Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information

Self-assembly of oppositely charged polylectrolyte block copolymers containing short thermoresponsive blocks

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1D NMR spectra of purified polymers

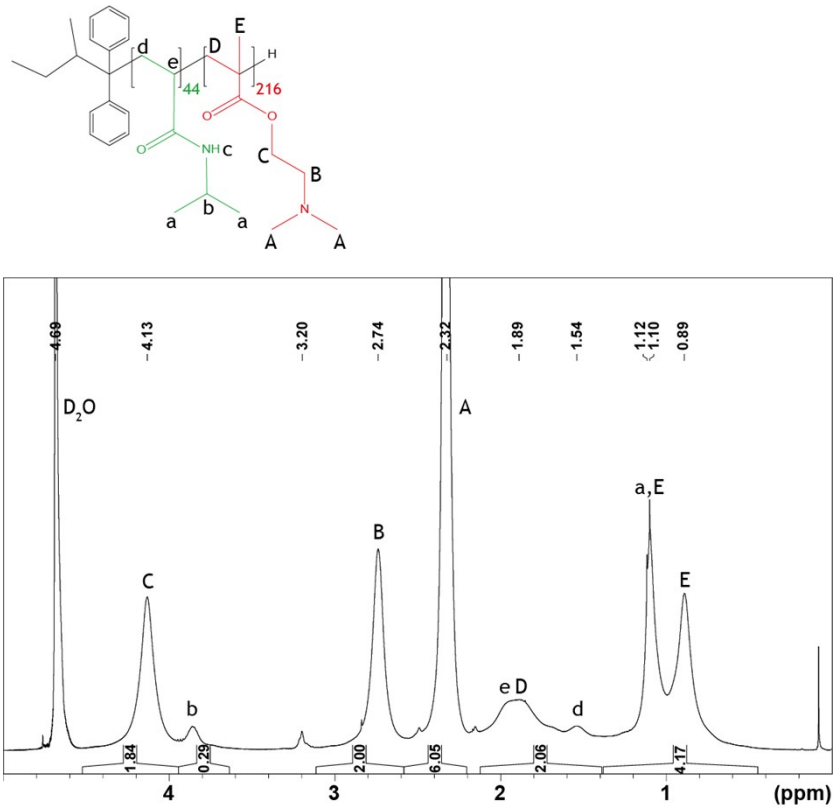

Figure 1 ^{1}H-NMR spectrum of PNIPAM-*b*-PDMAEMA, purchased from Polymer Source Ltd, in D_2O. As provided by the supplier; M_n 38.2 kDa, PDI 1.05.

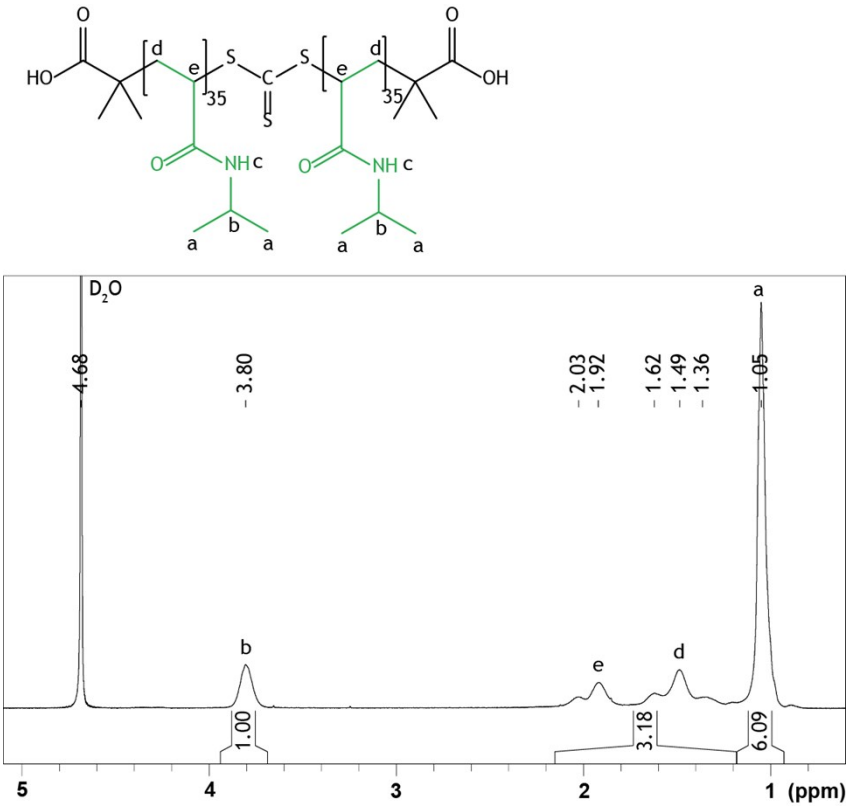

Figure 2 ^{1}H-NMR spectrum of the PNIPAM precursor used to synthesize PNIPAM-*b*-PAA-*b*-PNIPAM, measured in D_2O.

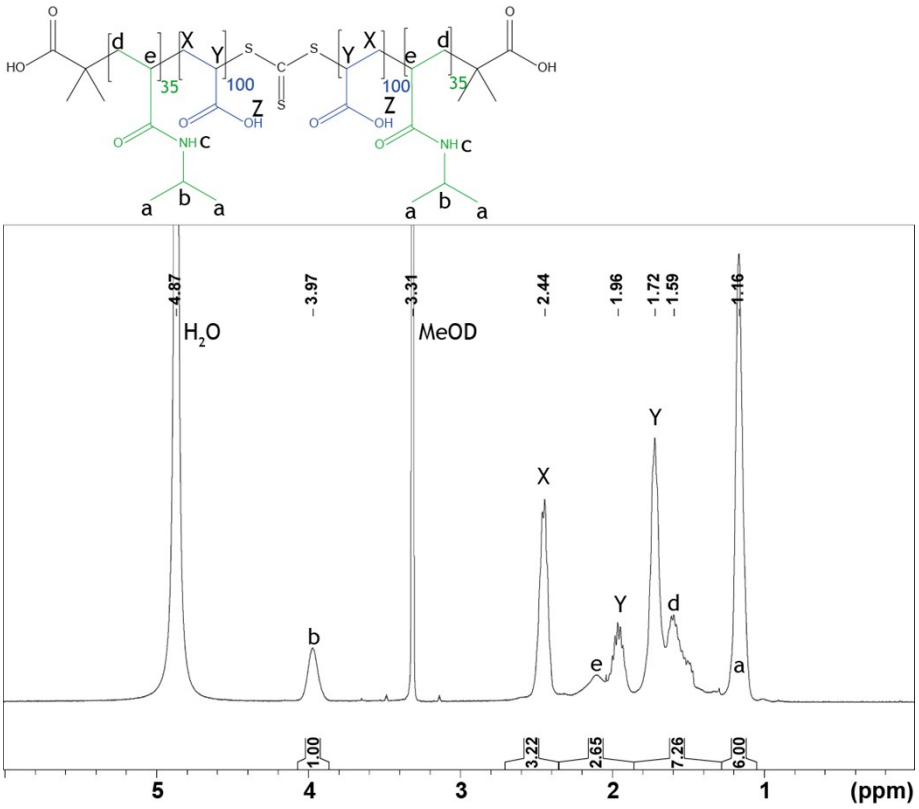

Figure 3 ^{1}H-NMR spectrum of PNIPAM-*b*-PAA-*b*-PNIPAM after deprotection in HFIP, measured in MeOD.

