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# Design rationale of thermally responsive microgel particle films that reversibly absorb large amounts of CO<sub>2</sub>: fine tuning the pK<sub>a</sub> of ammonium ions in the particles†

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Herein we revealed the design rationale of thermally responsive gel particle (GP) films that reversibly capture and release large amounts of CO<sub>2</sub> over a narrow temperature range (30–75 °C). The pK<sub>a</sub> value of ammonium ions in the GPs at both the CO<sub>2</sub> capture temperature (30 °C) and release temperature (75 °C) is found to be the primary factor responsible for the stoichiometry of reversible CO<sub>2</sub> capture by the amines in the GP films. The pK<sub>a</sub> values can be tuned by the properties of GPs such as volume phase transition temperature (VPTT), size, swelling ratio, and the imprinted microenvironment surrounding the amines. The optimal GP obtained according to the design rationale showed high capture capacity (68 mL CO<sub>2</sub> per g dry GPs, 3.0 mmol CO<sub>2</sub> per g dry GPs), although the regeneration temperature was as low as 75 °C. We anticipate that GP films that reversibly capture other acidic and basic gases in large amounts can also be achieved by the pK<sub>a</sub> tuning procedures.

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## Introduction

The accumulation of CO<sub>2</sub> in the atmosphere due to burning of fossil fuels is considered the main cause of global climate change.<sup>1</sup> Meanwhile, CO<sub>2</sub> is expected to be a carbon source for the production of liquid fuels, such as methanol and dimethyl ether, through the use of regenerative energy.<sup>2</sup> Thus, the development of energy-efficient CO<sub>2</sub> separation and recovery processes for point sources, such as fossil fuel power plants, is essential not only for minimizing climate change but also for the future use of carbon-based energy.

Conventional processes that recover CO<sub>2</sub> from the high humidity exhaust gases of power plants use aqueous solutions of ethanolamine as a CO<sub>2</sub> absorbent. CO<sub>2</sub> in the exhaust gases is selectively captured by the absorbent at a low temperature (~40 °C) and then recovered by heating the solution, typically above 140 °C.<sup>3–5</sup> Although the amine solution exhibits a high CO<sub>2</sub> absorption capacity, the high-energy consumption of the heating process limits its use in the environmentally friendly process.<sup>4–8</sup>

Porous solid adsorbents that can be regenerated under relatively mild conditions, such as metal–organic frameworks (MOFs),<sup>9,10</sup> zeolites,<sup>9,10</sup> and silica with physically or chemically supported amine polymers,<sup>9–13</sup> have recently been developed as alternatives to the aqueous amine solution. However, solid CO<sub>2</sub>

sorbents are rarely capable of efficiently capturing CO<sub>2</sub> from highly humid gases because the adsorption of water molecules competes with that of CO<sub>2</sub> on the pore surfaces. Furthermore, the capillaries and pores of the sorbents are easily blocked by the liquefied water, preventing CO<sub>2</sub> from diffusing into the pores.<sup>9–12</sup> Thus, the development of sorbents that absorb/adsorb large amount of CO<sub>2</sub>, even in humid environments, and desorb CO<sub>2</sub> at low temperatures (<100 °C) is of great importance.

It has been reported that poly-*N*-isopropylacrylamide (pNIPAm) undergoes a reversible volume phase transition from a hydrophilic swollen state to a hydrophobic collapsed state at temperatures below and above, respectively, the volume phase transition temperature (VPTT) of ~32 °C.<sup>14</sup> The phase transition is induced by the entropy-driven dissociation of water from pNIPAm chains after heating above the VPTT.<sup>14</sup> The temperature responsive pNIPAm-based functional hydrogels have been widely used as materials to reversibly capture targets, such as dyes,<sup>15,16</sup> drugs,<sup>17,18</sup> peptides,<sup>19</sup> proteins,<sup>20,21</sup> nucleotides,<sup>22</sup> cells,<sup>23</sup> and protons,<sup>24</sup> in aqueous media *via* the volume phase transition. The multipoint interactions are reversibly switched on/off by varying the volume density of hydrophobic functional groups,<sup>17,25,26</sup> the number of charged functional groups,<sup>22,27</sup> and/or the rigidity of the polymer chains<sup>28</sup> at temperatures above and below the VPTT.

Recently, we reported that hydrogel films composed of temperature-responsive microgel particles (GPs) consisting of NIPAm and *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPM) reversibly absorbed and released CO<sub>2</sub> *via* a volume phase transition during cooling (30 °C) and heating (75 °C) cycles, respectively.<sup>29</sup> Below the VPTT, amines in the swollen

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GPs were capable of forming ion pairs with absorbed bicarbonate ions. Above the VPTT, shrinkage of the GPs triggered CO<sub>2</sub> desorption.<sup>27</sup> The GP films showed faster CO<sub>2</sub> capture and release rate<sup>29</sup> than the conventional bulk hydrogel films due to the fast thermal responsibility of the GPs.<sup>30</sup>

However, guidelines to design GP films that reversibly absorb CO<sub>2</sub> with high capacity and stoichiometry have not been revealed.

In the case of reversible CO<sub>2</sub> absorption by the blood of animals, the pK<sub>a</sub> value of the Brønsted acid and base in the hemoglobin plays a crucial role for the control of CO<sub>2</sub> solution equilibrium: The pK<sub>a</sub> value of the ammonium and imidazolium cations decreases due to the drastic conformational change of the hemoglobin caused by oxygen binding to the heme. The shift of the pK<sub>a</sub> triggers the release of H<sup>+</sup> into the blood, leading to the release of CO<sub>2</sub> efficiently from lungs (Bohr effect).<sup>31,32</sup>

Inspired by the Bohr effect of hemoglobin, we hypothesized that the pK<sub>a</sub> value of the protonated amines (ammonium ions) within GPs (pK<sub>a</sub> value of GPs) at the CO<sub>2</sub> capture temperature (30 °C) and release temperature (75 °C) would contribute to the reversible capture efficiency of CO<sub>2</sub>.

In this study, in order to clarify the design rationale, we prepared a series of GPs with a variety of compositions using different polymerization conditions. The effects of the physical and chemical properties of GPs, such as VPTT, size, swelling ratio, on pK<sub>a</sub> values and the reversible CO<sub>2</sub> capture stoichiometry against amines were systematically investigated. pK<sub>a</sub> values of the ammonium ions in the GPs were also tuned by the “microenvironment-imprinting” strategy as we described in the recent report.<sup>24</sup> The reversible CO<sub>2</sub> capture capacity was maximized based on the design rationale revealed in this study. Humidified gas (60 °C) consisting of 10% CO<sub>2</sub> and 90% N<sub>2</sub>, which is comparable to the post-combustion gas of fire power plants after wet desulfurization process, was used as feed gas.<sup>6,33</sup> The CO<sub>2</sub> was captured at 30 °C and released at 75 °C under the same atmosphere (10% CO<sub>2</sub>, 90% N<sub>2</sub>, 60 °C water moisture).

## Experimental

### Preparation of GPs

A series of GPs containing NIPAm, a functional tertiary amine monomer DMPAM, and a crosslinker *N,N'*-methylenebisacrylamide (Bis) were synthesized by precipitation polymerization as reported (Scheme 1).<sup>29</sup> The amount of Bis was varied to prepare GPs with different degrees of crosslinking and swelling ratios. GPs with the same composition but different pK<sub>a</sub> values were synthesized *via* a “microenvironment-imprinting” strategy by adding HCl or NaOH into the monomer solution.<sup>24</sup> Larger GPs were obtained by decreasing the concentration of surfactant, while smaller GPs were prepared from solutions with a lower total monomer concentration. To decrease the VPTT of GPs, a more hydrophobic monomer, *N*-*tert*-butyl acrylamide (TBAm), was incorporated into the GPs. Details of the polymerization conditions of the GPs are summarized in Table 1. Polymerization process is described in ESI.†

### Quantification of hydrodynamic diameters, VPTTs, and swelling ratios of GPs

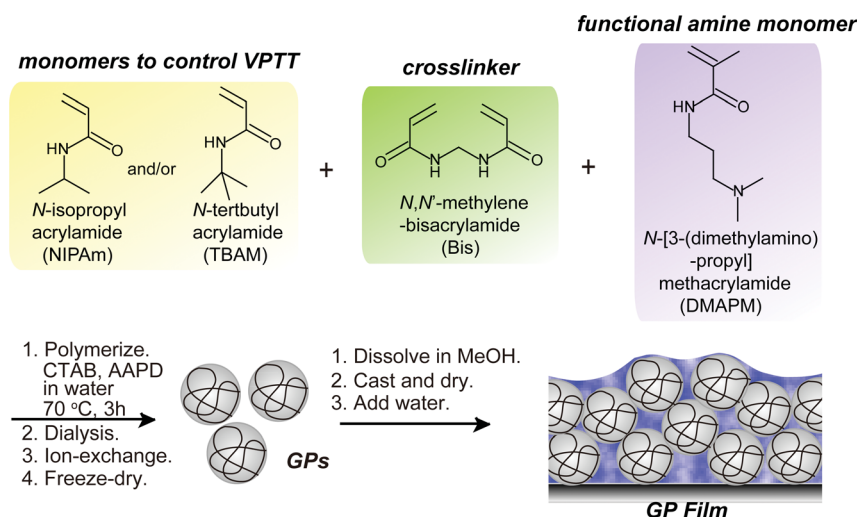
The hydrodynamic diameters and VPTT of GPs were measured by dynamic light scattering (DLS) as described.<sup>27,29</sup> The swelling ratio is defined as the ratio of the diameters at 30 °C (*D*<sub>30</sub>) and 75 °C (*D*<sub>75</sub>).

