Reversible Fixation and Release of Carbon Dioxide with a Binary System Consisting of Polyethylene Glycol and Polystyrene-Bearing Cyclic Amidine Pendant Group

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ABSTRACT: In this study, we investigated the CO_2 -capture/ release behavior of the polystyrene-bearing cyclic amidine pendant groups, which was synthesized via free radical polymerization of HCl salt of the corresponding styrene monomer followed by neutralization. For comparison, we also prepared the polystyrene bearing *N*-formyl-1,3-propanediamine pendant groups through the hydrolysis of the cyclic amidine group by treatment with an alkaline solution. First, we examined the CO_2 -capture/release behaviors of the amidine and amine monomers in aqueous solution in terms of conductivity. The conductivity of a wet DMSO solution of the amidine monomer increased upon CO_2 bubbling at 25 °C and reached a stationary value of about 11 mS/m, which indicated the formation of the bicarbonate salt. Conversely, the conductivity decreased to its

INTRODUCTION The last decade has witnessed an everincreasing interest in CO₂ fixation arising from global concern about the rising atmospheric CO_2 concentration as well as its potential utility as a green, renewable C1 source owing to its harmlessness and usefulness in organic transformations.¹⁻⁵ CO₂ capture with aqueous amine is a well-understood and widely used technology, efficiently absorbing CO2 from exhaust gases at low temperature via an exothermic reaction.⁶ However, the release process of the trapped CO₂ molecules requires heating, thereby consuming a large amount of energy.² Therefore, reversible and efficient CO2-absorbing systems need to be developed. A number of CO₂ absorbents that can capture and release CO₂ with relatively good efficiency have been reported to date, including metal-organic frameworks,7-9 amine-tethered silica,^{10–12} amine-appended mesoporous silica,^{13–15} aminetethered porous polymer networks,¹⁶ and ionic liquids.¹⁷⁻¹⁹

We reported a decade ago that polystyrene derivatives bearing cyclic amidine pendant groups captured CO_2 molecules at

original value upon N₂ bubbling at 50 °C, reflecting the complete release of the trapped CO₂ molecules. Both solutions showed the changes in the conductivity with quick responses, and no appreciable difference was observed between them. We then investigated the CO₂-capture/release behaviors of the amidine and amine polymers, by taking advantage of the binary system with polyethylene glycol, and found that the binary system with the amidine polymer captured and released CO₂ more efficiently than that with the amine polymer. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2025–2031

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a pressure of 1 atm in solution as well as in the solid state, and desorbed CO_2 under N_2 atmosphere at an elevated temperature, suggesting that amidines could be better alternatives for amines.²⁰⁻²³ Shortly thereafter, binary systems of amidines and organic alcohols or water were reported to efficiently capture CO_2 as alkyl carbonates or bicarbonates and release it under N_2 or Ar atmosphere.²⁴⁻²⁷ Amidines or guanidines were combined with hydroxy-functionalized ionic liquids, reversibly capturing and releasing CO_2 effectively.^{18,19} Based on the binary systems, reversibly coagulatable and redispersible latexes were developed using polyacrylamide or polystyrene scaffolds having aliphatic amidine pendant groups and were applied as switchable surfactants.^{28,29}

Polyethylene glycols (PEGs) are known to have interesting properties, such as good miscibility for common solids, thermal stability, nonvolatility, innocuousness, and environmentally benign characterization. In particular, PEGs have high affinity toward CO_2 and show some CO_2 -expansion effect that increases gas/liquid diffusion rates.³⁰ By taking

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SCHEME 1 Synthesis of polystyrene derivatives bearing cyclic amidine pendants (poly-1) and acyclic amine pendants (poly-2) and their unit models (1, 2A, and 2B).

advantage of this property, it was demonstrated that addition of PEG significantly enhances the rates of CO₂ absorption and desorption by ammonium salt/PEG mixtures.³¹ Combined mixture of PEG with amidine or guanidine superbases facilitated CO₂ capture and activated CO₂ molecules to catalyze some CO_2 -fixing organic reactions.³² We recently reported that a main chain-type polyamidine in which the amidine groups are connected through hexamethylene linkers was miscible with PEG to form a homogeneous mixture, which can reversibly capture and release CO₂.³³ A binary system of PEG and polyethyleneimine also captured and released CO₂ although its efficiency was much less than that of the polyamidine/PEG binary systems, suggesting that amidine is a better functionality for CO_2 absorbents than amino group. However, the main chain-type polyamidines are synthesized generally by polycondensation of $\alpha_{,\omega}$ -diamines and orthoformates, which limits the scope of further design of polyamidines. On the other hand, the polystyrene derivatives bearing amidine pendant groups can be prepared by radical polymerization of the corresponding styrene derivative.^{20,21} Therefore, the side chain-type polyamidines have potential advantage in incorporating various functionalities by molecular design and controlled radical polymerization techniques.

