Reversible Trap−Release of CO_2 by Polymers Bearing DBU and DBN Moieties

Bungo Ochiai,[†] Kensuke Yokota,[†] Asuka Fujii,[†] Daisuke Nagai,[†,‡] and Takeshi Endo*,[§]

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan, and Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka, 820-8555, Japan

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ABSTRACT: Copolymers bearing DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and DBN (1,5-diazabicyclo[4.3.0]-non-5-ene) moieties fixed carbon dioxide under atmospheric pressure. The copolymers bearing DBN moieties fixed carbon dioxide faster than those bearing DBU moieties owing to the lower steric hindrance around the imine structure. These copolymers held trapped CO_2 under a N_2 flow at 25 °C, whereas the corresponding low-molecular weight amidines release trapped CO_2 under the same conditions. The trapped CO_2 in the copolymers was quantitatively released by a N_2 flow at 120 °C. The CO_2 trapping efficiency of a copolymer bearing DBN moieties is competitive with that of an amidine-containing polymer, whereas the preparative method for the copolymer bearing DBN is easier. The higher CO_2 trapping abilities of the DBN derivatives were supported by computational calculation.

Introduction

Using CO_2 as a raw material is an important subject for reducing consumption of petroleum resources; hence, many reactions using CO_2 have been developed.[1−20] For the economical and practical use of CO_2, concentration of CO_2, which is the first step of using CO_2, should be conducted in a facile manner. A material that can trap and release carbon dioxide reversibly is a candidate meeting this requirement. For this purpose, materials for carbon dioxide fixation have been developed by many reseachers.[1−6,21−27] Among them, we have focused on cyclic amidine structures, which trap CO_2 by formation of carbonate or bicarbonate salts in the presence of water or alcohol, or zwitter ionic adducts.[1−6] Recent researches on the reaction of DBU with CO_2 revealed that trace amounts (e.g., 700 ppm) of water lead to the formation of the bicarbonate salt, although negligible interaction was observed between dry DBU (water content <0.5 ppm) and CO_2 even under high pressure.[5] We presume that the adduct of DBU and CO_2 can share trace amounts of water, considering the fact that the water content is significantly lower than the amounts of DBU and trapped CO_2. The CO_2 trap by amidines is reversible. Amidines trap CO_2 at ambient temperatures under CO_2 atmosphere in the presence of water to form bicarbonate salts, and the trapped CO_2 is released by heating or flowing other gases, such as nitrogen and argon.[2−6] The cyclic amidines we examined are 4-methyl-1,4,5,6-tetrahydropyrimidine (MTHP) and polymers bearing tetrahydropyrimide-1-yl structures that efficiently fix CO_2.[2] Thermal treatment of MTHP and the polymer trapping CO_2 release CO_2 to reproduce MTHP, and the polymer capable of trapping CO_2 again. In spite of the utility of the polymer bearing tetrahydropyrimide-1-yl moieties, its synthesis requires cumbersome processes. It is desirable if amidine-bearing polymers with good CO_2 fixation ability can be prepared from inexpensive and accessible amidines via simple procedures. Accordingly, we choose 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), whose derivatives can be prepared by lithiation of the 6-position followed by the reaction with electrophiles,[11,28,29] and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as the raw amidines. We herein report synthesis and CO_2-trapping behaviors of amidine-bearing polymers prepared easily by the reaction of lithiated amidines and copolymers derived from 4-chloromethylstyrene (Scheme 1).

Experimental Part

Materials and Measurements. Styrene, CMSt (4-chloromethylstyrene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), DBN (1,5-diazabicyclo[4.3.0]non-5-ene)), DMF (*N*,*N*-dimethylformamide), *n*-butyl benzene, and *N*,*N*-dimethyl acrylamide (DMA) were dried over CaH_2 and distilled under reduced pressure. THF (tetrahydrofuran) was dried over sodium and distilled under a nitrogen atmosphere. 6-Benzyl-1,8-diazabicyclo[5.4.0]undec-7-ene (BDBU) was prepared according to the literature.[29] CO_2 gas used contained 40 ppm of water, and was dried by passing through a column filled with calcium chloride and silica gel. Other materials were used as received.