### Quantification of amine content and pK<sub>a</sub> of ammonium ions in GPs

The amine content and pK<sub>a</sub> of amines in GPs was quantified by acid–base titration under N<sub>2</sub> purging as described.<sup>27,29</sup>

### Measurement of pK<sub>a</sub> shift curve during heating process

Since the apparent pK<sub>a</sub> can be approximated as the pH value at the half-neutralization point, the temperature dependent pK<sub>a</sub> shift of the GP solution was measured with the pH probe as follows. The half-neutralized GP solution was prepared by



Scheme 1 Synthesis of GPs and preparation of GP films.

Table 1 Polymerization conditions of the GPs

GPs	Feed ratio				Polymerization media	CTAB (mM)	AAPD (mM)	Concentration (mM)
	NIPAm (mol%)	DMAPM (mol%)	Bis (mol%)	TBAM (mol%)				
D5B2	93	5	2	0	Water	2.0	2.5	312
D5B0	95	5	0	0	Water	2.0	2.5	312
D5B5	90	5	5	0	Water	2.0	2.5	312
D5B10	85	5	10	0	Water	2.0	2.5	312
D5B2T40	53	5	2	40	Water	2.0	2.5	312
D5B10-1/4HCl	85	5	10	0	1/4 eq. HCl	2.0	2.5	312
D5B2-1/2HCl	93	5	2	0	1/2 eq. HCl	2.0	2.5	312
D5B2-1/1HCl	93	5	2	0	1/1 eq. HCl	2.0	2.5	312
D5B2-1/2NaOH	93	5	2	0	1/2 eq. NaOH	2.0	2.5	312
D5B2-L	93	5	2	0	Water	0.16	2.5	312
D5B2-S	93	5	2	0	Water	2.0	0.625	78
D5B2-1/2NaOH-S	93	5	2	0	1/2 eq. NaOH	2.0	0.625	78
D30B2	68	30	2	0	Water	2.0	2.5	312
D30B2T40	28	30	2	40	Water	2.0	2.5	312
D55B2	43	55	2	0	Water	2.0	2.5	312
D55B2T43	0	55	2	43	Water	2.0	2.5	312

adding 0.5 eq. of HCl to the GP solution. Then, under a N<sub>2</sub> atmosphere with stirring the pH value and temperature of the solution were recorded by the pH meter every 3 s during the heating process.

### Preparation of GP films

The lyophilized GPs were dissolved in methanol. The hydrogel films were then prepared by casting the methanol solutions containing 120 mg of GPs on the inner bottom surface of a stainless steel container with a surface area of 120 cm<sup>2</sup>. After completely evaporating the methanol, 4 mL of water was added per gram of GPs.

### Measurement of CO<sub>2</sub> absorption capacity of GP films

The CO<sub>2</sub> absorption capacities of the GP films are quantified as illustrated in Scheme S1.† 10% CO<sub>2</sub> (90% N<sub>2</sub>, 10 mL min<sup>-1</sup>) gas was passed through 60 °C water to generate saturated water vapor. The resulting 60 °C water-saturated gas mixture was channeled into a stainless steel container with the GP film on the inner surface, and then to a gas chromatograph after condensing the water moisture at 5 °C.

More detailed information about materials and experimental process are shown in ESI.†

## Results and discussion

### Effect of pK<sub>a</sub> values of GPs on the reversible CO<sub>2</sub> capture stoichiometry of GP films

The dynamic and reversible transition of the pK<sub>a</sub> values of Brønsted acid and base groups in proteins plays an important role in their functions, such as molecule/ion transfer, enzymatic reactions, and molecular recognition.<sup>32,34</sup> The pK<sub>a</sub> values are significantly influenced by the microenvironment around the functional groups, such as hydrophobicity, hydrogen bonding,

and distance to the neighboring charges.<sup>32,34–38</sup> Thus, the pK<sub>a</sub> value can be further dynamically shifted by the conformational change of polypeptides around the functional groups, which induces a microenvironment change.

In the case of CO<sub>2</sub> transfer through the bloodstream of animals, the pK<sub>a</sub> value of the ammonium and imidazolium cations in/on the hemoglobin decreases due to the drastic conformational change of the polypeptides caused by oxygen binding to the heme. The shift of the pK<sub>a</sub> value triggers the release of H<sup>+</sup> into the blood, lowers the pH of the blood, and drives the CO<sub>2</sub> efficiently from the lungs (Bohr effect).<sup>32,38</sup>

Inspired by the function of hemoglobin, we expected that the pK<sub>a</sub> value of the protonated amines (ammonium ions) within GPs (pK<sub>a</sub> value of GPs) at the CO<sub>2</sub> capture temperature (30 °C) and release temperature (75 °C) would contribute to the reversible capture efficiency of CO<sub>2</sub>.

To clarify the effect of the pK<sub>a</sub> value of GPs on the reversible CO<sub>2</sub> capture stoichiometry of GP films in the temperature swing process from 30 °C to 75 °C, a series of GPs with the same composition but different pK<sub>a</sub> values were prepared by the “microenvironment-imprinting” strategy.<sup>24,39</sup> Imprinting is a method to create polymers with specific microstructures that show strong affinity to target molecules and ions by cross-linking the polymer networks in the presence of targets.<sup>40,41</sup> It has been reported that pNIPAm-based acrylic acids (AAc) containing GPs with different pK<sub>a</sub> values can be prepared by the “proton-imprinted” strategy.<sup>24</sup> The GPs polymerized at a pH below the pK<sub>a</sub> of AAc showed a much higher pK<sub>a</sub> value at the collapsed state than those prepared at a high pH because stronger proton-affinity sites were incorporated into the relatively hydrophobic microenvironment around the protonated AAc. Note that the GPs were polymerized at the collapsed state in the temperature above the VPTT.

We anticipated that amine-containing GPs with different pK<sub>a</sub> values could also be prepared *via* the “microenvironment-



imprinting" strategy. Thus, the GPs were polymerized in the presence of acid (1 or 1/2 eq. of HCl against the amine monomer DMAPM) or base (1/2 eq. of NaOH). All GPs were polymerized in the aqueous monomer solution consisting of 5 mol% DMAPM, 2 mol% Bis and 93 mol% NIPAm at the temperature above the VPTT of the growing GPs (70 °C).

The VPTTs of the GPs were determined by monitoring the scattering intensity of the GP solutions during the heating process (Fig. S1a in ESI†). Despite the different polymerization conditions, all four GPs, **D5B2-1/1HCl** (1 eq. HCl), **D5B2-1/2HCl** (1/2 eq. HCl), **D5B2-1/2NaOH** (1 eq. NaOH), and **D5B2** (without HCl or NaOH), show similar VPTTs at about 38 °C. Similar swelling ratios in the range of 2.3–2.7 are also observed (Fig. S1b in ESI†), indicating the VPTTs and swelling ratios of GPs are independent of the polymerization conditions.

The apparent  $pK_a$  values of the GPs at 30 °C and 75 °C were determined by acid–base titration of the GP solutions and are plotted as the top and bottom, respectively, of the gray bars in Fig. 1a.<sup>27</sup> All GPs show lower  $pK_a$  values than the amine

monomer DMAPM, at both temperatures, indicating the relatively low dielectric constant and high steric hindrance around the amine groups in the GPs, as well as the high electrostatic repulsion between neighboring charges.<sup>42,43</sup> Moreover, in accordance with our expectation, the  $pK_a$  values of **D5B2-1/1HCl** and **D5B2-1/2HCl** at 75 °C (7.4 and 7.0, respectively) were significantly higher than those of **D5B2** and **D5B2-1/2NaOH** (5.3 and 4.9, respectively).

