

Supplementary information for

Thermoresponsive Behavior of Poly[trialkyl-(4-vinylbenzyl)ammonium] Based Polyelectrolytes in Aqueous Salt Solutions

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Experimental

Materials

4-Vinylbenzyl chloride (Aldrich, 90%, 500 ppm tertbutyl catechol as inhibitor), 2-cyano-2-propylbenzodithionate (CTA) (Aldrich, 97.0% HPLC grade), triethylamine (Merck KGaA, 99.0% GC), tripropylamine (Aldrich, 98.0%), tributylamine (Fluka, ≥99.0%), triamylamine (TCI, 98.0%), trihexylamine (Aldrich, 96%), lithium trifluoromethanesulfonate (Aldrich, 96%), lithium bis(trifluoromethane) sulfonimide (Aldrich, ≥99%), sodium 1-pentanesulfonate monohydrate (NaPS) (Alfa Aesar, HPLC grade), sodium dodecane sulfate (SDS) (Merck, ≥99%), NaCl (Fischer, 99.98%), NaNO₃ (VWR, 99%), NaH₂PO₄·2H₂O (VWR, 99%), NaSCN (Aldrich, 99%), Na₂SO₄ (Fischer, 99%), dimethylsulfoxide (Fisher, 99.98%), acetone (Aldrich, 99.8%), diethyl ether (VWR, 100%), MgSO₄·7H₂O (Merck, 99.5 %), Sigma-Aldrich (99.0 %) were used as received. N, N - dimethylformamide (Fluka, >99%) was distilled under reduced pressure and dried over 3 Å molecular sieves (VWR). Azobisisobutyronitrile (AIBN) (Fluka, 99.0%) was recrystallized from methanol. Deuterated solvents used for NMR were produced by Eurisotop. Water for dialysis was purified with Elix Essential 10 and water for samples with Elga purelab ultra.

Syntheses

Monomer synthesis. A series of trialkyl(4-vinylbenzyl)ammonium chlorides were synthesized. The synthesis of tributyl(4-vinylbenzyl)ammonium chloride is given as an example; other monomers were synthesized following the same procedure.

4-vinylbenzyl chloride (14.456 g, 94.7 mmol) and tributylamine (25.319 g, 137 mmol) dissolved in 50 mL of acetone. The reaction flask was immersed into an oil bath preheated to 40 °C and the reaction was allowed to proceed for 24 hours. The product was isolated by precipitation into diethyl ether and dried at 50 °C under high vacuum.

Polymerizations. The synthesized trialkyl(4-vinylbenzyl)ammonium chlorides were polymerized to yield the corresponding poly[trialkyl(4-vinylbenzyl)ammonium chlorides]. As an example, the polymerization of tributyl(4-vinylbenzyl)ammonium chloride is described below. The other monomers were polymerized using a similar methodology.

Tributyl(4-vinylbenzyl)ammonium chloride (10.10 g, 29.9 mmol), AIBN (0.0041 g, 0.0250 mmol) and 2-cyano-2-propylbenzodithionate (CTA) (0.0361 g, 0.163 mmol) were dissolved in 15 ml of DMF. The solution was purged with nitrogen and the reaction was allowed to proceed at 100°C for 23 hours. The reaction was stopped by freezing the solution with liquid nitrogen. After thawing the solution, a conversion sample was taken. The product was purified by dialyzing it against distilled water for 5 days in a dialysis bag with molecular weight cutoff of 3500 g/mol. The dialysis water was changed at least once per day. The polymer was isolated by freeze-drying the contents of the dialysis bag.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy. NMR spectra were measured with Bruker Avance III 500 MHz spectrometer. The structures of the products and the conversions of polymerizations were determined by measuring ^1H NMR spectra.

Transmittance measurements. The transmittance measurements were performed on Jasco V-750 spectrophotometer and Jasco J-815 CD spectrometer. The samples were prepared by mixing water, salt solution, and polymer stock solution to yield the target concentration. Polymer stock solution was always added last with vigorous stirring and the polymer concentration was kept at 1 mg/mL. The samples were degassed by subjecting them to a mild vacuum before measurements. The samples were equilibrated for 10 or 5 min at the start temperature. The temperature range between 5°C and 90°C was used for most heating and cooling measurements. With concentrated salt solutions, the heating started from 20 °C in order to avoid oversaturating the salt solutions at low temperatures. The temperature of the cuvette holder was continuously scanned at the rate of 1°C/min and the temperature was monitored with a temperature sensor immersed into the sample. The cloud points were determined from the intersection of two tangents (Fig. S1, supporting information). An analogous approach was used for determination of UCST type transitions. LCST type cloud points (T_{cL}) and UCST type cloud points (T_{cU}) were determined from heating and cooling curves respectively.

Differential Scanning microcalorimetry (DSC). Calorimetry measurements were conducted with a Microcal PEAQ-DSC calorimeter. The sample preparation procedure was identical to the one used for the transmittance measurements. The samples were degassed in vacuum before introducing them to the instrument. The samples were stabilized at 5 °C for 5 minutes. After the stabilization, the samples were heated to 85°C with the rate of 1°C/min. The reference cell was filled with deionized water. From the resulting thermograms, enthalpy of transition (ΔH) and the temperature of the maximum heat capacity (T_{max}) were determined as shown in Fig. S2.

Determination of number average molecular mass by UV spectroscopy. Jasco V-750 Spectrophotometer was used in determination of number average molar mass of the polymers. Polymers were dissolved in filtered methanol in concentrations of 1 mg/ml and their UV spectra were measured at 23 °C. The CTA was dissolved in methanol in nine different concentrations to determine the extinction coefficient.

Dynamic light scattering. Hydrodynamic diameters of the samples were measured with Zeta Sizer Nano. The samples were heated from 15 °C to 90 °C, with a two minutes stabilization time at each temperature before measuring. Three independent measurements were performed at each temperature.

Supplementary figures

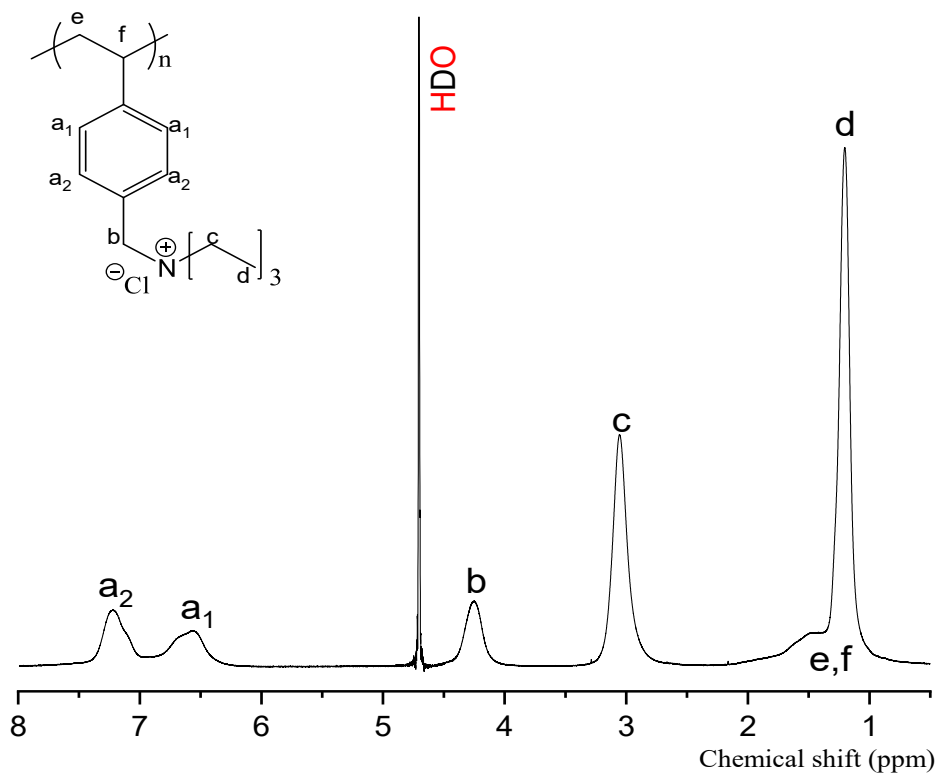


Figure S1. ^1H NMR-spectrum of PC2N in D_2O .