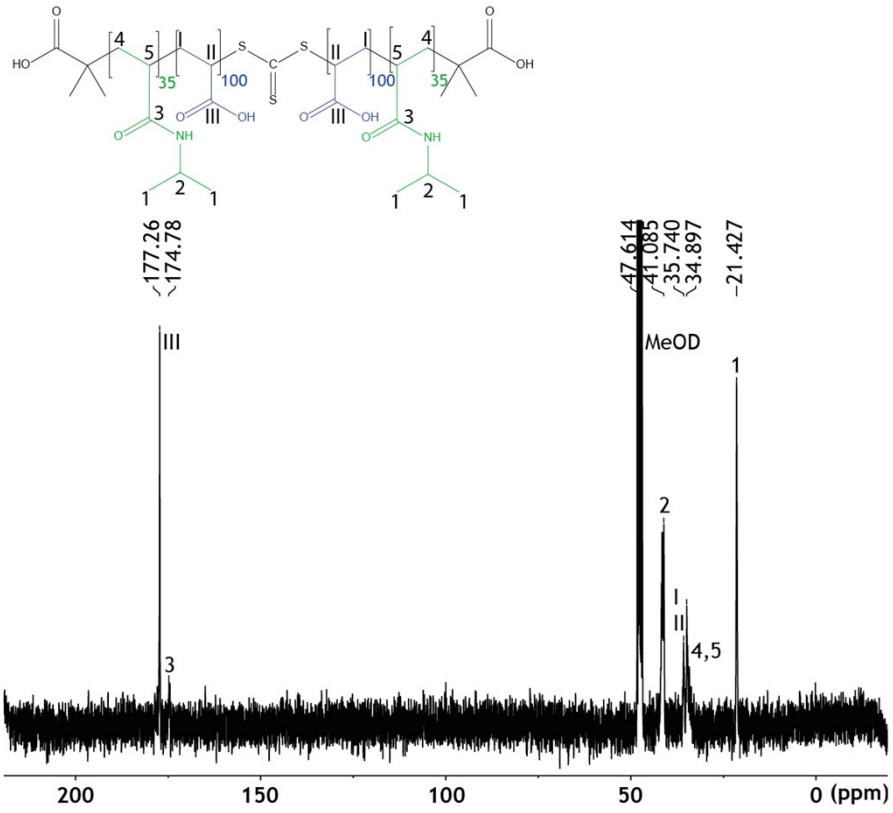

Figure 4 ^{13}C-NMR spectrum of NIPAM-*b*-AA-*b*-NIPAM after deprotection in HFIP, measured in MeOD. A clear carboxylic acid peak can be observed at 177 ppm, while tert-butyl is absent as it normally appears around 28 ppm.

COSY NMR spectra of purified polymers in D_2O

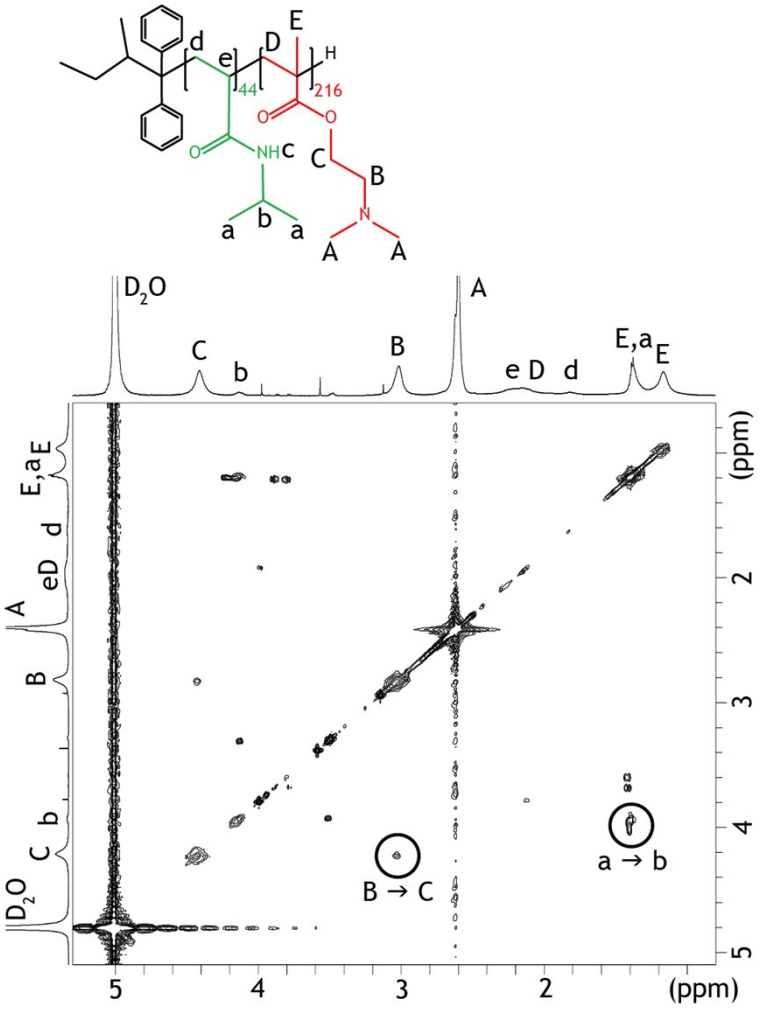

Figure 5 COSY spectrum of PNIPAM-*b*-PDMAEMA in D_2O. Two clear cross-peaks are observed, the first shows the ethyl group in the DMAEMA side chain, while the second shows the propyl group of the PNIPAM. Other cross-peaks are assigned to small impurities in the sample. As the backbone peaks have a relatively low intensity, cross-peaks cannot be observed.