Measurements. ^1H (400 MHz) and ^{13}C (100 MHz) nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a JEOL ECX-400 instrument using tetramethylsilane as an internal standard at ambient temperatures. ^{13}C cross-polarization magic angle scanning (CP MAS) spectroscopy measurements were performed on a JEOL ECX-400 at a spinning rate of 5 kHz using total suppression of side band (TOSS) technique. Size exclusion chromatography (SEC) measurements were performed on a Tosoh HLC-8220 GPC instrument equipped with four consecutive polystyrene gel column [Tosoh TSK-gel (bead size and exclusion limit molecular weight); G4000H_{XL} (5 μm and 4×10^5 g/mol), G3000H_{XL} (5 μm and 6×10^4 g/mol), G2000H_{XL} (5 μm and 1×10^4 g/mol), and a guard column H_{XL}-L] using THF (flow rate: 1.0 mL) as an eluent at 40 °C. Polystyrene standards were used for calibration. Fourier transform infrared (FT-IR) spectra were measured on a Horiba FT-210 spectrometer. High-resolution mass spectroscopy (HRMS) measurements were performed on a JEOL JMS-T100LC Accu-TOF (positive mode) using methanol as the solvent and reserpine (exact mass = 609.2812) as the internal

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* Correspondence to this author. Telephone and Fax: +81-948-22-7210. E-mail: tendo@me-henkel.fuk.kindai.ac.jp.

[†] Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University.

[‡] Present address: Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma, 376-8515, Japan.

[§] Molecular Engineering Institute, Kinki University.

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Scheme 1

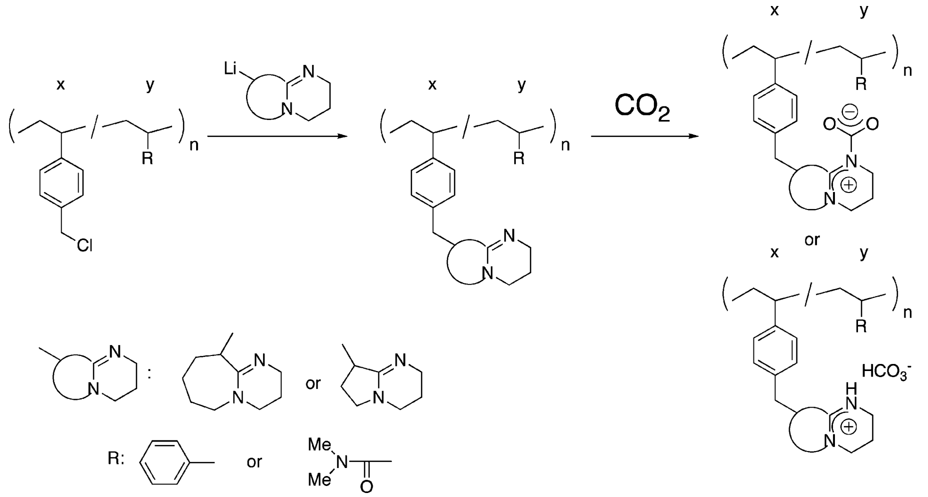


Table 1. Radical Copolymerization of 4-chloromethylstyrene (CMSt) and Styrene or DMA[a]

run	comonomer	feed ratio ([CMSt]/[comonomer])	yield (%)	M_n (M_w/M_n)	copolymer composition ([CMSt]/[comonomer])	abbreviation
1	none		96	60300 (2.37)		**P1**
2	styrene	50/50	94	64400 (3.17)	51/49	**P2**
3	styrene	30/70	91	55300 (3.39)	30/70	**P3**
4	DMA	50/50	89	29200 (1.82)	59/41	**P4**

[a] Conditions: AIBN (3 mol %), bulk, 60 °C, 24 h. [b] Insoluble part of *n*-hexane. [c] Estimated by SEC (THF, polystyrene standard). [d] Determined by ^{1}H NMR spectroscopy.

standard. Thermogravimetric analysis (TGA) was performed on a Seiko EXSTER6000 system with TGA-6200 instruments under nitrogen or CO_2 atmospheres (flow rates: 200 mL/min).

