Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information for

Upper or Lower Critical Solution Temperature, or Both? Studies on Cationic Copolymers of N-isopropylacrylamide

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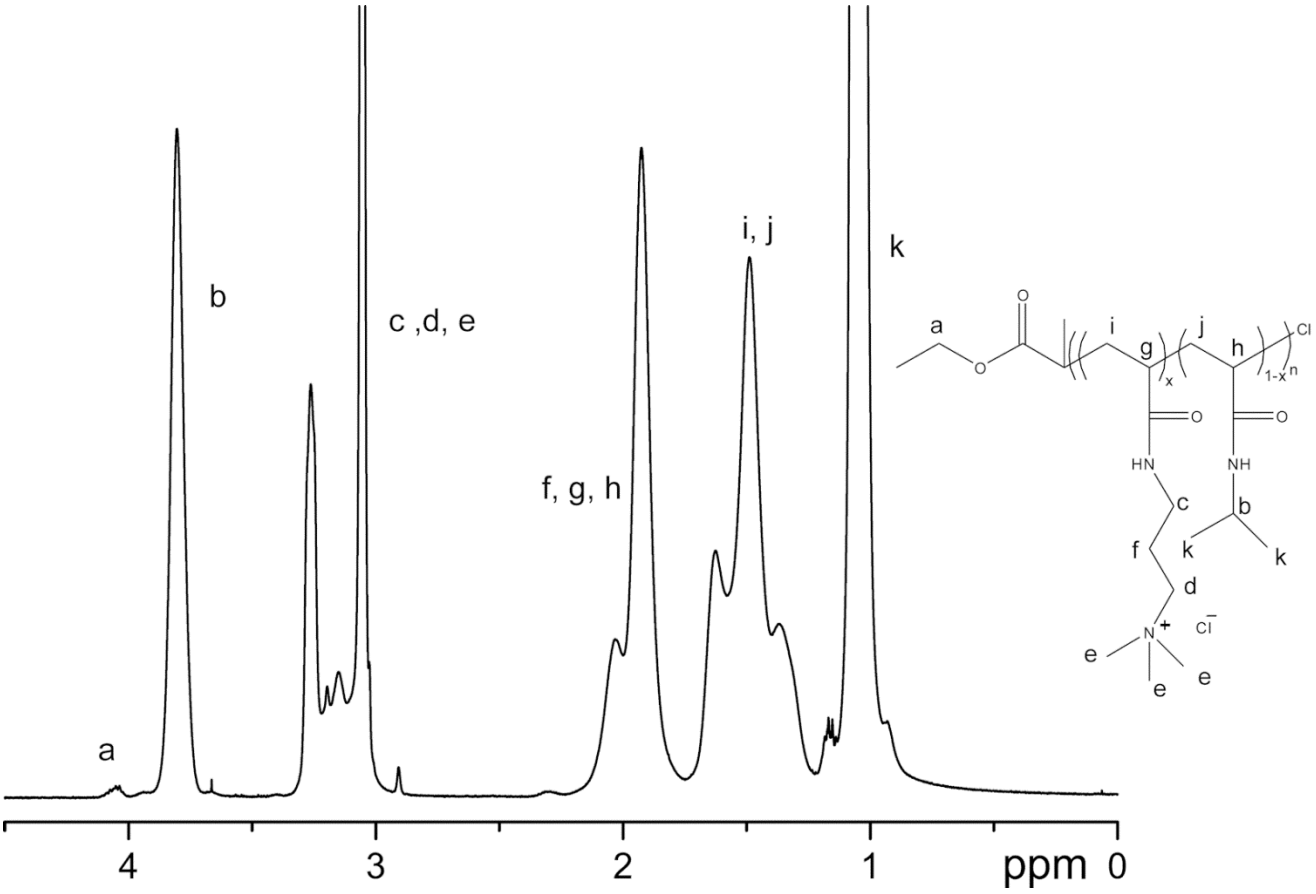