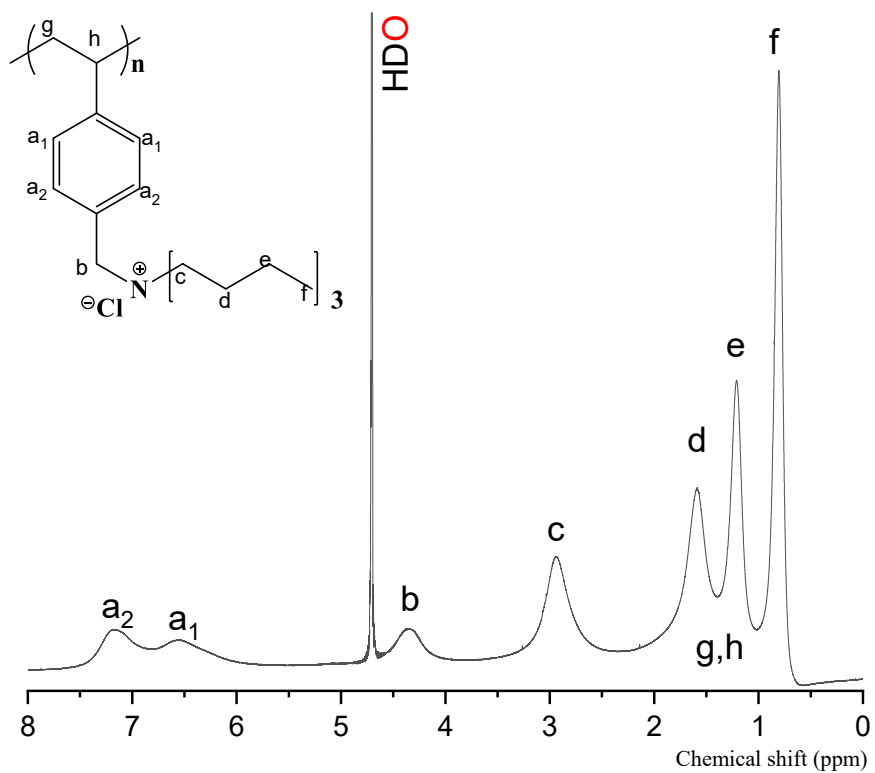


Figure S2. ^1H NMR-spectrum of PC4N in D_2O .

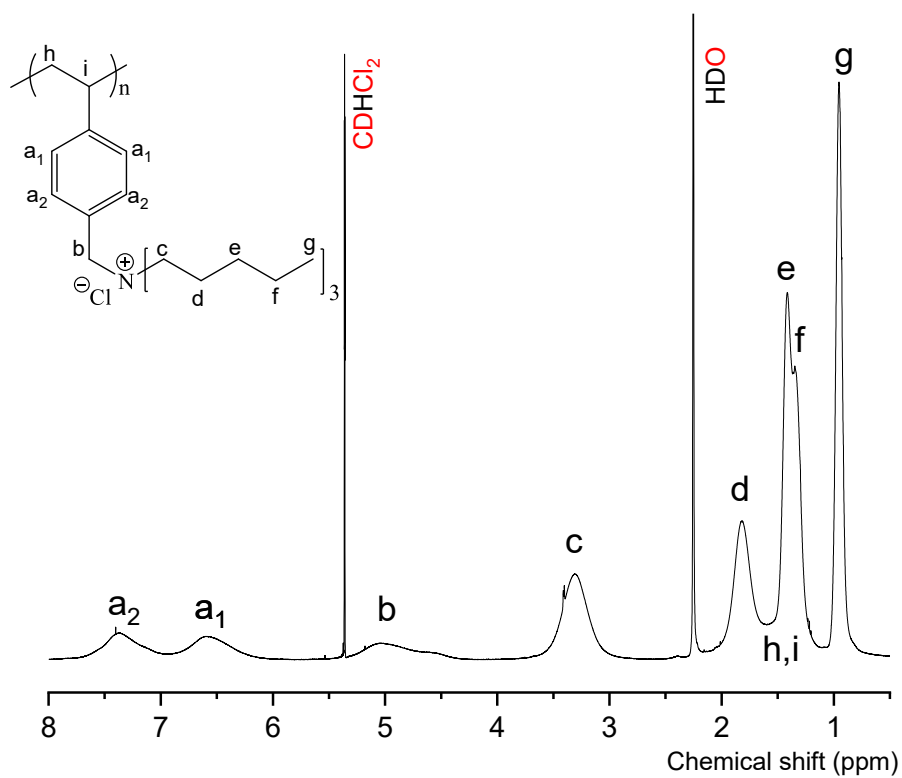


Figure S3. ¹H NMR-spectrum of PC5N in deuterated dichloromethane.

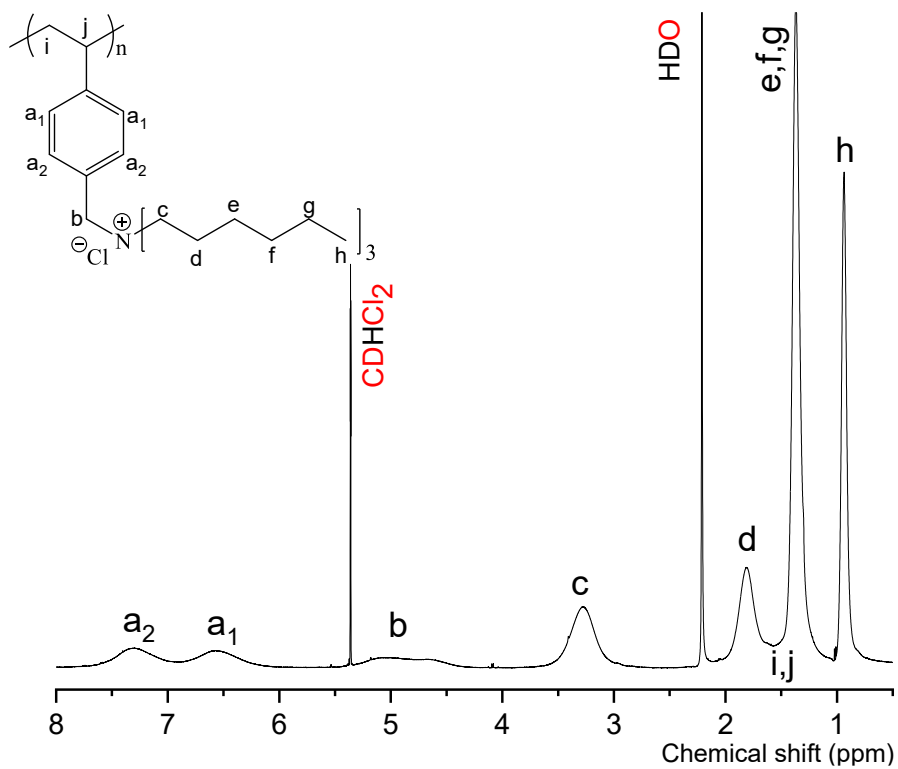


Figure S4. ¹H NMR-spectrum of PC6N in deuterated dichloromethane.

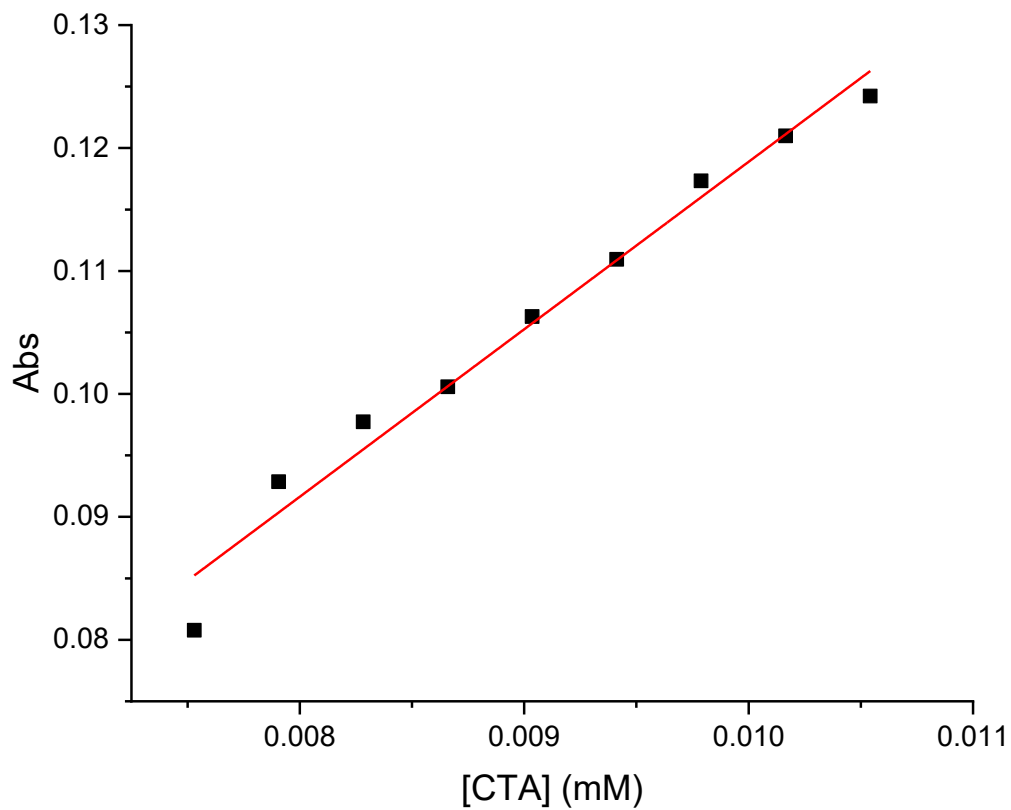


Figure S5. Absorbance CTA solution in methanol as a function of concentration at 310 nm. The value for the extinction coefficient ϵ obtained from the linear fit was $13622 \text{ M}^{-1}\text{cm}^{-1}$.