Computational Calculation. All the calculations were performed using Spartan ’04 for Windows (Wavefunction, Irvine, CA) run on a computer equipped with a Mobile Intel Pentium 4 processor (2.80 GHz). The conformations of the molecules were optimized as those with the lowest energies by MMFF 94 (Merck Molecular Mechanics Force Field) conformer calculation at 5000 K. All the molecules have C1 symmetries. The geometries and the energies were calculated with the 6-31G*-level calculations based on the restricted Hartree−Fock calculation (HF/6-31G*) or the 6-31G*-level calculation based on the B3LYP model of the density functional theory (DFT B3LYP/6-31G*) using Pulay DIIS extrapolation.

Synthesis of 9-Benzyl-1,5-diazabicyclo[4.3.0]non-5-ene (BDBN). BDBN was prepared by a modified method for synthesis of BDBU.[28] To a 500 mL three-neck flask equipped with a dropping funnel containing a magnetic stir bar, DBN (12.4 g, 100 mmol) and THF (100 mL) were added under a nitrogen atmosphere. Then, *n*-butyllithium in *n*-hexane (2.66 M, 150 mmol) was added from the dropping funnel at 0 °C, and the mixture was stirred for 1 h. Then, benzyl chloride (17.3 mL, 150 mmol) in THF (150 mL) was added from the dropping funnel, and the mixture was stirred for 12 h at that temperature. After the reaction, methanol (ca. 20 mL) was added for quenching. After an aqueous solution of NaCl was added, the organic layer was separated. The organic layer was washed three times with saturated aqueous solution of NaCl, and dried with $MgSO_4$. CO_2 was bubbled into the solution and the precipitate was collected by filtration. The solid was subjected to distillation under reduced pressure using a Kugelrohr distillation apparatus (yield = 8.09 g, 37.8 mmol, 37.8%).

^{1}H NMR (δ in ppm, $CDCl_3$): 1.55−2.01 (4H, $-NCH_2CH_2CH_2N-$, $-NCH_2CH_2CHC{=}N-$), 2.56 (dd, J = 10.42 and 13.59 Hz, 1H, $PhCH_2-$), 2.74−2.90 (m, 1H, $-NCH_2CH_2CH(Bn)C{=}N-$), 3.00−3.22 (4H, $-NCH_2CH_2CH_2N{=}C-$, $-NCH_2CH_2CHC{=}N-$), 3.27 (dd, J = 3.62 and 13.59 Hz, 1H, $PhCH_2-$), 3.35−3.46 (t, J = 11.33 Hz, 2H, $-NCH_2CH_2CH_2N{=}C-$), 7.17−7.30 (5H, C_6H_5-).

^{13}C NMR (δ in ppm, CD_3OD): 24.7 ($-NCH_2CH_2CH_2N-$), 29.5 ($-NCH_2CH_2CHC{=}N-$), 42.3 ($-NCH_2CH_2CHC{=}N-$), 46.9 ($PhCH_2-$), 47.2 ($-NCH_2CH_2CHC{=}N-$), 48.2 ($-NCH_2CH_2CH_2N{=}C-$), 53.9 ($-C{=}NCH_2CH_2CH_2N-$), 130.3, 132.4, 133.2, 144.2 (C_6H_5-), 166.8 ($-C{=}N-$).

IR (cm^{-1}): 1643 (C═N).

HRMS (*m/z*): Theoretical ($C_{14}H_{18}N_2$ + H) = 215.1548. Found = 215.1532.