Figure S1. NMR-spectrum of CP-17 in D_2O

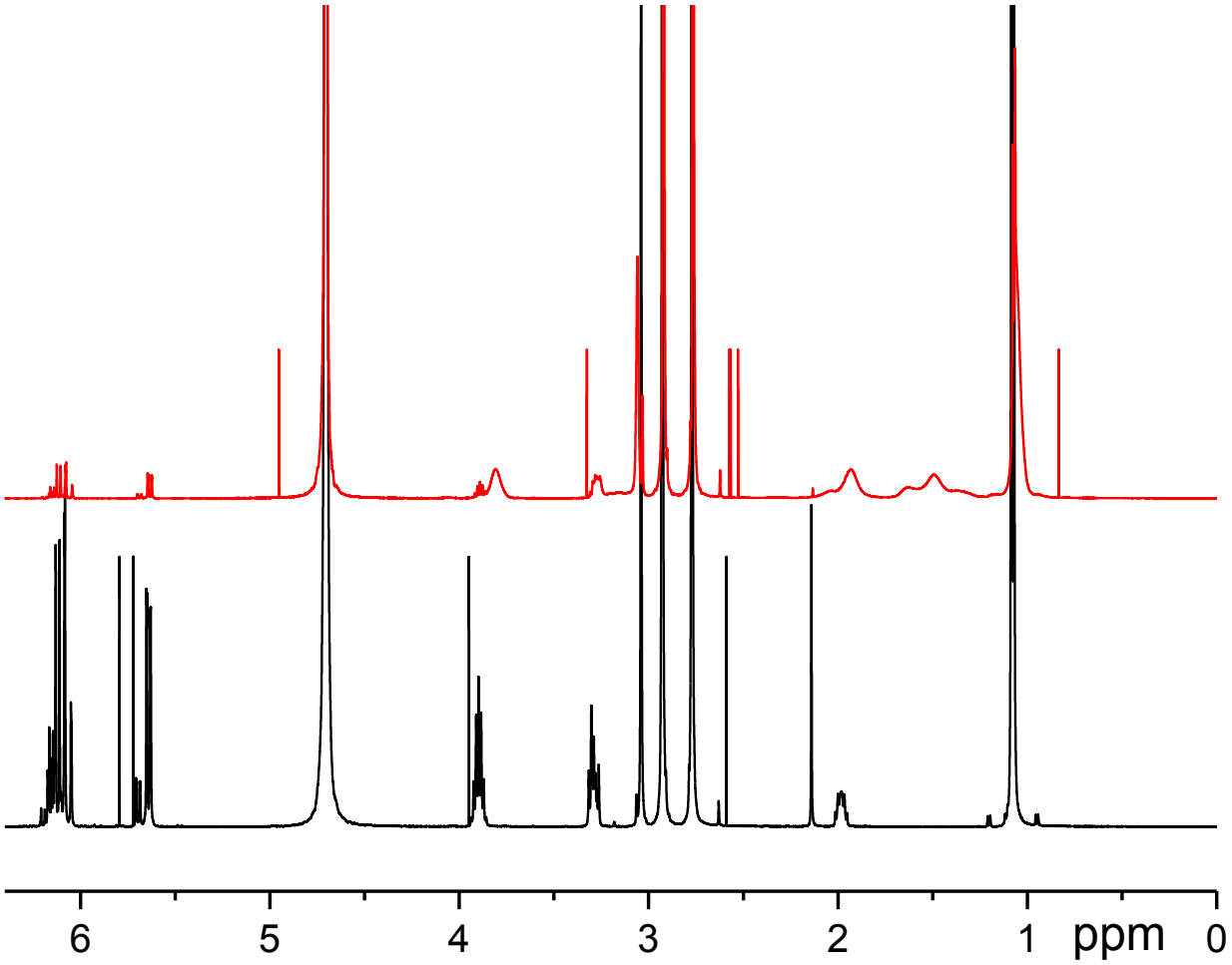

Figure S2. NMR-spectra of the zero sample (**black**) and conversion sample (**red**) of CP-17 in D_2O.

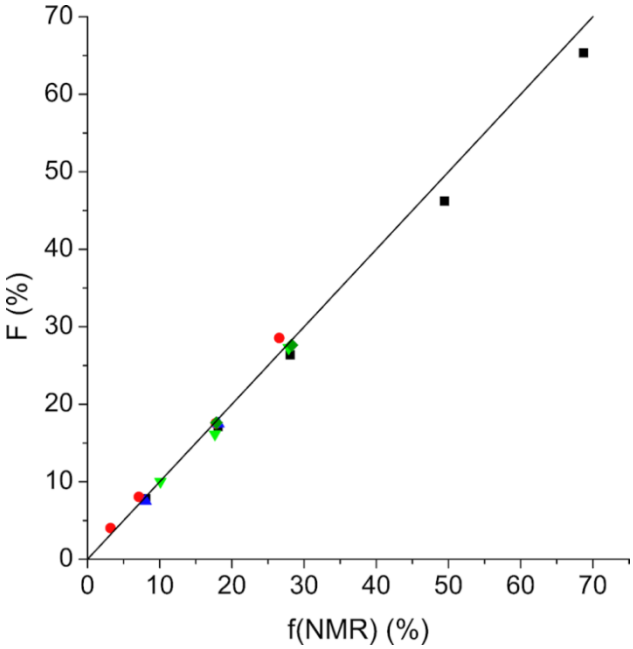

Figure S3. AMPTMA-content in the copolymer (F) as a function of AMPTMA-content in the feed (f(NMR)) as analyzed with NMR spectroscopy for the studied copolymers (■), copolymers without initial bubbling and three hours of reaction time (●), copolymers synthesized using metallic copper instead of CuCl at 25 °C (▲), at 40 °C (▼) or at 50 °C (♦). The line marks the theoretical curve with F=f(NMR).

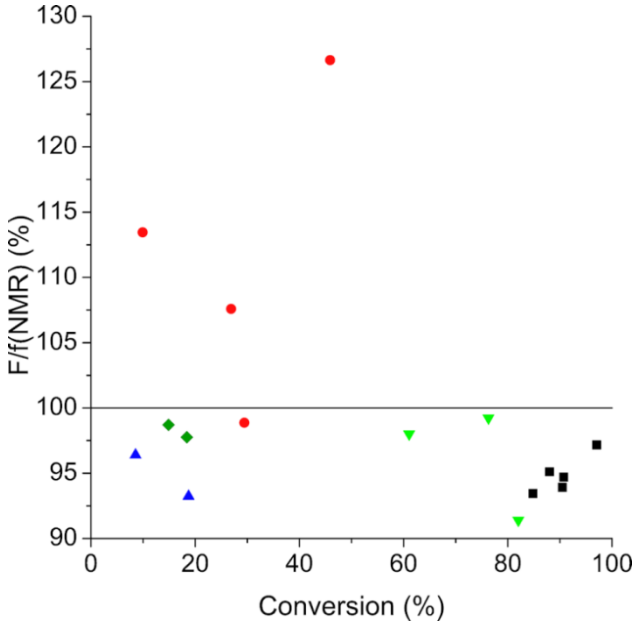

Figure S4. Relative difference between AMPTMA-content in the feed (f(NMR)) and in the purified copolymer (F) as analyzed with NMR spectroscopy for the studied copolymers (■), copolymers without initial bubbling and three hours of reaction time (●), copolymers synthesized using metallic copper instead of CuCl at 25 °C (▲), at 40 °C (▼) or at 50 °C (♦). The line marks the theoretical curve with F=f(NMR).

