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Reversible Absorption of CO_2 Triggered by Phase Transition of Amine-Containing Micro- and Nanogel Particles

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S *Supporting Information*

ABSTRACT: Herein we report that an aqueous solution of temperature-responsive micro- and nanogel particles (GPs) consisting of *N*-isopropylacrylamide (NIPAm) and *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPM) reversibly absorbs and desorbs CO_2 via a phase transition induced by cooling and heating cycles (30−75 °C). Below the phase-transition temperature, most of the amines in the swollen GPs are capable of forming ion pairs with absorbed bicarbonate ions. However, above the phase-transition temperature, shrinkage of the GPs lowers the pK_a and the number of amine groups exposed to water, thereby resulting in almost complete desorption of CO_2. The GPs can reversibly absorb more than the DMAPM monomer and polymer without NIPAm, which indicates the importance of the temperature-responsive phase transition of polymers in determining the degree of absorption. The results show the potential of temperature-responsive polymer solutions as absorbents to sequester CO_2 at a low energy cost.

The CO_2 level in the atmosphere has been increasing because of the combustion of fossil fuels since the Industrial Revolution, and this is considered to be one of the main factors behind global climate change.[1] Moreover, since fossil fuel reserves are diminishing, processes that can use CO_2 as a carbon source by reducing it—ideally using renewable energy—into liquid fuels such as methanol and dimethyl ether are of great interest.[2,3] Therefore, industrial processes that can capture and concentrate CO_2 selectively from exhaust gases (e.g., from fossil fuel power plants) have gained considerable attention.[2,3]

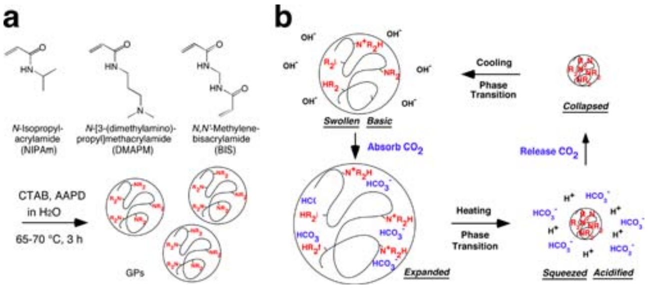
Aqueous solutions of amines are widely used as absorbents for CO_2 in industrial processes.[4] The solutions absorb large amounts of CO_2 from exhaust gases in low-temperature continuous reactors through an exothermic reaction and desorb this CO_2 when heated (typically at >100 °C).[4] However, this desorption process requires a large amount of energy, equivalent to 30% of the typical power plant output, which limits the use of such materials in power plants.[5] Recently, it has been reported that solutions with sterically hindered amines have dramatically lower energy requirements, although the required energy (22% of output) is still too large for power plants.[4] Therefore, CO_2 sorbents that can reversibly capture and release CO_2 under small temperature swings (ideally with a desorption temperature of <100 °C) are required.[4,6]

Recently, a number of CO_2 sorbents that can be regenerated at relatively low temperatures have been reported, including metal−organic frameworks,[7] solid amines,[8] solid amine polymers,[9−11] porous polymer networks,[12] and ionic liquids.[13] However, little has been reported about aqueous sorbents that can handle enormous amounts of water-saturated CO_2 gas reversibly through a small temperature swing. Here we report that an aqueous solution of temperature-responsive micro- and nanogel particles (GPs) consisting of *N*-isopropylacrylamide (NIPAm) and *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPM) can reversibly absorb and desorb CO_2 through a phase transition induced by small-temperature-interval cooling and heating cycles.

It has been reported that poly(NIPAm)-based hydrogels undergo a volume phase transition from a solvent-swollen "hydrophilic" state to a collapsed "hydrophobic" state at the lower critical solution temperature (LCST), which is typically ~31 °C.[14] Tanaka and co-workers reported that with cationic functional groups, poly(NIPAm) can reversibly catch and release polyanionic dyes through multipoint interactions under heating and cooling cycles across the LCST.[15] Lyon,[16] Shea,[17,18] and Okano[19,20] and co-workers have extended the concept to GPs and grafted films for targeting cancer drugs,[16] peptides,[17] proteins,[18] nucleotides,[19] and living cells.[20]

To capture and release CO_2 reversibly, we incorporated tertiary amine groups into the poly(NIPAm) GPs by copolymerizing NIPAm and DMAPM (Scheme 1a). It has been reported that the basicity of the amine groups incorporated in poly(NIPAm) copolymers can be reversibly altered by heating and