The large difference in  $pK_a$  values can be explained by the "microenvironment-imprinting" effect. When the GPs are polymerized in a proton-rich solution (in the presence of HCl), the protonated DMAPM is imprinted in the polar and hydrophilic microenvironment of the GPs (**D5B2-1/1HCl** and **D5B2-1/2HCl**), resulting in higher  $pK_a$  values than those of the GPs polymerized in the proton-poor solution (**D5B2** and **D5B2-1/2NaOH**). Although there is variation in the GP diameters (Fig. S1b in ESI†), the large difference in the  $pK_a$  values (>2) at 75 °C cannot be a result of the size differences because the smallest GP, **D5B2** (74 nm), and the largest GP, **D5B2-1/2NaOH** (136 nm), show a  $pK_a$  difference of only 0.4 (5.3–4.9).

Fig. 1a also shows that the  $pK_a$  difference between 30 °C and 75 °C ( $\Delta pK_a$ ) of all GPs (1.5–2.5) is larger than that of the monomer (0.9). For better understanding of the temperature dependent  $pK_a$  difference, the apparent  $pK_a$  values of **D5B2** and the monomer DMAPM, were recorded during the heating process. Fig. 1b shows that a sharp  $pK_a$  transition of **D5B2** occurs at a temperature around its VPTT, and a steep  $pK_a$  decrease continues over a wide temperature range above the VPTT. However, this sharp  $pK_a$  transition is not observed in the case of the monomer, indicating that the sharp  $pK_a$  decrease was induced by a volume phase transition of GPs, during which the increased hydrophobicity and steric hindrance, and the decreased dielectric constant at high temperature make the amine groups more difficult to be protonated.<sup>42</sup>

In Fig. 1a, the  $\Delta pK_a$  values between 75 °C and 30 °C of the GPs polymerized with HCl, **D5B2-1/1HCl** (1.5) and **D5B2-1/2HCl** (1.6), are significantly lower than those of **D5B2** (2.5) and **D5B2-1/2NaOH** (2.3), although the swelling ratios are similar (2.3–2.7). We hypothesize that in comparison with **D5B2** and **D5B2-1/2NaOH**, which were polymerized with 0 and 0.5 eq. of NaOH, respectively, the protonated DMAPM groups (ammoniums) within **D5B2-1/1HCl** and **D5B2-1/2HCl** are relatively distant from the hydrophobic pNIPAm moieties and backbones in the collapsed GPs. This is because the protonated amine groups are relatively polar and hydrophilic. In other words, the amine groups of the GPs prepared with HCl are located in a "pseudo-swollen" microenvironment analogous to the swollen state even at the collapsed state. After the volume phase transition from the collapsed to the swollen state, swelling has less effect on the amines within the "pseudo-swollen" GPs. As a result, the  $\Delta pK_a$  values of the GPs prepared with HCl are less than those of the GPs prepared without HCl.

The reversible  $\text{CO}_2$  capture stoichiometries of the GP films are presented as red plots in Fig. 1a. **D5B2-1/1HCl** and **D5B2-1/2HCl** show very low reversible  $\text{CO}_2$  capture stoichiometries (0.18 and 0.27 mol  $\text{CO}_2$  per mol amine, respectively), while the values for **D5B2** and **D5B2-1/2NaOH** are both  $\sim 0.97$  mol  $\text{CO}_2$  per mol amine.

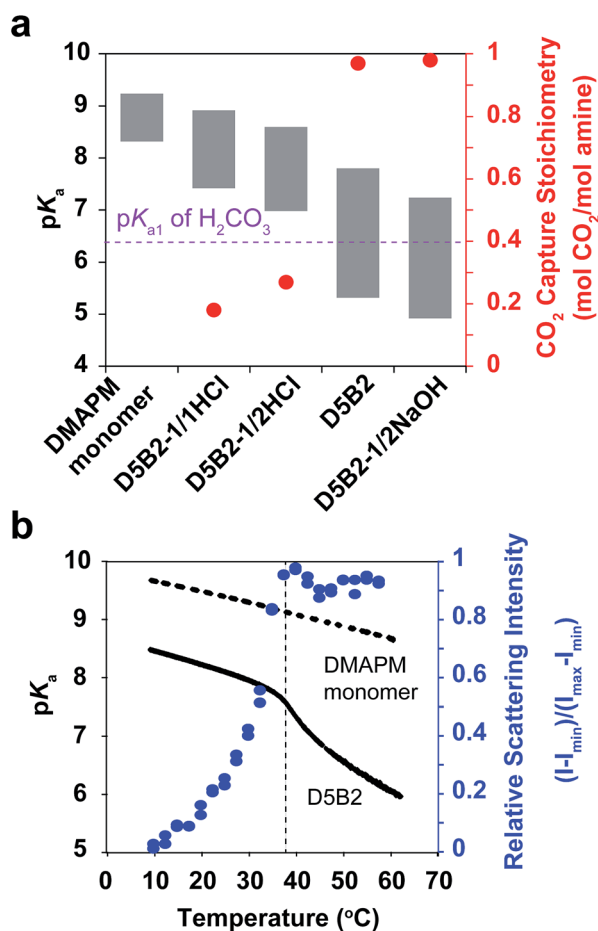


Fig. 1 (a)  $pK_a$  values (left Y-axis) of **D5B2-1/1HCl**, **D5B2-1/2HCl**, **D5B2**, **D5B2-1/2NaOH** and the monomer DMAPM at 75 °C (bottom of bar) and 30 °C (top of bar), and the reversible  $\text{CO}_2$  capture stoichiometries (right Y-axis, red dot) of the GP films in the temperature range 30–75 °C. (b)  $pK_a$  shift (left Y-axis) of **D5B2** (black solid line) and the monomer DMAPM (black dashed line) during the heating process, and the temperature dependent relative scattering intensity (right Y-axis, blue dot) of **D5B2**.





The difference in the stoichiometry can be interpreted by the acid–base theory as follows. It has been reported that the tertiary amines in GPs and CO<sub>2</sub> form ammonium ions (RN<sub>3</sub>H<sup>+</sup>) and bicarbonate ions (HCO<sub>3</sub><sup>−</sup>) *via* base-catalyzed reactions.<sup>44,45</sup> In aqueous media containing RN<sub>3</sub>H<sup>+</sup> and HCO<sub>3</sub><sup>−</sup>, there is always an equilibrium between their corresponding conjugated base–acid, as described in Scheme 2.

When the pK<sub>a</sub> of NR<sub>3</sub>H<sup>+</sup> is above the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, which indicates that NR<sub>3</sub>H<sup>+</sup> holds a proton more tightly than H<sub>2</sub>CO<sub>3</sub> does, the proton will move from the stronger acid, H<sub>2</sub>CO<sub>3</sub>, to the stronger base, NR<sub>3</sub>. As a result, more R<sub>3</sub>N will be consumed and more CO<sub>2</sub> will be captured, as presented by the blue arrows in Scheme 2. In contrast, when the pK<sub>a</sub> of NR<sub>3</sub>H<sup>+</sup> is below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, more CO<sub>2</sub> will be released, as indicated by the red arrows in Scheme 2.<sup>46</sup>

The pK<sub>a1</sub> value of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is in the range of 6.35 ± 0.05 at both 30 °C and 75 °C, as determined by Harned and Davis,<sup>47</sup> however, the pK<sub>a</sub> values of the amine-containing thermal responsive GPs dramatically depend on the temperature, as presented in Fig. 1. The high pK<sub>a</sub> values of **D5B2-1/HCl** and **D5B2-1/2HCl** at 75 °C (7.4 and 7.0, respectively) are higher than the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub> (6.35) and inhibit the release of CO<sub>2</sub>. As a result, the reversible CO<sub>2</sub> capture stoichiometries of **D5B2-1/HCl** and **D5B2-1/2HCl** are low (0.18 and 0.27 mol CO<sub>2</sub> per mol amine, respectively), although the pK<sub>a</sub> values at 30 °C (8.9 and 8.6, respectively) are high enough to capture CO<sub>2</sub> efficiently. For **D5B2** and **D5B2-1/2NaOH**, the high reversible CO<sub>2</sub> capture stoichiometries (0.97 mol CO<sub>2</sub> per mol amine for both) are achieved due to the low pK<sub>a</sub> values at 75 °C (5.3 and 4.9, respectively), which are below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, and meanwhile, the high pK<sub>a</sub> values at 30 °C (7.8 and 7.2, respectively), which are above the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>.