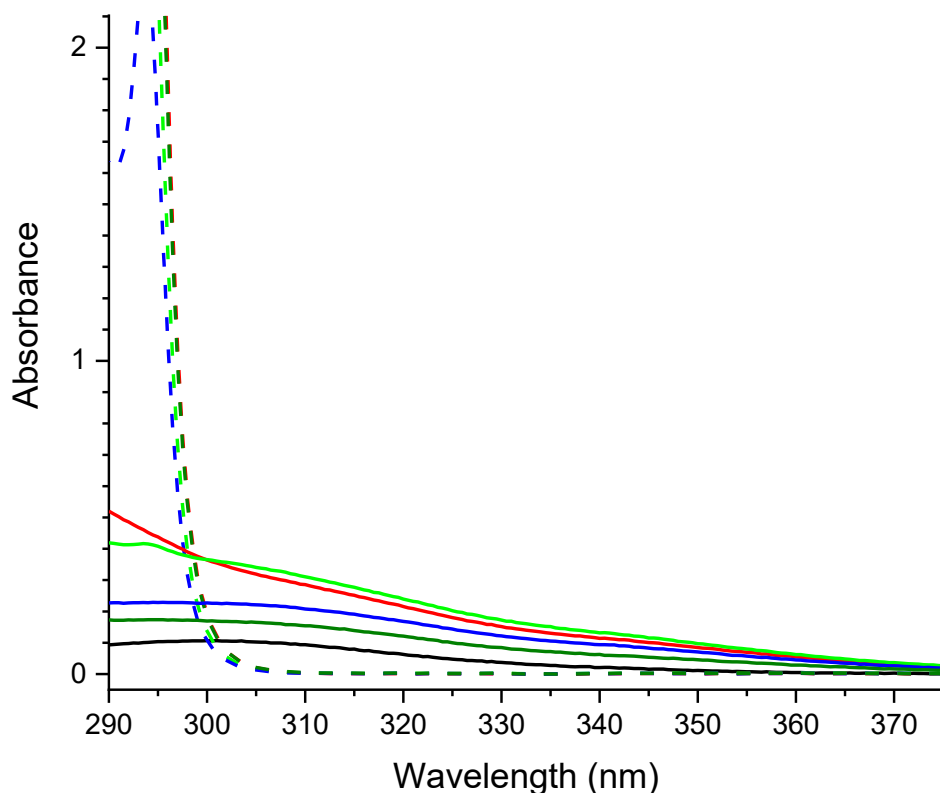


Figure S6. UV spectra for CTA (black solid line), PC2N (red solid line), PC3N (green solid line), PC4N (blue solid line) and PC4N (olive solid line). The spectra of the monomers are drawn with dashed lines with the same colors as the corresponding polymers. All spectra have been measured in methanol.

Determination of number average molecular weight for UV spectra

Combining the results from Figures S5 and S6 allows one to determine the molecular weight of the polymer.¹ If one assumes that the extinction coefficients of a CTA molecule and an end group derived from the CTA, then it is possible to determine the concentration of the end groups in the samples shown in S6 using the extinction coefficient from Figure S5. This is done with the Lambert-Beer law (equation S1), where A is the absorbance of the sample, b is the length of the optical path, ϵ is the extinction coefficient, and c is the concentration of the end groups.

$$c = \frac{A}{b\epsilon} \quad (\text{S1})$$

Concentration of the polymer chains in the sample solution can be expressed using equation S2. In the equation n is the amount of polymer chains in the solution in moles, M_n is the number average molecular weight of the polymer, and V is the volume of the sample.

$$c = \frac{n}{V} = \frac{m}{M_n V} \quad (\text{S2})$$

If one assumes that every polymer chain in the sample has exactly one end group that arises from the CTA and the polymer is made only of the repeating units, then equations S1 and S2 can be combined as equation S3.

$$M_n = \frac{m}{V} \times \frac{b\varepsilon}{A} \quad (S3)$$

Since the mass concentration of the sample (m/V) and optical path length (b) are known, the extinction coefficient (ε) can be determined from Figure S5, and the absorbance is determined from the UV spectra (Figure S6), equation S3 can be used to calculate the number average molecular weight (M_n).

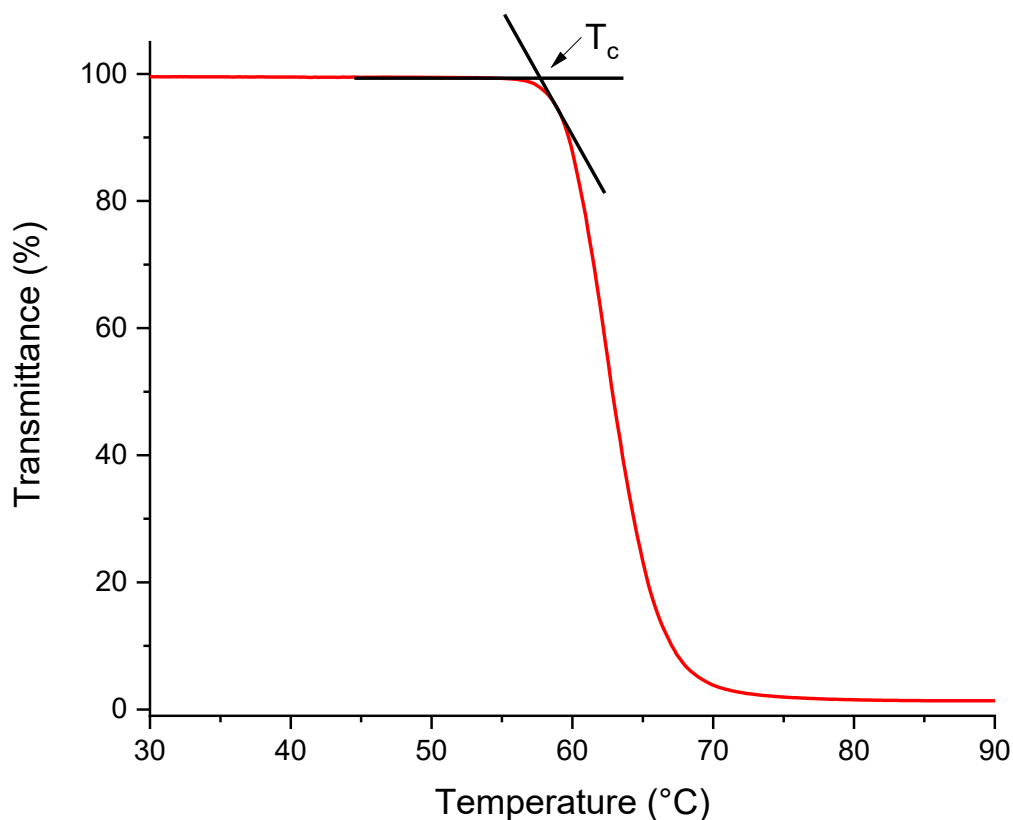


Figure S7. Determination of the cloud point (T_c) from a sample with an LCST type transition, PC4N in 1 M NaCl as an example.