Scheme 1. (a) Preparation of Poly(NIPAm-*co*-DMAPM) GPs and (b) Proposed Mechanism for Reversible Absorption of CO_2 by Poly(NIPAm-*co*-DMAPM) GPs



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cooling cycles:[19,21,22] because of the decrease in the dielectric constant around the amine groups in the collapsed phase, protonation of the amine group is suppressed, and thus, the pK_a of the amine-containing poly(NIPAm) is lower above the LCST than below it.[21] We expected that this temperature-dependent pK_a shift could enable the effective capture and release of CO_2 across the LCST. DMAPM, an acrylamide derivative having tertiary amine group, was selected as a model amine-containing monomer, since the CO_2 absorption mechanism of tertiary amines is relatively simple in comparison with primary and secondary amines: unlike primary and secondary amines,[23] tertiary amines do not react with CO_2 directly to form a variety of species such as carbamates and carbamides;[24,25] instead, they mostly facilitate CO_2 hydrolysis through base-catalyzed reactions to form ammonium bicarbonate.[24,25]

A pseudoprecipitation polymerization process was employed to prepare the GPs.[26−28] The GPs (**GP5**, **GP20**, and **GP30**) were synthesized by a thermally initiated free-radical copolymerization of NIPAm, DMAPM (5, 20, and 30 mol %, respectively), and the cross-linker *N*,*N*′-methylenebis(acrylamide) (2 or 5 mol %) in an aqueous solution containing a free radical initiator and surfactant (Scheme 1 and Table S1 in the Supporting Information). As controls, poly(NIPAm) GPs without DMAPM (**GP0**) and poly(DMAPM) without NIPAm (**pDMAPM**) were prepared.

Dynamic light scattering (DLS) confirmed monomodal size distributions for **GP0**, **GP5**, **GP20**, and **GP30** with hydrodynamic diameters of 313 ± 5, 198 ± 2, 387 ± 6, and 1972 ± 21 nm, respectively, at 30 °C. All of the GPs showed a clear phase-transition temperature that was dependent on the feed ratio of DMAPM (Figure S1a and Table S1). The differences in LCST can be explained by the variation in the intraparticle electrostatic repulsion between the protonated ammonium cations.[26] The hydrodynamic diameter and LCST of **pDMAPM** could not be determined because **pDMAPM** does not have hydrophobic side chains that enable the polymers to collapse as GPs.

When the solution of **GP5** was heated and cooled between 10 and 50 °C, the pH of the solution reversibly dropped and jumped, respectively, near the LCST (32−38 °C) (Figure 1a). Since no drop/jump in pH was observed for the solution of DMAPM monomers (**mDMAPM**) or for **pDMAPM**, it appears that the conformational change in the GPs at the LCST induced a reversible pH shift of the solution of amine-containing GPs.

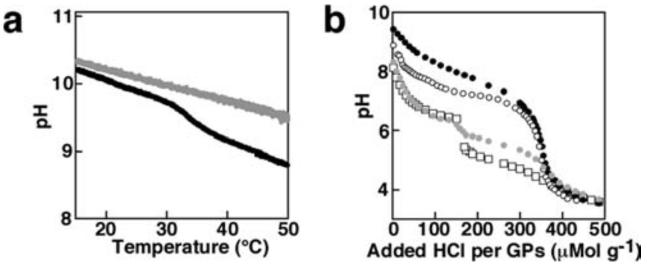

Figure 1. (a) pH of aqueous solutions of **GP5** (4 mg mL^{-1}; black) and **mDMAPM** (93 mM; gray) as functions of temperature. (b) pH titration of aqueous solutions of **GP5** (4 mg mL^{-1}) against HCl at (black ●) 30, (○) 45, (gray ●) 60, and (□) 75 °C.