### Effect of ΔpK<sub>a</sub> values of GPs on the reversible CO<sub>2</sub> capture stoichiometry of GP films

Despite the low pK<sub>a</sub> values of **D5B2** and **D5B2-1/2NaOH** at 75 °C (Fig. 1a), their larger ΔpK<sub>a</sub> values between 30 °C and 75 °C (2.5 and 2.3, respectively) than those of **D5B2-1/HCl** and **D5B2-1/2HCl** (1.5 and 1.6, respectively) may also be responsible for their high reversible CO<sub>2</sub> capture stoichiometries.

In order to distinguish the effects of the pK<sub>a</sub> value and the ΔpK<sub>a</sub> on the reversible CO<sub>2</sub> capture stoichiometry of the GP films, a GP with a smaller ΔpK<sub>a</sub> than **D5B2** was prepared by increasing the Bis cross-linker to 10 mol% into the GP that contains 5 mol% DMAPM (**D5B10**), since it has been reported that the crosslink degree influences the ΔpK<sub>a</sub> of the GPs.<sup>24</sup>

The pK<sub>a</sub> values of **D5B2** and **D5B10** at 30 °C and 75 °C are plotted as the top and bottom of the gray bars in Fig. 2. The ΔpK<sub>a</sub> of **D5B10** (1.4) is apparently less than that of **D5B2** (2.5). However the pK<sub>a</sub> value of **D5B10** (5.9) at 30 °C is below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>. Thus the possible reason for the lower reversible CO<sub>2</sub>

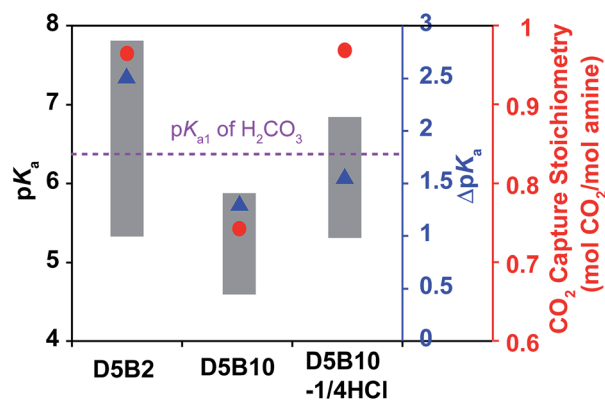


Fig. 2 pK<sub>a</sub> values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar), and ΔpK<sub>a</sub> values (blue right Y-axis, blue triangle) between 75 °C and 30 °C of **D5B2**, **D5B10**, and **D5B10-1/4HCl**, reversible CO<sub>2</sub> capture stoichiometries (red right Y-axis, red dot) of GP films in the temperature range 30–75 °C.

capture stoichiometry of **D5B10** than **D5B2** (0.74 and 0.97 mol CO<sub>2</sub> per mol amine, respectively), the smaller ΔpK<sub>a</sub> of **D5B10** than **D5B2** and/or the low pK<sub>a</sub> value of **D5B10** at 30 °C which is below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, still cannot be distinguished.

To identify the main factor that governs the reversible CO<sub>2</sub> capture stoichiometry, we designed another GP with a greater pK<sub>a</sub> value than **D5B10** and a lower ΔpK<sub>a</sub> than **D5B2**, using the “microenvironment-imprinting” strategy described above. The GPs were prepared by polymerizing **D5B10** in the presence of an appropriate amount of HCl (**D5B10-1/4HCl**).

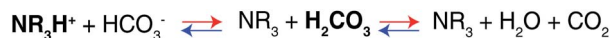
Fig. 2 shows the pK<sub>a</sub> values and ΔpK<sub>a</sub> of **D5B10-1/4HCl**. The pK<sub>a</sub> values at 30 °C and 75 °C of **D5B10-1/4HCl** (6.8 and 5.3, respectively) are higher than those of **D5B10** (5.9 and 4.5, respectively), but the ΔpK<sub>a</sub> of **D5B10-1/4HCl** (1.5) is comparable to that of **D5B10** (1.4). **D5B10-1/4HCl** shows a much higher CO<sub>2</sub> capture stoichiometry (0.97 mol CO<sub>2</sub> per mol amine) than **D5B10** (0.74 mol CO<sub>2</sub> per mol amine), despite the similar ΔpK<sub>a</sub> values.

On the other hand, as displayed in Fig. 2, the pK<sub>a</sub> value of **D5B10-1/4HCl** at 75 °C (5.3) is similar to that of **D5B2** (5.3), while the ΔpK<sub>a</sub> of **D5B10-1/4HCl** (1.5) is much less than that of **D5B2** (2.5). However, both GPs exhibit comparably high reversible CO<sub>2</sub> capture stoichiometries (0.97 mol CO<sub>2</sub> per mol amine), even though the ΔpK<sub>a</sub> values are much different.

We conclude from these results that the ΔpK<sub>a</sub> has a minor influence on the reversible CO<sub>2</sub> capture stoichiometry, and a high reversible CO<sub>2</sub> capture stoichiometry is possible for GPs that exhibit reduced ΔpK<sub>a</sub> values as long as the pK<sub>a</sub> values lie within the appropriate range. The pK<sub>a</sub> value of the GPs must be tuned above the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub> (6.35) at the CO<sub>2</sub> capture temperature (30 °C) and below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub> (6.35) at the CO<sub>2</sub> release temperature (75 °C) in order to achieve a high reversible CO<sub>2</sub> capture stoichiometry.

### Effect of VPTT of GPs on the reversible CO<sub>2</sub> capture stoichiometry of GP films

As shown in Fig. 1b, the thermal responsive volume phase transition of the GPs leads to a sharp pK<sub>a</sub> transition. In



Scheme 2 Equilibrium of the tertiary amine–CO<sub>2</sub> reaction.



addition, the  $pK_a$  value of the GPs has been revealed essential for the reversible  $\text{CO}_2$  capture stoichiometry. Therefore, it is interesting to observe the effect of the VPTT of GPs on the reversible  $\text{CO}_2$  capture stoichiometry of the GP films.

A GP with a lower VPTT than **D5B2** was synthesized by polymerizing 40 mol% of TBAm, which is more hydrophobic than NIPAm, together with 5 mol% DMAPM and 2 mol% Bis (**D5B2T40**). The relative scattering intensity of the GP solutions is shown in Fig. 3a. Compared with **D5B2** (VPTT = 38 °C), the VPTT of **D5B2T40** is only 12 °C. The higher intra-particle hydrophobic interaction of the GPs containing 40 mol% TBAm causes the entropy-driven collapse of **D5B2T40** to occur at a lower temperature.<sup>48,49</sup>

Fig. 3b shows the temperature dependent  $pK_a$  values of **D5B2** and **D5B2T40**. Similar to **D5B2**, **D5B2T40** shows a sharp  $pK_a$

transition at a temperature around its VPTT (12 °C) and a steep  $pK_a$  decrease continues over a wide temperature range above the VPTT. As a result, the  $pK_a$  values of **D5B2T40** at 30 °C and 75 °C (6.0 and 4.8, respectively) are both low. The lower reversible  $\text{CO}_2$  capture stoichiometry of **D5B2T40** (0.60 mol  $\text{CO}_2$  per mol amine) than that of **D5B2** (0.97 mol  $\text{CO}_2$  per mol amine), can be explained by the low  $pK_a$  value of **D5B2T40** at 30 °C (6.0), which is below the  $pK_{a1}$  of  $\text{H}_2\text{CO}_3$ .

Besides **D5B2** and **D5B2T40**, another pair of GPs with different VPTTs were prepared by increasing the feed ratio of DMAPM to 30 mol% (**D30B2** and **D30B2T40**).<sup>48,49</sup> Fig. 3c shows that the VPTT of **D30B2** is above 60 °C. To lower the VPTT, 40 mol% of TBAm was incorporated into the 30 mol% DMAPM-containing GP (**D30B2T40**). In comparison, the VPTT of **D30B2T40** is only 40 °C (Fig. 3c).