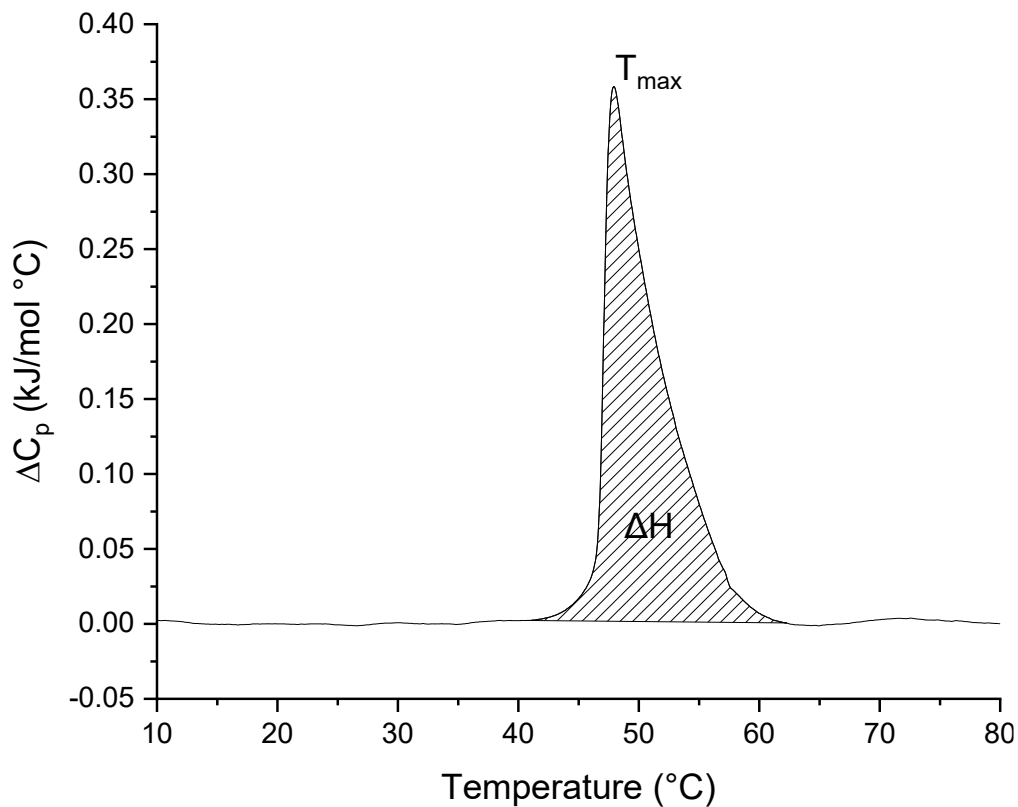


Figure S8. Determination of the temperature of maximum heat capacity (T_{\max}) as the peak value and the enthalpy of the transition (ΔH) as the area under the peak. PC4N in 700 mM NaPS as an example.

Table S1. Comparison of T_{cU} values for 1 mg/mL polycation solutions with LiNTf₂ and 500 mM NaCl.

Polymer	[LiNTf ₂] (mM)	T_{cU} (°C)	Reference
Poly[triethyl(4-vinylbenzyl)ammonium chloride] (PC2N)	0.40	78	This work
Poly(2-methacryloyloxyethyl trimethylammonium iodide)	2.0	55	²
Poly(3-methyl-1-(4-vinylbenzyl)-imidazolium chloride)	0.85	62	²
Poly[(3-acrylamidopropyl)trimethylammonium chloride]	7.0	22	³

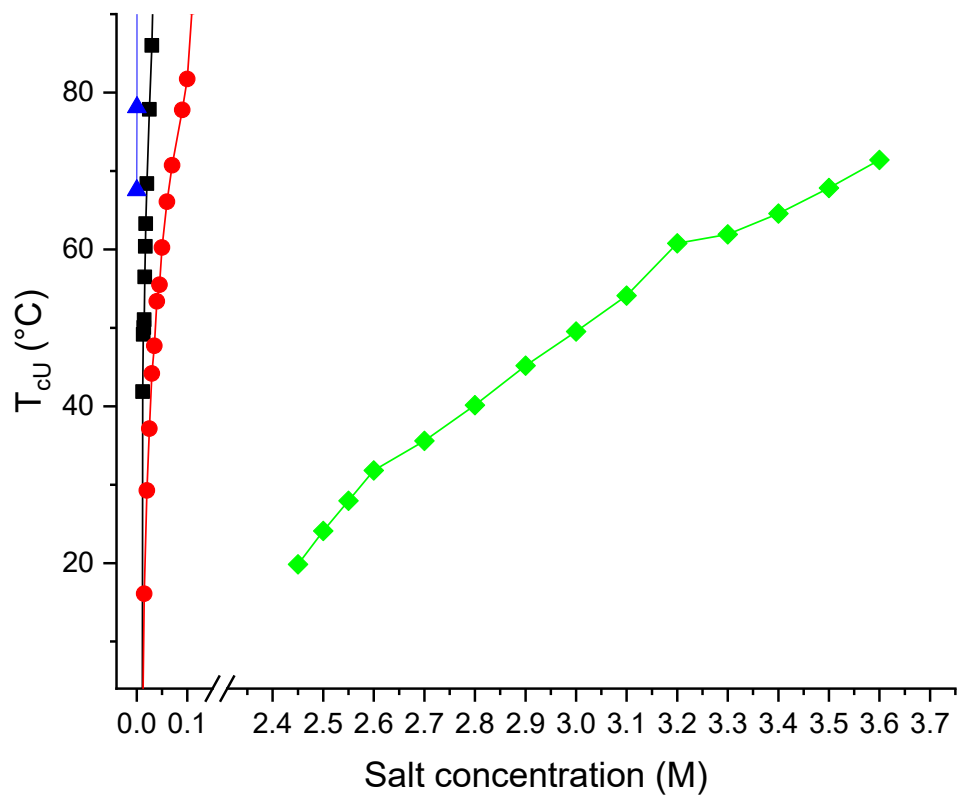


Figure S9. T_{cU} as a function salt concentration for 1 mg/mL PC2N solution with LiOTf (■), with NaSCN (●), with LiNTf₂ in 500 mM NaCl (▲), and with NaNO₃ (◆). The NaCl added to the LiNTf₂ solutions is not taken into account in the salt concentration. All the curves, except the one with NaNO₃, are shown in Figure 2 in the main text as well.

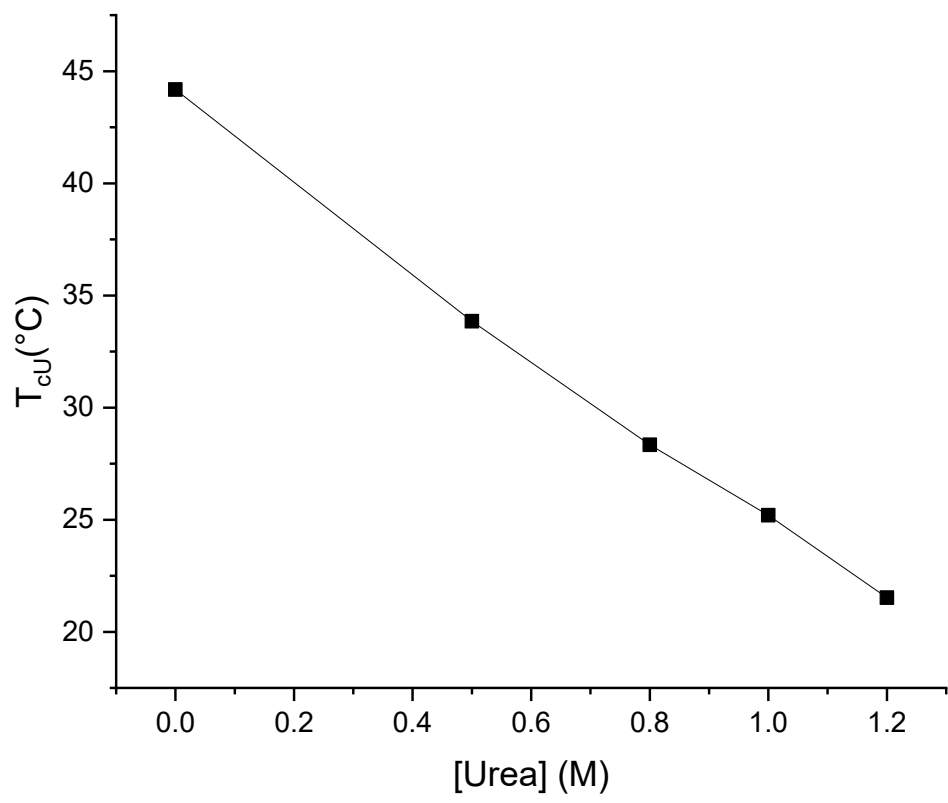


Figure S10. T_{cU} as a function of concentration of urea in 1 mg/mL solution of PC2N in 30 mM NaSCN.