Synthesis of Prepolymers. Prepolymers were prepared by radical copolymerization of CMSt and styrene or DMA in the presence of 2,2′-azobis(isobutyronitrile) (3 mol % with respect to total monomers) at 60 °C for 24 h. The resulting solid was dissolved in THF, and the solution was poured into *n*-hexane. The precipitate was collected by filtration and dried under reduced pressure to obtain the prepolymers (Table 1).

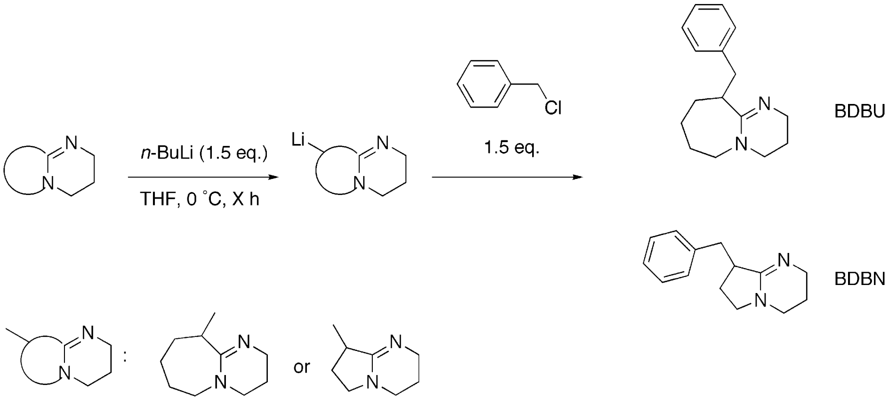
Reaction of Lithiated Amidines with Prepolymers. The introduction of amidine structures was conducted in a similar manner with the reaction using cross-linked polystyrene bearing chloromethyl groups.[28] To a 50 mL two-neck flask equipped with a dropping funnel containing a magnetic stir bar, DBN (500 mg, 4.0 mmol) and THF (15 mL) were added under a nitrogen atmosphere. Then, *n*-butyllithium in *n*-hexane (1.6 M, 6.0 mmol) was added from the dropping funnel at 0 °C, and the mixture was stirred for 1 h. Then, **P2** (poly(chloromethylstyrene$_{51}$-*co*-styrene$_{49}$)) (259 mg, 2.0 mmol amount of $-CH_2Cl$) in THF (10 mL) was added from the dropping funnel, and the mixture was stirred for 24 h at that temperature. After the reaction, methanol (ca. 2.0 mL) was added for quenching. The resulting homogeneous solution was poured into an excess amount of acetone, and the precipitate was collected by filtration. The solid was dried under reduced pressure to obtain **P2DBN** (310 mg, 45%).

IR (cm^{-1}): 1650 (C═N).

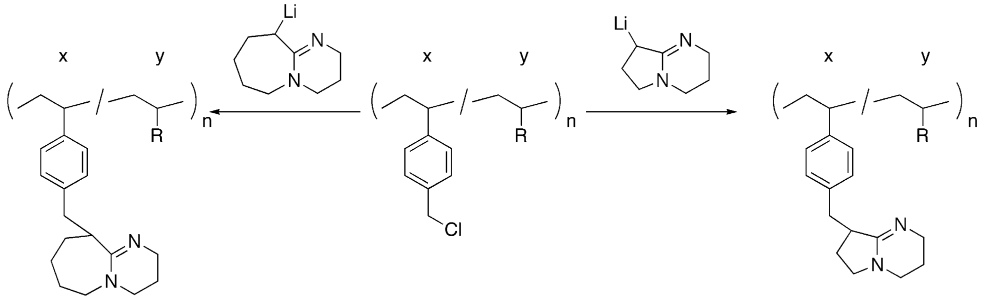
Other polymers: **P1DBN** (yield 95%; IR 1643 cm^{-1}); **P3DBN** (yield 58%; IR 1648 cm^{-1}); **P4DBN** (yield 89%; IR 1635 cm^{-1}); **P2DBU** (yield 38%; IR 1635 cm^{-1}).

