

Electronic Supplementary Information

Temperature- and CO₂ Responsive Polyethylenimine for Highly Efficient Carbon Dioxide Release[†]

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Materials and methods

Materials

Chemicals were purchased from Sigma Aldrich or Acros Organics and used without further purification unless stated otherwise. Branched polyethylenimine (*b*-PEI) ($M_n = 10\,000$ g/mol and $M_w = 25\,000$ g/mol) was obtained from Sigma-Aldrich. NMR spectra were recorded on a Bruker ARX-300 or AV-500C spectrometer. ^1H and ^{13}C NMR chemical shifts δ are reported in ppm relative to tetramethylsilane and calibrated by the residual proton signal of the deuterated solvent. Deuterated solvents were obtained from Euroisotop.

Synthesis of *N*-acylated polyethylenimine

b-PEI (30 g; 684 mmol of total amine residues¹) was dissolved in 600 mL of methanol. The solution was cooled with an ice bath and 0.75eq. or 1.0 eq. of Triethylamine and butyric anhydride (moles of anhydride / moles of reactive amines in *b*-PEI) were added dropwise under rapid stirring to achieve thermosensitive behaviour. During the acylation reaction, the same molar equivalent of Triethylamine relative to the anhydride was used in order to quench the protons. The reaction mixture was subsequently stirred overnight at room temperature.

nBu-PEI-0.75 and nBu-PEI-1.0 were purified by precipitation in 1.5 L of diethyl ether. After the precipitation the polymer was dissolved in 100 mL of methanol. The described procedure of precipitation was repeated two times and then methanol was removed under vacuum. The final acylated polymer was obtained as yellow high viscous gel. The reaction equation is given in Figure S1.

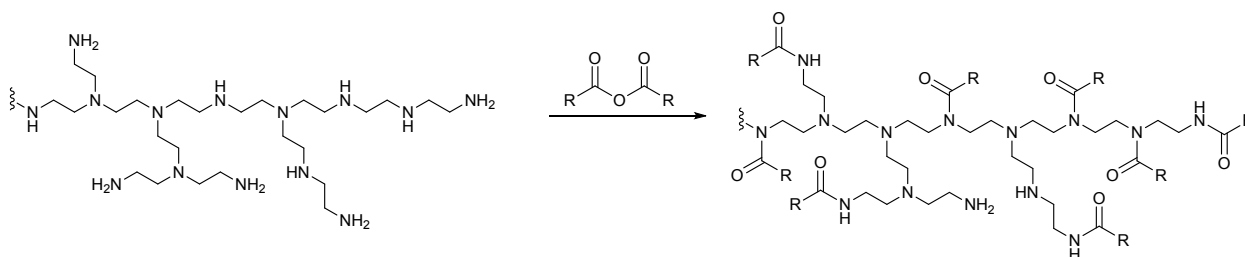


Fig. S1 Acylation of branched Polyethylenimine with butyric anhydride. $R = \text{CH}_2\text{CH}_2\text{CH}_3$

Before the acylation of branched Polyethylenimine ^1H - and ^{13}C - NMR spectra were recorded of the purchased *b*-PEI from Sigma Aldrich. The results are shown in Figure S2 and S3 together with the assignment of the chemical shifts. These data are in agreement with recently published data from *Holycross et al.*²

