

Amidine-functionalized poly(2 vinyl-4,4-dimethylazlactone) for selective and efficient CO₂ fixing

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ABSTRACT

Development of novel polymeric materials capable of efficient CO₂ capture and separation under ambient conditions is crucial for cost-effective and practical industrial applications. Here we report the facile synthesis of a new CO₂-responsive polymer through post-polymerization modification of poly(2 vinyl-4,4-dimethylazlactone) (PVDMA). The reactive pendant azlactone groups of PVDMA are easily modified with 4-(*N*-methyltetrahydropyrimidine) benzyl alcohol (PBA) without any by-product formation. FTIR and TGA experiments show the new PBA functionalized polymer powder can reversibly capture CO₂ at room temperature and under atmospheric pressure. CO₂ capture was selective, showing a high fixing efficiency even with a mixed gas system (20% CO₂, 80% N₂) similar to flue gas. CO₂ release occurred at room temperature and release profiles were investigated as a function of temperature. Density Functional Theory (DFT) calculations coupled with modeling and simulation reveal the presence of two CO₂ binding sites in the PBA functionalized polymer resulting in a two-step CO₂ release at room temperature. The ease of material preparation, high fixing efficiency, and robust release characteristics suggest that post-polymerization modification may be a useful route to designing new materials for CO₂ capture.

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1. INTRODUCTION

Carbon dioxide (CO₂) emissions from the burning of fossil fuels have grown exponentially since the industrial era,¹ and increasing atmospheric concentrations of CO₂ have been linked to global warming.² According to the International Energy Agency (IEA), selective carbon capture and sequestration (CCS) from flue gas could play an important role in reducing CO₂ emissions.³⁻⁶ There are three major approaches to CCS, namely post-combustion capture, pre-combustion

capture and the oxyfuel process. The post-combustion capture processes have several advantages due to compatibility with existing combustion technologies. The most common method of post-combustion capture involves absorbing CO₂ from exhaust gases at low temperature using a concentrated aqueous solution of amines (generally, concentrations of 20-30%). Drawbacks to this method include a high heat load because the amine solution needs to be heated to 150 °C in order to liberate CO₂^{1,7} and operational challenges caused by the corrosive nature of amine solutions.⁸ This has led to an increased interest in developing solid phase absorbent or adsorbent materials that can capture and release CO₂ in an energy efficient and environmentally benign way.

In this pursuit, a variety of material systems have been investigated, including metal-organic frameworks,⁹⁻¹¹ amine-functionalized silica particles,¹²⁻¹⁵ amine-functionalized porous polymer networks,¹⁶ mesoporous phenol networks,¹⁷ ionic liquids,¹⁸⁻²⁰ and temperature sensitive amine based micro- and nanogel particles.^{21,22} These solid sorbents have several advantages, including high capture density due to their high surface area-to-volume ratios and favorable release characteristics because CO₂ molecules are distributed mostly along the surface. In general, amine-based polymeric sorbents are preferred candidates for CO₂ capture because of their inherent basicity to bind with CO₂, which is a Lewis acid, and also because they can be constructed using a vast pool of monomeric building blocks with the synthetic diversity providing a route to fine-tune material properties such as surface area, stability, responsivity etc.²³⁻²⁶

However, compared to amines, amidines typically have a higher tendency to bind CO₂ because they are more nucleophilic and stabilize the resulting cation via delocalization in the amidine system.²⁷ Recently, Furusho *et al.* synthesized an aliphatic polyamidine system and demonstrated

that in the solid state,⁷ 3.4% of the amidine groups captured CO₂, compared to 1.8% of the amino groups in polyethyleneimine. However, the synthesis of amidine functionalized polymers is a cumbersome process. Therefore, the development of a facile and robust synthetic method to synthesize polyamidine based materials would be of great interest for the design of new systems capable of efficient and reversible CO₂ capture.

Another route to generating polymers with desirable properties involves post-polymerization modification strategies. For example, Rhe and co-workers reported that succinimide ester functionalized polymer brushes could be modified with n-alkyl amines,²⁸ Klok *et al.* has shown the modification of both PHEMA and poly(glycidyl methacrylate) (PGMA) brushes,²⁹⁻³¹ Bruening *et al.* modified poly(2-hydroxyethyl methacrylate) (PHEMA) brushes using a nickel complex and histidine,³² and Hawker and Wooley used Click chemistry to functionalize acetylene block copolymers.³³ We are particularly interested in post-polymerization modification of poly(2 vinyl-4,4 dimethylazlactone) (PVDMA) due to the polymer's hydrolytic stability, its facile reaction with nucleophilic groups such as thiols, alcohols and primary amines, and because no side products are generated during the modification reactions.³⁴⁻³⁷ Herein, we report the synthesis of a new amidine-based alcohol, 4-(*N*-methyltetrahydropyrimidine) benzyl alcohol (PBA) and its utilization for post-polymerization modification of well-defined PVDMA homopolymers. The resulting new, solid state powdered polymeric material is capable of CO₂ capture at room temperature and reversible release, including selective capture from a mixed gas (similar to flue gas) system. In addition, we examine the binding interaction between CO₂ molecules and the active amidine groups in the PBA-modified PVDMA with temperature dependent CO₂ release using thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) experiments coupled with theoretical modeling and simulation.

2. EXPERIMENTAL SECTION

2.1 Materials

All reagents, including 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT), were purchased from Aldrich at the highest purity available and used as received unless stated otherwise. 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) was purchased from Wako Specialty Chemicals and recrystallized from methanol before use. 2 vinyl-4,4-dimethylazlactone monomer (VDMA; Isochem North America, LLC) was fractionally distilled under reduced pressure and the middle fraction (~70%) was used. Cylinders of CO₂ (99% by volume) and 20% CO₂/80% N₂ were purchased from Airgas and used as received.

2.2 Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H and ^{13}C NMR spectra were collected on a Varian VNMRS 500 MHz multinuclear spectrometer. Chloroform-*d* (CDCl_3) was used as the solvent and residual solvent peak served as internal standard.

Size Exclusion Chromatography (SEC). Absolute molecular weights and dispersities were measured by size exclusion chromatography (SEC) using an Agilent 1310B 1260 Infinity HPLC instrument (equipped with an isocratic pump, degasser, autosampler, thermostatted column compartment and instant pilot controller); four Phenomenex Phenogel columns in series (each 300 mm \times 7.8 mm in dimension with 10 μm particle size and porosities of 2×10^5 Å, 1×10^4 Å, and 1×10^3 Å respectively); a Wyatt DAWN HELEOS II ambient 18-angle light scattering detector; and a Wyatt Optilab T-rEX differential refractive index detector. THF was used as the mobile phase at a flow rate of 1 mL/min.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were recorded using a Bruker Optics Vertex 70 spectrometer with a deuterated L-alanine doped triglycine sulfate (DLATGS) detector. Bulk polymer samples were analyzed *via* ATR-FTIR using a Harrick Scientific MVP Star accessory equipped with a diamond internal reflection element (IRE). A background spectrum of the clean ATR crystal was collected as the average of 64 scans, and the polymer sample spectra was collected as the average of 64 scans with 4 cm^{-1} resolution.