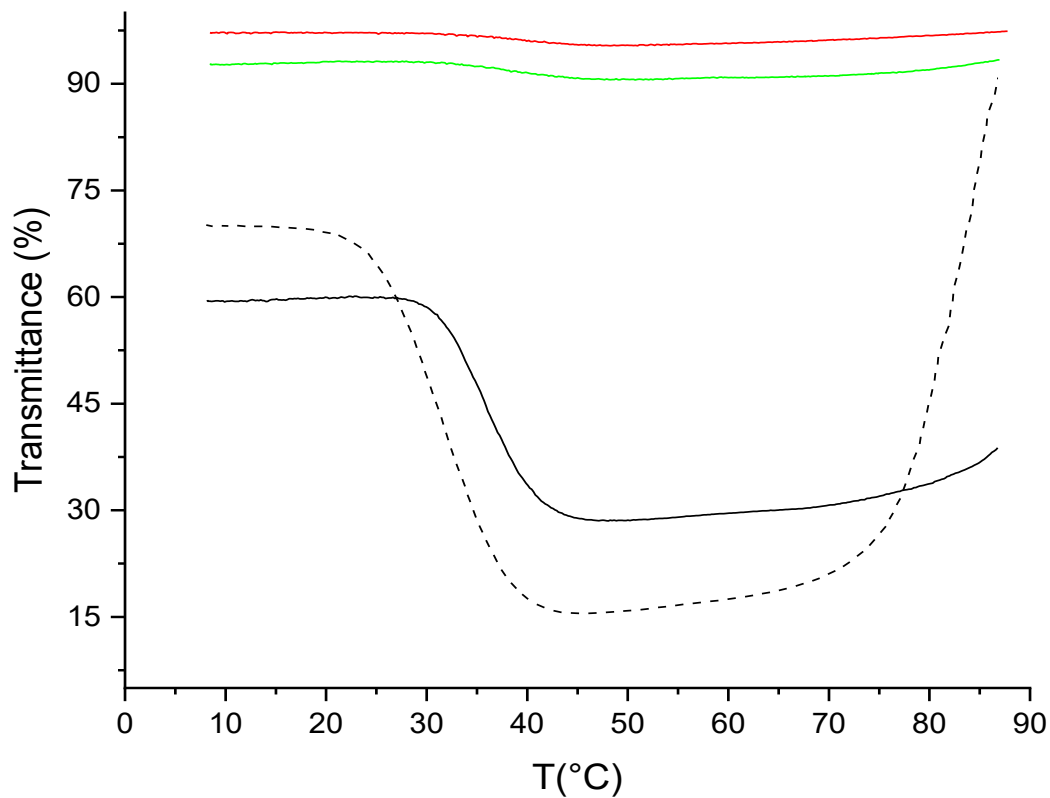


Figure S11. Transmittance curves as a function of temperature for concentrations of NaSCN 5 mM (red), 7 mM (green), 8 mM (solid black line) and 8 mM with the addition of 1 M of urea (dashed black line) 1mg/ml aqueous solution of PC3N.

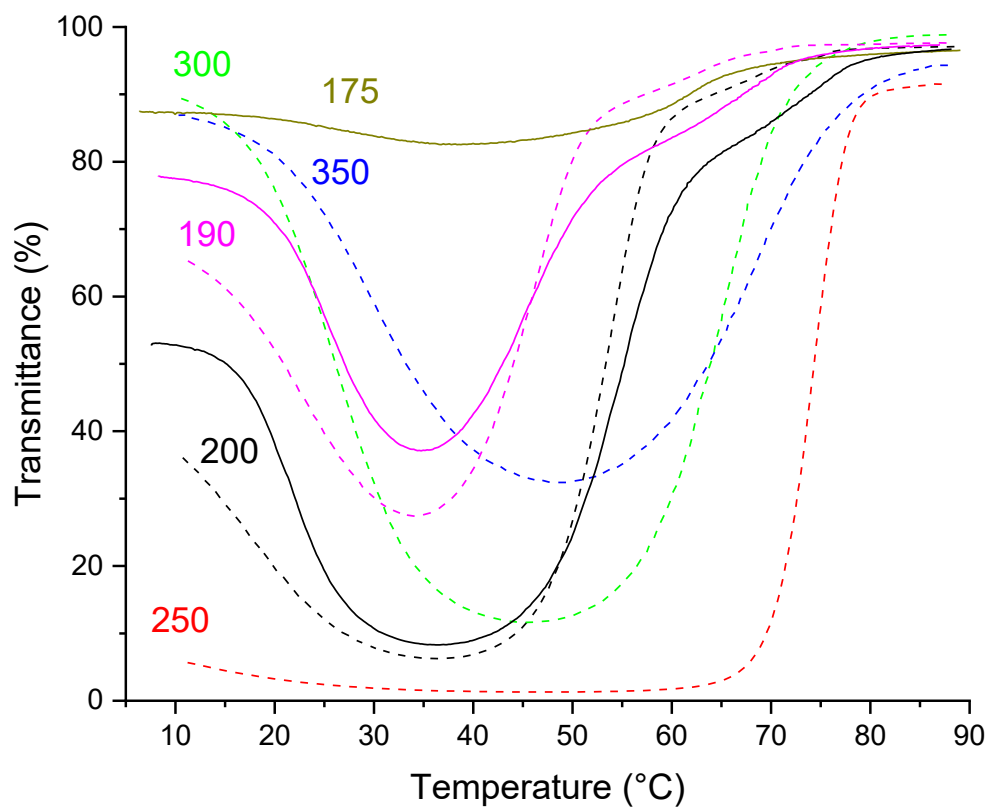


Figure S12. Transmittance as a function of temperature for 1 mg/mL PC3N solutions with varying concentrations of NaNO₃ on heating (solid) and on cooling (dashed). The NaNO₃ concentration for each solution is give as mM next to each curve.

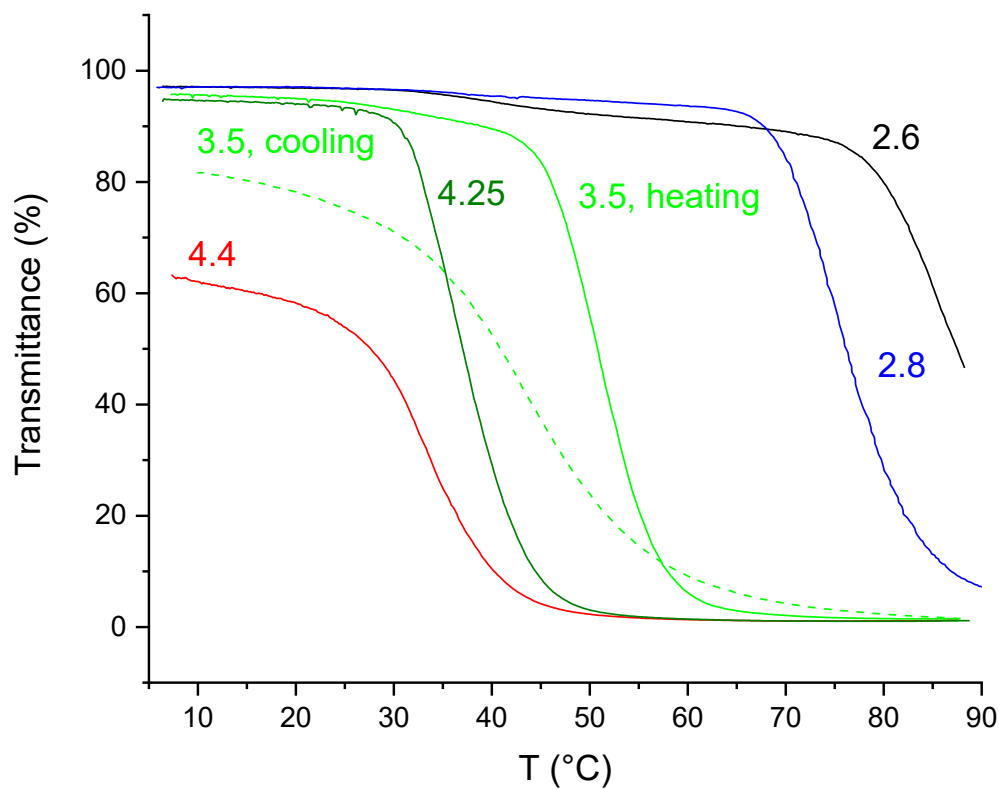


Figure S13. Transmittance as a function of temperature for 1 mg/mL PC3N solutions in aqueous NaCl with variable concentrations. The concentration is given as M next to each curve. The dashed line represents a cooling run for 3.5 M solution. The cooling run was conducted directly after the heating run.