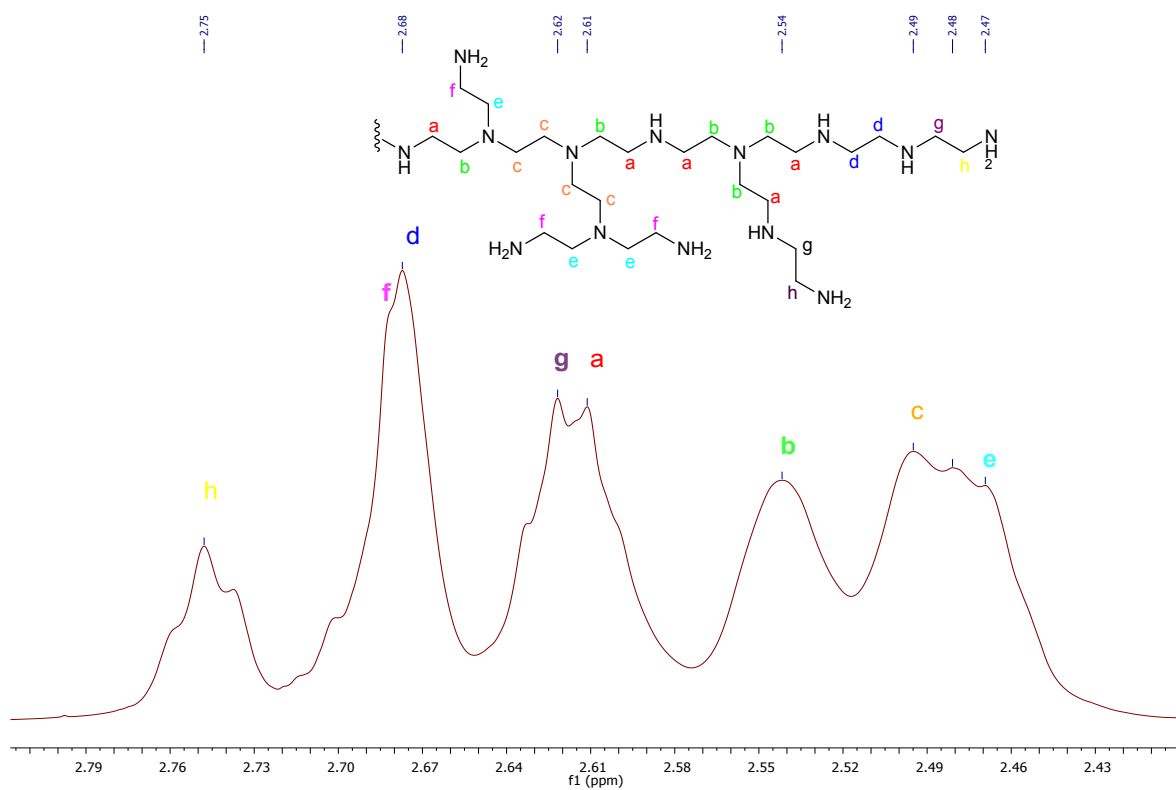


Fig. S2 ^1H -NMR spectrum and assignment of the chemical shifts for *b*-PEI received from Sigma Aldrich.