To investigate further the temperature-dependent change in basicity, solutions of **GP5**, **pDMAPM**, and **mDMAPM** were titrated against HCl. Titration of the solutions at 30 °C showed the typical titration curves of polymers and monomers with a single equivalence point (Figures 1b and S1b). The apparent pK_a values for **GP5**, **pDMAPM**, and **mDMAPM**, which were estimated from the 50% equivalence points of the titration curves, are 7.8, 7.7, and 9.3, respectively. The pK_a difference between the polymers (**GP5** and **pDMAPM**) and **mDMAPM** is due to the density of charges: the electrostatic repulsion of the ammonium cations on the polymers destabilizes the formation of these cations, since the amines on the polymers are much closer to each other than are the amines on the monomers in solution.[29] When the solutions were titrated at higher temperatures (75 °C), moderate shifts in pK_a were observed for **pDMAPM** (ΔpK_a = 0.6) and **mDMAPM** (ΔpK_a = 0.8), although little change in the equivalence point was observed (Figure S1b). However, the titration of **GP5** showed a two-stage equivalence curve at temperatures above 60 °C (Figure 1b). Both of the apparent pK_a values obtained from the two-stage titration curve at 75 °C (pK_{a1} = 6.6 and pK_{a2} = 4.9) are significantly lower than the pK_a of 7.8 at 30 °C (ΔpK_{a1} = 1.2, ΔpK_{a2} = 2.9). This decrease in pK_a at higher temperature can be explained by the phase change of the GPs: since the dielectric constant around the amine groups decreases for the collapsed (dehydrated)-phase GPs, protonation of the amine group is disfavored, and thus, the pK_a of **GP5** is lower at temperatures above the LCST.[21,22] The two-stage titration curves indicated the presence of two different amine environments in **GP5**: one is highly hindered (pK_{a2} = 4.9), and the other is relatively closer to the environment in water (pK_{a1} = 6.6). Importantly, the basicities of all of the amines in **GP5** at temperatures above 60 °C were significantly weaker than at 30 °C, whereas those of **pDMAPM** and **mDMAPM** showed only a moderate difference.

When CO_2 gas (in a mixture of 10% CO_2 and 90% N_2) was bubbled into a solution of **GP5**, the hydrodynamic diameter of the GPs approximately doubled (from ∼200 to ∼400 nm) and the LCST increased by ∼20 °C (from 35 to 55 °C) (Figure 2a). However, the size and LCST of **GP0** did not change after bubbling of CO_2. These results suggest that CO_2 was absorbed in the solution as carbonic acid (CA), which protonated the amine groups on the GPs,[30] forming a number of ammonium salts in the GPs. The GPs thus expanded as a result of the intraparticle electrostatic repulsion of ammonium cations. Importantly, the particle size at 75 °C was equal to that without bubbling of CO_2, suggesting that the absorbed CO_2 was released at higher temperature.

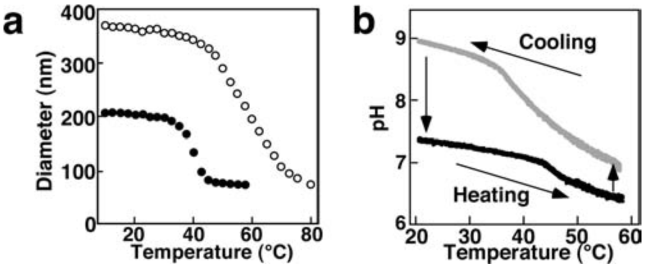

Figure 2. (a) Hydrodynamic diameter of **GP5** as a function of temperature in water (2 mg mL^{-1}) (●) before and (○) after bubbling of 10% CO_2 for 2 h. The solution was equilibrated at each temperature for ∼6 min in N_2 and a 10/90 CO_2/N_2, respectively. (b) pH of an aqueous solution of **GP5** (10 mg mL^{-1}) under a 10% CO_2 (2 mL min^{-1}) as a function of temperature during the heating (black) and cooling (gray) processes. The solution was equilibrated at 20 and 58 °C after cooling and heating, respectively, until the pH stabilized.

To estimate the protonation ratio of the amine groups and protonation state of CA species in the solution in the presence of