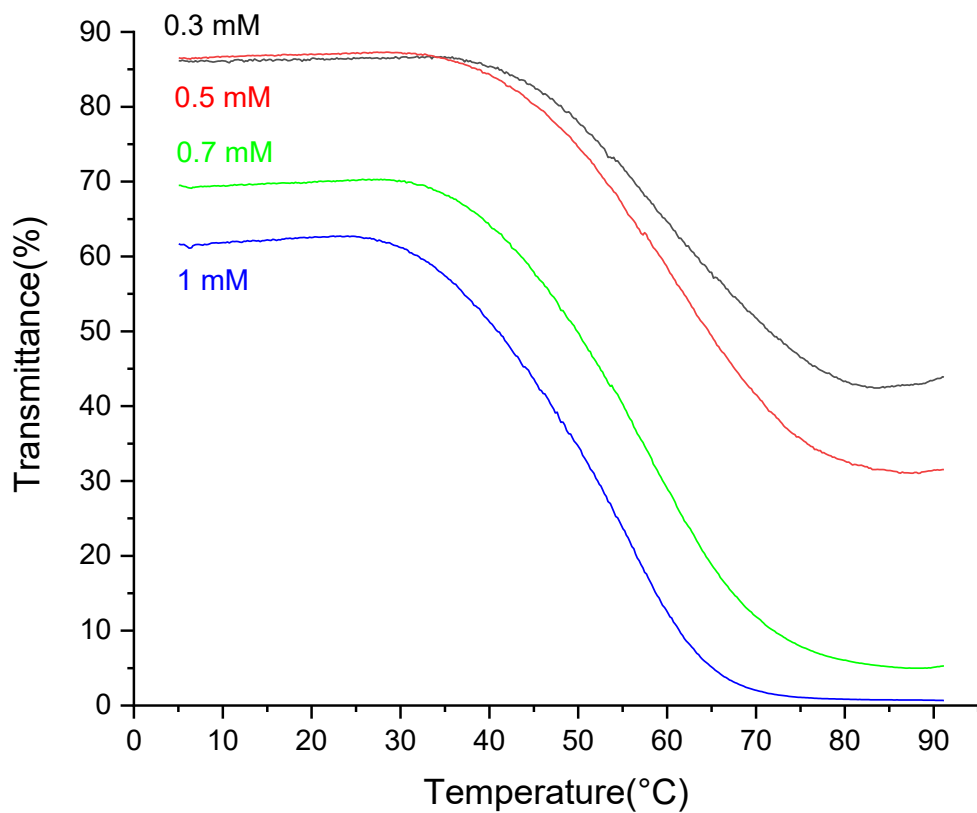


Figure S14. Transmittance as a function of concentration for 1 mg/mL solution of PC4N in 500 mM NaCl with variable concentrations of LiNTf₂ (written next to each curve).

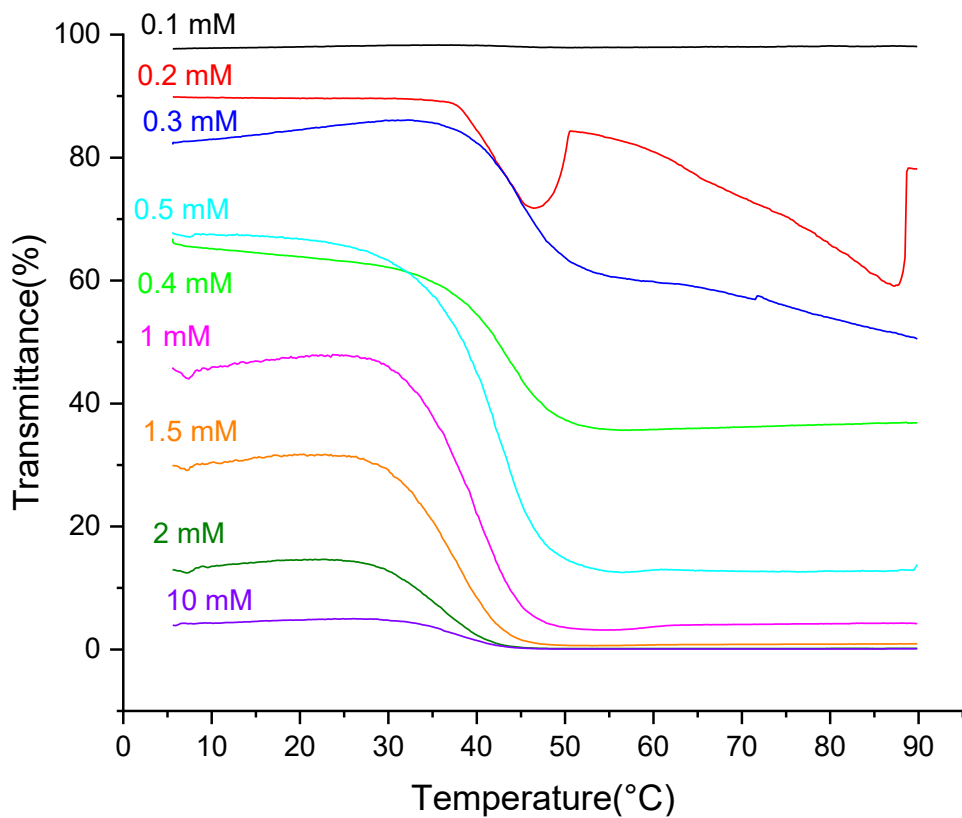


Figure S15. Transmittance curves as function of temperature for 1 mg/mL solutions of PC4N in presence of various concentrations of SDS. The SDS concentration is written next to each curve.

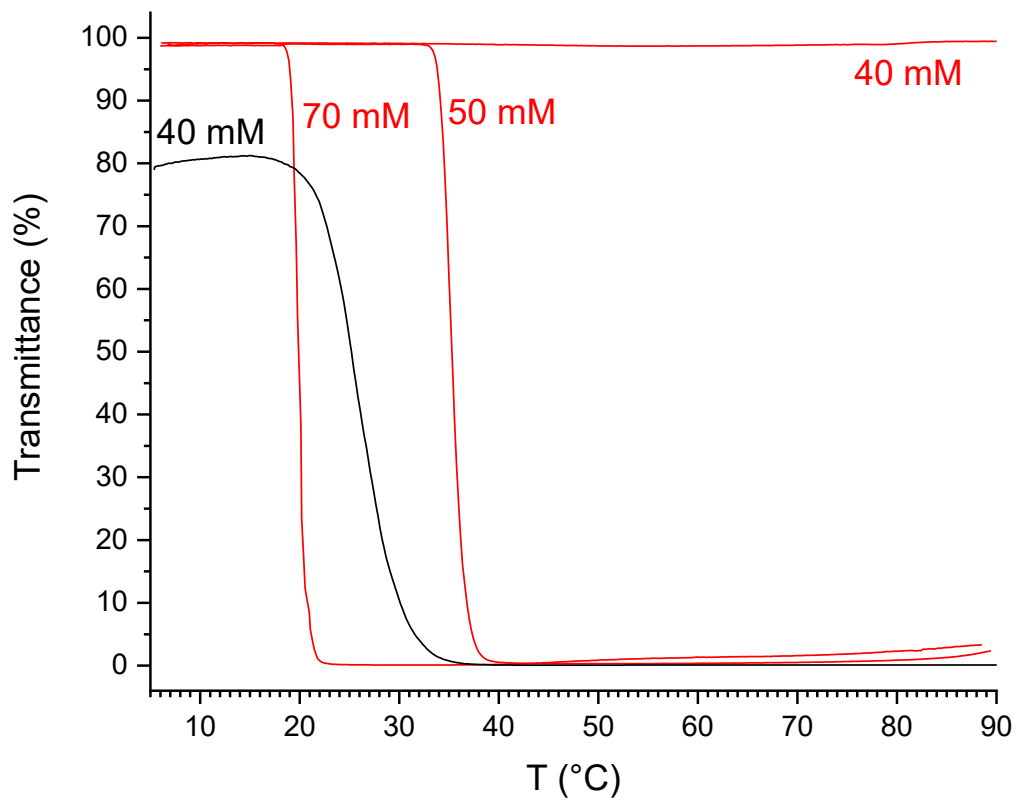


Figure S16. Transmittance as a function of temperature for a 1 mg/mL solution of PC4N in NaNO₃ (black) and in NaNO₃ with 250 mM NaCl (red). The concentration of NaNO₃ is written next to each curve.