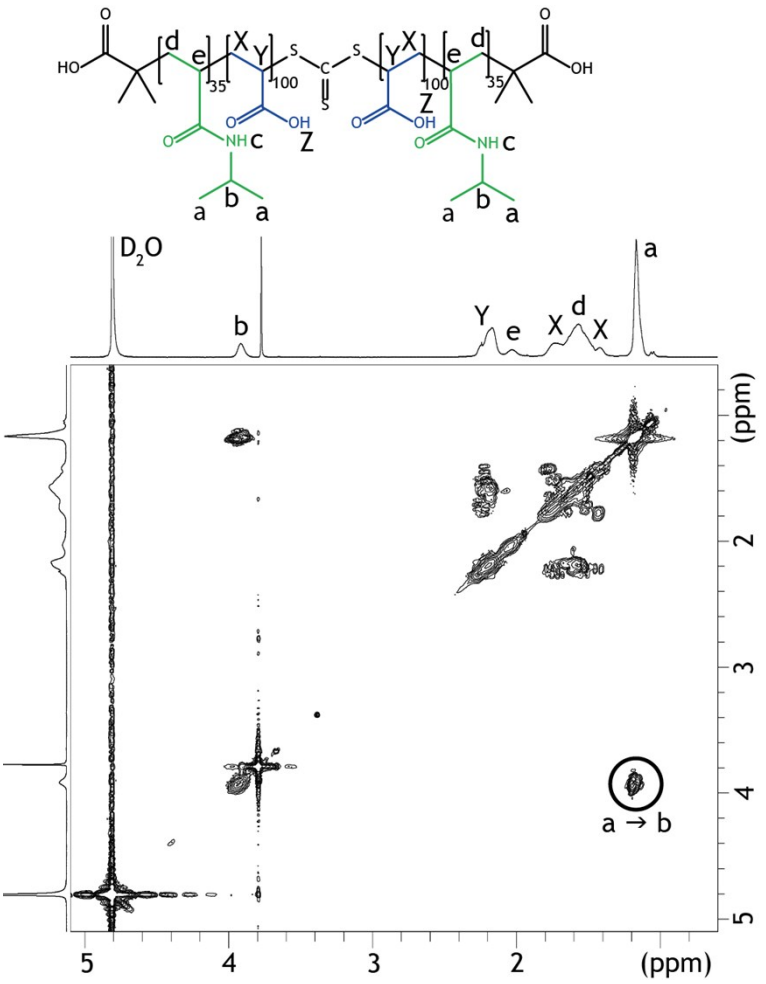

Figure 6 COSY spectrum of PNIPAM-*b*-PAA-*b*-PNIPAM in D_2O. Only one clear cross-peak is observed, that shows the propyl group of the PNIPAM. As the backbone peaks of the PNIPAM have a relatively low intensity, cross-peaks cannot be observed.

Zeta potential measurements

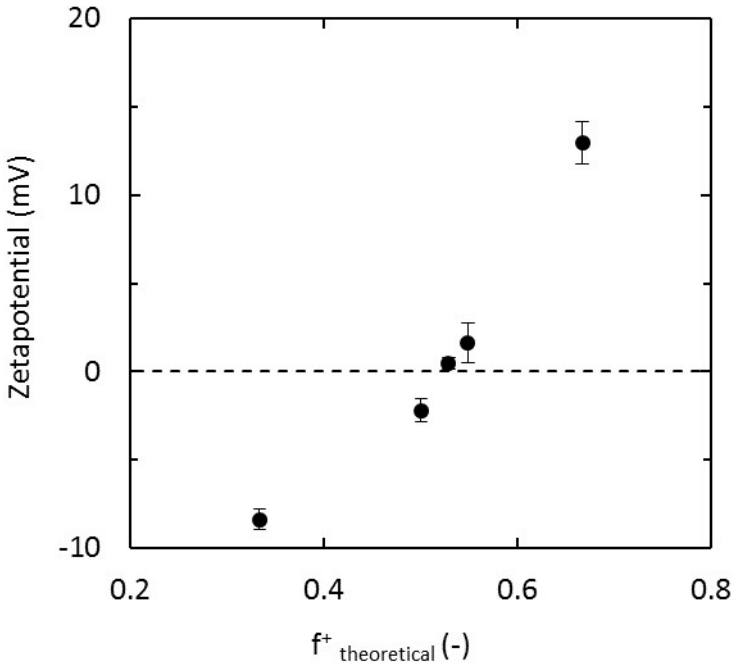

Figure 7 Representative determination of equal charge by zeta potential determination, based on the charge fraction f^+. Using $f^+ = \frac{n^+}{n^+ + n^-}$, with n^+ being the number of cationic monomers and n^- the number of anionic monomers present in solution. For every new combination of stock solutions, the fraction of equal charge has to be determined.

Light scattering

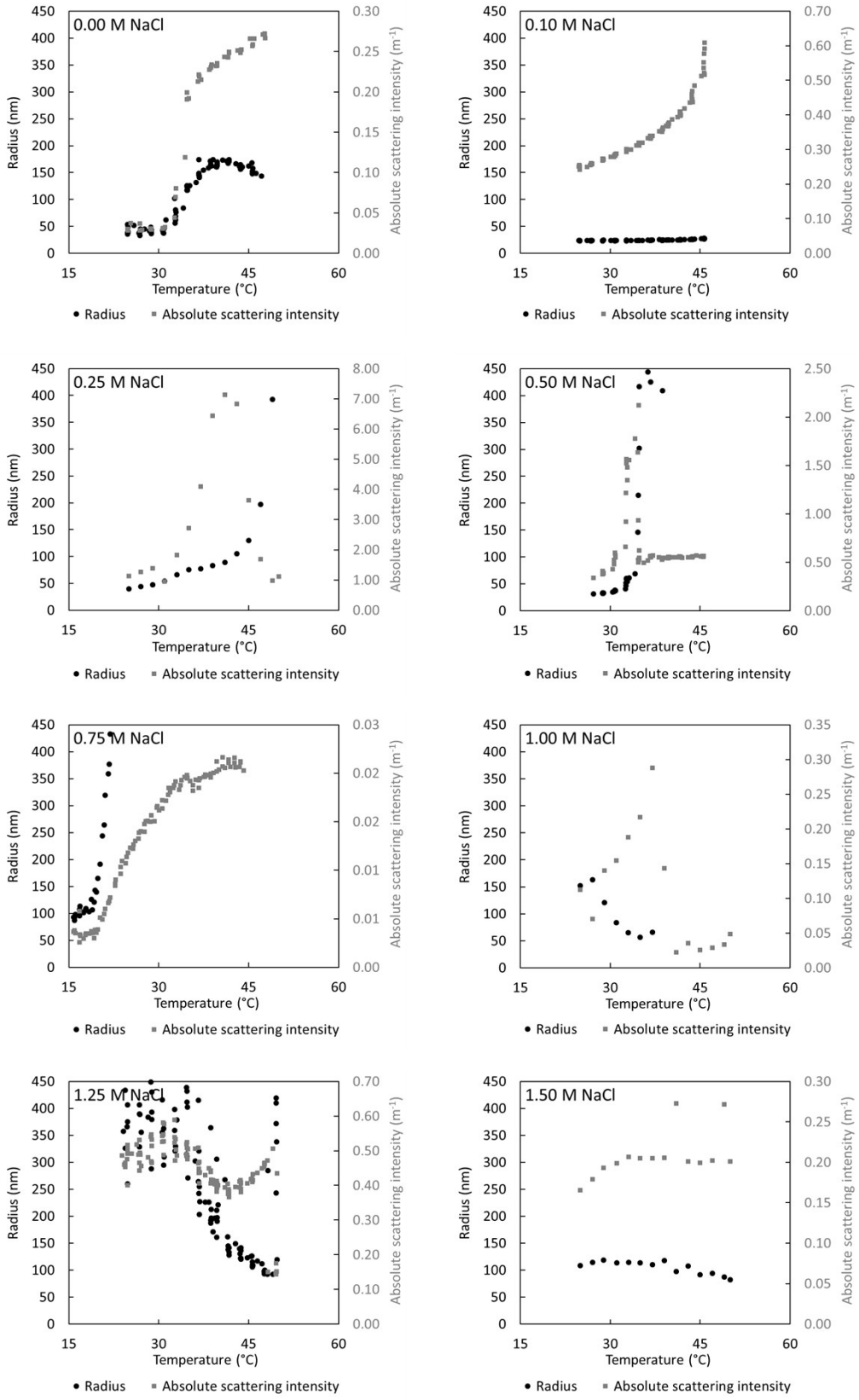

Figure 8 Overview of dynamic light scattering results of charge balanced polymer solutions, containing varying concentrations of NaCl, measured while the temperature was increased with 2°C per 10 minutes. The data points shown are averages of 5 measurements for the 0.00, 0.10, 0.50, 0.75 and 1.25 M NaCl samples. Samples of 0.25, 1.00 and 1.50 M NaCl were measured on the Malvern Zetasizer Nano ZS and are averages of three consecutive measurements existing of multiple data points.

