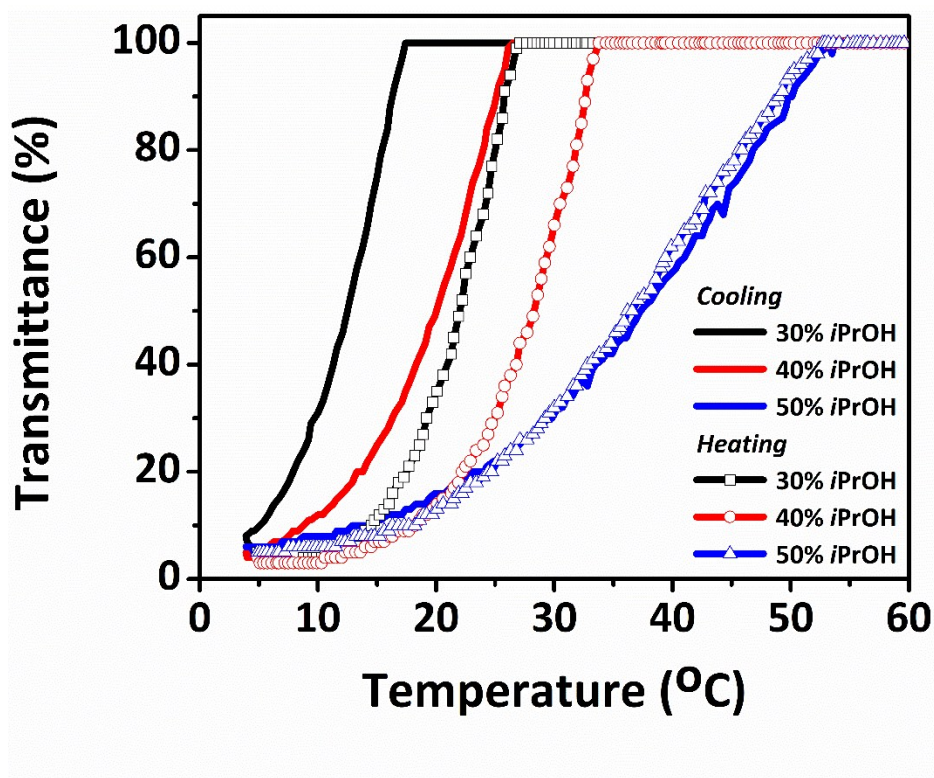


Fig. S20. UCST behavior of P(DMAMSt-*alt*-CEMI) in *i*PrOH/H₂O mixtures (Concentration: 1 mg mL⁻¹; Heating and Cooling Rate: 5°C min⁻¹).

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