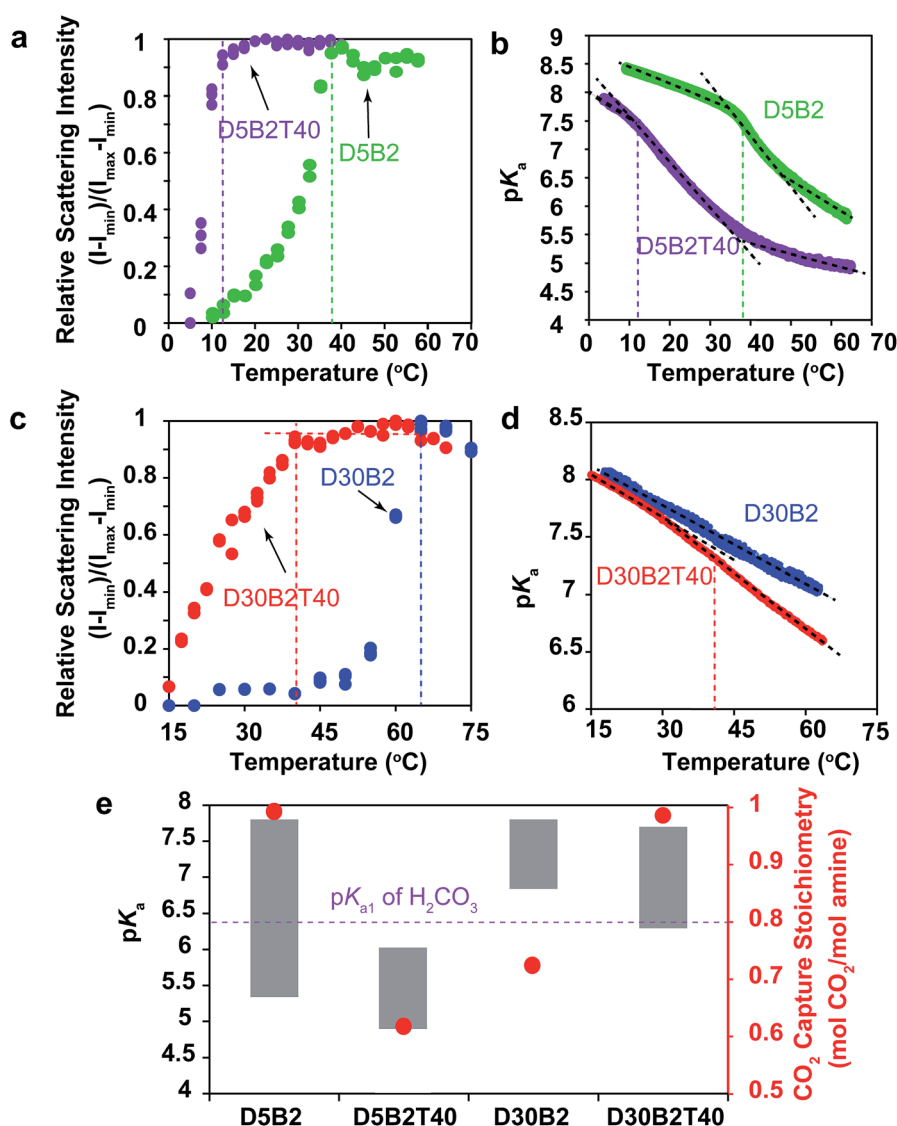


Fig. 3 (a) Relative scattering intensity as a function of temperature for **D5B2** (green) and **D5B2T40** (purple). (b)  $pK_a$  shift of **D5B2** (green) and **D5B2T40** (purple) during the heating process. (c) Relative scattering intensity as a function of temperature for **D30B2** (blue) and **D30B2T40** (red). (d)  $pK_a$  shift of **D30B2** (blue) and **D30B2T40** (red) during heating process. (e)  $pK_a$  values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar) of the GPs, and reversible  $\text{CO}_2$  capture stoichiometries (right Y-axis, red dot) of the GP films in the temperature range 30–75 °C.



In Fig. 3d, the  $pK_a$  value of **D30B2** is linearly dependent on temperature, and no obvious sharp transition is observed in the temperature range due to the high VPTT. However, the  $pK_a$  value of **D30B2T40** exhibits a transition from the temperature around its VPTT (40 °C), and a steeper  $pK_a$  decrease than that of **D30B2** is observed at the temperatures above the VPTT. As a result, **D30B2T40** has lower  $pK_a$  values at higher temperatures (>40 °C) and a larger  $\Delta pK_a$  between 30 °C and 75 °C than **D30B2** (Fig. 3e).

The degree of  $pK_a$  transition of **D30B2T40** (Fig. 3d) induced by the phase transition is less significant than **D5B2** and **D5B2T40** (Fig. 3b). This may be a result of the increased intra-GP charge repulsion within **D30B2T40** caused by the smaller amine–amine distance.

The  $pK_a$  values at 30 °C and 75 °C of **D30B2** (7.8 and 6.8, respectively) and **D30B2T40** (7.7 and 6.3, respectively) are shown in Fig. 3e. The reversible CO<sub>2</sub> capture stoichiometry (0.72 mol CO<sub>2</sub> per mol amine) of **D30B2** is quite low; however, that of **D30B2T40** is much higher at 0.97 mol CO<sub>2</sub> per mol amine. The improved stoichiometric efficiency can be explained by the relatively low  $pK_a$  value of **D30B2T40** at 75 °C (6.3), which is below the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub>. The VPTT of **D30B2T40**, which is close to 30 °C, induces a sharp  $pK_a$  transition and a steep  $pK_a$  decrease over a wide temperature range above the VPTT, lowers the  $pK_a$  value at 75 °C, and consequently improves the reversible CO<sub>2</sub> capture stoichiometry.

In summary, the results in Fig. 3 lead to a comparable conclusion to those of Fig. 1 and 2: the  $pK_a$  values of the GPs at 30 °C and 75 °C govern the reversible CO<sub>2</sub> capture stoichiometry. However, the VPTT of the GPs also plays a crucial role. The GPs with a much lower VPTT than the CO<sub>2</sub> capture temperature (30 °C) show low reversible CO<sub>2</sub> capture stoichiometries due to the low  $pK_a$  value. Meanwhile, to achieve a high reversible CO<sub>2</sub> capture stoichiometry, the VPTT should be above and as close to 30 °C as possible to generate a large  $pK_a$  transition over a wide temperature range above the VPTT.

However, a VPTT above and close to 30 °C is not enough for a high CO<sub>2</sub> capture stoichiometry if the  $pK_a$  values at 30 °C and 75 °C lie at an improper level. For example, in Fig. 1, though the VPTTs of **D5B2-1/1HCl** and **D5B2-1/2HCl** are both 38 °C, the high  $pK_a$  values at 75 °C (7.4 and 7.0, respectively) considerably restrict efficient CO<sub>2</sub> release (0.18 and 0.27 mol CO<sub>2</sub> per mol amine, respectively).

### Effect of GP size on the reversible CO<sub>2</sub> capture stoichiometry of GP films

We have reported that the GP films exhibited larger CO<sub>2</sub> capture capacities than conventional bulk hydrogel films due to the small dimensions of GPs, which lead to a fast response and fast ion diffusion.<sup>29</sup> Herein, the effect of GP size on the reversible CO<sub>2</sub> capture stoichiometry is discussed.

Larger GPs can be prepared by increasing the concentration of monomer or by decreasing the concentration of surfactant.<sup>50</sup> In this study, GPs with the same composition (5 mol% DMAPM and 2 mol% Bis) but different size were designed. A GP with a larger hydrodynamic diameter (**D5B2-L**) than **D5B2** was

prepared by decreasing the concentration of surfactant, while a smaller GP (**D5B2-S**) was synthesized using a monomer solution with a lower total concentration.

The diameters of the GPs at 30 °C and 75 °C are shown in Fig. 4a. As expected, **D5B2-L** (638 nm at 30 °C and 322 nm at 75 °C) has a larger diameter than **D5B2** (196 nm at 30 °C and 74 nm at 75 °C), and **D5B2-S** has the smallest diameter (115 nm at 30 °C and 49 nm at 75 °C). The  $pK_a$  values of the GPs at 30 °C and 75 °C are presented as the top and bottom, respectively, of the bars in Fig. 4b. It can be seen clearly that the  $pK_a$  values of the GPs at both temperatures increase with the decreasing diameter.

The amine groups located at the exterior of the GPs are expected to show higher  $pK_a$  values than those of the interior groups because of the high dielectric constant of water, as well as the reduced steric hindrance. In the meantime, the amine groups of the exterior of the smaller GP account for a much larger percentage than those of the larger GPs. Therefore, smaller GPs show higher  $pK_a$  values than the larger GPs.

Fig. 4b also shows that the three GPs exhibit similar, high reversible CO<sub>2</sub> capture stoichiometries (0.96–1.0 mol CO<sub>2</sub> per mol amine), despite the difference in GP diameters and  $pK_a$  values.