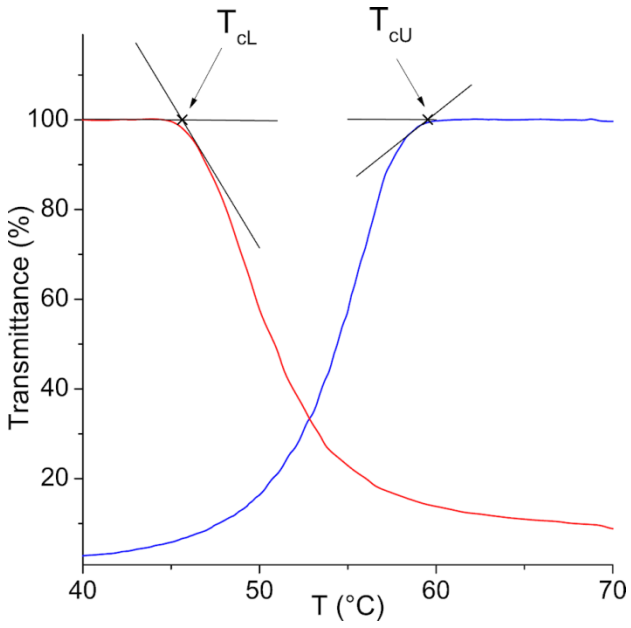

Figure S5. Illustration of definitions used in this study. T_{cL} as an intersection of two tangents from heating curve of CP-8 in 1 mM $LiNTf_2$ without any NaCl (**red**) and T_{cU} as an intersection of two tangents from cooling curve of PAMPTMA-1 in 100 mM NaCl with 6 mM $LiNTf_2$ (**blue**).

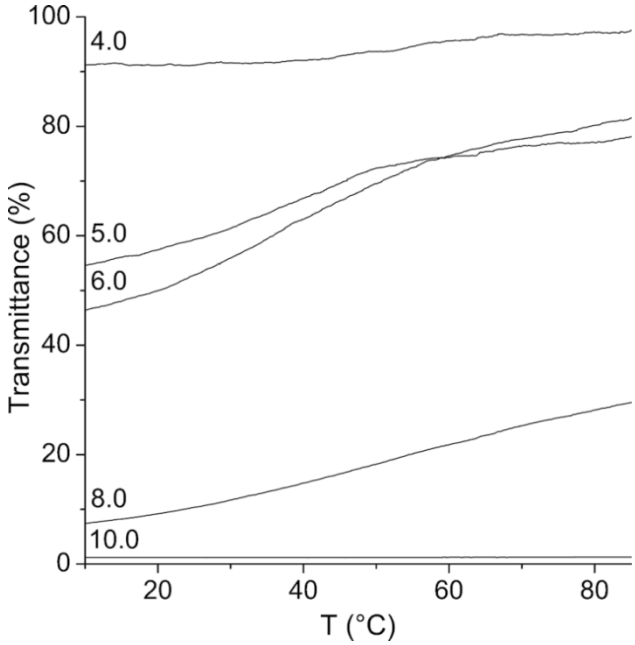

Figure S6. Cooling curves of PAMPTMA-1 in water with various amounts of $LiNTf_2$. The $LiNTf_2$-concentrations are given as mM above each curve.

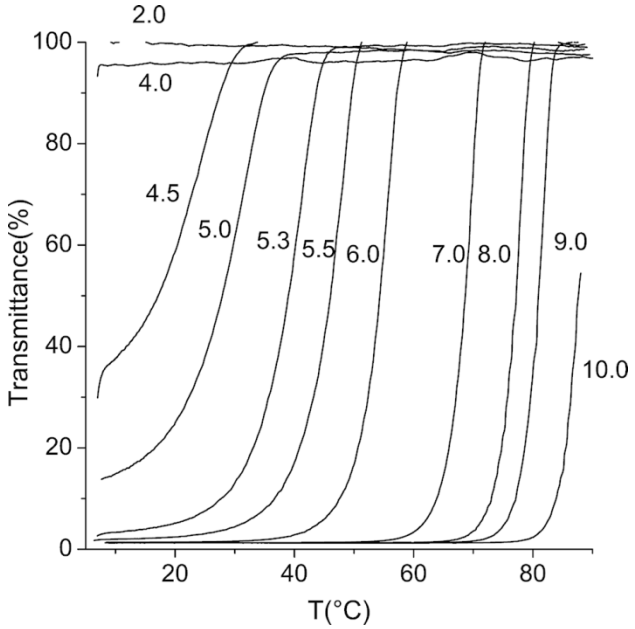

Figure S7. Cooling curves for PAMPTMA-1 as 1 mg/mL solution in 100 mM NaCl with various concentrations of $LiNTf_2$ (written as mM next to the curves).