Thermogravimetric Analysis (TGA). A TA Instruments Q5000 TGA instrument was used to analyze CO_2 adsorption and desorption from the PBA-modified PVDMA. The CO_2 desorption from the modified polymer was examined at 25, 55 and 100 $^\circ\text{C}$ using CO_2 gas (99% purity) and a 20% CO_2 /80% N_2 gas mixture. In a typical experiment, ~ 10 mg of PBA-modified PVDMA was

added to a platinum pan and loaded into the TGA instrument. The sample was initially heated under a pure N₂ atmosphere at a flow rate of 20 mL/min to 100 °C, where the temperature was maintained for 40 minutes to desorb any absorbed moisture or CO₂. After this protocol, the temperature was lowered to room temperature (nominally 25 °C) while maintaining N₂ flow.

To examine CO₂ capture and release properties, the sample was exposed for 40 minutes to 99% CO₂ at a flow rate of 20 mL/min. After CO₂ exposure, the gas flow was switched to pure N₂, and the temperature was increased to 55 °C and held constant for 40 minutes while CO₂ desorption was monitored. To investigate repeatability, each sample was subjected to three CO₂ absorption and desorption cycles. At the conclusion of the third cycle, the temperature was increased from 55 °C to 100 °C under N₂ to fully desorb the CO₂.

2.3 Synthetic Procedures

Synthesis of 4-(1,3-N-propane diamine)benzyl alcohol (2). A 3 mL solution of 4-chloromethyl benzyl alcohol (1) (200 mg, 1.28 mmol) in anhydrous dichloromethane was added drop-wise to a round bottom flask containing 10 mL solution of 1,3-propane diamine (475 mg, 6.4 mmol) in dichloromethane at 0°C under a nitrogen atmosphere. The temperature was maintained at 0 °C for 1 h and then slowly allowed to come to room temperature. The reaction was allowed to proceed at room temperature for 24 h under a nitrogen atmosphere. After 24 h, the reaction flask was placed in the freezer for 3 h. The cooled reaction mixture was filtered using a sintered glass funnel to remove the precipitate from the homogenate. The homogeneous filtrate was concentrated by rotary evaporation to obtain the crude product. The crude product was dried under vacuum at 40 °C to remove the excess diamine, yielding the desired product **2** as an oily liquid. (199 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃): δ(ppm) 7.28-7.35 (m, 4H), 4.66-4.69 (s, 2H), 3.7-3.8(s, 2H), 2.74-2.79(t, 2H), 2.66-2.71 (t, 2H), 1.85-2.1 (s, 4H), 1.50-1.80 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ(ppm) 140.1, 139.4, 129.3, 128.3, 127.0, 127.4, 64.6, 53.7, 47.0, 40.5, 33.5. FTIR: ν (cm⁻¹) 3280, 2925, 2848, 1595, 1513, 1454, 1418, 1361, 1211, 1104, 1033, 1016, 942, 804, 749.

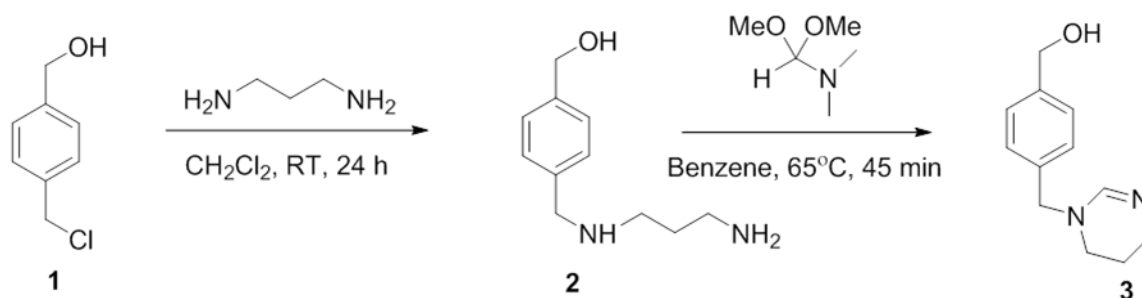
Synthesis of 4-(N-methyltetrahydropyrimidine)benzyl alcohol (PBA)(3). *N,N*-dimethylformamide dimethylacetal (0.460 mL, 3.46 mmol) was added to a solution of **2** (672 mg, 3.46 mmol) in 30 mL of benzene. The mixture was stirred for 45 minutes in a thermostatted oil bath set at 65°C. The crude product was then concentrated by rotary evaporation to remove the solvent and the unreacted *N,N*-dimethylformamide dimethylacetal. The remaining crude product was then dried under vacuum at room temperature to obtain **3** as a waxy solid (600 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃): δ(ppm) 7.26-7.28 (d, 2H), 7.03-7.05 (d, 2H), 6.91 (s, 1H), 4.51 (s, 2H), 4.04 (s, 2H), 3.70-3.82 (s, 1H), 3.10 (t, 2H), 2.89 (t, 2H), 1.63 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ(ppm) 155.1, 150.2, 141.6, 135.7, 128.8, 127.7, 126.8, 64.1, 56.6, 43.1, 42.2, 20.7. FTIR: ν (cm⁻¹) 3092, 2927, 2840, 2678, 1624, 1444, 1410, 1348, 1315, 1302, 1275, 1225, 1209, 1187, 1175, 1103, 1045, 1018, 996, 977, 923, 757, 740, 709, 537, 482.

Synthesis of poly(2-vinyl-4,4 dimethylazlactone)(PVDMA) (4). The reaction was formulated in a single-neck 50 mL Airfree® round bottom reaction flask equipped with a Teflon-coated magnetic stir bar. In a typical reaction, VDMA monomer (5.64 g, 4.00×10^{-2} mol) was combined with CPDT (243.33 mg, 7.05×10^{-4} mol; VDMA: DMP = 56.74), V-70 (72.48 mg, 2.35×10^{-4} mol; molar ratio of CPDT: V-70 = 3:1) and benzene (40.0 mL). The reaction vessel was capped with a rubber septum and the solution was sparged with dry argon for ~30 min. The reaction vessel was then placed in an oil bath thermostatted at 30 °C and allowed to react for 24 h, after which the reaction vessel was immersed in liquid nitrogen to quench the polymerization. The solution was then precipitated in cold hexanes to recover the PVDMA. The recovered polymer was re-dissolved in benzene and then re-precipitated in cold hexanes to isolate and purify the PVDMA. With the refractive index increment known from our previous work,³⁴ the absolute weight-average molecular weight, M_w , was found to be 6,480 g/mol with a dispersity (\mathcal{D}) of 1.08, as determined by MALLS-SEC.