Another pair of GPs showing different  $pK_a$  ranges from those of the GPs in Fig. 4a and b was polymerized using the “micro-environment-imprinting” strategy by adding 0.5 eq. of NaOH to the monomer solution (**D5B2-1/2NaOH** and **D5B2-1/2NaOH-S**). **D5B2-1/2NaOH-S**, having a smaller diameter than **D5B2-1/2NaOH**, was prepared by lowering the total monomer concentration.

Fig. 4c and d show the diameters and  $pK_a$  values, respectively, of the GPs at 30 °C and 75 °C. In good agreement with the results in Fig. 4a, the diameters of **D5B2-1/2NaOH-S** (83 nm at 30 °C and 57 nm at 75 °C) are much smaller than the diameters of **D5B2-1/2NaOH** (715 nm at 30 °C and 349 nm at 75 °C). The  $pK_a$  values of the smaller GP are also higher than those of the larger GP. However, the reversible CO<sub>2</sub> capture stoichiometry of **D5B2-1/2NaOH-S** (0.74 mol CO<sub>2</sub> per mol amine) is lower than that of **D5B2-1/2NaOH** (0.98 mol CO<sub>2</sub> per mol amine), as shown in Fig. 4d.

The different results from Fig. 4b and d could also be ascribed to the different  $pK_a$  values of the GPs. The high  $pK_a$  values of **D5B2-L**, **D5B2**, **D5B2-S**, and **D5B2-1/2NaOH** at 30 °C (7.0, 7.8, 8.5, and 7.2, respectively), which are above the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub> (6.35), and the low  $pK_a$  values at 75 °C (4.8, 5.3, 6.1, and 4.9, respectively), which are below the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub>, result in high reversible CO<sub>2</sub> capture stoichiometries. However, the  $pK_a$  values of **D5B2-1/2NaOH-S** at 30 °C and 75 °C are 8.4 and 6.6, respectively. Its high  $pK_a$  value at 75 °C (6.6), which is above the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub>, restricts the efficient release of CO<sub>2</sub>, resulting in a low reversible CO<sub>2</sub> capture stoichiometry (0.74 mol CO<sub>2</sub> per mol amine).

In general, the results of Fig. 4 lead to the conclusion that the reversible CO<sub>2</sub> capture stoichiometry of GPs can be improved by regulating their  $pK_a$  values at both 30 °C and 75 °C through varying their diameter. The smaller diameter leads to a higher  $pK_a$  value.



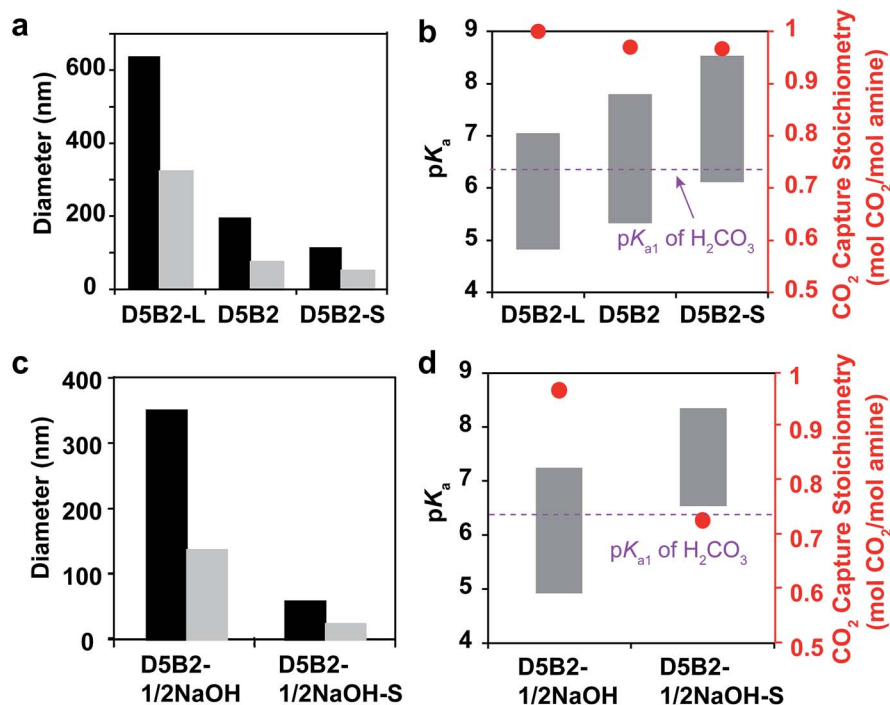


Fig. 4 (a) Diameters at 30 °C (black bar) and 75 °C (gray bar) of D5B2-L, D5B2, and D5B2-S. (b)  $pK_a$  values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar) of the GPs, and the reversible  $\text{CO}_2$  capture stoichiometries (right Y-axis, red dot) of the GP films in the temperature range 30–75 °C. (c) Diameters at 30 °C (black bar) and 75 °C (gray bar) of D5B2-1/2NaOH and D5B2-1/2NaOH-S. (d)  $pK_a$  values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar) of the GPs, and the reversible  $\text{CO}_2$  capture stoichiometries (right Y-axis, red dot) of the GP films in the temperature range 30–75 °C.

### Effect of swelling ratio of GP on the reversible $\text{CO}_2$ capture stoichiometry of GP films

The swelling ratio of thermal responsive GPs plays an important role in their function such as the reversible target binding.<sup>26,51,52</sup> The swelling ratio of GPs is typically controlled by the crosslink degree.<sup>53</sup> Herein, we prepared a series of GPs containing 5 mol% of DMAPM with 0, 2, 5, and 10 mol% Bis crosslinker (D5B0, D5B2, D5B5, and D5B10, respectively) to investigate the effect of the swelling ratio on the reversible  $\text{CO}_2$  capture stoichiometry of GPs.

The diameters at 30 °C and 75 °C, and the swelling ratios of the GPs are plotted in Fig. 5a. It is noteworthy that GP can be obtained without Bis crosslinker (D5B0), possibly due to the slight self-crosslinking.<sup>54</sup> As expected, the swelling ratios of D5B2 (2.7), D5B5 (2.0), and D5B10 (1.6) decrease with the increasing crosslink degree. The diameters of the GPs at 75 °C increase slightly with the increasing amount of Bis crosslinker, indicating that Bis influences the nucleation process during polymerization, as observed by Pelton's group.<sup>50</sup>

Fig. 5b shows the  $pK_a$  values of the GPs at 30 °C and 75 °C, and the  $\Delta pK_a$  values. The  $\Delta pK_a$  values of D5B2 (2.5), D5B5 (2.1), and D5B10 (1.3) between 30 °C and 75 °C show a positive correlation with the swelling ratios of the GPs (2.7, 2.0, and 1.6, respectively). This suggests that from 30 °C to 75 °C the microenvironmental changes, such as the change of dielectric constant and polymer density, around the less cross-linked amines are greater than those of the highly cross-linked amines in the GPs. At 30 °C, the  $pK_a$  values of the swollen GPs, D5B2

(7.8), D5B5 (6.7), and D5B10 (5.9), decrease with the reduction in the swelling ratio, indicating the GP with a smaller swelling ratio is in a relatively collapsed state at 30 °C compared to those with higher swelling ratios, because swelling of the GP is inhibited by the high crosslink degree. The  $pK_a$  value of D5B2 at 30 °C (7.8) is similar to that of D5B0 (7.7), although D5B0 exhibits a much larger swelling ratio, indicating that D5B2 is also fully swollen at 30 °C.

In Fig. 5b, D5B0, D5B2, and D5B5 exhibit similar reversible  $\text{CO}_2$  capture stoichiometries (0.97–1.0 mol  $\text{CO}_2$  per mol amine), while that of D5B10 (0.74 mol  $\text{CO}_2$  per mol amine) is much lower. The difference in the reversible  $\text{CO}_2$  capture stoichiometries can also be explained by their  $pK_a$  values. The higher  $pK_a$  values of D5B0, D5B2, and D5B5 at 30 °C (7.7, 7.8, and 6.7, respectively), which are above the  $pK_{a1}$  of  $\text{H}_2\text{CO}_3$ , and the lower  $pK_a$  values at 75 °C (5.2, 5.3, and 4.4, respectively), which are below the  $pK_{a1}$  of  $\text{H}_2\text{CO}_3$ , lead to high reversible  $\text{CO}_2$  capture stoichiometries. However, the  $pK_a$  value of D5B10 at 30 °C (5.9) is too low and the basicity is too weak to capture  $\text{CO}_2$  efficiently.

Conclusively, the swelling ratio ( $D_{30}/D_{75}$ ), which can be controlled by crosslink degree, is an important factor to tune the  $\Delta pK_a$  and consequently the  $pK_a$  values of GPs to improve the reversible  $\text{CO}_2$  capture stoichiometry.