In this study, we synthesized the polystyrene-bearing cyclic amidine pendant groups (poly-1) via free radical polymerization of the hydrochloride of the corresponding styrene monomer (1·HCl) followed by neutralization, according to our previous method (Scheme 1).²⁰ For comparison, we also prepared the polystyrene-bearing *N*-formyl-1,3-propanediamine pendant groups (poly-2) through the hydrolysis of the cyclic amidine group by treatment with an alkaline solution of which the structure was characterized by ¹H, ¹³C, and 2-D NMR, and IR along with the studies using its unit models (2A and 2B) prepared by the hydrolysis of the cyclic amidine group of 1·HCl. Another reason to study the hydrolytic products of 1 and poly-1 is that we had been aware of the possibility of hydrolysis of poly-1 by a small amount of water during experimental manipulation. It was necessary to investigate it in detail for further development of the polyamidine-based system. We investigated the CO_2 fixation-release behaviors of **1** and **2** in wet solution in terms of conductivity. Moreover, we prepared binary systems PEG with poly-**1** or poly-**2** of which the CO_2 -capture/release efficiencies were estimated by thermogravimetric analysis (TGA) technique.

EXPERIMENTAL

General

The NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C. Chemical shifts are reported in parts per million (δ) based on the residual proton peaks of the deuterated solvents. The electron spray ionization mass spectra (ESI-MS) were recorded using a JEOL JMS-T100CS spectrometer. The conductivities of the DMSO solutions of 1 and a mixture of 2A and 2B were measured using an electric conductivity meter (MM60R with a conductivity sensor CT-57101C, TOADKK, Japan) after the solutions were bubbled with N_2 for 30 min at 50 °C to obtain a stable conductivity. The TGA of the polymers was performed with an EXSTAR TG/DTA 6200 instrument (Seiko Instruments) with a flow of CO_2 or N_2 at a rate of 200 mL/min. Gel permeation chromatography was carried out with a JASCO LC-Net II high-performance liquid chromatography with TOSOH TSKgel ALPHA-M and phosphatebuffered saline as eluent. Molecular weights were evaluated using PEG standards.

Materials

Hydrochloride **1**·HCl was prepared from *p*-chloromethylstyrene according to our previously reported method.²⁰ The polystyrene-bearing 6-membered cyclic amidinium hydrochloride (poly-**1**·HCl) was synthesized by free radical polymerization of **1**·HCl in water according to a slightly modified procedure of our previous article.²⁰ Polyethylene glycol ($M_w = 400$, **PEG**₄₀₀) was purchased from Wako Pure Chemical Industries (Osaka, Japan), and used as received. CO₂ was purchased from Fukuho Teisan (Fukuoka, Japan). Other reagents and solvents were purchased from commercial suppliers and used without further purification.

Methods

Synthesis of 1-(4-Vinylbenzyl)-1,4,5,6tetrahydropyrimidine (1)

A 0.1-M solution of sodium methoxide in methanol (20 mL, 2 mmol) was added slowly to a 0.2-M solution of 1·HCl in methanol (10 mL, 2 mmol). The solvent was removed by evaporation after being stirred at room temperature for 10 min under nitrogen. The residue was dissolved in chloroform (10 mL) and the insoluble part was filtered off. The filtrate was evaporated to dryness to afford 1 as a colorless oil in 98% yield after drying under vacuum.

¹H NMR (400MHz, CD₃OD): δ = 7.43 (d, *J* = 8.24 Hz, 2H), 7.27 (s, 1H, disappeared after H/D exchange), 7.23 (d, *J* = 8.24 Hz), 6.73 (dd, *J* = 11.0, 17.4 Hz, 1H), 5.78(d, *J* = 17.4 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 4.30 (s, 2H), 3.21 (t,



FIGURE 1 ¹H NMR (400 MHz, CD_3OD) spectra of (a) **1**, and poly-**1** (b) right after and (c) 1 day after dissolving, (d) a mixture of **2A** and **2B**, and (e) poly-**2**.