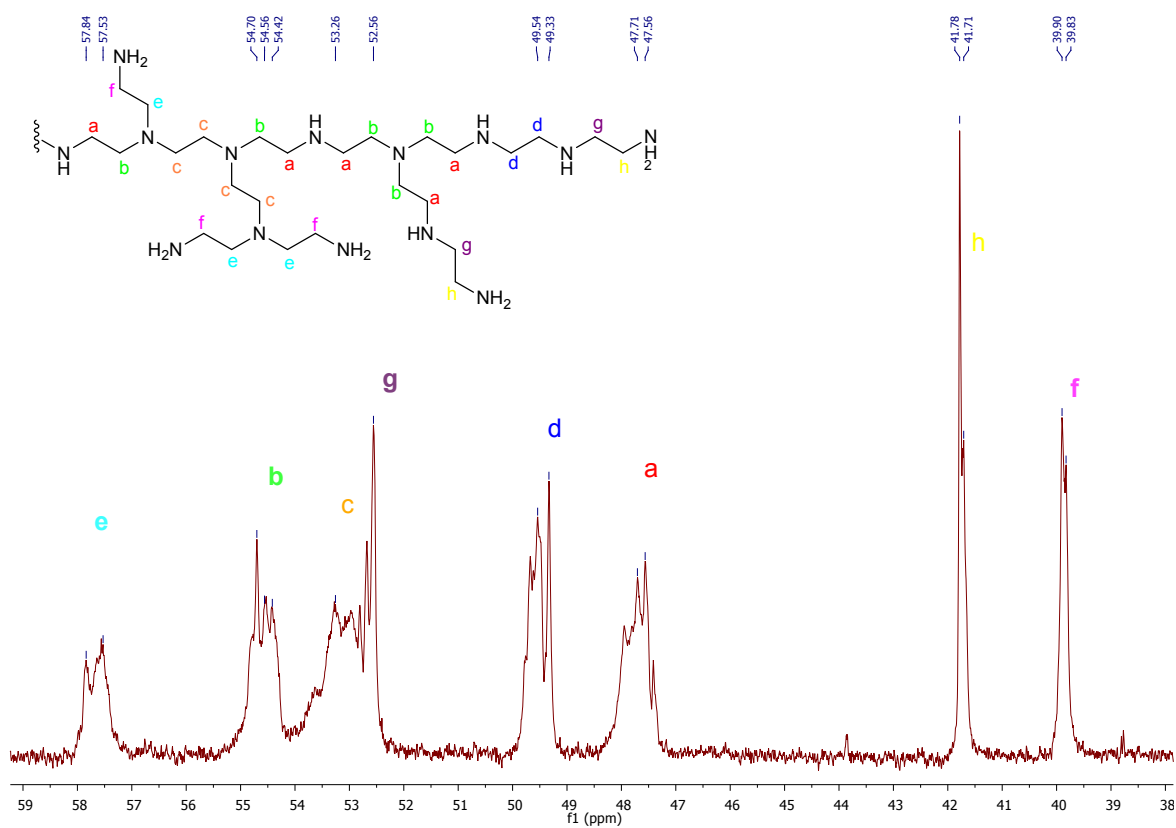


Fig. S3 ^{13}C -NMR spectrum and assignment of the chemical shifts for *b*-PEI received from Sigma Aldrich.

The final obtained acylated polymer was analyzed via ^1H - and ^{13}C -NMR spectroscopy, too. Figure S4 and S5 demonstrate the ^1H - and ^{13}C - NMR spectra of nBu-PEI-0.75 and nBu-PEI-1.0 in comparison to the non acylated *b*- PEI.