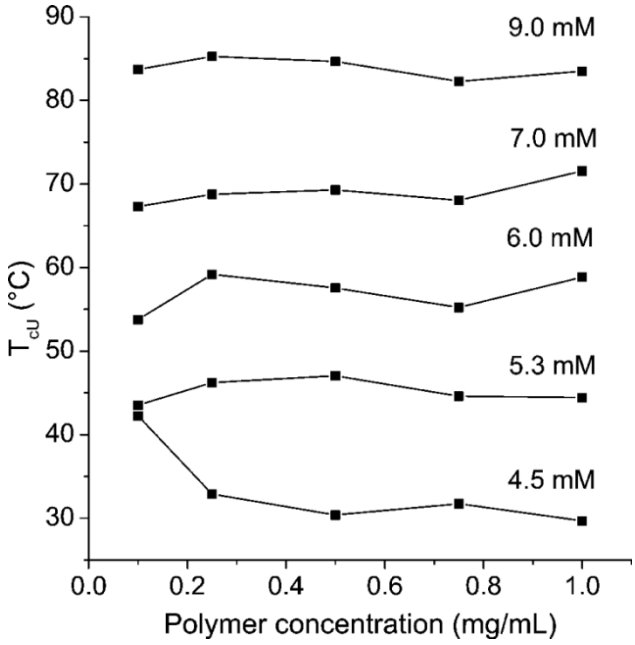

Figure S8. TcU of PAMPTMA in 100 mM NaCl with various concentrations of LiNTf2 as a function of polymer concentration. The $LiNTf_2$ concentration is given above each series.

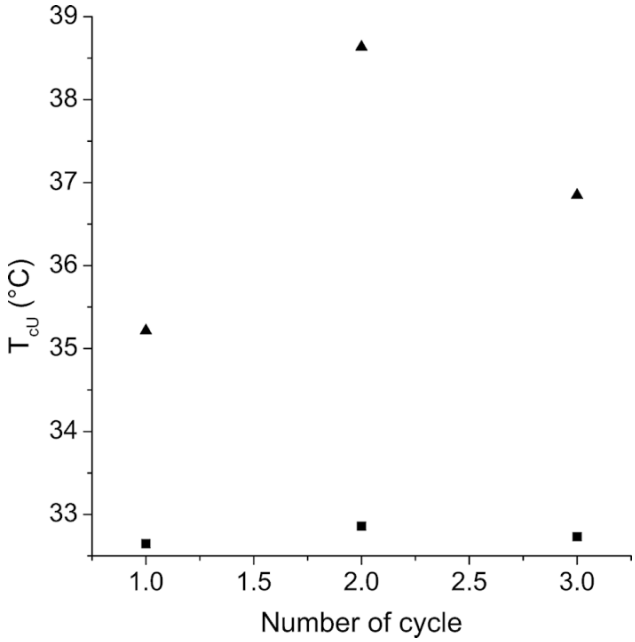

Figure S9. T_{cU} on both cooling (■) and heating (▲) of PAMPTMA-1 in 500 mM NaCl with 10 mM $LiNTf_2$ over three cycles. The measurement has been started with cooling.

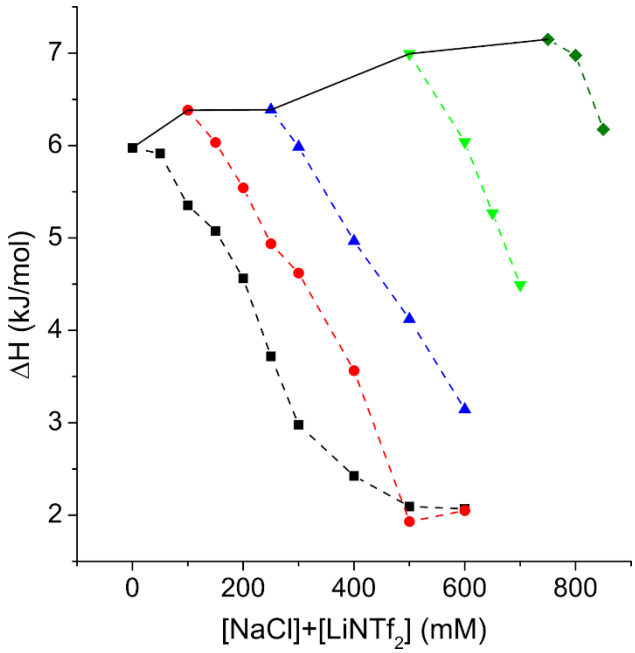

Figure S10. ΔH as function of total concentration of salts for 1 mg/mL PNIPAM-1 solutions containing LiNTf2 with no added NaCl (■), with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼) and with 750 mM NaCl (♦). The solid black line connects the points with only NaCl as the added salt.