J = 5.5 Hz, 2H), 3.07 (t, J = 6.0 Hz, 2H), 1.80 (quint, J = 5.73 Hz, 2H) ppm, ¹³C NMR (100 MHz, CD₃OD): $\delta = 152.16$ (split into a triplet after H/D exchange), 138.64, 138.00, 137.64, 128.88, 127.60, 114.29, 57.28, 44.09, 42.89, and 21.82 ppm.

Free Radical Polymerization of 1 HCl (Synthesis of Poly-1 HCl)

1·HCl (1.050 g, 4.4 mmol), 2,2'-azobis (2-amidinopropane) dihydrochloride (V-50, 36 mg, 0.133 mmol), and H₂O (10 mL) were fed into round flask. Then, the mixture was cooled, degassed, and heated at 75 °C for 20 h. The product was precipitated from tetrahydrofuran and collected by filtration. The product was dissolved in a small amount of methanol, and precipitated from diethyl ether several times and collected by filtration, and then in a vacuum oven to dry for 24 h. The yellow powder was obtained with the yield of 99%. SEC-analysis (eluent, H₂O) of the polymer was carried out to estimate the number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) ($M_n = 83,000$, $M_w/M_n = 1.99$). IR (ATR), 1675 cm⁻¹.

¹H NMR (400 MHz, CD₃OD): $\delta = 8.53$ (d, J = 27.9 Hz, 1H), 7.21 (m, 2H), 6.58 (m, 2H), 4.71 (brs, 2H), 3.11–3.60 (m, 4H), 1.98 (brs, 2H), 0.89–2.55 (m, 3H), ¹³C NMR (100 MHz, CD₃OD): $\delta = 153.77$, 147.06, 132.75, 129.83, 129.30, 59.18, 45.67, 44.47, 41.83, 38.51, and 19.73 ppm.

Synthesis of Poly-1

A 0.1-M solution of sodium methoxide in methanol (5 mL, 0.5 mmol) was added slowly to a 0.2-M solution of poly-1·HCl (2.5 mL, 0.5 mmol) in methanol. After being stirred at room temperature for 10 min under nitrogen, the mixture was poured into dry diethyl ether (50 mL). The resulting precipitate was collected by suction filtration under nitrogen, and then dried in a vacuum oven for 24 h to afford poly-1 in 87% yield as a white powder. IR (ATR), 1626 cm⁻¹. ¹H NMR (400 MHz, CD₃OD): δ = 7.26 (brs, 1H, disappeared after H/D exchange), 7.00 (brs, 2H), 6.52 (brs, 2H), 4.24 (brs, 2H), 3.17 (brs, 2H), 3.01 (brs, 2H), 1.72 (brs, 2H), 1.20–2.10 (brs, 3H) ppm, ¹³C NMR (100 MHz, CD₃OD): δ = 152.10 (s, before H/D exchange, and highly broadened after H/D exchange), 145.91, 136.02, 129.09, 128.68, 57.31, 45.89, 44.12, 42.82, 41.68, and 21.83 ppm.

Synthesis of a Mixture of N-(3-((4-vinylbenzyl)amino)propyl) formamide (2A) and N-(3-aminopropyl)-N-(4-vinylbenzyl) formamide (2B)

An aqueous solution of potassium hydroxide (3 wt %, 4.0 mL) was added to a 0.2-M solution of **1**·HCl in water (5 mL, 1 mmol). The water was removed by evaporation after being stirred at room temperature for 10 min. The residue was dissolved in chloroform (10 mL) and the insoluble part was removed by suction filtration. The filtrate was evaporated to dryness to give a mixture of **2A** and **2B** as a colorless oil in 55% yield (**2A**:**2B** = 59:41).

For the characterization, these two isomers were separated by preparative TLC (SiO₂, MeOH/CHCl₃ = 2/1 v/v, R_f values: 0.5 (2A); 0.13 (2B)). 2A: ¹H NMR (400 MHz, CD₃OD, two conformers arising from the *E*/*Z* isomerism of the formamide group were present (*E*:*Z* = 7.5:92.5).