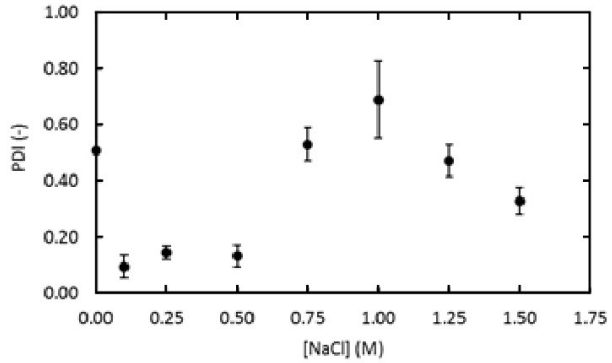

Figure 9 Overview of the PDI values below LCST as measured by DLS and calculated using ALV-7004 Correlator software or using Zetasizer software (version 7.02, Malvern Instruments, U.K.) using the second cumulant. For the samples containing 0.10, 0.25 and 0.50 M NaCl, narrow PDI values, comparable to values found in literature., were observed.[1, 2] From this, it can be concluded that the radii for these can be used as realistic values for the objects present in solution below LCST. Also, for these samples at low salt monomodal decorrelation curves have been observed using CONTIN. However, the variation in radii of the other samples is too high to determine the objects sizes from these values. Therefore, only qualitative comparisons are made. Additionally, multimodal decorrelation curves have been observed for CONTIN analysis, meaning that objects with multiple sizes are present in solution and therefore the value for the radius from the ALV software cannot be used. Error bars show the standard deviation from the calculated average PDI of all measurements below LCST.

Figure 10 Picture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM at 1 wt% in 0.5 M NaCl at 50°C. As a result of the elevated temperature, a white concentrated phase coexists with a dilute solvent phase. The solid phase sticks to the bottom of the tube when the tube is inverted.

^{1}H NMR spectra in deuterated salt solutions

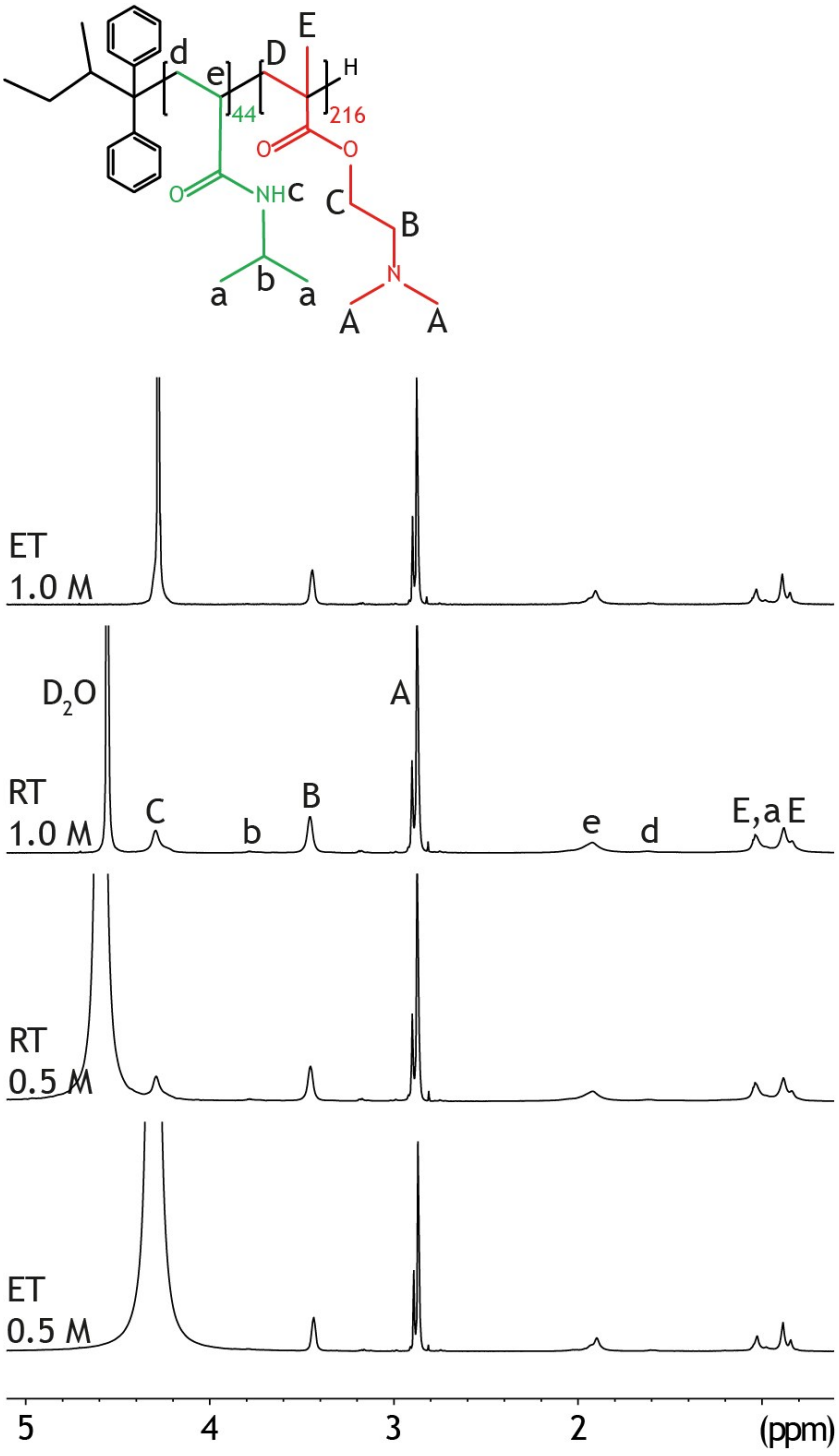

Figure 11 ^{1}H NMR in 0.5 M and 1.0 M NaCl at room temperature (RT) and 67°C (ET) of NIPAM-*b*-DMAEMA. The peak intensities are normalized by the intensity of DMAEMA, peak A. Due to storage of the samples water was attracted by the samples. This effect was more severe for the 0.5 M NaCl sample than for the 1.0 M NaCl sample, causing a broader solvent peak at low salt. Increasing temperature causes minor differences in the NIPAM peaks. When comparing to the polymer mixtures, peak broadening can be observed at 2.9 ppm for the DMAEMA side group, and between 2.1 and 1.7 ppm for the backbone area in the spectrum of the mixture, MT Figure 3.