### Design rationale of GP film with large reversible $\text{CO}_2$ capture stoichiometry

The above discussion has revealed the design rationale of GPs that show large reversible  $\text{CO}_2$  capture stoichiometry within a





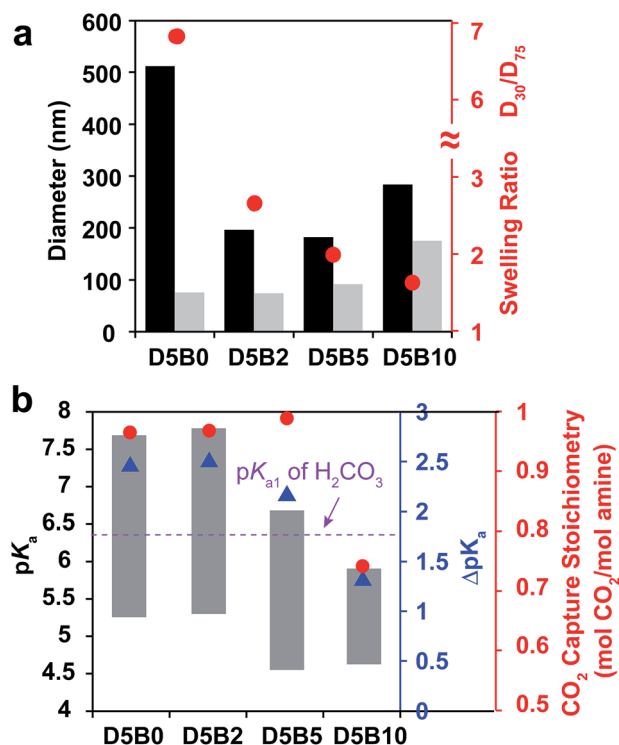


Fig. 5 (a) Diameters (left Y-axis) at 30 °C (black bar) and 75 °C (gray bar) and swelling ratios (right Y-axis, red dot) between 30 °C and 75 °C of D5B0, D5B2, D5B5, and D5B10. (b)  $pK_a$  values (left Y-axis) at 75 °C (bottom of bar) and 30 °C (top of bar), and  $\Delta pK_a$  values (blue right Y-axis, blue triangle) between 75 °C and 30 °C of D5B0, D5B2, D5B5, and D5B10, reversible CO<sub>2</sub> capture stoichiometries (red right Y-axis, red dot) of the GP films in the temperature range 30–75 °C.

narrow temperature range of 30 °C to 75 °C. The  $pK_a$  values of the GPs at 30 °C and 75 °C are the principal factors that govern the reversible CO<sub>2</sub> capture stoichiometry. Higher  $pK_a$  values at 30 °C, above the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub> (6.35), and lower  $pK_a$  values at 75 °C, below the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub>, enable high reversible CO<sub>2</sub> capture stoichiometries of GP films. This is because the GPs are capable of capturing CO<sub>2</sub> efficiently at 30 °C due to the stronger basicity of the amine than HCO<sub>3</sub><sup>−</sup>, and then releasing CO<sub>2</sub> sufficiently at 75 °C because of the weaker basicity. High reversible CO<sub>2</sub> capture stoichiometry can be achieved for GPs that exhibit a smaller  $\Delta pK_a$ , as long as the  $pK_a$  values lie within the appropriate range.

The  $pK_a$  value of the GPs can be readily adjusted to the desired level by varying the VPTT of the GPs above and close to the CO<sub>2</sub> capture temperature (30 °C in this study), because the volume phase transition of GPs always brings out a large  $pK_a$  transition throughout a wide temperature range above the VPTT. The  $pK_a$  value of the GPs can also be tuned by controlling the size of the GPs since smaller GPs show higher  $pK_a$  values. Another method is to regulate the GP swelling ratio, which influences  $\Delta pK_a$  and consequently the  $pK_a$  value of GPs. Finally, the imprinted microenvironment around the amine groups in the GPs can also influence the  $pK_a$  values of the GPs because the GPs synthesized in the presence of a large amount of protons

exhibit higher  $pK_a$  values. The inter-relationship between these factors is illustrated by Scheme 3.

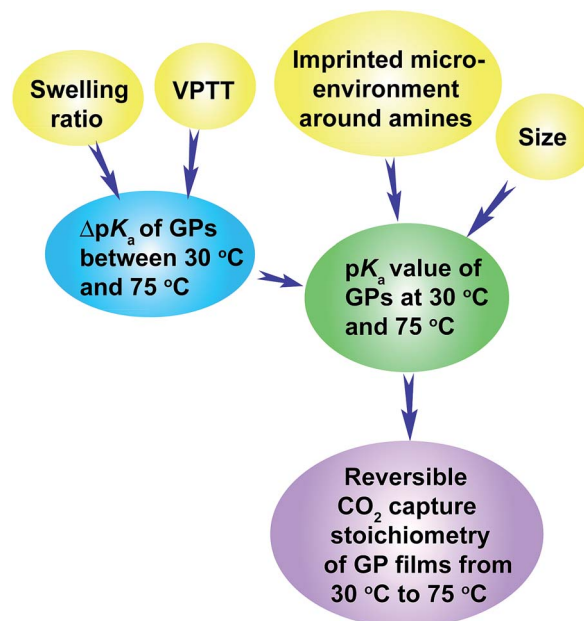
### Optimization of GPs to maximize reversible CO<sub>2</sub> capture capacity

In order to improve the CO<sub>2</sub> capture capacity by GP films, the ratio of functional amine monomer, DMAPM, was maximized to 55 mol% (GPs with a higher DMAPM concentration precipitated during polymerization process). However, D55B2 exhibited a low CO<sub>2</sub> capture stoichiometry (0.73 mol CO<sub>2</sub> per mol amine) due to its high  $pK_a$  value at 75 °C (6.8) (Fig. 6a). According to the design rationale described above, highly efficient CO<sub>2</sub> capture cycles could be achieved if the  $pK_a$  value of the 55 mol% DMAPM-containing GP at 75 °C is below the  $pK_{a1}$  of H<sub>2</sub>CO<sub>3</sub> (6.35).

Since the VPTT of D55B2 is greater than 75 °C, one approach to reducing the  $pK_a$  value of the 55 mol% DMAPM-containing GP at 75 °C is to lower its VPTT. Thus, 43 mol% TBAm was incorporated into the 55 mol% DMAPM-containing GP (D55B2T43).

In accordance with the design rationale, the  $pK_a$  value of D55B2T43 at 75 °C decreases to about 6.35 (Fig. 6a) due to the reduced VPTT *via* the incorporation of TBAm. Consequently, a high reversible CO<sub>2</sub> capture stoichiometry (0.93 mol CO<sub>2</sub> per mol amine) is obtained. As a result of the high amine content and the high stoichiometric efficiency, as shown in Fig. 6b, D55B2T43 shows the largest reversible CO<sub>2</sub> capture capacity (68 mL CO<sub>2</sub> per g dry GPs, 3.0 mmol CO<sub>2</sub> per g dry GPs) in this study.

Though the GP D55B2T43 showed high CO<sub>2</sub> capture capacity (68 mL CO<sub>2</sub> per g dry GPs, 3.0 mmol CO<sub>2</sub> per g dry GPs), taking into account of water and support that are necessary for the GP films, the CO<sub>2</sub> capture capacity of the GP film is lower than the



Scheme 3 Illustration of the design rationale for GPs that show large reversible CO<sub>2</sub> capture stoichiometry.