Chemical shift values belonging to the major *Z*-conformer are underlined: $\delta = 8.02 + 7.97$ (s+s, 0.925H+0.075H), 7.40 (m, J = 8.0 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.72(dd, J = 11.0, 17.9 Hz, 1H), 5.76 (d, J = 20 Hz, 1H), 5.2 (d, J = 9.4 Hz, 1H), 3.730+3.729 (s+s, 2H), 3.27 (t, J = 6.9 Hz, 2H), 2.62 (t, J = 8.4 Hz, 2H), 1.74+1.73 (quin+quin, J = 7.1 Hz, 2H) ppm, ¹³C NMR (100 MHz, CD₃OD): $\delta = 163.84$, 140.27, 137.99, 137.86, 129.73, 127.26, 113.74, 54.16, 47.11, 36.86, and 30.11 ppm. ESI-MS (MeOH, positive): Calcd for



 $[C_{13}H_{16}D_2N_2NaO 2A+Na]^+$: m/z = 243; Found: m/z = 243(The two NH protons were replaced with deuterium as the solution of 2A in CD₃OD used for the NMR measurements was subjected to ESI-MS analysis). 2B: ¹H NMR (400 MHz, CD₃OD, two conformers arising from the *E/Z* isomerism of the formamide group were present (*E*:*Z* = 57.5:42.5).

Chemical shift values belonging to the major conformer are underlined: $\delta = 8.34 + 8.23$ (s+s, 0.57H+0.43H), 7.45+7.40 (d+d, J = 7.8, 8.2 Hz, 1.14H+0.86H), 7.26+7.24 (d+d, I = 7.3, 7.8 Hz, 1.14H+0.86H), 6.75+6.71 (dd+dd, I = 7.1, 10.1 Hz and J = 7.32, 11.0 Hz, 0.43H+0.57H), 5.80+5.76 (d+d, J = 10.5, 10.1 Hz, 0.57H+0.43H), 5.25+5.22 (d+d,J = 11.0, 10.0 Hz, 0.57H+0.43H, 4.55+4.49 (s+s, 0.43H+0.57H), 3.28 (t+t, J = 3.64 Hz, 1.14H+0.86H), 2.60 (t+t, J = 6.88 Hz, 1.14H + 0.86H), 1.70 + 1.63 (quint + quint, J = 7.08, 6.86 Hz, 1.14H+0.86H) ppm, ¹³C NMR (100 MHz, MeOD): $\delta = 165.53 + 165.34$, 138.95 + 138.45, 137.64 + 137.54, 137.45 + 137.21, 129.50 + 129.24, 127.74 + 127.68, 114.55 + 114.21,52.00, 46.04 + 45.98, 40.31 + 39.45, 32.23, 30.77 ppm. ESI-MS (MeOH, positive): Calcd for $[C_{13}H_{16}D_2N_2NaO \mathbf{2B}+Na]^+$: m/z = 243; Found: m/z = 243 (The two NH protons were replaced with deuterium as the solution of 2B in CD_3OD used for the NMR measurements was subjected to ESI-MS analysis).

Synthesis of Poly-2

An aqueous solution of potassium hydroxide (3 wt %, 2.0 mL) was added to a 0.25-M solution of poly-1·HCl (2 mL, 0.5 mmol) in water. The resulting precipitate was collected by suction filtration and dried under vacuum to give poly-2 in 66.4% yield as a white solid. IR (ATR), 1651 cm⁻¹.

¹H NMR (400 MHz, CD₃OD). The chemical shifts belonging to the primary amine unit (corresponding to **2B**) are doubleunderlined: $\delta = \underline{8.24} + 8.05 + 7.95$ (br s+s+s, 0.475H+ 0.495H+0.03H), 7.02 (brs, 2H), 6.50 (brs, 2H), <u>4.41</u>+3.65 (brs+brs, 0.95H+1.05H), 3.26 (brs, 2H), 1.71 (brs, 5H) ppm.

