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COMMUNICATION

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

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Post combustion carbon dioxide capture with aqueous polymer solutions is a field of major interest. Via acylation of commercially available polyethylenimine (*b*-PEI) with butyric anhydride, lower critical solution temperature (LCST) behaviour together with a reversible pH shift was found in water as well as in CO₂ containing aqueous solutions. As expected, a low CO₂ absorption capability of the acylated thermosensitive *b*-PEI was measured in a stirred tank reactor. However, the observed improved CO₂ release in the desorption process associated with the LCST behaviour of the polymer is a “green” tool to face high efficiency loss in standard CO₂ capturing processes.

Climate change is a major problem of mankind. Since the industrial revolution the combustion of fossil fuels like coal, natural gas and oil led to an accumulation of carbon dioxide in the atmosphere.¹ In 2011, 35 gigatons of CO₂ were emitted from fuel burning devices and the cement industry, corresponding to a 54 % increase as compared to the level of 1990.¹ Carbon dioxide capture and storage (CCS) is considered as one of the options to reduce atmospheric emissions of CO₂ from human activities.^{2–3} The captured CO₂ is a renewable C1 feedstock⁴ and can be utilized, *e. g.* for the production of green fuels⁵ or CO₂ containing polymers.^{6–8} Within the CCS technology, the post combustion CO₂ capture shows the greatest potential because it can be retrofitted to existing fossil fuelled power plants and other CO₂ emitting devices.⁹ Usually, aqueous solutions

of monoethanolamine react with CO₂ at 40 °C¹⁰ through a zwitterion mechanism to form bicarbonates.¹¹ The regeneration of the monoethanolamine at elevated temperatures (100–140 °C),¹⁰ is a high energy consuming process and leads to an efficiency penalty.¹² Said high energy consumption is the main drawback of this standard amine process, so that sorbents like metal-organic frameworks,^{13, 14} solid porous absorbent materials,^{14, 15} porous polymer networks¹⁶ and ionic liquids¹⁷ have been studied intensively in order to overcome the aforementioned problem.

Thermo- and CO₂- responsive polymers^{18, 19} are studied intensively to improve the regeneration of aqueous sorbents and, therefore, the temperature dependent solubility of a polymer known as lower critical solution temperature (LCST) is addressed. This entropically driven effect can only be observed in polymer systems and may be seen as the most promising tool to reduce the high efficiency loss during the regeneration process which is mainly caused by the high heat capacity of the aqueous amine solutions.²⁰ Below the LCST, the solution is a one phase system and above said specific temperature, the polymer chains collapse and precipitate from solution. In 2012, *Bergbreiter et al.* reported that the LCST behaviour of polymers with acidic or basic side groups correlates with a pH shift.²¹ *Zhao et al.* outlined a reversible thermosensitive behaviour in CO₂ containing solutions.²² Recently, *Hoshino et al.* reported the absorption and desorption behaviour of CO₂ in micro- and nanogel particles (GPs) consisting of a copolymer of *N*-isopropylacrylamide (NIPAm) and *N*-[3-(diethylamino)propyl]methacrylamide (DMAPM)²³ and extended this concept of micro- and nanogel particles to microgel films in a wet environment.²⁴

In 2011, *Kim et al.* reported that branched polyethylenimine can be equipped with thermosensitive behaviour by simple acylation with several anhydrides.²⁵ Polyethylenimines (PEIs) are commercially available, wherein it is known that the linear form is capable to absorb CO₂.²⁶ Several publications^{27–30} report on PEI as an absorbing material for CO₂ immobilized on solid materials.

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Herein, we present the improved release of carbon dioxide within the regeneration process in an aqueous solution of thermosensitive acylated polyethylenimine. Our goal is to provide thermosensitive behaviour and the ability of CO₂ absorption in a commercially available homopolymer in order to design a polymer based high efficient CO₂ capturing process.

Branched polyethylenimine obtained via cationic polymerisation of aziridine is commercially available as Lupasol[®] and is a well-known polymer with primary, secondary and tertiary amine groups in the polymer backbone.³¹ *b*-PEI purchased from Sigma-Aldrich was dissolved in methanol, mixed with triethylamine and was acylated using 0.75 and 1.0 equivalents, respectively, of butyric anhydride according to the procedure of Kim *et al.*²⁵. ¹H- and ¹³C-NMR of the purchased polymer samples (Fig S2, Fig S3 in the ESI †) are in agreement with recently published data.³² An excerpt of the structure of the acylated polymer is given in Figure 1.