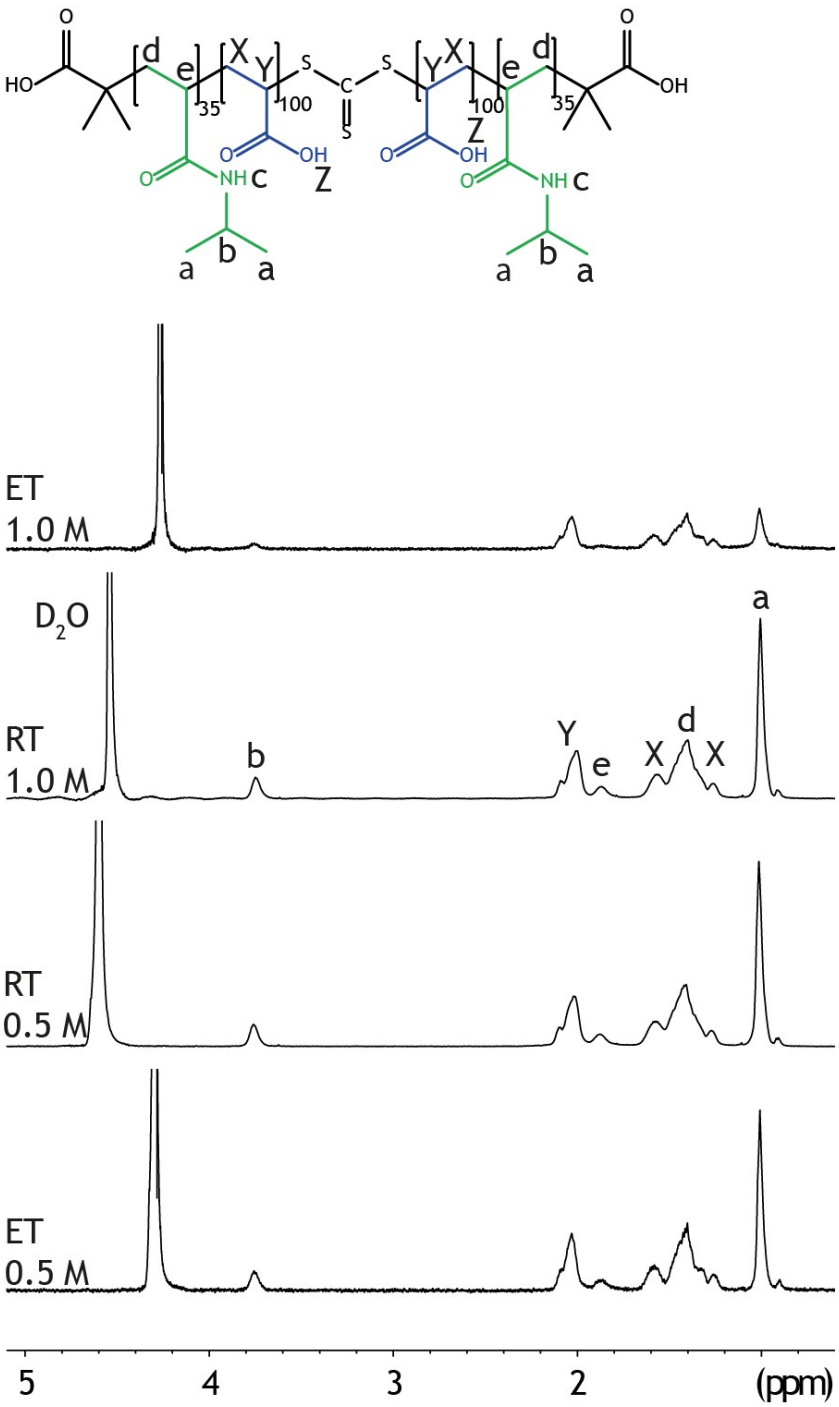

Figure 12 ^{1}H NMR in 0.5 M and 1.0 M NaCl at room temperature (RT) and 67°C (ET) of NIPAM-*b*-AA-*b*-NIPAM. The peak intensities are normalized by the area of the solvent peak. Increasing temperature results in decreasing peak intensities for peaks at 1.0 M NaCl. When comparing to the polymer mixtures, peak broadening can be observed between 2.1 and 1.2 ppm for the backbone area in the spectrum of the mixture, MT figure 3.

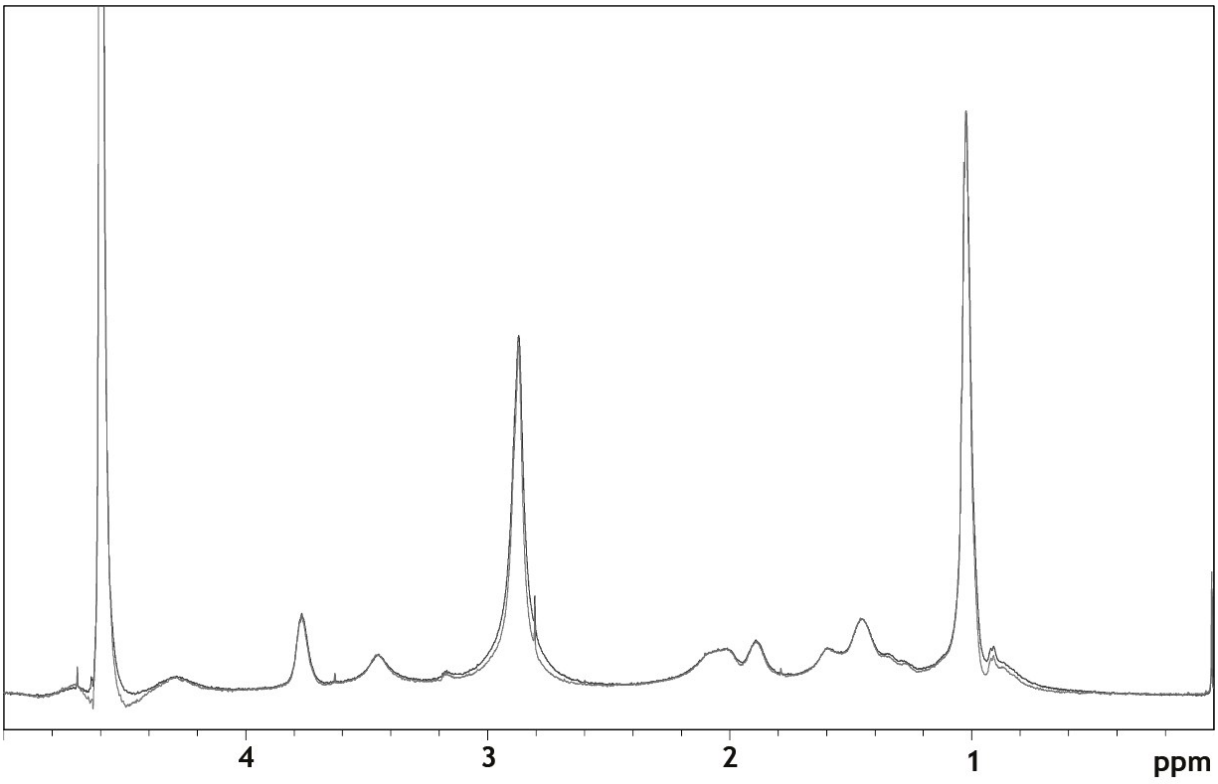

Figure 13 ^{1}H-NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 0.5 M NaCl at room temperature, before (dark grey) and after (light grey) heating. Both spectra largely overlap, showing the full reversibility of the system