Functionalization of PVDMA(4) with PBA(3) to form PVDMA/PBA conjugate 5. PBA (291.41 mg, 7.14×10^{-3} mol) was added to a solution of PVDMA (200 mg, 2.86×10^{-5} mol) in chloroform (nominally 10.0 mL). The mixture was stirred overnight at room temperature, after which time the reaction mixture was precipitated in hexanes. The precipitate was collected by decanting the solvent mixture. When attempting to purify the polymer by re-dissolving into chloroform, it was found that the polymer was insoluble. The polymer was then poured into 50 mL of chloroform and shaken vigorously in a vortex mixture, allowed to settle and the filtrate decanted to remove any unreacted PVDMA and/or PBA. This purification step was repeated three times to isolate the PVDMA/PBA conjugate, which is shown and identified as **5** in Scheme 2. The PVDMA/PBA conjugate **5** was then dried under vacuum to remove residual solvent. The isolated, purified PVDMA/PBA conjugate **5** was found to have very low solubility in common organic solvents.

3. RESULTS AND DISCUSSION

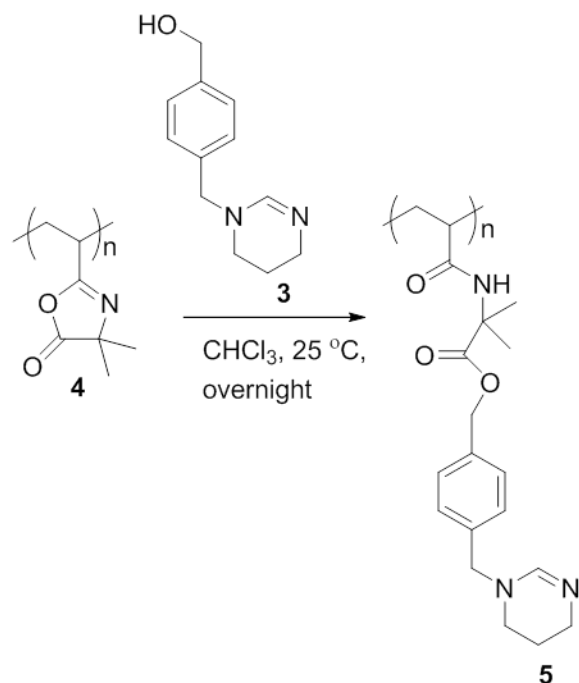
Materials Synthesis and Characterization. PVDMA was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization according to our previous reports.^{34,38} 4-(*N*-methyltetrahydropyrimidine)benzyl alcohol (PBA) (**3**), a new compound that is similar to the structure of (*N*-methyltetrahydropyrimidine), MTHP,²⁷ was designed and synthesized as shown in *Scheme 1*.



Scheme 1. Synthesis of PBA (**3**)

First, 4-(1,3-*N*-propane diamine)benzyl alcohol (**2**) was synthesized by nucleophilic substitution of 4-chloromethyl benzyl alcohol (**1**) with 1,3-propane diamine. Compound **2** was then reacted with *N,N*-dimethylformamide dimethylacetal followed by ring closure to form PBA (**3**) in high yield (90 %). The hydroxyl group of PBA provides a useful reactive handle for the subsequent modification of PVDMA.

Previously, we utilized PVDMA to generate functional polymer surfaces and investigated the resultant structure-property relationships.^{34,38-42} Facile modification of the azlactone moiety is possible under relatively mild conditions in the presence of good nucleophiles such as alcohols, amines, and thiols.^{34,37} The solution phase modification of PVDMA with PBA, as shown in *Scheme 2* proceeded at room temperature and was confirmed by FTIR spectroscopy (**Figure 1**).



Scheme 2. Modification of PVDMA (4) with 3 to form PVDMA/PBA conjugate 5

The band at 1820 cm^{-1} assigned to the carbonyl ($\text{C}=\text{O}$) of the azlactone disappeared when PVDMA reacted with PBA. The conversion was 98.3% as evaluated from the ratio of the peak areas at 1820 cm^{-1} before and after the functionalization. Functionalization of PVDMA to PVDMA/PBA conjugate 5 was further evidenced by the broad absorption band from 1560 cm^{-1} to 1700 cm^{-1} which indicated the presence of amidine ($\text{C}=\text{N}$) and amide ($-\text{NH}-\text{C}=\text{O}$) functional groups, and the band at 1744 cm^{-1} , indicating an ester ($-\text{O}-\text{C}=\text{O}$) functional moiety. Functionalization of PVDMA with weaker nucleophiles such as alcohols usually requires a catalyst, such as 1,8-diazabicyclo[7.1.1]undec-7-ene (DBU).^{34,37} However, functionalization of PVDMA using PBA proceeded efficiently without any catalyst due to the ability of the basic amidine group in PBA to self-catalyze the reaction.

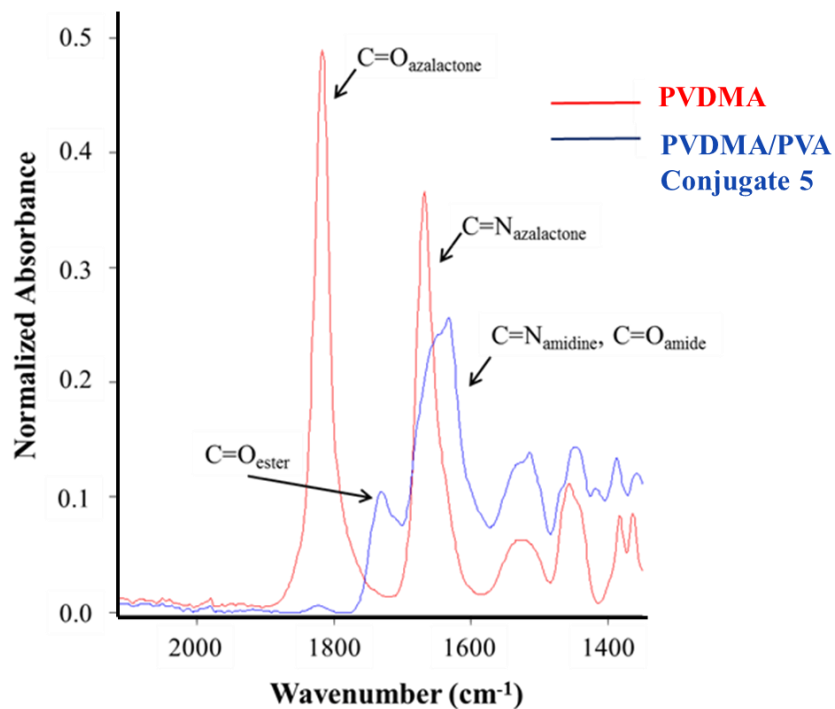


Figure 1. Partial ATR-FTIR spectra highlighting the portion of the spectra where changes associated with functionalization of PVDMA with PBA appear.