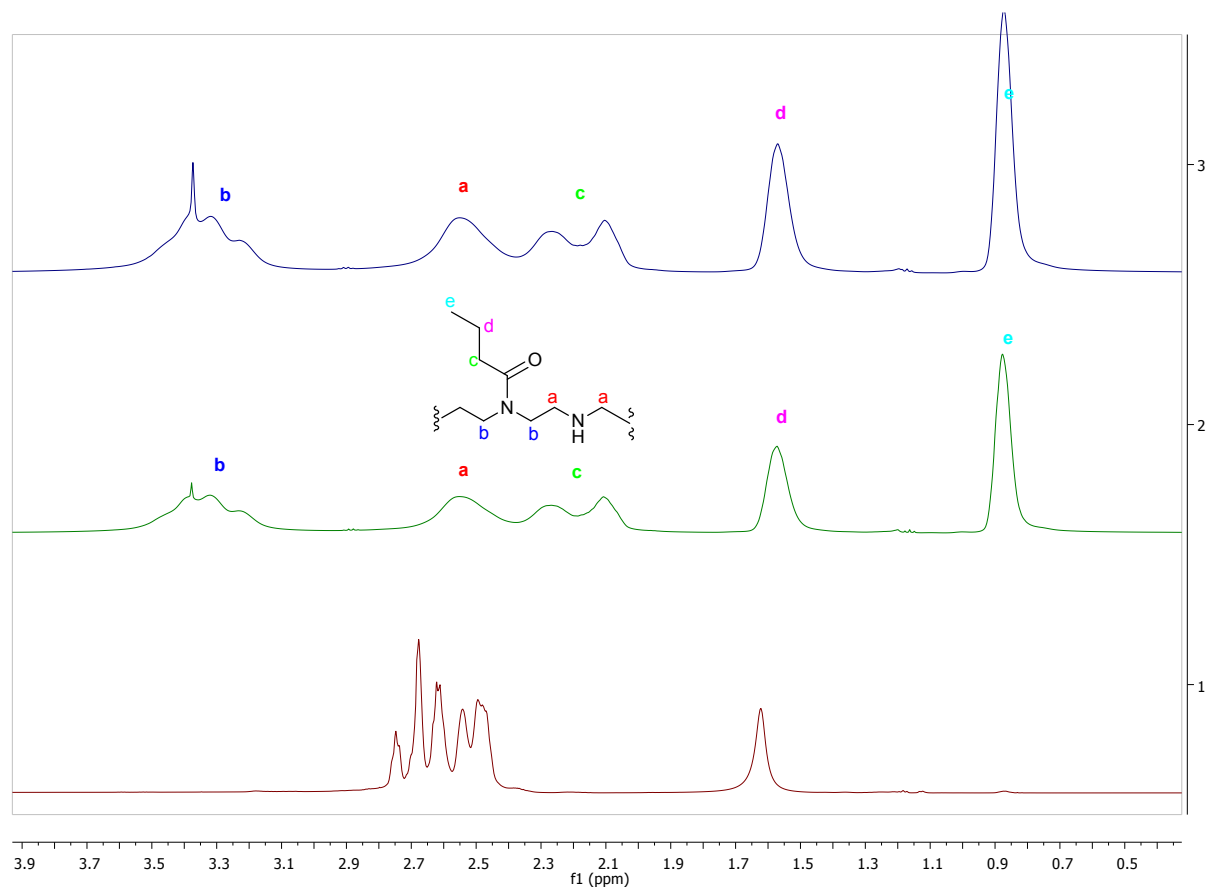


Fig. S4 ^1H - NMR spectrum of nBu-PEI-0.75 (2) and nBu-PEI-1.0 (3) in comparison with *b*- PEI (1).