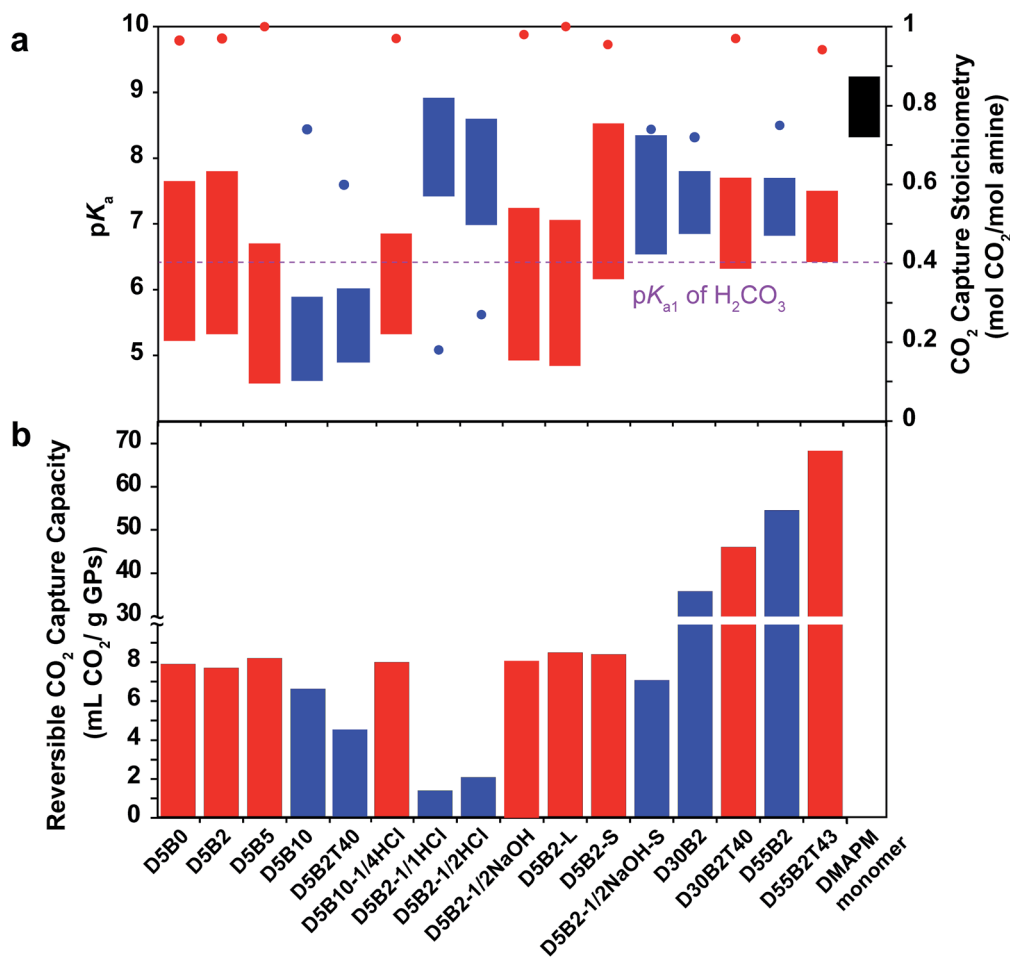


Fig. 6 (a)  $pK_a$  values (left Y axis) at 75 °C (bottom of bar) and 30 °C (top of bar) of the GPs studied in this paper, and the reversible  $CO_2$  capture stoichiometries (right Y axis, red dot) of the GP films in the temperature range 30–75 °C. (b) Reversible  $CO_2$  capture capacities of the GP films in the temperature range 30–75 °C. Red represents GPs with high reversible  $CO_2$  capture stoichiometries (>0.9 mol  $CO_2$  per mol amine) and blue represents those with low stoichiometries (<0.75 mol  $CO_2$  per mol amine).

best adsorbents.<sup>55</sup> However the GP films can be used directly to capture  $CO_2$  from desulfurized post-combustion exhausted gas, without pre-treatment of the exhausted gas to remove water vapor inside, nor to decrease the temperature of the water vapor. Furthermore, the low regeneration temperature of the GP films (75 °C) enables the utilization of abundant and low cost waste heat (<100 °C) of factories as an energy source. Consequently the energy consumption of the GP films might be lowered.

Fig. 6a summarizes the  $pK_a$  values and the reversible  $CO_2$  capture stoichiometries of the GPs studied in this paper. Overall, it can be concluded that the GPs with  $pK_a$  values at 30 °C above the  $pK_{a1}$  of  $H_2CO_3$ , and  $pK_a$  values at 75 °C below the  $pK_{a1}$  of  $H_2CO_3$  (red) generally show larger reversible  $CO_2$  capture stoichiometries than other GPs (blue).

#### Reversibility of the optimized GPs as $CO_2$ absorbent in wet environment

In order to show the cycle stability of the GP film, the reversible  $CO_2$  capture-release by D55B2T43 film was carried out for 10 cycles. The result is shown in Fig. 7 red plots. The reversible  $CO_2$

capture capacity decreased gradually from 0.93 mol  $CO_2$  per mol amine of the 1<sup>st</sup> cycle to 0.71 mol  $CO_2$  per mol amine of the 10<sup>th</sup> cycle. The reason is that the GP film partly dried out, as can be

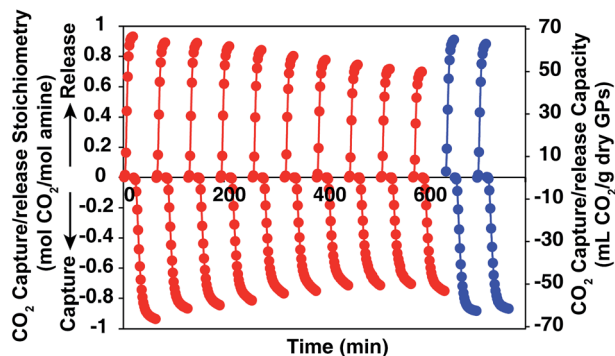


Fig. 7  $CO_2$  capture/release stoichiometry (right Y axis) and  $CO_2$  capture/release capacity (left Y axis) of GP D55B2T43 film with 4 mL water per g GPs. Red: first 10 cycles of  $CO_2$  release/capture by the GP film. After the first 10 cycles, 4 mL water per g GPs was supplied to the dried part of the GP film. Blue: the  $CO_2$  release-capture by the GP film after supplying 4 mL water per g GPs to the dried part of the GP film.

seen in Fig. 2S in ESI.† However, by supplying 4 mL water per g GPs to the dried part of the GP film after 10 CO<sub>2</sub> release/capture cycles, the reversible CO<sub>2</sub> capture capacity can be completely recovered (Fig. 7 blue plots).

We believe the problem of cycle stability can be solved by tuning mass balance of water carefully by engineering the CO<sub>2</sub> capture processes, such as reactor shape and operation condition optimization.

## Conclusions

Inspired by the efficient CO<sub>2</sub> transport mechanism of hemoglobin, known as the Bohr effect, here we revealed the design rationale of amine-functionalized thermo-responsive gel particle (GP) films that reversibly capture and release large amounts of CO<sub>2</sub> efficiently from a model of the exhaust gas of fire power plants over a narrow temperature range (30–75 °C). Appropriate pK<sub>a</sub> values of the GPs at the CO<sub>2</sub> capture and release temperatures (30 °C and 75 °C, respectively) are essential for the reversible CO<sub>2</sub> capture stoichiometry of the GPs films. At 30 °C, a high pK<sub>a</sub> value, above the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, is required for efficient CO<sub>2</sub> capture. Simultaneously, a low pK<sub>a</sub> value at 75 °C, below the pK<sub>a1</sub> of H<sub>2</sub>CO<sub>3</sub>, is required for the efficient release of CO<sub>2</sub>.

The pK<sub>a</sub> value of the GPs can be readily adjusted to the desired level *via* four methods. (1) Controlling the VPTT of the GPs above and close to 30 °C – the phase transition induces a large pK<sub>a</sub> transition over a wide temperature range above the VPTT. (2) Controlling the size of the GPs – smaller GPs show higher pK<sub>a</sub> values. (3) Controlling the swelling ratio, which influences ΔpK<sub>a</sub>, and consequently the pK<sub>a</sub> value of the GPs. (4) Controlling the imprinted microenvironment of the GPs – the GPs synthesized in the presence of a large amount of protons exhibit higher pK<sub>a</sub> values.

We successfully designed and acquired the GP, **D55B2T43**, which exhibited a large reversible CO<sub>2</sub> capture capacity (68 mL CO<sub>2</sub> per g dry GPs, 3.0 mmol CO<sub>2</sub> per g dry GPs) as well as a high reversible CO<sub>2</sub> capture stoichiometry (0.93 mol CO<sub>2</sub> per mol amine), by optimizing the pK<sub>a</sub> value of GPs containing a maximum amount of amine-monomer. We believe GPs with an even larger CO<sub>2</sub> capture capacity could be designed by incorporating co-monomers that are more hydrophobic than TBAm into the tertiary amine-containing GPs, and/or by using more hydrophobic tertiary amine monomers such as *N*-[3-(diethylamino)propyl] methacrylamide. The advantages of amine functionalized GP films, such as the large capture capacity, the low regeneration temperature (75 °C), and the unique ability to work in wet environments, would enable the use of GP films as energy efficient CO<sub>2</sub> absorbents for the exhaust gas of fire power plants. We anticipate that GP films that can reversibly capture other acidic and basic gases with a large capacity can also be achieved by the same strategy inspired by the Bohr effect of hemoglobin.

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