An NMR spectrum of PVDMA/PBA conjugate **5** could not be obtained because it became insoluble in common organic solvents after precipitation of the reaction mixture in hexanes. This was not completely unexpected: Endo *et al.* reported poor solubility for a polystyrene derivative bearing an amidine moiety.²⁷ We attribute the loss of solubility of the PVDMA/PBA conjugate **5** to the formation of aggregates caused by the physical cross-linking between polymer chains via ionic interactions between amidinium moieties and bicarbonate anions formed from the protonation of trapped CO₂, a phenomenon that also has been observed by Ochiai *et al.* in their studies of polystyrene derivatives bearing amidine moieties.⁴³ Optical microscopy and SEM images of the dried powder samples for PVDMA as well as the PVDMA/PBA conjugate **5** (see

Figures S1a, S1b, S2a, and Figure S2b in the Supporting Information) reveal large aggregates with non-uniform pore size distributions (less than 1.4 μm to $\sim 14 \mu\text{m}$) and have disorganized and amorphous structures due to the lack of any structural motifs for templating controlled pore formation. For practical applications, the polymer could be processed directly from the reaction mixture to form membranes, composites or blends.

CO₂ Capture and Release Monitored by Thermogravimetric Analysis (TGA). TGA has proven to be a reliable technique for measuring the ability of solid sorbents to capture CO₂.^{27,44,45} Here, we used TGA to study the ability of PVDMA/PBA conjugate **5** to capture CO₂ from either a stream of 99% CO₂ or from a 20% CO₂/80% N₂ mixture at a flow rate of 20 mL/min at 25 °C (room temperature) followed by measuring CO₂ release at 25 °C, 55 °C, and/or 100 °C under N₂ atmosphere. In order to compare the CO₂ sorption/release characteristics of the PVDMA/PBA conjugate **5** with previous reports of amidine based polymers, we selected experimental conditions that are similar to those used and reported by Endo and co-workers.^{7,27,43} The results of the CO₂ capture experiments, expressed in terms of the % CO₂ fixing efficiency, are summarized in **Figure 2**. The % CO₂ fixing efficiency is defined as the number of moles of CO₂ captured per mole of amidine functional groups in PVDMA/PBA conjugate **5**, taking into account that 98.3% of the azlactone groups in the PVDMA are functionalized with PBA to yield conjugate **5**. The CO₂ fixing efficiency is the fraction of amidine groups in PVDMA/PBA conjugate **5** that capture CO₂ under the given experimental conditions.

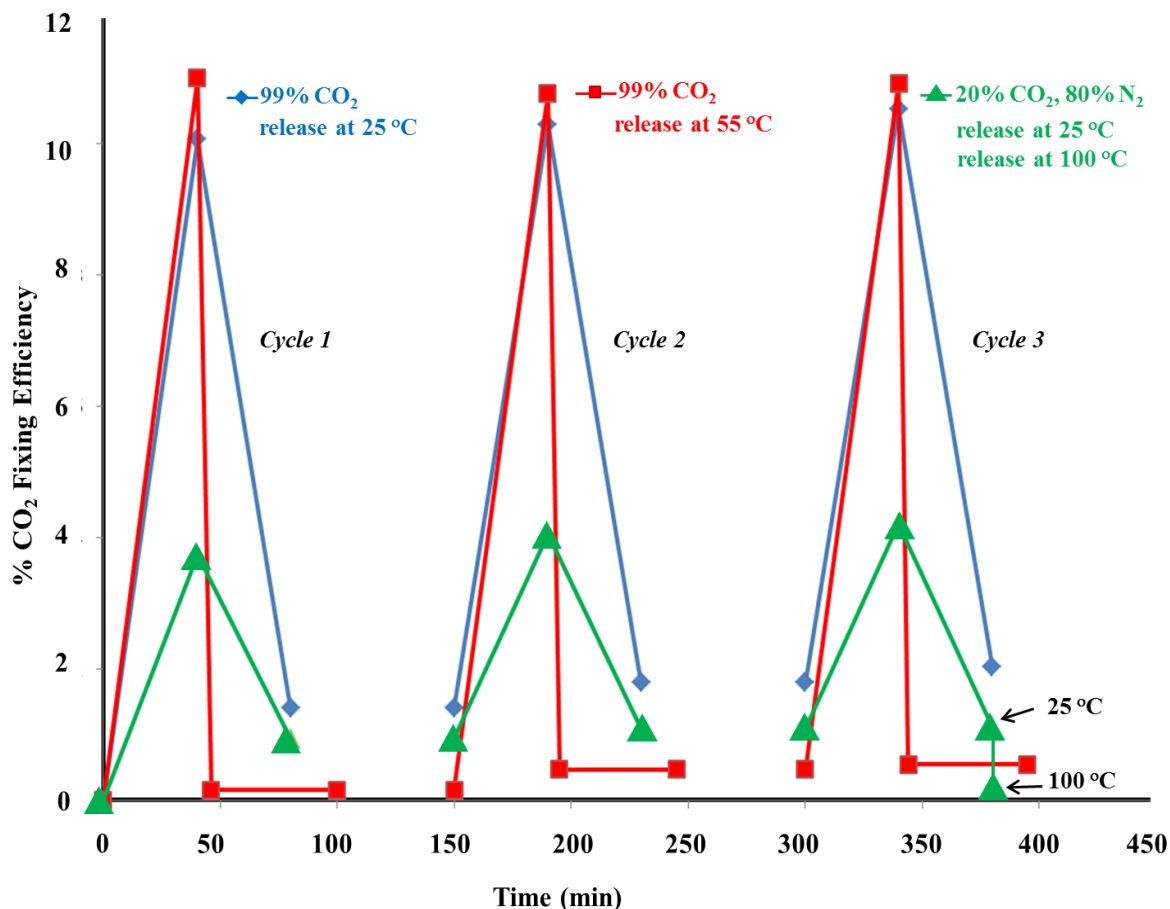


Figure 2. % CO₂ fixing efficiency versus time for capture and release of CO₂ by PVDMA/PBA conjugate **5**. The colors of the lines denote the conditions used for capture and release: Blue: capture and release of CO₂ (99% CO₂ stream) at room temperature (25 °C); Red: capture of CO₂ (99% CO₂) at room temperature with release at 55 °C; Green: capture of a mixed feed stream (20% CO₂, 80% N₂) and release at room temperature, with a heating to 100 °C at the end of the third cycle.