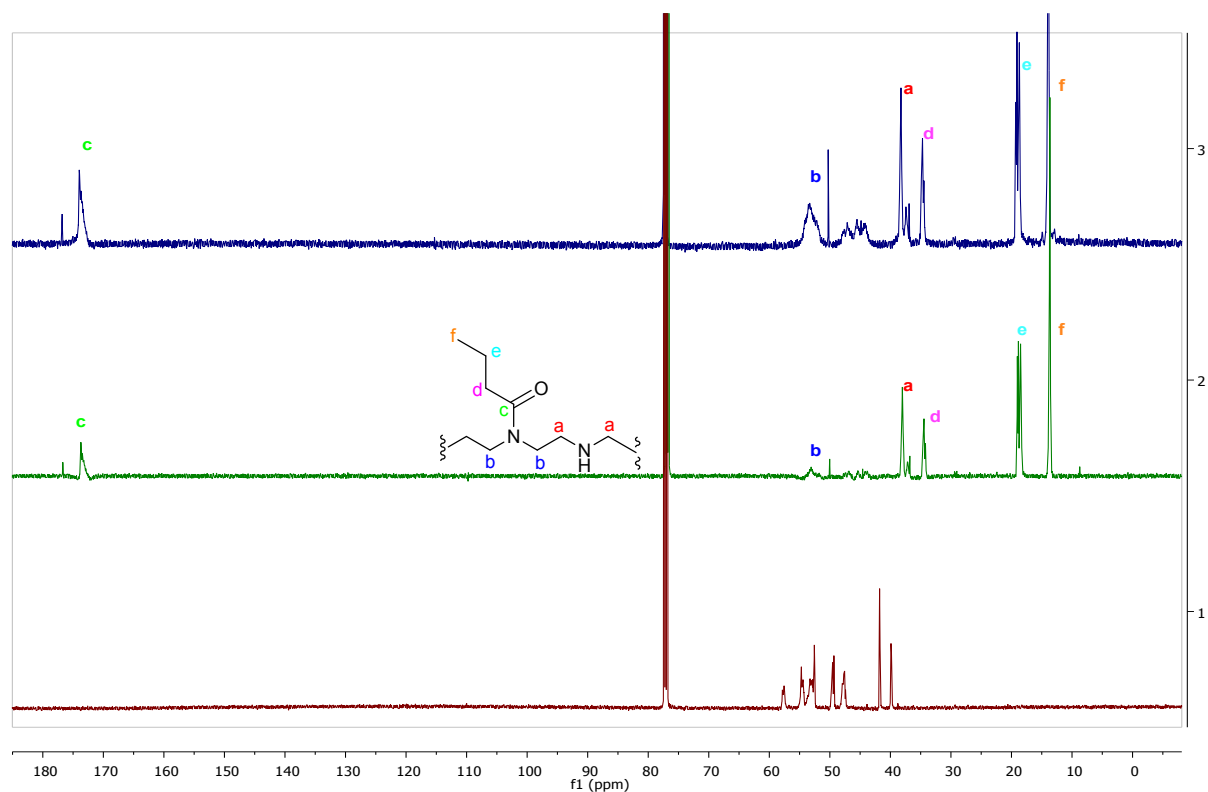


Fig. S5 ^{13}C - NMR spectrum of nBu-PEI-0.75 (2) and nBu-PEI-1.0 (3) in comparison with *b*- PEI (1).

Reactor setup

CO₂ absorption and desorption measurements were performed in a 1 L Büchi glass stirred tank reactor equipped with a magnetic coupled stirring unit and a gas entrainment impeller. Temperature (Julabo ATS3) was kept constant during the absorption measurement at 10 °C and was increased to 95 °C during desorption measurement after the release of the CO₂ overpressure of 1 bar.

The CO₂ flow was detected by digital gas flow meters (Bronkhorst M12-RGD-11-0-S) and the pressure (Bronkhorst pressure controller P-602C-6KOR-RGB-33-Z) was set to 1 bar for the CO₂ absorption measurement. The pH value was measured with digital pH electrode (METTLER TOLEDO HA405-DPA-SC-S8/225) and monitored with a device of HANNA instruments (HI2215 pH/ORP Meter). CO₂ flow, pressure, temperature, and pH value were monitored and recorded online during the whole absorption and desorption process. CO₂ flow and pressure were measured every 0.5 seconds and temperature together pH values were plotted every second.

For absorption and desorption measurements Millipore® water degassed with argon in order to remove CO₂ traces from air was used. 500 g of a two weight percent solution of acylated polymer in water was analysed during the absorption and desorption measurements. In Figure 6 a piping and instrumentation diagram (P&ID) is shown for the reactor system:

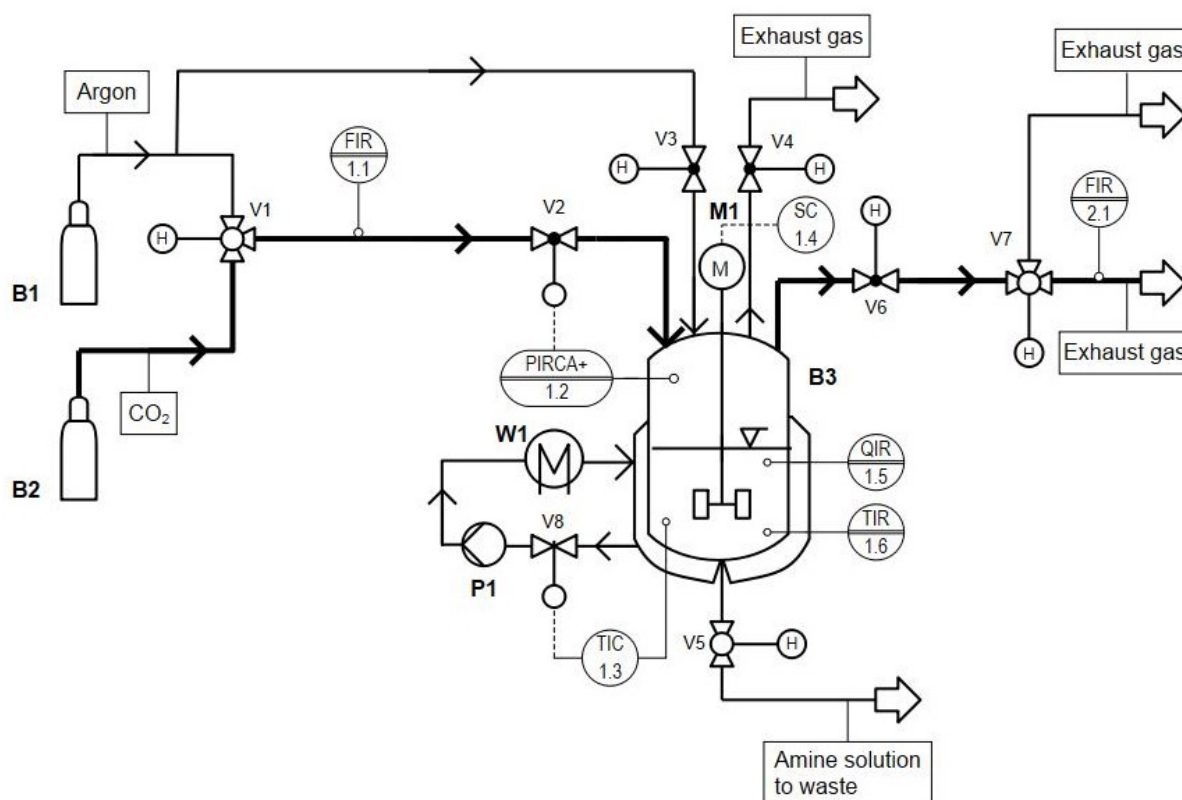


Fig. S6 Stirred tank reactor for the CO₂ absorption and desorption measurements. Temperature, pH, CO₂ flow and pressure were monitored online.

Said stirred tank reactor setup is versatile tool to outline CO₂ flow, pressure, temperature, and pH online during the whole absorption and desorption process. With this unique research setup the absorption and desorption of CO₂ on several systems were elevated and simulated closely to the real conditions in a CO₂ emitting power plant. In Figure 7 a complete overview of all recorded data is plotted in one diagram for nBu-PEI-0.75.