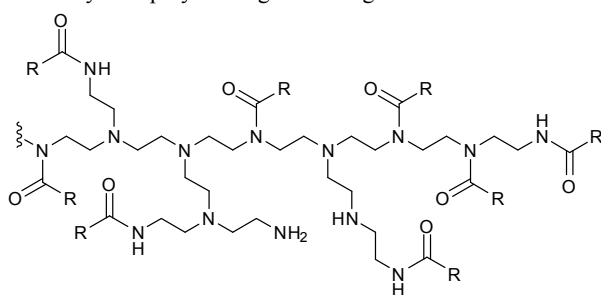


Fig. 1 Excerpt of the structure of acylated branched polyethylenimine with butyric anhydride. R = CH₂CH₂CH₃

The acylation reaction was confirmed by ¹H- and ¹³C NMR (Fig. S4, Fig. S5 †). Thermosensitive properties especially cloud point and lower critical solution temperature were determined by recording the transmittance 2 wt% polymer solutions of nBu-PEI-0.75 and nBu-PEI-1.0 in a standard UV-Vis spectrometer. Differential scanning calorimetry (DSC) measurements were performed as well to determine T_g. The LCST and DSC data are shown in Table 1.

Table 1 LCST data and DSC measurements of branched PEI and the acylated compounds (T in °C)

polymer	<i>b</i> -PEI	nBu-PEI-0.75	nBu-PEI-1.0
T _{LCST}	-	19	14
T _g	-54	-9	-8

As reported earlier by Kim *et al.*, the acylated compounds exhibit a LCST below room temperature (nBu-PEI-0.75 T_{LCST} = 19 °C and nBu-PEI-1.0 T_{LCST} = 14 °C). As expected, the LCST of the *b*-PEI acylated with 1.0 eq. butyric anhydride shows a lower LCST as compared to the nBu-PEI-0.75 due to the higher degree of acylation. The DSC results indicate a clear shift in the glass transition point after the acylation of the *b*-PEI. The implementation of unpolar alkyl group via treatment of polyethylenimine with butyric anhydride led to lower mobility of the polymer chains and therefore to a higher glass transition point.

To further address the thermosensitive behaviour, to show the improved carbon dioxide release and the CO₂ absorption and desorption capability of nBu-PEI-0.75 and nBu-PEI-1.0, a stirred tank reactor was used. With this unique reactor system, it is possible to get a detailed and complete overview of all relevant parameters (CO₂ flow, pressure, temperature, pH) in the polymer solutions during the absorption and desorption of CO₂ (Fig. S6 †).

The polymer samples (2 wt% polymer solutions of nBu-PEI-0.75 and nBu-PEI-1.0 in Milipore[®] water) were charged into the reactor and carbon dioxide was added to the solution. UV-Vis measurements after release of the CO₂ overpressure were recorded to determine the LCST in CO₂ containing aqueous solution (Figure 2).

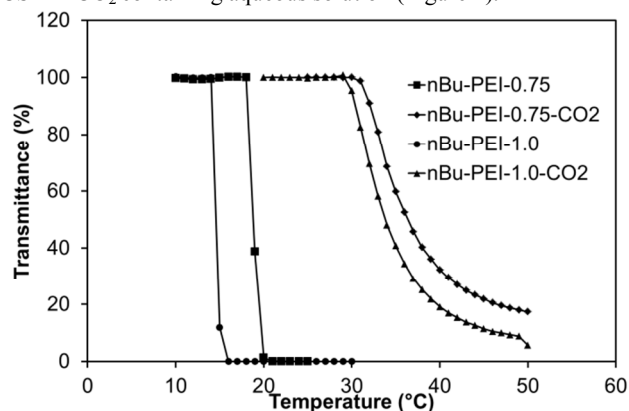


Fig. 2 Determination of Lower Critical Solution Temperature of nBu-PEI-0.75 and nBu-PEI-1.0 before and after CO₂ absorption samples (2 wt% polymer solutions of nBu-PEI-0.75 and nBu-PEI-1.0 in Milipore[®] water).