Figure 2 shows that PVDMA/PBA conjugate **5** has a CO₂ fixing efficiency of ~10-11% (~ 0.34 mmol CO₂ captured/g polymer) after exposure to 99% CO₂ at a flow rate of 20 mL/min at room temperature for 40 minutes. The process is highly efficient, with 65% of the total CO₂ capture (0.22 mmol CO₂ captured/g of polymer) occurring within the first 5 minutes of the exposure as shown in **Figure 3**. In comparison, Furusho *et al.* reported that aliphatic polyamidine and

polyethyleneimine (PEI) achieved CO₂ fixing efficiencies of 3.4% and 1.8%, respectively, when exposed to feed streams of 99% CO₂ at a flow rate of 200 mL/min for 500 h.⁷ We also measured the CO₂ adsorbing capacity of a commercial PEI sample (M_w ~ 4000 g/mol) under the same experimental conditions as that of the PVDMA/PBA conjugate **5**, and found that it had a CO₂ fixing efficiency of 1.33% (data not shown) which is in agreement with the values reported by Furusho *et al.*⁷

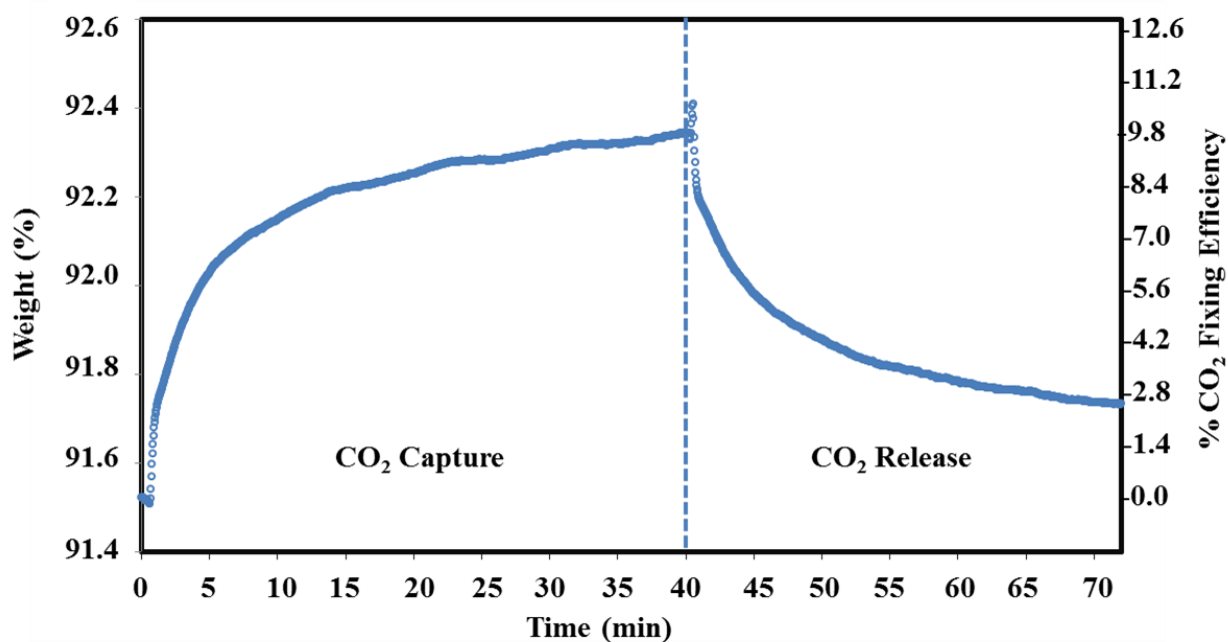


Figure 3. TGA profile of PVDMA/PBA Conjugate **5** showing % CO₂ capture efficiency and change in % weight versus time during capture and release of CO₂ at 25 °C.

PVDMA/PBA conjugate **5** also is able to capture CO₂ selectively from a mixed gas stream (80% N₂, 20% CO₂) that is similar in CO₂ content to flue gas (~15% CO₂). As shown by the green traces in **Figure 2**, a fixing efficiency of ~3.74 % (~0.11 mmol CO₂ captured/ g polymer) is observed. The PVDMA/PBA conjugate **5** demonstrates a higher CO₂ fixing efficiency when

exposed to the mixed gas stream with 20% CO₂ content compared to the fixing efficiencies reported for polyamidine and polyethyleneimine polymers that were exposed to 99% CO₂.⁷ This indicates that the PVDMA/PBA conjugate **5** is highly selective towards binding CO₂, even at dilute CO₂ concentrations. Because post-combustion carbon capture of flue gas from coal-fired plants is carried out at temperature between 40 °C and 60 °C,⁴⁶ it is reasonable to investigate the performance of the PVDMA/PBA conjugate **5** to capture CO₂ over a similar temperature range. PVDMA/PBA conjugate **5** demonstrated a CO₂ fixing efficiency of 7% (0.20 mmol CO₂ captured/g polymer) and 6% (0.18 mmol CO₂ captured/g polymer) at 40 °C and at 60 °C, respectively, when exposed to a 99% CO₂ atmosphere for 40 minutes at a flow rate of 20 mL/min. (See **Table S1** in the *Supporting Information*.)

As shown in **Figure 2**, the efficiency of CO₂ release also depends on temperature. After flowing 99% CO₂ over PVDMA/PBA conjugate **5**, the gas was switched to N₂, and CO₂ release was monitored at different temperatures. As observed from **Figure 2**, the release is much faster at 55 °C than at room temperature. Also, at both room temperature and at 55 °C, (blue and red traces in **Figure 2**, respectively) some CO₂ remains bound to PVDMA/PBA conjugate **5** and the amount of CO₂ released decreases with each consecutive capture cycle at room temperature and at 55 °C. However, if the polymer is exposed to a pure N₂ stream at 100 °C, all of the CO₂ is released from PVDMA/PBA conjugate **5** (data not shown). This behavior is also observed from the final cycle (3rd cycle in **Figure 2**) in which a mixed gas (20% CO₂, green trace) was used: The release of CO₂ is complete when PVDMA/PBA conjugate **5** is heated to 100 °C. At room temperature, PVDMA/PBA conjugate **5** released 86% and 76% of the captured CO₂ from sources that contained 99% and 20% CO₂ respectively in 40 minutes under a N₂ flow of 20 mL/min. Under similar conditions, PVDMA/PBA conjugate **5** released 93% of the captured CO₂ at 55 °C. For

CO₂ capture and release experiments at 40 °C and 60 °C, PVDMA/PBA conjugate **5** released 91% and 95% of the captured CO₂. Although the release experiments were run for 40 minutes, more than 50% of the total CO₂ released at room temperature (**Figure 3**) and 98% of the total CO₂ released at 55 °C occurs within the first 5 minutes of the release step (**Figure 2**). From **Figure 2** it is evident that at 55 °C (red traces), only a small amount of additional bound CO₂ is not released after the first 5 minutes. However, when the polymer conjugate **5** is heated to 100 °C, all of the captured CO₂ is released. Considering the demand for solid sorbents with efficient CO₂ capture-and-release characteristics, materials similar to PVDMA/PBA conjugate **5** may find practical applications in post-combustion processes.