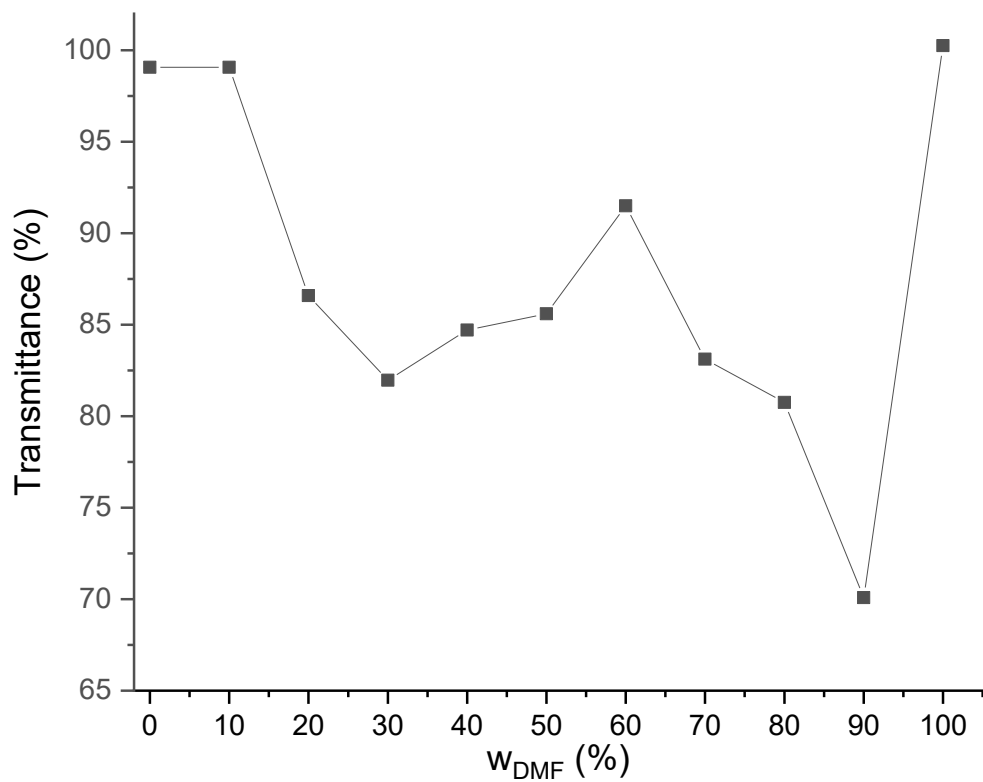


Figure S17. Transmittance for a 0.1 w-% solution of PC4N as a function of DMF weight fraction in DMF-water mixtures. The measurements have been conducted at 20 °C and reported as an average of 300 measurements measured with 1 second intervals. The error bars are smaller than the symbols.

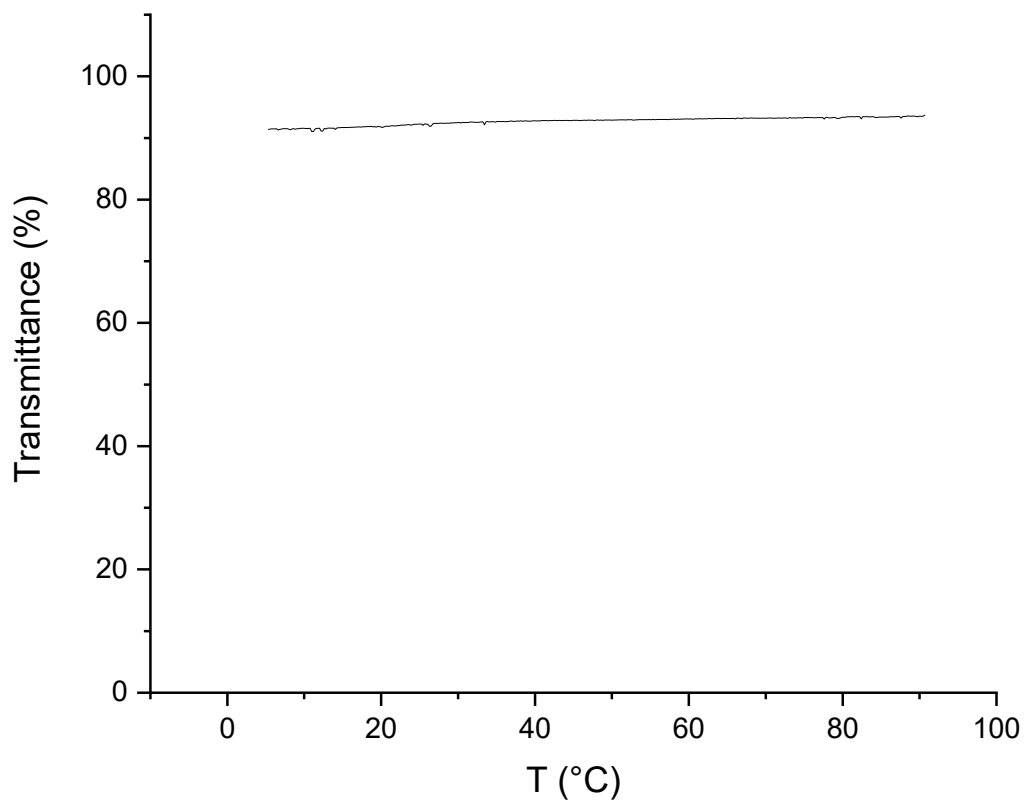


Figure S18. Transmittance as a function of temperature for a 1 mg/mL solution of PC4N in a solution with 20 w-% DMF in water.

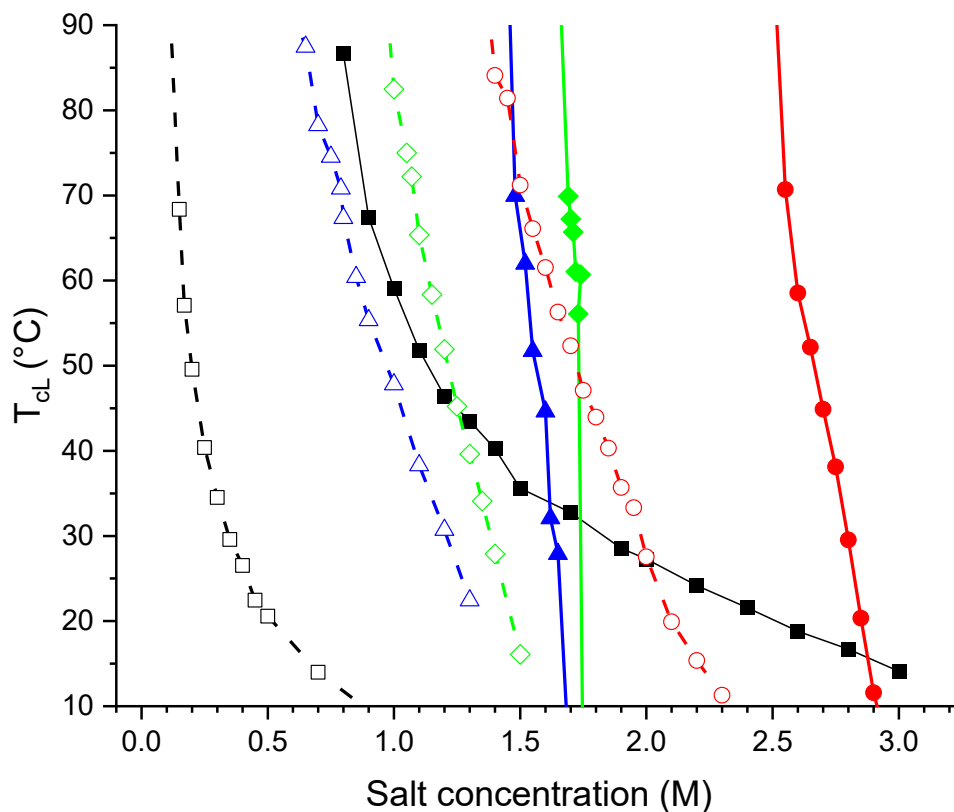
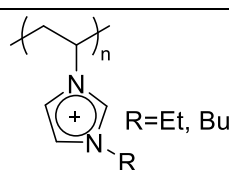
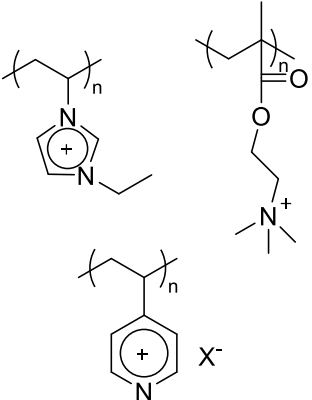
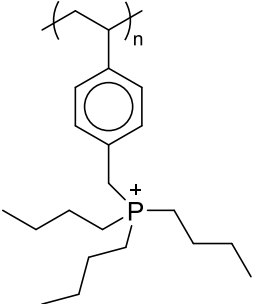
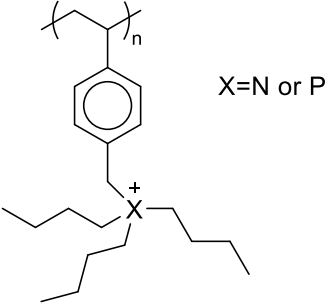
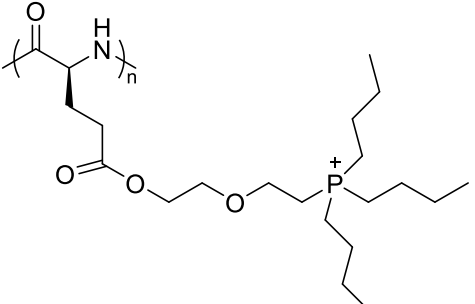
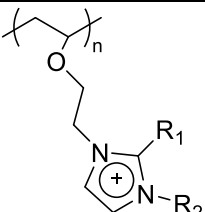
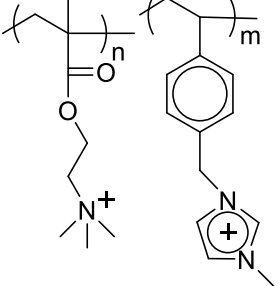
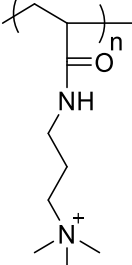
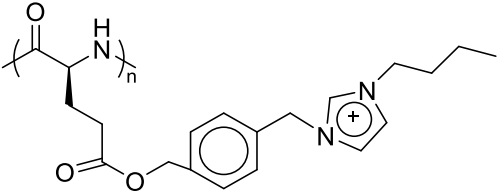
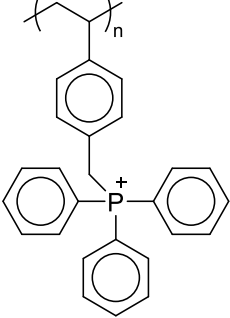
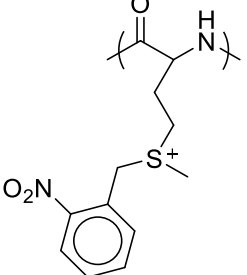