The cloud point in carbon dioxide containing water is shifted to higher temperatures compared to the CO₂ free system. Furthermore, the observed phase transition is broadened in the presence of CO₂.²² As a result, these measurements clearly indicate that it is possible to introduce thermosensitive properties to branched polyethylenimine in a CO₂ containing aqueous solution.

The additional pH shift in connection with the LCST effect is of particular relevance for the release of CO₂ in the desorption process because of the proton driven decomposition of bicarbonate moieties.²¹ Due to the fact that the acylated *b*-PEI has some basic groups within the polymer even after acylation, a connection between the phase transition above the LCST temperature and a shift in the pH value was expected in the present case. In order to demonstrate this correlation, the polymer solution was charged into our reactor setup. The pH value was measured and plotted against the temperature in the solution using a digital pH electrode. To ensure a one phase system, of nBu-PEI-0.75 and nBu-PEI-1.0 solutions were cooled below their LCST to 10 °C. Subsequently, each polymer solution was heated above the LCST to 50 °C and then cooled to 10 °C again. This procedure was repeated five times. A pH shift of more than one unit was observed and obviously correlated with the LCST of the two acylated species (Figure 3). The pH shift was reversible for five heating and cooling cycles and was almost in the same range for both polymer samples.

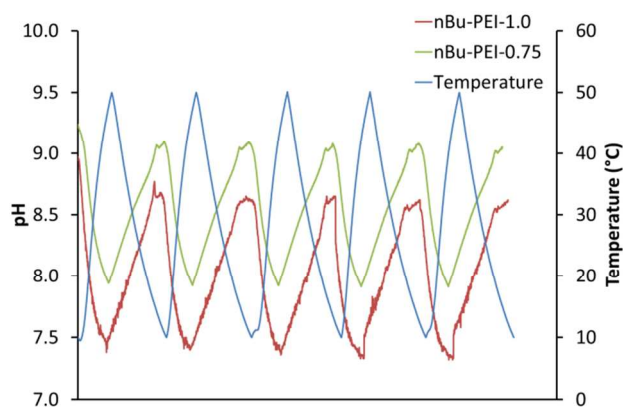


Fig. 3 Reversible change in pH of nBu-PEI-0.75 and nBu-PEI-1.0 before CO₂ absorption over five heating and cooling cycles.

According to the transmittance curves in Figure 2, we were able to address a LCST behaviour in water and in CO₂ containing solutions. Additionally, the phase transition before the absorption was correlated with a reversible shift in pH over five heating and cooling cycles. However, we had to analyse the CO₂ absorbed and desorbed with the thermosensitive *b*-PEI polymer solution. As described by *Theoto et al.*,¹⁸ thermosensitive and CO₂ responsive amine containing polymer systems show a low absorption capacity.²⁷ The amount of CO₂ was measured by two digital flow meters and recorded online. For the absorption reaction, the CO₂ pressure was set to one bar. The pressure was regulated by a digital pressure valve. The temperature was kept constant at 10 °C below the LCST of nBu-PEI-0.75 and nBu-PEI-1.0 during the absorption process and during the release of the overpressure at the beginning of desorption. After the release of the overpressure, the temperature was set to 95 °C and monitored together with the pH value during the absorption and desorption process (Fig. S7 †). The amount of CO₂ absorbed and desorbed is calculated from the integral of the flow curves. In order to determine the amount of CO₂ absorbed or desorbed by the polymer, the CO₂ absorbed by water is subtracted from the calculated values (Table 2). 490 g water desorbed 3.36 g CO₂ and water vapour due to the high desorption temperature of 95 °C corresponding to 2.71 g absorbed CO₂. In order to relate the outlined absorption and desorption capacity of the acylated polymer systems with a standard amine system, the amount of CO₂ adsorbed and desorbed by a 2wt% Monoethanolamine solution is also given (Table 2).