¹³C NMR (100 MHz, CD₃OD). The chemical shifts belonging to the primary amine unit (corresponding to **2B**) are double underlined: $\delta = \underline{165.37 + 165.21} + 163.81$, 138.40, 135.35, 129.40, 128.94, 54.29+ $\underline{51.79}$, 48.36+ $\underline{45.81}$, 44.12, 41.49, $\underline{40.08 + 39.48} + 36.92$, and $\underline{32.11 + 30.77} + 30.21$ ppm.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polystyrene Derivatives having 6-Membered Cyclic Amidine or *N*formyl-1,3-propanediamine Pendant Groups

The hydrochloride of the styrene derivative bearing hydrochloride of 6-membered cyclic amidine group (1·HCl) was prepared from *p*-chloromethylstyrene according to our previously published method.²⁰ Although we reported previously that we neutralized successfully the cyclic amidinium hydrochloride moiety of 1·HCl by using potassium hydroxide,²⁰ we could not reproduce the result and the most of the cyclic amidine moiety was hydrolyzed as described below (Scheme 1).³⁴ In this study, the neutralization was achieved by using an equimolar amount of NaOMe to afford the styrene with a



FIGURE 2 ¹H NMR spectra of (a) 2A, (b) 2B, and (c) a mixture of 2A and 2B.

free cyclic amidine group (1) of which the ¹H NMR spectrum is shown in Figure 1(a). In CD_3OD , the methine proton underwent H/D coupling so that its ¹H signal at 7.27 ppm disappeared and its ¹³C singlet at 152.16 ppm was split into a triplet as a result of the ¹³C-D coupling (Supporting Information Fig. S1). As the free radical polymerization of the styrene with the neutral amidine group (1) did not proceed at all, we synthesized poly-1.HCl by free radical polymerization of the hydrochloride monomer (1·HCl) according to a slightly modified procedure of our previously published study.²⁰ The polystyrene with amidinium hydrochloride pendant groups (poly-**1**·HCl) was neutralized with an equimolar amount of NaOMe to afford the polystyrene with free cyclic amidine groups (poly-1) in 87% yield. The structure of poly-1 was characterized by 1-D and 2-D ¹H NMR spectra (Fig. 1 and Supporting Information Figs. S2–S4). The ¹H NMR spectrum in CD₃OD was in good agreement of the polymer structure; the vinyl proton signals disappeared and the signals of the methine and methylene proton of the polymer backbone were newly appeared [Fig. 1(a,b)]. The methine proton of the cyclic amidine moiety underwent H/D exchange reaction with CD₃OD, and its ¹H signal almost disappeared within 1 day [Fig. 1(c)]. The ¹³C NMR spectrum was also in good agreement with the structure, and the singlet owing to the methine carbon highly broadened after 1 day as a result of ¹³C-D coupling after the H/D exchange reaction with CD₃OD (Supporting Information Fig. S2). The IR spectrum of poly-1 showed a strong peak attributable to the C=N stretching at a lower wavenumber of 1626 cm⁻¹ than that of poly-**1** HCl (1675 cm⁻¹). The molecular weight of poly-**1**·HCl was determined to be $M_n = 83,000$ $(M_w/M_p = 1.99)$ by SEC analysis (H₂O, PEG standards).

As mentioned above, the cyclic amidine was highly susceptible to hydrolysis in alkaline solution. We treated **1**·HCl with an excess of KOH in water to completely hydrolyze the amidine moiety, and obtained a mixture of two *N*-formylated propanediamines, secondary amine **2A**, and primary amine **2B** [Fig. 1(d)]. The molar ratio of **2A** and **2B** was calculated to be 59:41 based on the integrals of the ¹H NMR spectrum.



FIGURE 3 Partial NOESY spectrum of 2B (mixing time = 0.5 s).

As it was difficult to assign all the signals of the ¹H NMR spectrum owing to its complexity, we separated the two isomers by preparative TLC with SiO₂ stationary phase (eluent: $MeOH/CHCl_3 = 2/1 v/v$). Both isomers were characterized by ¹H, ¹³C, and 2-D NMR as well as ESI-MS (Fig. 2 and Supporting Information Figs. S5–S7). The ¹H NMR spectra of the two isomers, 2A and 2B, showed the absence of NH signals as a result of the H/D exchange reaction with CD_3OD . The CHO proton of 2A appeared as two singlets at 8.02 and 7.97 ppm with an integral ratio of 92.5:7.5, respectively, arising from the existence of the two conformers owing to the E/Zisomerism of the formamide moiety [Fig. 2(a)]. The major isomer was assigned to be the Z-conformer according to Petride's report on analogous mono-formylated ethylenediamines.³⁵ On the other hand, the isomer 2B exhibited two singlets for its CHO proton at 8.34 and 8.23 ppm, which are comparable in integral intensity [Fig. 2(b)]. The assignment of the signals to the two isomers was achieved based on the measurements of NOESY of 2B (Fig. 3 and Supporting Information Fig. S6). A distinct crosspeak was observed between

the signals at 8.1 and 3.2 ppm, indicating the *Z*-conformation. The signal at 8.2 ppm showed a crosspeak with 4.37 ppm, which indicated the *E*-conformation. The abundance ratio of the two conformers was evaluated to be E:Z = 57:43. The bias in conformation was quite small when compared to **2A**, as reported for analogous *N*-formylated ethylenediamines.³⁵