Effective CO₂ Release Monitored by TGA. The TGA profile for PVDMA/PBA conjugate **5** shown in **Figure S3** (*Supporting Information*) indicates a two-step CO₂ release process at room temperature: a sharp weight loss due to CO₂ release was observed immediately after switching from CO₂ to N₂ followed by a second, slower CO₂ release. However, at 55 °C, the CO₂ release occurs in a single step (**Figure S4**, *Supporting Information*). The faster, single-step release of CO₂ at 55 °C compared to the release behavior at room temperature is attributed to the increased thermal energy supplied to the system at elevated temperature. The two-step release at room temperature, and the temperature dependence of CO₂ release suggests that CO₂ molecules can interact with the polymer surface with different binding energies. The TGA profiles for the CO₂ release at room temperature and at 55°C were fitted using exponential decays to determine the effect of temperature on CO₂ effective release. Here, the term “effective release” at a particular temperature is used to quantify the amount of CO₂ released from the surface of PVDMA/PBA conjugate **5** as a function of time. The CO₂ release at room temperature was first fit using a single exponential; however as shown in **Figure 4**, it showed poor agreement with the

experimental data. A double exponential decay was used to accurately capture the experimental data, which supports the hypothesis of a two-step CO₂ release mechanism. Effective decay time constants were extracted from the fits, with the first release step (0.32 min⁻¹) being more than five times faster than the second release step (0.06 min⁻¹).

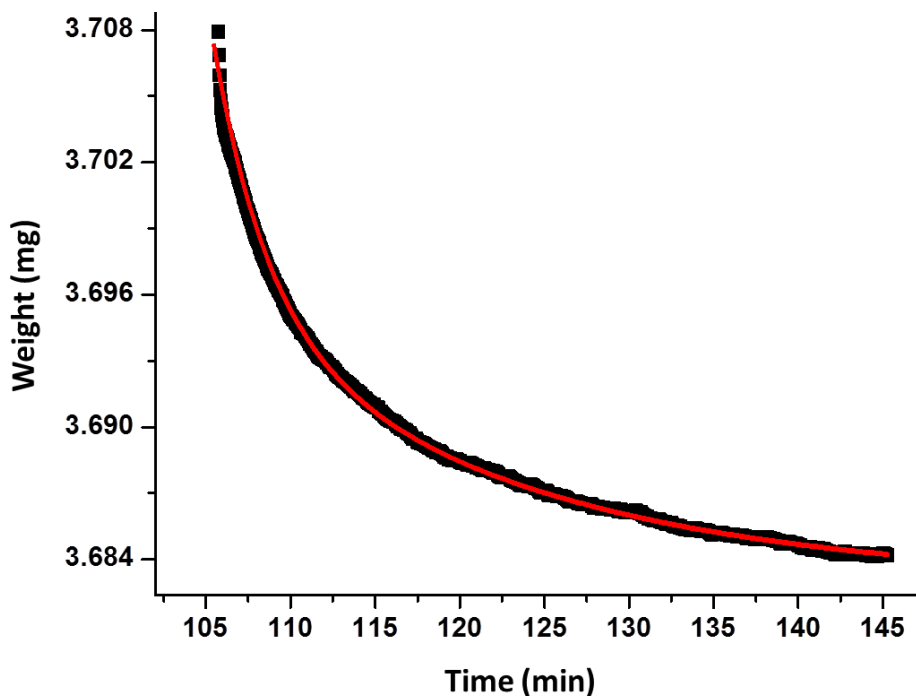


Figure 4. CO₂ release (data, black squares) at room temperature and the best-fit double exponential decay (data, red line).

The CO₂ release data at 55 °C were adequately described by a single exponential decay function, as shown in **Figure 5**. This suggests a single step CO₂ release process, and the effective decay time constant for CO₂ release at 55 °C was determined to be 0.96 min⁻¹.

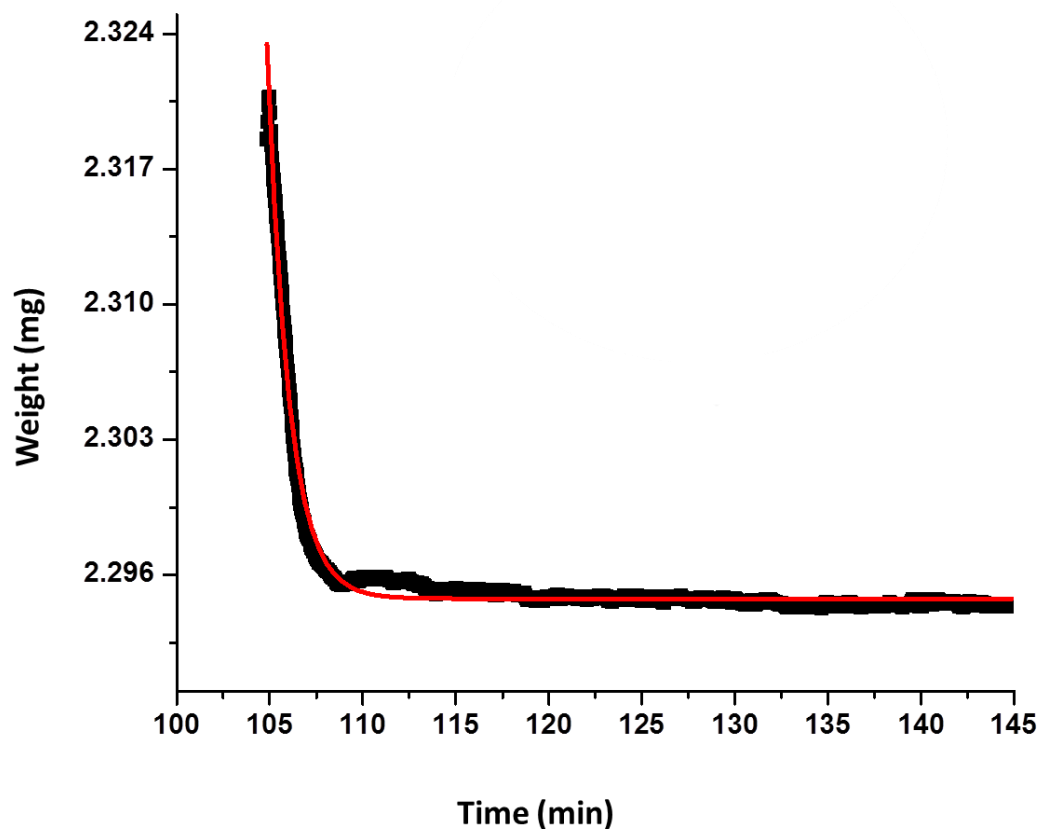


Figure 5. CO₂ release (data, black squares) at 55°C and the fit with a single exponential decay (data, red line).