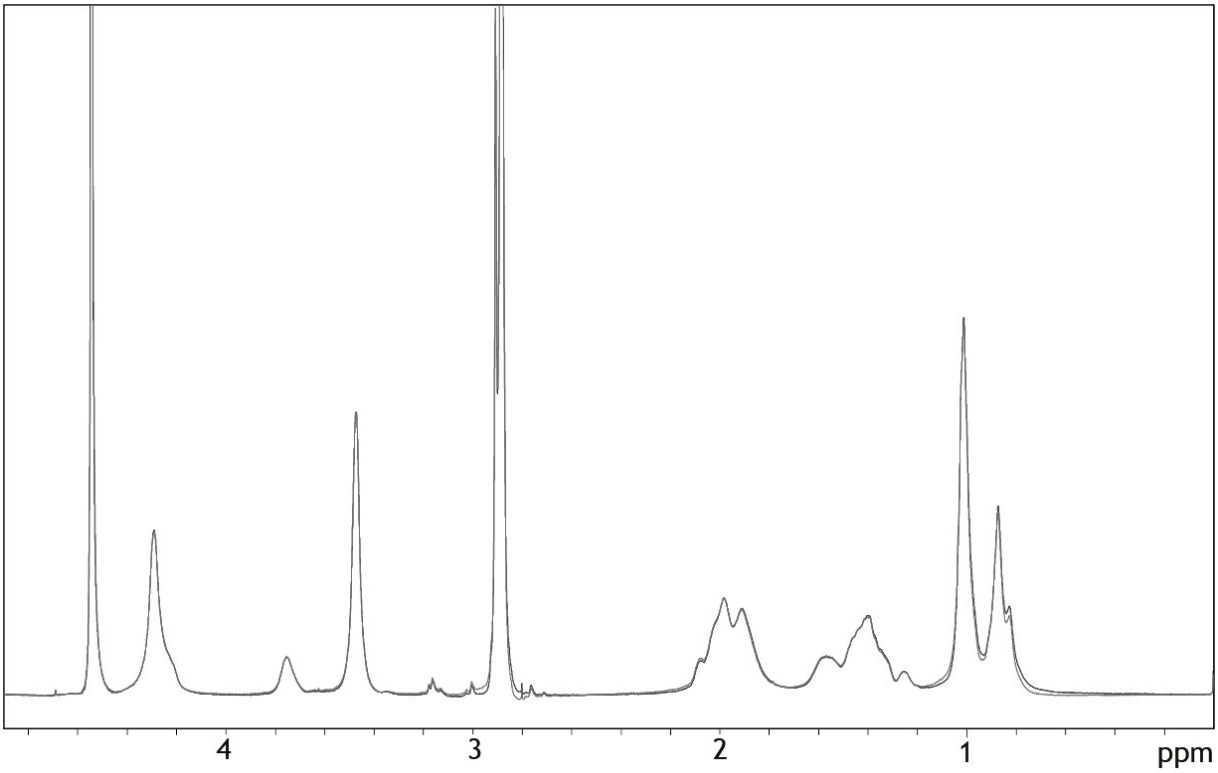

Figure 14 ^{1}H-NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 1.0 M NaCl at room temperature, before (dark grey) and after (light grey) heating. Both spectra largely overlap, showing the full reversibility of the system.

NOESY NMR spectra in deuterated salt solutions

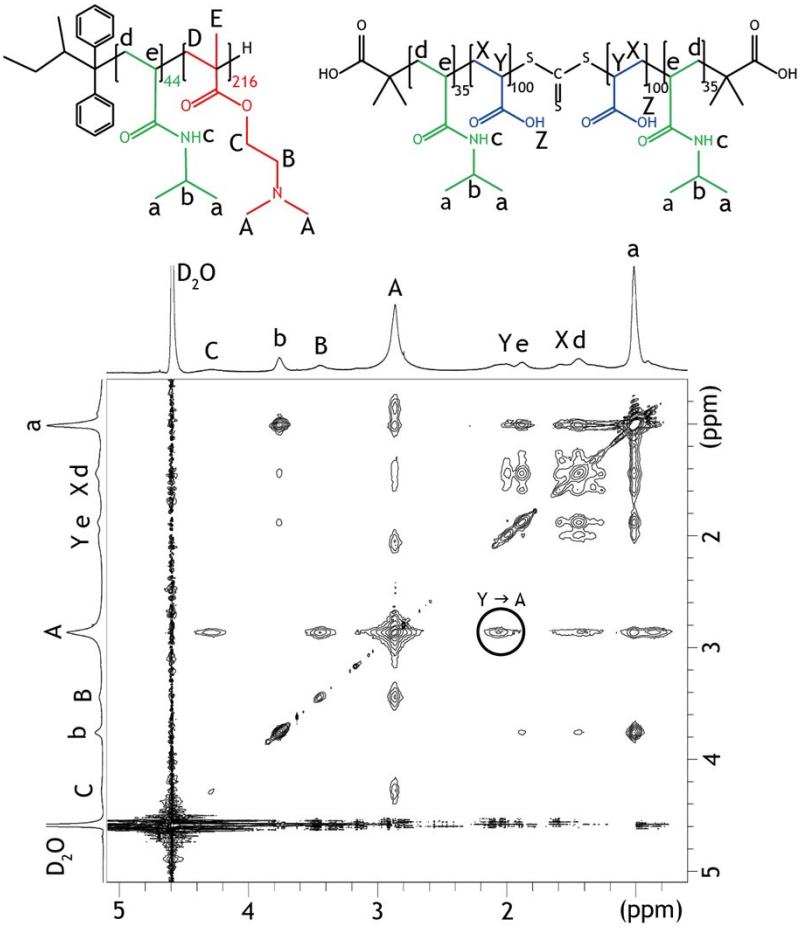

Figure 15 NOESY NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 0.5 M NaCl at room temperature. A cross-peak between the blocks is present between PAA and PDMAEMA (black circle).