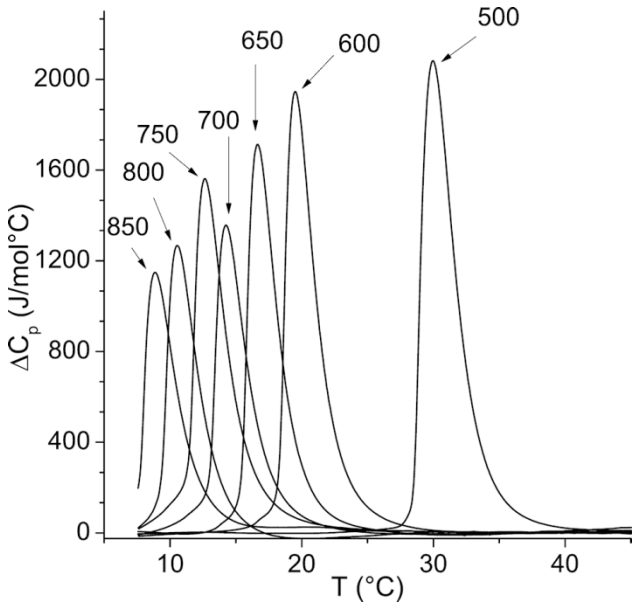

Figure S11. The micro-DSC-thermograms for the PNIPAm-1-series with 500 mM NaCl. The total concentration of salts is marked as mM to each peak.

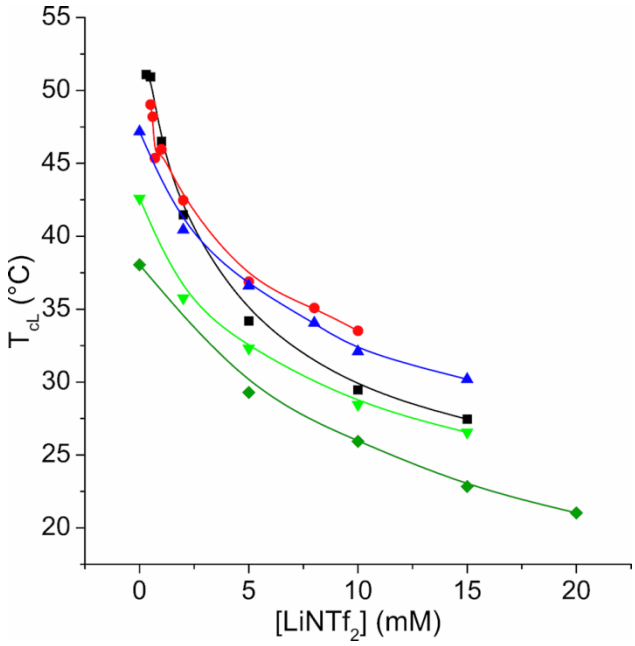

Figure S12. T_{cL} of CP-8 as a function of $LiNTf_2$-concentration with no added NaCl (■), with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼), and with 750 mM NaCl (♦). The lines are to guide the eye.

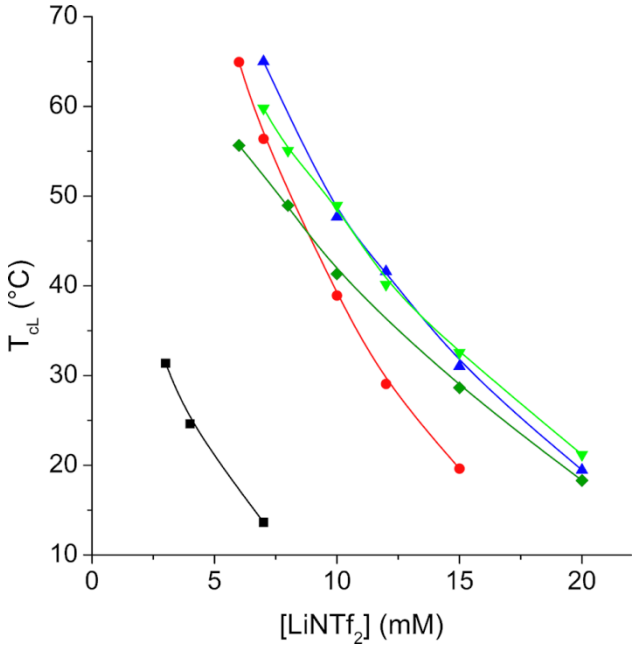

Figure S13. T_{cL} of 1 mg/mL solution of CP-26 as a function of $LiNTf_2$-concentration with no added NaCl (■), with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼), and with 750 mM NaCl (♦). The lines are to guide the eye.

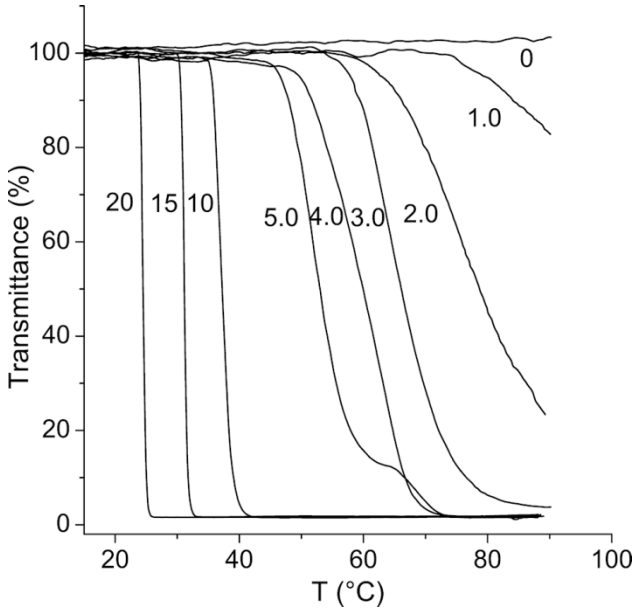

Figure S14. Transmittance as a function of temperature for 1 mg/mL CP-8-solutions with different amounts of $LiNTf_2$ and with 500 mM NaCl. $LiNTf_2$ concetration is written next to each curve.