The temperature dependent CO₂ release profiles shown in **Figure 4** and **Figure 5** and the calculated decay time constants were also investigated utilizing DFT calculations, theoretical modeling, and simulations to gain a more comprehensive understanding of CO₂ release. (These are described in **Method S1** in the *Supporting Information*). Using DFT, the binding energy of a single CO₂ molecule physisorbed at the basic amidine (-C=N) N-atom (*Supporting Information, Figure S5a*) of PVDMA/PBA conjugate **5** is calculated to be 9.51 kcal/mol, which is more than five times greater than the binding energy for a CO₂ molecule absorbed at the N-atom in

unmodified PVDMA which was calculated to be 1.83 kcal/mol. The significant increase in binding energy is largely due to the ability of a CO₂ molecule to be in close proximity to the N-heteroatoms of the highly basic amidine structure on PVDMA/PBA conjugate **5**. The N-heteroatoms of the attached amidine on PVDMA/PBA conjugate **5** has considerably less steric hindrance compared to the ring azlactone N-atom on un-modified PVDMA. DFT calculations also show that PVDMA/PBA conjugate **5** has two accessible binding positions for CO₂: one is ~2.7 Å from the amidine N atom (**Figure S5a**) having a binding energy of 9.51 kcal/mol and a second at ~4.1 Å from the amidine N that has a binding energy of 2.56 kcal/mol (**Figure S5b**). These two “positions” comprise an “inner” and “outer” CO₂ shell for each PBA group. Results obtained from *Ab Initio* Molecular Dynamics Simulations (AIMD), which explicitly accounts for entropic effects, indicate that two-1st order release/desorption steps occur: (1) CO₂ molecules in the “outer shell” associated with the N-heteroatom of the amidine release/desorb first, followed by (2) desorption of CO₂ molecules in the “inner shell” of the N-heteroatom of the amidine. In order for CO₂ from both “shells” to desorb, activation energy greater than 9.51 kcal/mol (which correspond to the inner shell binding energy) is required. We note that the binding energies obtained from DFT are likely representative of an upper bound (overestimated); these should not be considered quantitative, but the trends for the relative energy differences of the two CO₂ adsorption sites/states should be valid. Also, while there are a variety of energy transfer pathways by which release can occur, the salient point is that theory identifies two states that reinforce the excellent binding capacity of the PVDMA-PBA conjugate and a trend of increased desorption at two different temperatures.

Study of polymer-CO₂ interaction by FTIR analyses. The calculated binding energies (9.51 kcal/mol and 2.56 kcal/mol) for the inner and outer shells of PVDMA/PBA conjugate **5** are

lower than the energy of a C-N bond (~ 73 kcal/mol). Therefore, structural and/or compositional changes for PVDMA/PBA conjugate **5** before and after CO₂ exposure are not expected. **Figure S6** shows the full FTIR spectra for PVDMA/PBA conjugate **5** after 7 cycles of CO₂ capture (at 25 °C) and release (both at 25 °C and at 100 °C), and across these cycles, there are no significant changes in the spectra. The FTIR data thus supports the findings of DFT calculations that no bonds are formed between the amidine and CO₂ molecules during uptake. Therefore, it can be concluded that the weight changes observed in thermal gravimetric studies (**Figure 2**) are only due to physisorption of CO₂ onto PVDMA/PBA conjugate **5**.

The -C=N of the amidine group and C=O of an amide absorb around 1650 cm⁻¹ and analysis of the FTIR spectra shown in **Figure 6** show that before CO₂ capture, two peaks are observed at 1650 cm⁻¹. These peaks appear to merge, forming a single peak after CO₂ capture, indicating that a resonance stabilized amidinium structure, $[-N-CH=N^+ \leftrightarrow -N^+=CH-N-]$ is formed upon absorption. The resonance stabilized structure might be due to the formation of a zwitterion in the absence of moisture or due to the formation of an amidinium bicarbonate in the presence of moisture upon adsorption of CO₂ onto PVDMA/PBA conjugate **5**^{48,49,7} Recently, Endo *et al.* reported that monocyclic amidines such as MTHP, whose structure is similar to PBA, capture CO₂ to form zwitterionic products which can be fully reversed at 60°C under inert conditions.⁴⁷ However, the amidine moiety in MTHP might also form amidinium bicarbonate through hydrolysis of the initial zwitterionic adducts by trace amount of moisture present during an experiment. Amidinium bicarbonates are more difficult to reverse than zwitterions.^{45,48} The FTIR spectra in **Figure 6** show that after the 7th cycle of CO₂ release, it was difficult to reverse the formation of the amidine structure in PVDMA/PBA conjugate **5** thereby indicating that as the number of CO₂ capture-release cycles increased, amidinium bicarbonate was formed. This

observation is also consistent with the gradual upward trend observed with increasing number of CO₂ absorption/release cycles that was seen for PVDMA/PBA conjugate **5** both at 55 °C and also at room temperature (**Figure 2**).