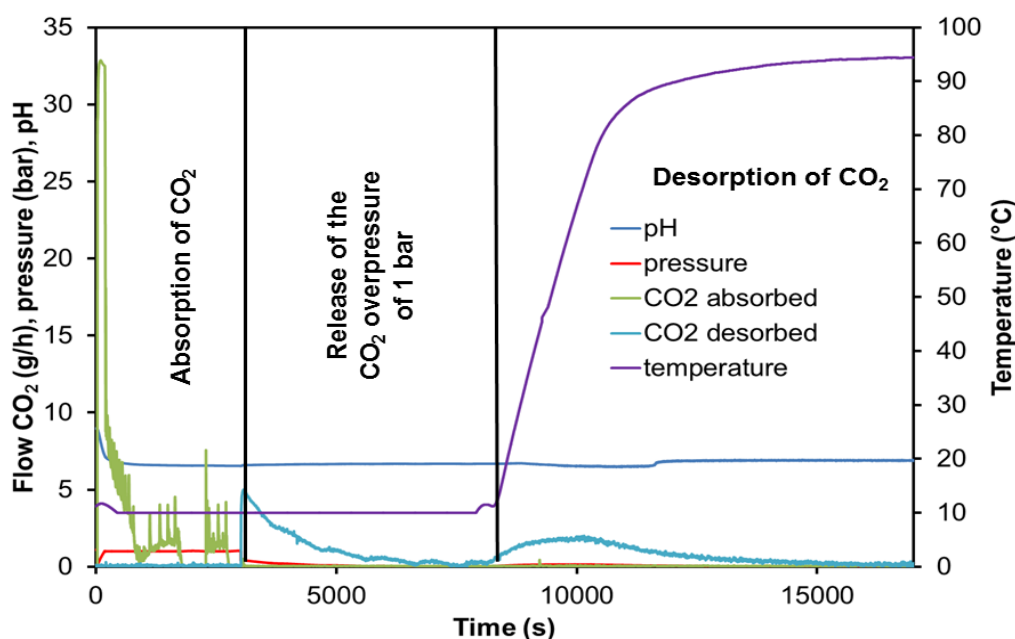


Fig. S7 Flow CO₂ (g/h), pressure (bar), pH () and temperature (°C) during the absorption and desorption measurement of a 2wt% solution of nBu-PEI-0.75 in Milipore® water.

Determination of the Cloud Points

Turbidity measurements were carried out on a Cary 50 UV–vis spectrophotometer from Varian. The cloud point was determined by spectrophotometric detection of the changes in transmittance at $\lambda = 500$ nm of the 2wt% solutions of nBu-PEI-0.75 and nBu-PEI-1.0. The heating/cooling rate was 1.0 K/min in steps of 1 K followed by a 3 min period of constant temperature to ensure equilibration. The cloud point was defined as the temperature corresponding to a 10% decrease in optical transmittance. Solutions of 2 wt% of polymer in milipore water are analysed.

DSC measurement

Differential scanning calorimetry (DSC) measurements were performed on TA instruments DSC-Q2000 with *b*-PEI, nBu-PEI-0.75 and nBu-PEI-1.0 with a heating rate of 10 K/min.

Comparison of acylated *b*-PEI and Poly(NIPAm-co-DMAPM)

Table S1 Thermosensitive properties, absorbed and desorbed CO₂ and pH values of acylated branched polyethylenimine and Poly (*N*-isopropylacrylamide(NIPAm)-co-*N*-[3-(diethylamino)propyl] methacrylamide (DMAPM))³:

	T _{LCST} (°C) (without CO ₂)	T _{LCST} (°C) (with CO ₂)	CO ₂ (ml/L) absorbed	CO ₂ (ml/L) desorbed	pH (10 °C)	pH (50 °C)
acylated <i>b</i> -PEI	14 ^a , 19 ^b	32 ^a , 34 ^b	600 ^a , 508 ^b	376 ^a , 112 ^b	8.9 ^a , 9.2 ^b	7.5 ^a , 7.9 ^b
Poly(NIPAm-co-DMAPM)	35 ^c , 45 ^d , 57 ^e		150 ^e	150 ^e	10.2 ^c	8.8 ^c

^anBu-PEI-1.0, ^bnBu-PEI-1.0, ^cGP5, ^dGP20, ^eGP30 (Poly(NIPAm-co-DMAPM) with 5, 20, 30 mol% DMAPM)

References

1. H. Kim, S. Lee, M. Noh, S. H. Lee, Y. Mok, G.-w. Jin, J.-H. Seo and Y. Lee, *Polymer*, 2011, **52**, 1367-1374.
2. D. R. Holycross and M. Chai, *Macromolecules*, 2013, **46**, 6891-6897.
3. Y. Hoshino, K. Imamura, M. Yue, G. Inoue and Y. Miura, *Journal of the American Chemical Society*, 2012, **134**, 18177-18180.