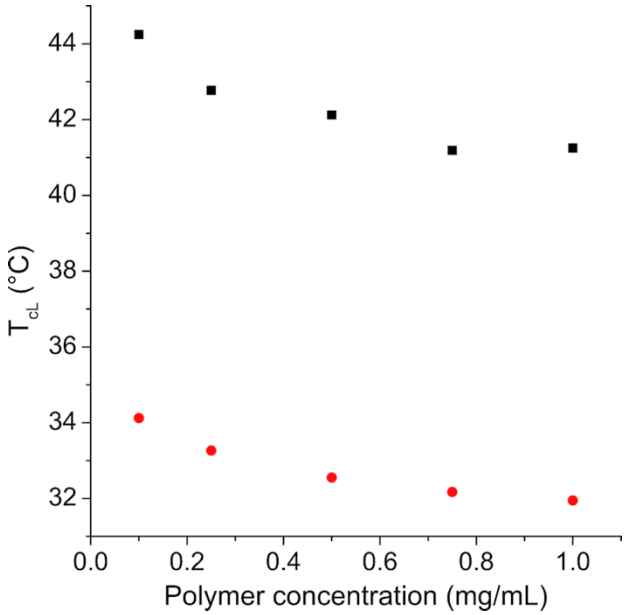

Figure S15. T_{cL} as a function of polymer concentration for CP-8 in 2 mM $LiNTf_2$ without NaCl (■) and for copolymer 8 in 250 mM NaCl with 10 mM $LiNTf_2$ (●).

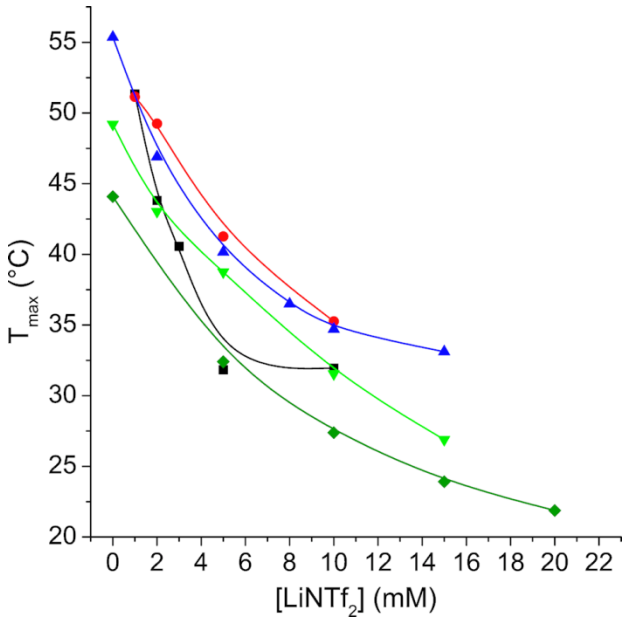

Figure S16. T_{max} of 1 mg/mL solution of CP-8 as a function of $LiNTf_2$-concentration with no added NaCl (■), with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼), and with 750 mM NaCl (♦). The lines are to guide the eye.

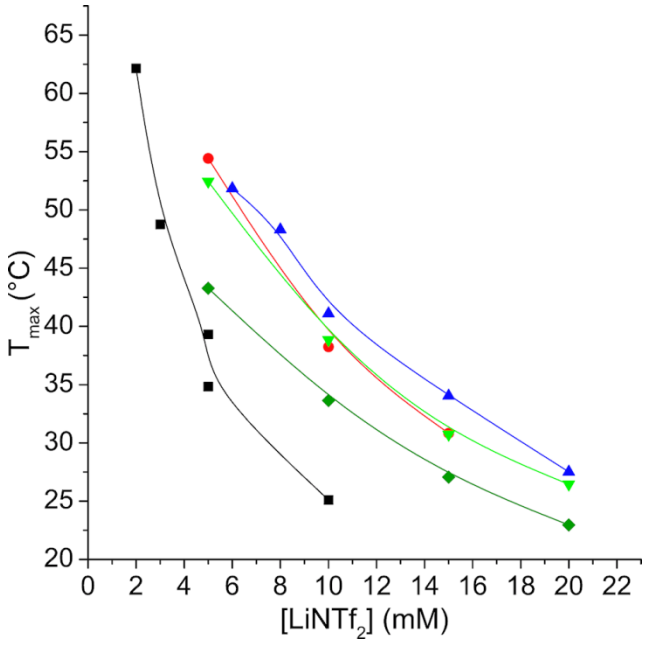

Figure S17. T_{max} of 1 mg/mL solution of CP-17 as a function of $LiNTf_2$-concentration with no added NaCl (■), with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼), and with 750 mM NaCl (♦). The lines are to guide the eye.