10% CO_2 gas, the pH of the **GP5** solution was monitored during the temperature swing process (Figure 2b). As expected, the solution pH of 7.2 after bubbling of 10% CO_2 at 30 °C was lower than the pK_a of 7.8 for **GP5** obtained from the titration at 30 °C, indicating that most of the amines were protonated. The pH of 7.2 at 30 °C was higher than the first acid dissociation constant of CA ($pK_{a1,CA} = 6.4$) and lower than the second dissociation constant ($pK_{a2,CA} = 10.3$),[31] indicating that majority of the CA molecules were deprotonated as monovalent bicarbonate anions, forming ammonium bicarbonate salt. When the solution was heated to 60 °C under 10% CO_2 gas, the pH of the solution slightly decreased in a linear fashion until the temperature reached 45 °C and then dropped dramatically (Figure 2b). The temperature at which the drop occurred (45 °C) is close to the LCST observed by DLS in the presence of 10% CO_2 (Figure 2a). The degree of the pH drop is comparable to the pH drop of the solution of **GP5** observed around the LCST (32−38 °C) in the absence of CO_2 (Figure 1a). These results suggest that the phase change of GPs induced deionization of the amine groups in the GPs because of the decreased dielectric constant around the amine groups in the collapsed phase, resulting in a release of bicarbonate ions from the GPs into the water as CA, which in turn led to acidification of the solution. The solution pH of 6.5 right after the temperature reached ~60 °C was higher than the amine pK_{a2} of 5.5 at 60 °C, corresponding to the amines expected to be highly hindered by the polymer chains, and close to the amine pK_{a1} of 6.6 at 60 °C, corresponding to amines in an environment relatively close to that in water. These results suggest that all of the amines in the hindered position and about half of the amines in the water-like environment (~73% of all the amines in the GPs) were deprotonated in this state.

When the temperature was kept at ~60 °C under 10% CO_2, the pH of the solution increased to 7.0 (Figure 2b), which is higher than both pK_a's of **GP5** at 60 °C ($pK_{a1} = 6.6$ and $pK_{a2} = 5.5$), indicating that most of the amines in **GP5** were deprotonated as a result of CO_2 release. It should be noted that CA readily dehydrated to give CO_2 because of its low hydration constant.[31] When the solution was cooled, its pH dramatically increased to 8.6 at 35 °C because of the pK_a increase of the amines in the GPs induced by the temperature-dependent swelling (hydration) of **GP5** (Figure 2a). Importantly, 35 °C is close to the LCST observed in the absence of CO_2 (Figure 1a), indicating that CO_2 was almost completely released in the equilibration process at 60 °C. Moreover, the pH of 8.8 at 30 °C in the cooling process (Figure 2b) is much higher than the pK_a of **GP5** ($pK_a = 7.8$ at 30 °C) (Figure 1b), indicating that most of the amines were deprotonated and that the basic CO_2 sorbent was regenerated.

Absorption of CO_2 was confirmed by ^{13}C NMR spectroscopy. As shown in Figure S2, a D_2O solution of **GP30** after bubbling of 10% CO_2 at 25 °C showed a signal at 160.4 ppm, which corresponds to the carbonyl carbon of bicarbonate ion.[32] The corresponding peaks of CO_2 (126 ppm) and CO_3^{-2} (169 ppm) were not observed.[32] The signal at 160.4 ppm was not osbserved for the same solution before CO_2 bubbling or after heating at 75 °C overnight, providing evidence of the CO_2 absorption mechanism proposed in the pH experiment. It should be noted that tertiary amines do not form carbamates or carbamides.[24,25]

To quantify the absolute amounts of CO_2 captured and released during the temperature swing process, 10% CO_2 was bubbled continuously through the solution of **GPs**, and the level of CO_2 in the gas downstream was quantified every 2.5 min by a gas chromatograph (GC) equipped with a thermal conductivity detector (Figure S3). Here, the GPs with high amine content (**GP20** and **GP30**) were used. All of the solutions were equilibrated with 10% CO_2 for ~8 h at 30 °C prior to the experiment. When the solution of **GP30** was heated from 30 to 75 °C, the CO_2 level in the outgas increased gradually for 25 min up to 18% and decreased back to 10% in ~2 h, indicating that CO_2 was released from the solution (Figure 3a). The solution was then cooled back to 30 °C. During this process, the CO_2 level in the outgas gradually decreased to 6% over 30 min and then increased back to 10% in ~4 h, indicating that CO_2 was dissolved in the solution (Figure 3a). Importantly, the amount of CO_2 released from the GPs consisting of both DMAPM and NIPAm was much larger than those from pure water and solutions of **GP0**, **pDMAPM**, and **mDMAPM** (Figure S4a and Table S1). Precipitation was not observed in any of the solutions. From these results, it can be concluded that the pK_a shift triggered by the swelling−collapse phase change of the amine-containing poly(NIPAm) is critical to the release of CO_2 in this small-temperature-swing process. At 30 °C, a comparable amount of CO_2 absorption was observed (Figure S4b). Binding stoichiometry calculations revealed that each amine in **GP20** and **GP30** caught and released ~1 equiv of CO_2, whereas **pDMAPM** and **mDMAPM** captured only ~0.2 and ~0.1 equiv, respectively (Table S1). These results support the reversible CO_2 binding mechanism suggested by the DLS, pH, and ^{13}C NMR experiments. Interestingly, the binding stoichiometries of **GP20** and **GP30** were almost consistent, although the hydrodynamic diameter of **GP30** (1972 nm) was 5 times larger than that of **GP20** (387 nm). This indicates that most amines, including the ones in the micrometer-sized GPs, can be used to capture CO_2 because of the low polymer density and high diffusion rate in the swollen hydrogel particles.[28,33]