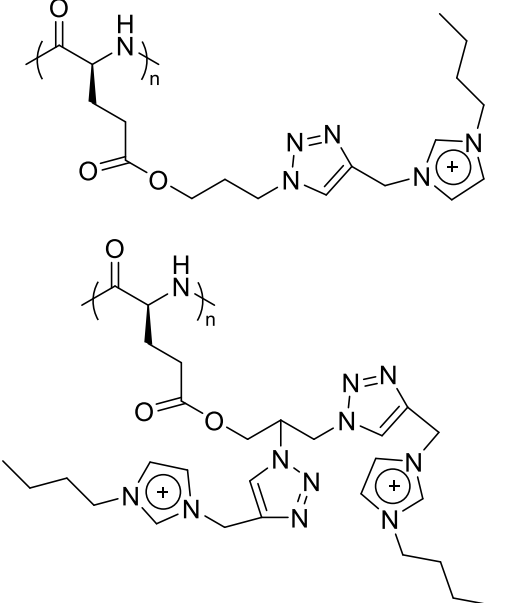
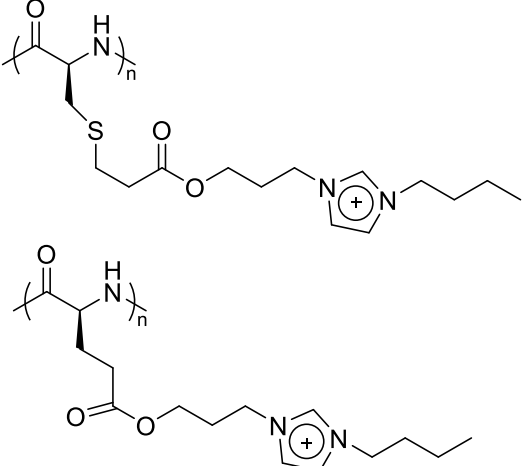
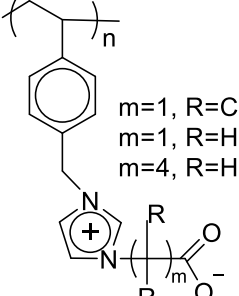
Figure S19. LCST type cloud points as a function of salt concentration for 1 mg/mL solutions PC4N (solid lined, filled symbols) and PC5N (dashed lines, empty symbols) in aqueous NaCl (■), in NaH₂PO₄ (●), in Na₂SO₄ (▲), and in Na₂CO₃ (◆).

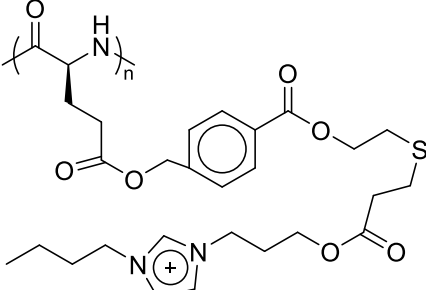
Table S2. Examples of strong polycations with anion-tunable water solubility and their order of anion interaction strength.

Polycations ^a	Type of transition	Order of anions	Reverse Hofmeister for monovalent ions?	Series in this article?	Ref.
 R=Et, Bu	I/S ^b	Br ⁻ /Cl ⁻ <BF ₄ ⁻ , PF ₆ ⁻ , OTf, NTf ₂ ⁻ , (CF ₃ SO ₂) ₂ N ⁻	NA	Yes	4

	I/S ^b	Br ⁻ /Cl ⁻ <BF ₄ ⁻ , PF ₆ ⁻ , OTf ⁻ , NTf ₂ ⁻ , (CF ₃ SO ₂) ₂ N ⁻ , C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ ⁻ , CH ₃ C ₆ H ₄ SO ₃ ⁻ , C ₁₆ H ₃₄ PO ₄ ⁻	NA	Yes	5
	LCST	Cl ⁻ <C ₃ H ₅ SO ₃ ⁻ < C ₄ H ₉ SO ₃ ⁻ < C ₅ H ₁₁ SO ₃ ⁻ < C ₆ H ₁₃ SO ₃ ⁻	NA	Yes	6
	LCST	C ₄ H ₉ SO ₃ ⁻ < C ₅ H ₁₁ SO ₃ ⁻ < C ₆ H ₁₃ SO ₃ ⁻	NA	NA	7
	LCST/UCST	I ⁻ <BF ₄ ⁻	NA	NA	8
	UCST	CO ₃ ²⁻ <Cl ⁻ <BF ₄ ⁻ < NTf ₂ ⁻ , SbF ₆ ⁻	Yes	Yes	9

	UCST	Cl ⁻ <OTf ⁻ < C ₄ F ₉ SO ₃ ⁻ <NTf ₂ ⁻	NA	Yes	2
	UCST	Cl ⁻ <NTf ₂ ⁻	NA	Yes	3
	UCST	Cl ⁻ <I ⁻ <BF ₄ ⁻	Yes	NA	10
	UCST	Cl ⁻ <Br ⁻	Yes	NA	11
	UCST (only precipitation for SO ₄ ²⁻)	I ⁻ <ClO ₄ ⁻ <SO ₄ ²⁻ <SCN ⁻	Yes	NA	12

	UCST	$\text{Cl}^- < \text{I}^- < \text{BF}_4^-$	Yes	NA	13
	UCST	$\text{Cl}^- < \text{I}^- < \text{BF}_4^-$	Yes	NA	14
 <p> $m=1, R=\text{CH}_3$ $m=1, R=\text{H}$ $m=4, R=\text{H}$ </p>	UCST	Varies with R and m	Mostly, but not in all cases.	NA	15

	UCST	Cl ⁻ /I ⁻ /BF ₄ ⁻	Yes	NA	16
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a. Limited to studies with several anions. b. No temperature dependence was studied, only solubility and insolubility in water.

References

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