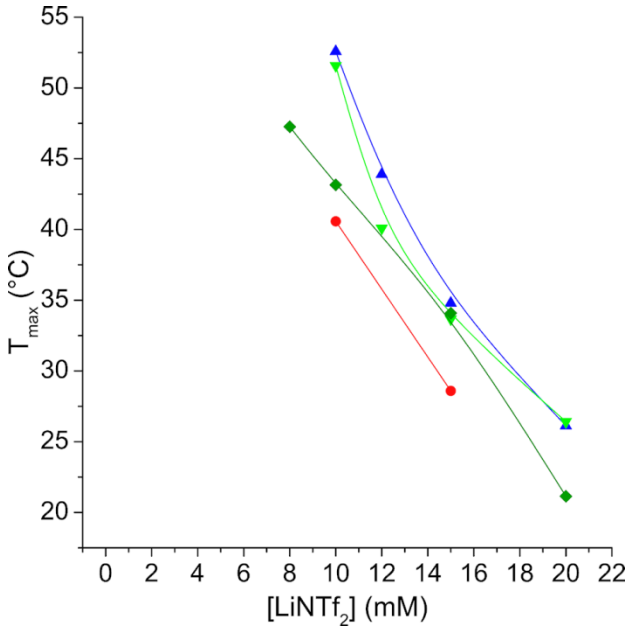

Figure S18. T_{max} of 1 mg/mL solution of CP-26 as a function of $LiNTf_2$-concentration with 100 mM NaCl (●), with 250 mM NaCl (▲), with 500 mM NaCl (▼), and with 750 mM NaCl (♦). The lines are to guide the eye.

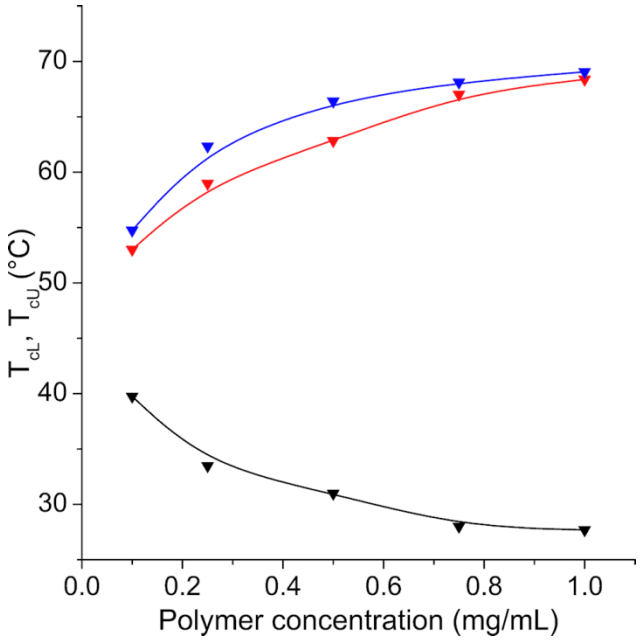

Figure S19. TcL (**black**), TcU on heating (**red**) and TcU on cooling (**blue**) for copolymer 46 in 500 mM NaCl with 14 mM $LiNTf_2$. The lines are to guide the eye.

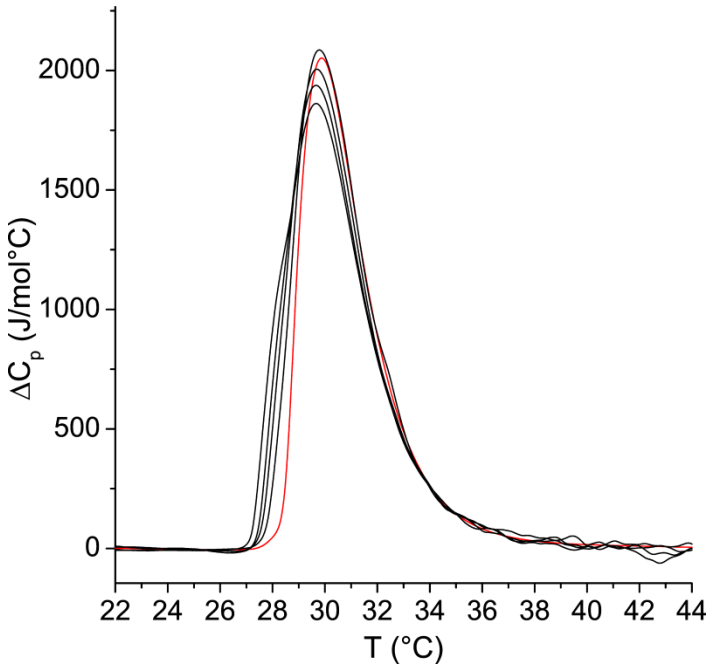

Figure S20. Micro-DSC-thermograms of PNIPAm-1 in 500 mM NaCl. The red line shows the initial measurement. The stabilization times between the measurements for the black lines in the order of increasing onset of the peak: 4 hour, 8 hours, 12 hours, and 16 hours. All the thermograms are from heating runs.

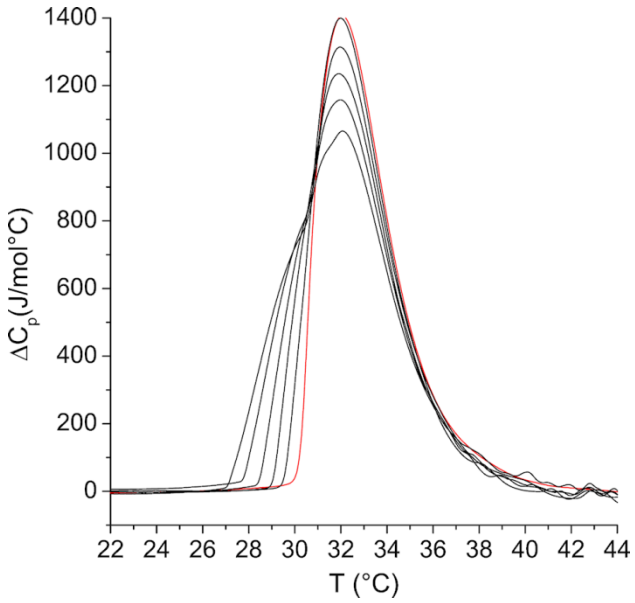

Figure S21. Micro-DSC-thermograms of CP-8 in 10 mM $LiNTf_2$ with no NaCl. The red line shows the initial measurement. The stabilization times between the measurements for the black lines in the order of increasing onset of the peak: 1 hour, 2 hours, 4 hours, 8 hours, and 12 hours. All the thermograms are from heating runs.