Table 2 Absorbed and desorbed CO₂ of 2wt% nBu-PEI-0.75 and nBu-PEI-1.0 solution and 2wt% Monoethanolamine solution in g in total and corrected by 490 g water. Absorption at 10 °C and 1 bar CO₂ overpressure and desorption at 95 °C.

	nBu-PEI-0.75	nBu-PEI-1.0	MEA	n-Bu-PEI-0.75	n-Bu-PEI-1.0	MEA
absorbed CO ₂ (g)	3.31	3.00	8.74	0.59 ^b	0.28 ^b	5.58 ^b
desorbed CO ₂ (g)	3.73 ^a	3.43 ^a	6.73 ^a	0.37 ^b	0.11 ^b	4.02 ^b
	^a CO ₂ and water vapour			^b corrected values		

As expected, rather low amounts of CO₂ were absorbed and desorbed by the acylated polymers compared to a 2wt% Monoethanolamine solution due to the high degree of acylation in case of nBu-PEI-0.75 and nBu-PEI-1.0. Reactive primary and secondary amine side groups were blocked and were not available for the absorption reaction. Low polymer concentrations of two weight percent for nBu-PEI-0.75 and nBu-PEI-1.0 were another reason for the observed values. A comparison of the 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))²³ is given in Table S1 †.

To provide evidence for the impact of the proton driven decomposition of HCO₃⁻ within the desorption process, the desorption curves and the pH value during this process were considered in detail. To remove non-absorbed CO₂ in the gas phase, the overpressure was reduced to atmospheric pressure first. Then the temperature was continuously increased to 95 °C and the CO₂ flow was recorded during this continuous increase in temperature together with the pH value. The proof for thermosensitive properties of acylated *b*-PEI and a correlated decrease in pH during the continuous increase of temperature in the regeneration process is shown in Figure 4.

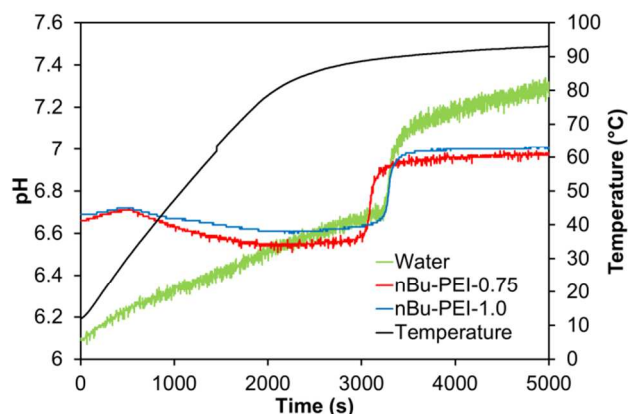


Fig. 4 pH trend of nBu-PEI-0.75, nBu-PEI-1.0 and water versus a continuous rise in temperature during the regeneration process.

While the pH value of water increases continuously due to desorption of CO₂, the pH values of the polymer solutions decrease during increase in temperature to 90 °C. This pH drop must obviously be caused by the LCST effect of the acylated polymers nBu-PEI-0.75 and nBu-PEI-1.0 in the CO₂ containing solutions. The LCST effect is associated with a release of protons and a reduction in pH during the phase transition of the acylated polyethylenimine. Apart from the decrease in pH associated with the LCST effect, a pH rise was observed for both the acylated *b*-PEIs and water caused by the additional thermal decomposition of bicarbonate at 95 °C.

In addition to the thermally driven desorption of CO₂, the LCST effect contributes to a stronger increase in the CO₂ flow

due to the H^+ -induced decomposition of bicarbonate moieties. In Figure 5, desorption curves of water together with nBu-PEI-0.75 and nBu-PEI-1.0 are shown in correlation to the temperature of the solution.

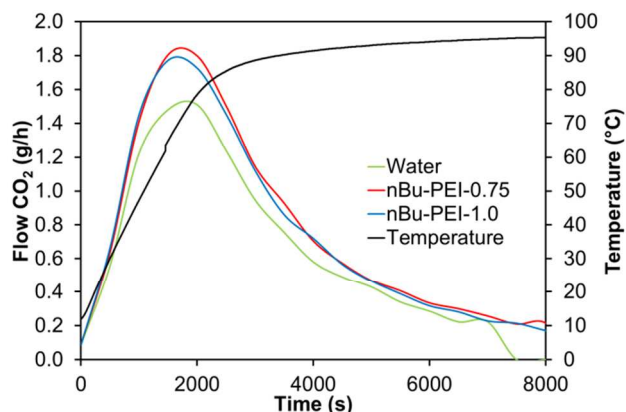


Fig. 5 Desorption flows of nBu-PEI-0.75, nBu-PEI-1.0 and water in correlation with the temperature of the polymer solution.