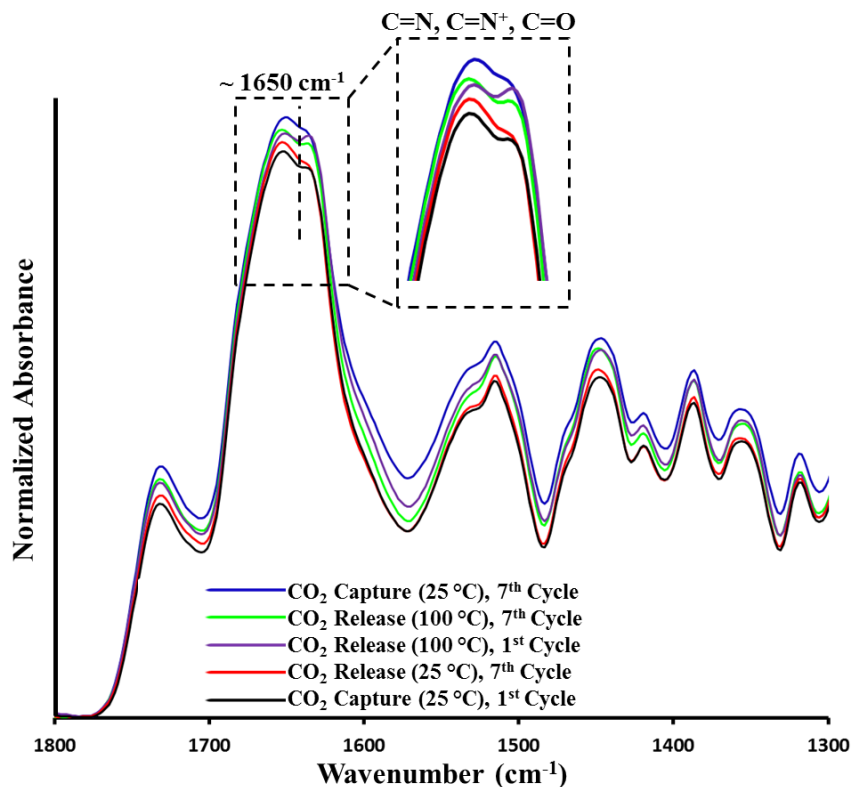


Figure 6. Partial FTIR spectra of PVDMA/PBA conjugate **5** after CO₂ absorption and desorption. The region where changes associated with formation of amidinium bicarbonate would appear is expanded.

The CO₂ used in the experiments had a purity of 99%, but it is possible that a small amount of moisture was present under the experimental conditions. Amidinium bicarbonate formation would decrease the number of active CO₂ capturing amidine sites on the surface of PVDMA/PBA conjugate **5**, and contribute to the gradual decrease in the effective decay time constant for CO₂ release at 55 °C (*Supporting Information, Figure S7*). It has been previously reported that supported amine-sorbents form bicarbonates upon CO₂ adsorption in humid

conditions which leads to an increase in CO₂ adsorbing efficiency.⁵⁰ We also expect the CO₂ capturing ability of PVDMA/PBA conjugate **5** to be impacted by the presence of humidity. The ability of PVDMA/PBA to capture and release CO₂ in the presence of humidity and/or SO_x and NO_x type gases under various conditions is currently being investigated in our labs and will be the subject of a future publication.

4. CONCLUSIONS

We report a facile method of preparing new polyamidine based polymers using post-polymer modification of PVDMA. The new polymer, PVDMA/PBA conjugate **5**, is capable of selective and reversible CO₂ capture at room temperature (25 °C) from a nearly-pure (99%) CO₂ source and from a mixed source (20% CO₂ content) that is similar to flue gas. The PVDMA/PBA conjugate **5** exhibits rapid absorption and release of CO₂ and high fixing efficiency compared to PEI and values previously reported for aliphatic polyamidine. The incomplete release of CO₂ at 25 (room temperature) and 55 °C is attributed to amidinium bicarbonate formation caused by small amounts of moisture present in the system. Additionally, the CO₂ release was shown to be dependent on temperature and the time constant for release increased with increasing temperature. DFT calculations suggest the presence of two sites for CO₂ physisorption and support the observed differences in CO₂ release efficiencies as a function of temperature. The ease of material preparation, high fixing efficiency, and robust release characteristics suggest that post-polymerization modification is a useful route to designing new materials for CO₂ capture. The efficient and cost-effective capture and separation of CO₂ under ambient conditions are crucial for practical applications, and this work opens additional possibilities for utilizing PVDMA-based polymers to develop new CO₂ responsive materials.

5. SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publication website at DOI:

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Optical microscopy images of PVDMA and PVDMA/PBA conjugate **5**; SEM images of dried powder sample of PVDMA/PBA conjugate **5** showing non-uniform distribution of pore sizes; TGA profile of PVDMA/PBA conjugate **5** showing CO₂ capture and release at room temperature; TGA profile of PVDMA/PBA conjugate **5** showing CO₂ capture at room temperature and release at 55°C; Fully optimized structure for a model of PVDMA/PBA conjugate **5** with (a) one CO₂ or (b) two CO₂ molecules physisorbed on the amidine (C=N), N-atom of the attached PBA on functionalized PVDMA; Full FTIR spectra of PVDMA/PBA conjugate **5** after CO₂ capture and release; Graph showing effective decay time constants of CO₂ release by PVDMA/PBA conjugate **5** at 55 °C versus number of CO₂ capture-release cycles in TGA; Table showing amount of CO₂ captured/release by PVDMA/PBA conjugate **5** from 99% CO₂ source as a function of temperature; Method for First Principles Theoretical Modeling, Calculation and Simulation.

6. ACKNOWLEDGEMENTS

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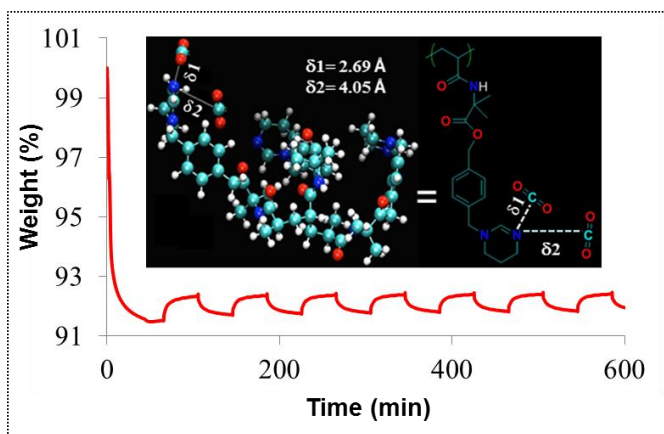
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Table of Contents Graphic

Amidine-functionalized poly(2 vinyl-4,4-dimethylazlactone) for selective and efficient CO₂ fixing

Balaka Barkakaty,^{1*} Katie L. Browning,² Bobby Sumpter,¹ David Uhrig,¹ Ivana Karpisova,³ Kevin W. Harman,¹ Ilia Ivanov,¹ Dale K. Hensley,¹ Jamie M. Messman,¹ S. Michael Kilbey II,⁴ Bradley S. Lokitz^{1*}

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Herein we report the facile synthesis of a new amidine-functionalized polymer using post-polymer modification of poly(2 vinyl-4,4-dimethylazlactone). In solid state, the new polymer is capable of efficient and selective capture of CO₂ from both concentrated (99% CO₂) and dilute (20% CO₂ content) sources. The ability of the polymer to reversibly release CO₂ at room temperature and under atmospheric pressure makes it particularly interesting for post-combustion carbon capture applications. Theoretical and experimental studies revealed the presence of two binding sites for CO₂ with the basic amidine N-atom present in the amidine-functionalized polymer.