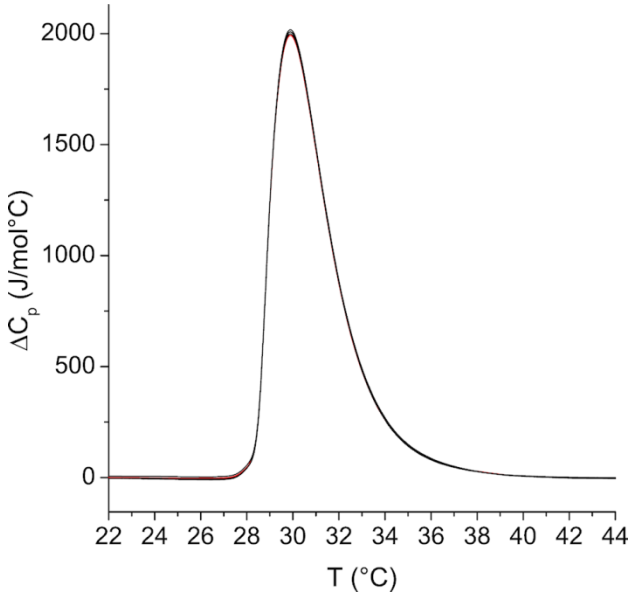

Figure S22. Micro-DSC-thermograms of PNIPAm-1 in 500 mM NaCl with fast cooling. The red line shows the initial measurement. The black lines show measurements with stabilization time of 4 hours, 8 hours, and 12 hours between the measurements. All the thermograms are from heating runs.

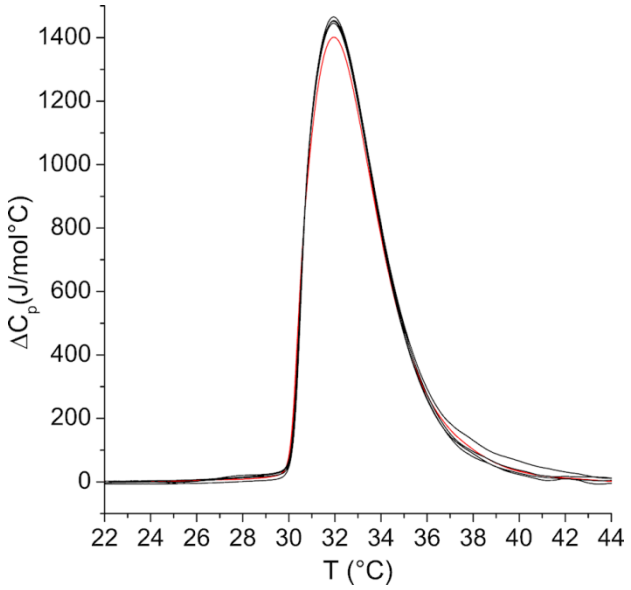

Figure S23. Micro-DSC-thermograms of CP-8 in 10 mM $LiNTf_2$ with no NaCl and with fast cooling. The red line shows the initial measurement. The black lines show measurements with stabilization time of 1 hour, 2 hours, 4 hours, and 8 hours between the measurements. All the thermograms are from heating runs.

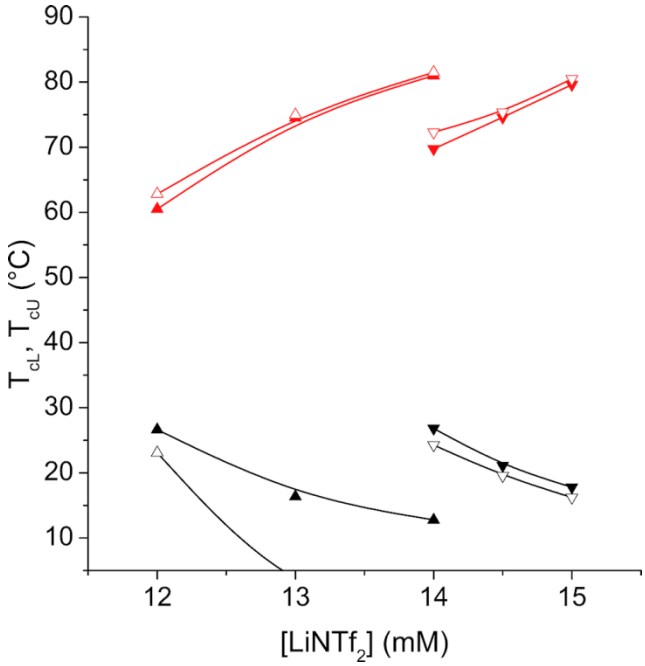

Figure S24. T_{cL} (**black**) and T_{cU} on heating (**red**) as a function of $LiNTf_2$-concentration for CP-46 in 250 mM NaCl (▲) and 500 mM NaCl (▼). After the initial measurement (filled symbols) the samples have been quickly cooled back to 5 °C and the measurement has been repeated (open symbols). The lines are to guide the eye.