The desorption behaviour of the acylated polymers is compared with water as there is only a small difference in the amounts of desorbed CO_2 of the acylated compounds compared to the desorption behaviour of water. However, we observed a significant increase of about 20 % in the desorption flows of the acylated species. Due to the LCST effect of nBu-PEI-1.0 in CO_2 containing solution compared with nBu-PEI-0.75, on the one hand, the decomposition of bicarbonate species started earlier in the desorption process. On the other hand, a lower amount of carbon dioxide was desorbed by nBu-PEI-1.0 (Table 2), which led to similar desorption flows for both acylated species. The entropically driven LCST behaviour of nBu-PEI-0.75 and nBu-PEI-1.0 resulted in a significant decrease in pH and to a clear increase in desorption flows. Thermosensitive polymers, especially acylated branched PEIs, are shown to be versatile “green” tools to face the problem of an efficient carbon dioxide release.

Conclusions

Acylated branched polyethylenimine is the first commercially available polymer that shows thermosensitive behaviour in water and also in CO_2 containing aqueous solution. This reversible phase transition called lower critical solution temperature is correlated with a shift in pH and a proton release. If used during a desorption process in a standard CO_2 capturing unit, said thermosensitive properties of acylated branched polyethylenimine (nBu-PEI-0.75 and nBu-PEI-1.0) represent a novel and highly efficient “green” tool to generate a proton driven decomposition of bicarbonate. In this context, a significant increase in desorption flow of CO_2 is reported within this study.

b- PEI is the first commercial available homopolymer which can be used as a novel energy efficient CO_2 absorbent in aqueous solutions in a standard postcombustion capturing

process. Hence, thermosensitive polymers, especially acylated branched PEIs, are shown to be versatile “green” tools to face the problem of an efficient carbon dioxide release.

Acknowledgements

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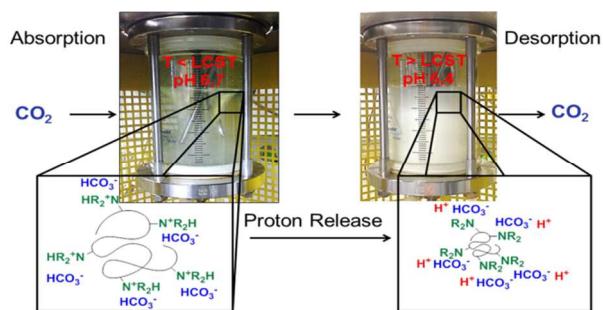
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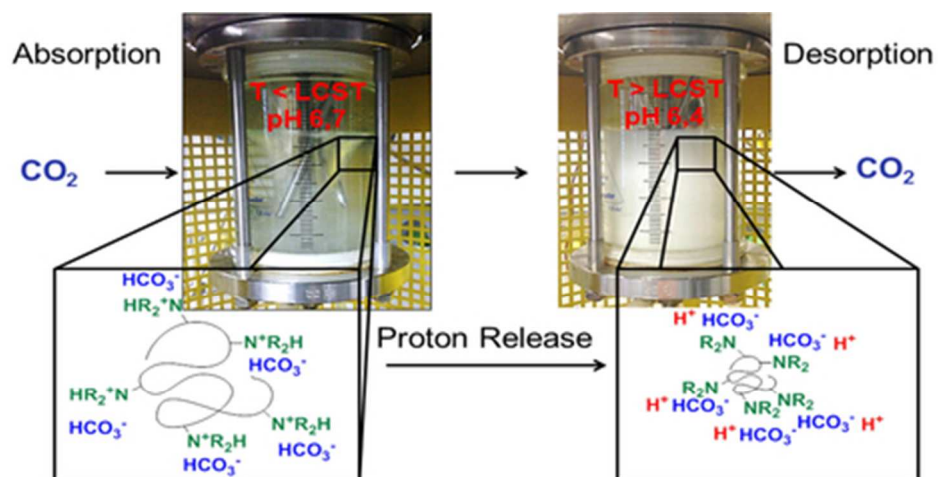
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Temperature- and CO_2 responsive behaviour and highly efficient carbon dioxide release was achieved via acylation of commercial available Polyethylenimine.





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