We prepared poly-2 from poly-1.HCl by treatment with an excess of KOH in water by a similar procedure to that for the 2A/2B mixture from 1 HCl. The IR spectrum showed a strong absorption at 1651 cm^{-1} , which was attributed to the C=O stretching of amide functionalities. The ¹H NMR of poly-2 showed its signals at chemical shifts similar to those for 2A and **2B** except for disappearance of the vinyl proton signals as well as appearance of the signals of the newly formed polymer backbone (Fig. 1(e) and Supporting Information Figs. S7 and S8). The ¹³C NMR spectrum was also consistent with the structure of poly-2 (Supporting Information Fig. S9). The molar ratio of the secondary amine unit (corresponding to 2A) and the primary amine unit (corresponding to 2B) was estimated to be 47.5:52.5 based on the relative integral values of the benzylic proton signals, which was comparable to that for the 2A/2B mixture obtained by the hydrolysis of 1·HCl although the bias in the regioselectivity was inverted.

CO₂ Capture and Release by Styrenes having a 6-Membered Cyclic Amidine or an *N*-formyl-1,3propanediamine Moiety

The CO₂ capture and release behaviors of **1** and **2A/2B** in aqueous solution were investigated in terms of conductivity (Fig. 4). Upon bubbling CO₂ gas through a solution of the cyclic amidine monomer **1** in wet DMSO containing 1% of water (10 mM) at 25 °C, its conductivity increased rapidly and reached a saturated value within approximately 3 min [Fig. 4(a)]. The maximum value of about 11 mS/m was comparable to those for analogous amidines,^{24,29} indicating the formation of the bicarbonate of **1** (**1**H·HCO₃). When N₂ was bubbled through the DMSO solution saturated with CO₂ at 50 °C, its conductivity decreased to almost the initial value within approximately 4 min, meaning all the captured CO₂ was released. The CO₂ capture and release cycle could be



FIGURE 4 Changes in the conductivity of (a) **1** and (b) a mixture of **2A** and **2B** in DMSO containing 1 vol % of H_2O (10 mM) with bubbling CO_2 at 25 °C and N_2 at 50 °C in an alternate manner.



FIGURE 5 TG profiles of homogeneous mixtures of (a) poly-1 and **PEG**₄₀₀ (black) and (b) poly-2 and **PEG**₄₀₀ (gray) with flowing CO₂ at 25 °C and N₂ at 45 °C in an alternate manner (200 mL/min).

repeated three times with quick responses. However, the maximum conductivity value showed a slight decrease at every step, which could be attributed to hydrolysis of the cyclic amidine moiety in the wet DMSO solution. On the other hand, CO₂ gas was bubbled through a solution of a mixture of 2A and 2B in wet DMSO containing 1% of water (10 mM) at 25 °C, its conductivity increased promptly, and reached a saturated value within approximately 7.5 min [Fig. 4(b)]. The maximum value of about 3 mS/m was much smaller than that of 1 in wet DMSO, reflecting that the reaction of 2A or 2B with CO_2 formed an electronically neutral carbamic acid instead of the bicarbonate salt formation from **1** and CO₂. Upon purging with N₂ gas at 50 $^{\circ}$ C, the conductivity of the wet DMSO solution was reduced quickly to the original value, indicating a complete release of CO₂. The cycle could also be repeated three times without decrease in the maximum conductivity value. Thus, the mixture of the amines 2A and 2B in aqueous solution captured and released CO_2 as efficiently as that of the cyclic amidine **1**, as it is the case of wet DMSO solutions of a linear polyamidine and polyethyleneimine.³³

CO₂ Capture and Release by Polystyrenes Bearing 6-Membered Cyclic Amidine or *N*-formyl-1,3propanediamine Pendant Groups