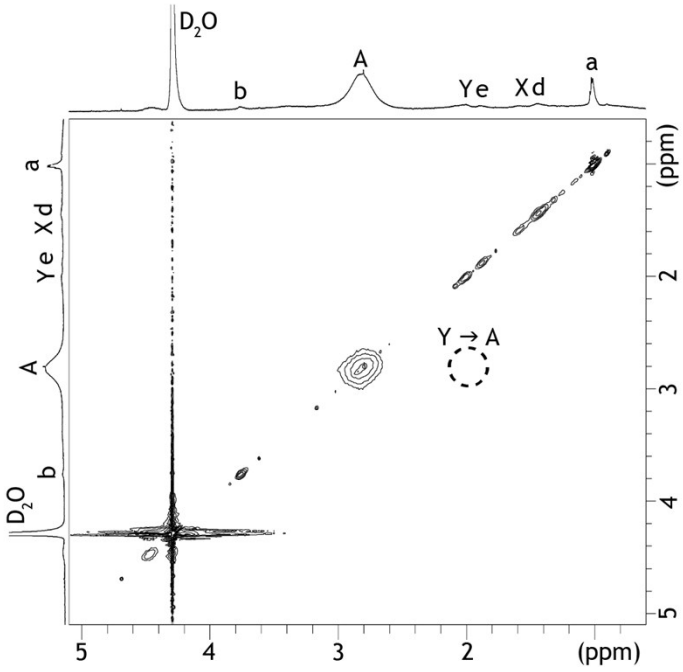

Figure 16 NOESY NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 0.5 M NaCl at 67°C. Cross-peaks between the blocks are absent.

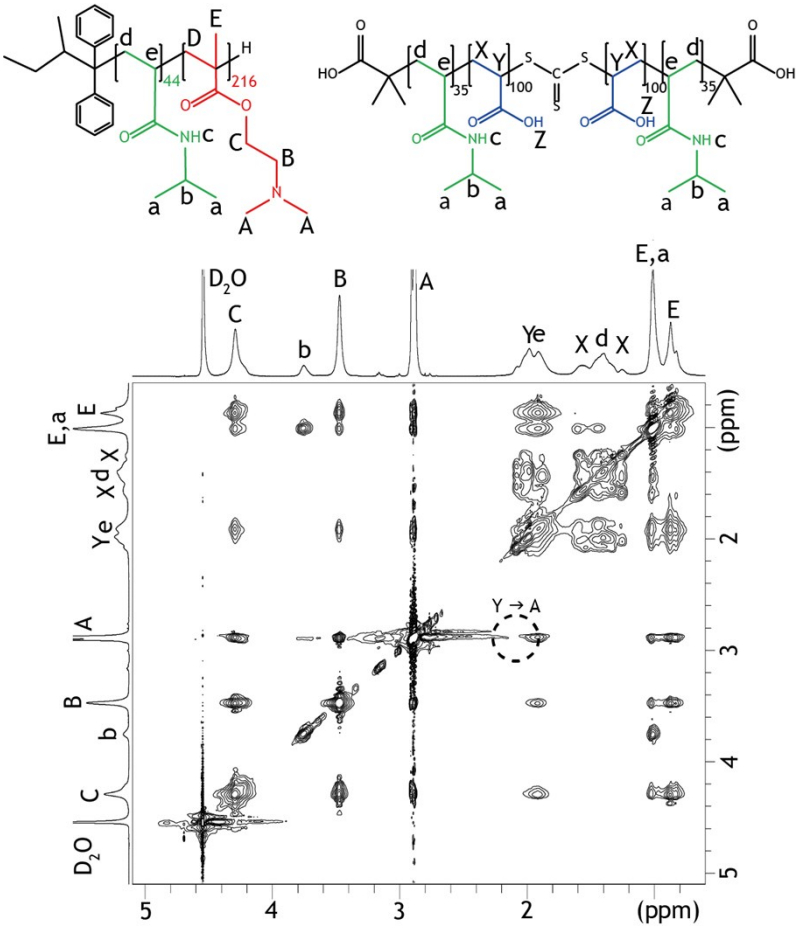

Figure 17 NOESY NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 1.0 M NaCl at RT. Cross-peaks between the blocks are absent.

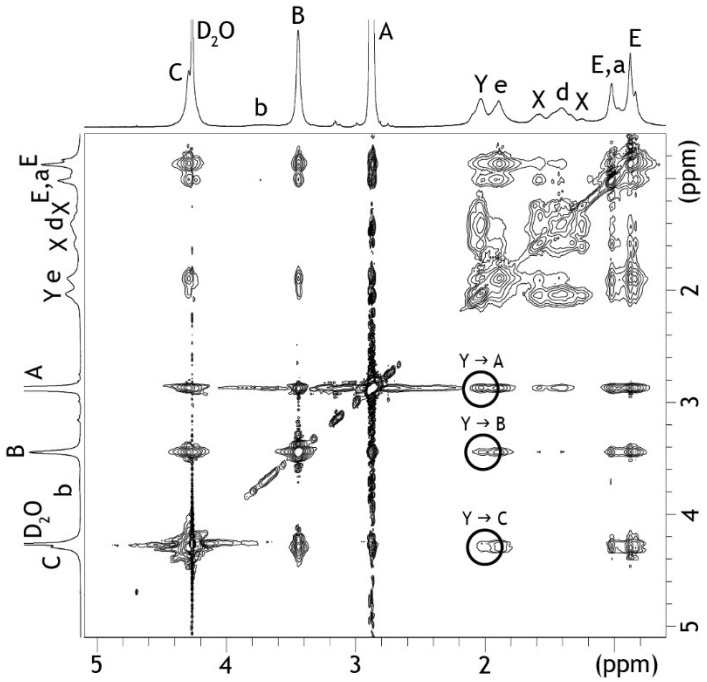

Figure 18 NOESY NMR of the mixture of PNIPAM-*b*-PDMAEMA and PNIPAM-*b*-PAA-*b*-PNIPAM in 1.0 M NaCl at 67°C. Cross-peaks between the polyelectrolytes blocks are present.