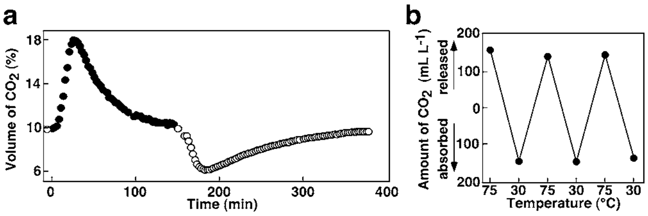

Figure 3. (a) Desorption−absorption cycle of CO_2 by **GP30** solution (2.1 mM amine, 500 mL). The partial volume of CO_2 in the gas downstream (20 mL min^{-1}) was quantified by GC. The temperatures of the solution were (●) 75 and (○) 30 °C. (b) Desorption−absorption of CO_2 by **GP30** solution (2.1 mM amine, 500 mL) for three cycles.

Figure 3b shows the amounts of CO_2 desorbed and absorbed from a **GP30** solution over three consecutive heating and cooling cycles. As can be clearly seen, **GP30** could capture and release CO_2 repeatedly in a temperature-responsive manner. The process was reversible, as the GPs did not form precipitates or lose their binding capability. Furthermore, no volatile compounds besides CO_2 and N_2 were detected by GC in the outgas during the cycles (Figure S5), indicating the advantage of using polymer materials in an aqueous system in a low-temperature process.

From these results, we conclude that aqueous solutions of temperature-responsive GPs consisting of NIPAm and DMAPM can reversibly absorb and desorb almost 1 equiv of CO_2 per amine during the cooling and heating cycles. Below the phase-transition temperature (30 °C), most amines in the swollen GPs are capable of forming ion pairs with absorbed bicarbonate ions.

However, above the phase-transition temperature (75 °C), shrinkage of the GPs lowers the pK_a and the number of amine groups that are exposed to water, resulting in almost complete desorption of CO_2. The amount of CO_2 that was reversibly absorbed by the GPs was greater than those by DMAPM monomers and the polymer without NIPAm, showing the importance of the temperature-responsive phase transition for reversible absorption.

Although the CO_2 absorption capacity per amine in this study is comparable or superior to that of the CO_2 absorbent in the current industrial process, which consists of methanolamines, the absorption capacity per unit volume of solution was much smaller than that of the optimized absorbent. The absorption rate of our solution was also lower than for the industrialized solution.[4−6] These results are due to the much lower concentration of amines in this study (<1 g L^{-1}) compared with the optimized system (~300 g L^{-1}) and the use of tertiary amines in our system to simplify the absorption mechanism.

Despite the relatively low CO_2 absorption capacity and slow kinetics in this work compared with the traditional absorbents, we believe that the reversible absorption mechanism proposed in this study provides a novel strategy for the design of energy-efficient CO_2 sorbents. The low regeneration temperature in this work (75 °C), which could be further lowered by tuning the LCST,[26,33] should enable the utilization of abundant and low-cost waste heat (<100 °C) of factories as an energy source as well as a decrease in the sensible heat of the whole system and the latent heat of boiling water and amines. Moreover, the absorption capacity per volume of sorbent would be dramatically enlarged, reduce the heat required to raise the temperature of the absorbent by maximizing the concentration of GPs and optimizing the composition of the amines in the GPs. The absorption−desorption kinetics could be accelerated by incorporation of more nucleophilic amines, such as primary and secondary amines, and tuning of the LCST and the swell/collapse ratio of the GPs.[33] Thus, temperature-responsive nano- and microgel-based sorbents that sequester CO_2 at a low energy cost should be accessible.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, synthetic and analysis procedures, and supporting data (Table S1 and Figures S1−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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