Finally, we compared the CO₂ capturing and releasing abilities of poly-1 and poly-2 by TGA (Fig. 5 and Supporting Information Fig. S10).³⁶ Mixing poly-1 with PEG with an average molecular weight of 400 (**PEG**₄₀₀) gave a colorless, highly viscous oil of which the sample weight was monitored by TG apparatus under CO₂ or N₂ atmosphere. When exposed to a CO₂ flow at 25 °C, the mixture of poly-1 and **PEG**₄₀₀ showed an increase in the weight as a result of the

formation of the alkylcarbonate salt.^{32,33} The molar ratio of captured CO_2 to the amidine unit was calculated based on the weight increase of the binary mixture, reaching 45% after 240 min under the conditions. Then the mixture was exposed to a N_2 flow at 45 $^\circ\text{C}\textsc{,}$ showing a decrease in the trapped CO₂ down to 12% after 240 min. Similarly, the binary homogeneous mixture prepared from poly-2 and PEG₄₀₀ was subjected to a CO₂ flow at 25 °C. After 240 min, the trapped CO_2 reached 29%, which was 16% less than that of poly-1. The mixture was then exposed to a N₂ flow at 45 °C. However, the binary system released CO_2 after 240 min to a lesser extent when compared with the binary system of poly-1. Although both the binary systems could be repeated at least three times, the mixture with poly-1 captured and released CO₂ more efficiently than that with poly-2 as it is clearly shown in Figure 5. However, the TG profile of the binary mixture of poly-1 became closer to that of poly-2 with each cycle. Then we examined the binary samples by IR spectroscopy (Supporting Information Fig. S11). The freshly prepared binary sample of poly-1 showed a strong absorption at 1632 cm^{-1} assignable to C=N stretching of the amidine group, whereas the binary sample of poly-2 showed an absorption peak at 1659 cm^{-1} , which was assigned to C=0 stretching of the N-formyl-1,3-propannediamine group. On the other hand, the binary sample of poly-1 that had been stored in air at ambient temperature for 2 weeks showed an absorption peak at 1650 cm^{-1} , which was in between those of poly-1 and poly-2, indicating that the amidine group was partially hydrolyzed to yield the amino group after the sample was stored in air at ambient temperature for a long period of time. Therefore, the deterioration in the CO_2 capture and release of the binary system of poly-1 could be attributed to the partial hydrolysis of the amidine group by a small amount of moisture contained in CO₂ or N₂ gas during the TG measurements.

CONCLUSIONS

In this study, we carried out the comparison of the CO_2 capturing and releasing abilities of the cyclic amidines and their hydrolyzed products, N-formyl-1,3-propanedimaines in solution as well as in the solid state. We synthesized the polystyrene having 6-membered cyclic amidine pendant groups by free radical polymerization of the corresponding styrene monomer as the HCl salt. In the course of the polymer synthesis, we found that treatment of the polymer with an excess of KOH resulted in hydrolysis of the cyclic amidine unit to form N-formyl-1,3-propanedimaine moiety. The structure of the resulting polymer with N-formyl-1,3-propanediamine pendant groups was characterized by ¹H, ¹³C, 2-D NMR, and IR along with the studies using its unit models prepared from the styrene monomer with the cyclic amidine. Using the styrene monomer having the cyclic amidine group and its hydrolyzed N-formyl-1,3-propanediamines, we investigated their CO₂-capturing and -releasing abilities in solution in terms of conductivity, and found that both efficiently captured and released CO_2 with a quick response, and no appreciable difference was observed between them. We then examined the CO₂-capturing and -releasing behaviors of the



amidine polymer and the amine polymer in the solid state by taking advantage of the binary system with PEG, and found that the binary system with the amidine polymer captured and released CO_2 more efficiently than the binary system with the amine polymer, in contrast with the results on the solution study. Amidines are known to be versatile synthons for supramolecular chemistry, owing to their high affinity toward oxo acids, such as carboxylic acids and sulfonic acids, as well as their coordinating ability toward transition metals.³⁷⁻⁴¹ We believe that further investigation of the binary system studied here could lead to more sophisticated CO_2 absorbing systems with highly ordered nanostructure by utilizing amidine units for both CO_2 capture and supramolecular synthons with acidic groups or transition metals. Such studies are ongoing in our group.

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