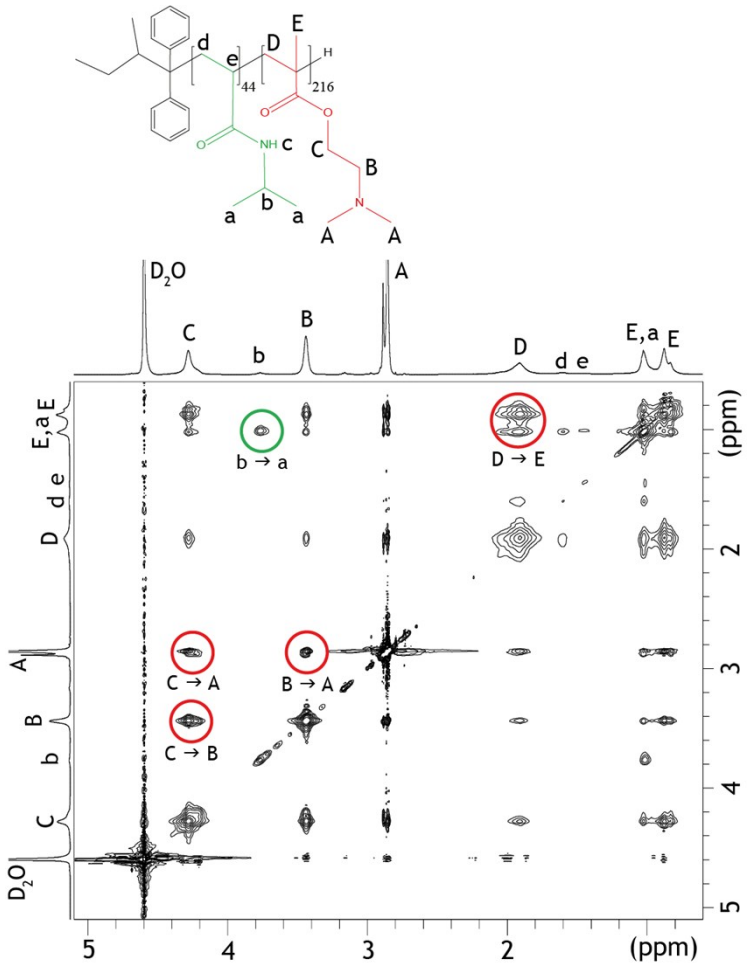

Figure 19 NOESY NMR of PNIPAM-*b*-PDMAEMA in 0.5 M NaCl at room temperature. Cross-peaks can be observed between the DMAEMA peaks (red circles) e.g. at 1.9;0.9, 1.9;2.9, 1.9;3.4 and 1.9;4.3 ppm, or between the NIPAM peaks (green circle) at 1.0;3.8 ppm.

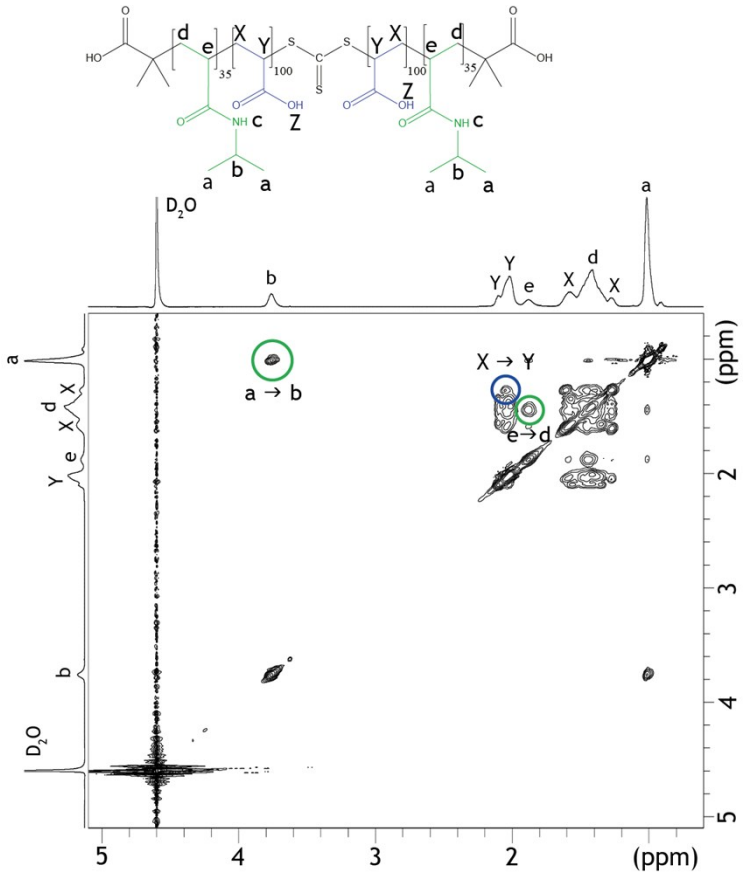

Figure 20 NOESY NMR of PNIPAM-*b*-PAA-*b*-PNIPAM in 0.5 M NaCl at room temperature. Two cross-peaks between the PNIPAM compounds (green circles) are present in the spectrum at 1.0;3.8 and 1.9;3.8 ppm. A cross-peak between PAA and PNIPAM (black circle) can be found at 1.4;3.8 ppm.

PNIPAM solubility

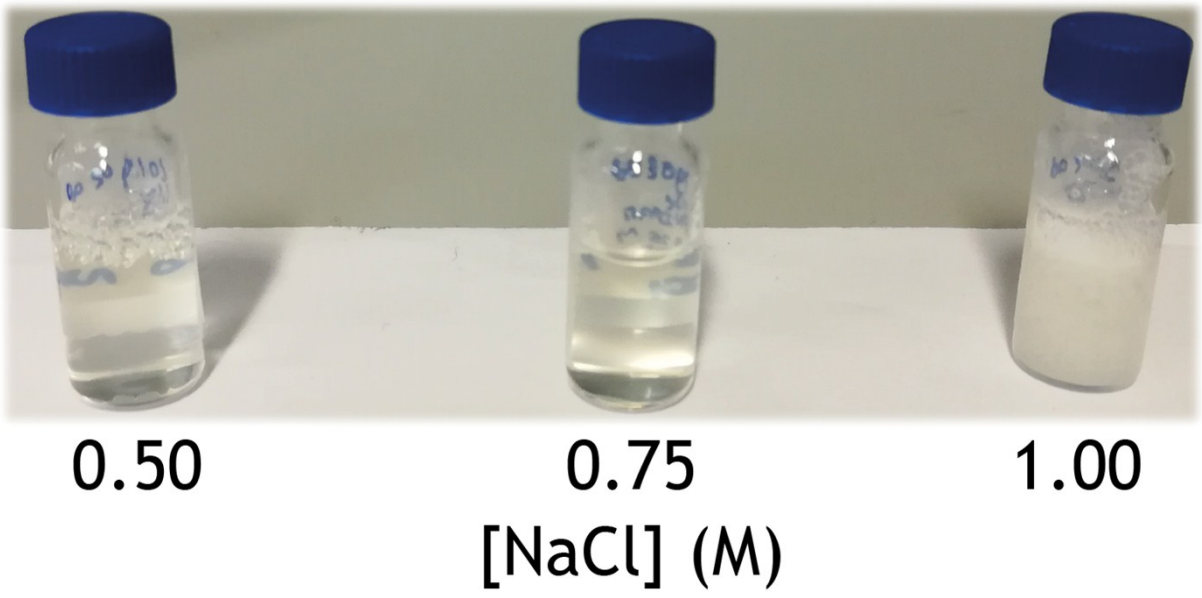

Figure 21 Solubility of 1 wt% PNIPAM, which was used as precursor to synthesize PNIPAM-*b*-PAA-*b*-PNIPAM, in NaCl solutions with changing concentrations. At 0.50 and 0.75 M NaCl clear solutions are observed, while at 1.00 M NaCl turbidity is seen. This indicates that the PNIPAM is soluble at 0.50 and 0.75 M NaCl, but insoluble at 1.00 M NaCl. At the moment the picture was taken, the temperature in the room was 19°C.

References

1. J. S. Park, Y. Akiyama, Y. Yamasaki and K. Kataoka, *Langmuir*, 2007, **23**, 138-146.
2. H. Dautzenberg, Y. B. Gao and M. Hahn, *Langmuir*, 2000, **16**, 9070-9081.