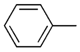
Reaction of Amidines with CO_2 in DMF. A 50 mL round-bottom flask with a three-way stopcock was filled with nitrogen, and a DMF solution of amidine (1.0 M, 10 mmol) was added. CO_2 dried by passing through $CaCl_2$ and silica gel was allowed to flow

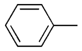
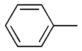
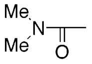
Scheme 2



Scheme 3



	R	x/y
P2DBU		51/49

	R	x/y
P1DBN	none	100/0
P2DBN		51/49
P3DBN		30/70
P4DBN		59/41

into the flask (200 mL/min) at 25 °C. In the same manner, CO_2 was allowed to flow into a flask containing the same amount of DMF as a control. The gravimetric increase was quantified as the difference in the weights of the sample and the control flasks. The degrees of CO_2 fixation was calculated based on the postulation that all of the CO_2 was fixed as bicarbonate salts.[30]

Reaction of Polymers Bearing Amidine Moieties with CO_2. Copolymers were dried at 120 °C under reduced pressure for at least 2 days before use, and stored under a nitrogen atmosphere. A TGA sample pan containing copolymers (ca. 5.0 mg) was placed in the TGA instrument. The sample was heated at 120 °C under a nitrogen atmosphere to remove absorbed CO_2 for 1000 min. Then, temperature was raised to the reaction temperature and the CO_2 fixation behavior was monitored as gravimetric changes under a CO_2 flow (200 mL/min). CO_2 releasing experiments were conducted by changing the flow-gas to nitrogen (200 mL/min). The increase in the weights was postulated to originate from fixation of equimolar amounts of CO_2 and water.[30]

Results and Discussion

Synthesis of Benzylated Cyclic Amidines and Polymers Bearing Cyclic Amidine Structures. We choose the reaction of lithiated amidines with active halogen compounds as the method for the incorporation of amidine structures into polymers. In a similar manner with 6-benzyl-1,8-diazabicyclo[5.4.0]-undec-7-ene (BDBU), 9-benzyl-1,5-diazabicyclo[4.3.0]non-5-ene (BDBN) was obtained by the reaction of lithiated DBN with benzyl chloride (Scheme 2).

The cyclic amidine structures were incorporated into polymers through the reaction of copolymers containing 4-chloromethylstyrene units with lithiated cyclic amidines in similar manners with the synthesis of BDBU and BDBN (Scheme 3). The copolymers are abbreviated as, for example, **P1DBN** and **P1DBU** for the copolymers prepared from **P1** and DBN and DBU, respectively. After the isolation of the resulting polymers, all the polymers became insoluble in common organic solvents, although the polymers are soluble before isolation. A plausible reason is the intermolecular cross-linking through the ionic interactions between amidinium structures and trapped CO_2 or bicarbonate originating from the protonation of the trapped CO_2 with water. The structures of the polymers were evaluated by IR and ^{13}C CP-MAS NMR (cross-polarization magic angle spinning nuclear magnetic resonance) spectroscopy. Figure 1 shows the ^{13}C NMR spectra of BDBN, BDBN under CO_2 atmosphere, **P2DBN**, and **P2**. The presence of the cyclic amidine structures could be confirmed by the clear IR absorption at 1650 cm^{-1} and ^{13}C NMR signals around 160−170 ppm. The splitting ^{13}C signals suggest the presence of trapped CO_2 in the polymer, which can be observed in the ^{13}C NMR spectrum of BDBN in CD_3OD (not dried) under a CO_2 atmosphere existing as the bicarbonate salt,[5] although the ^{13}C NMR spectrum of BDBN in CD_3OD under an air atmosphere does not show the signals of trapped CO_2 (discussed later). The small IR absorption around 1680 cm^{-1} supports the formation of the amidinium structure.

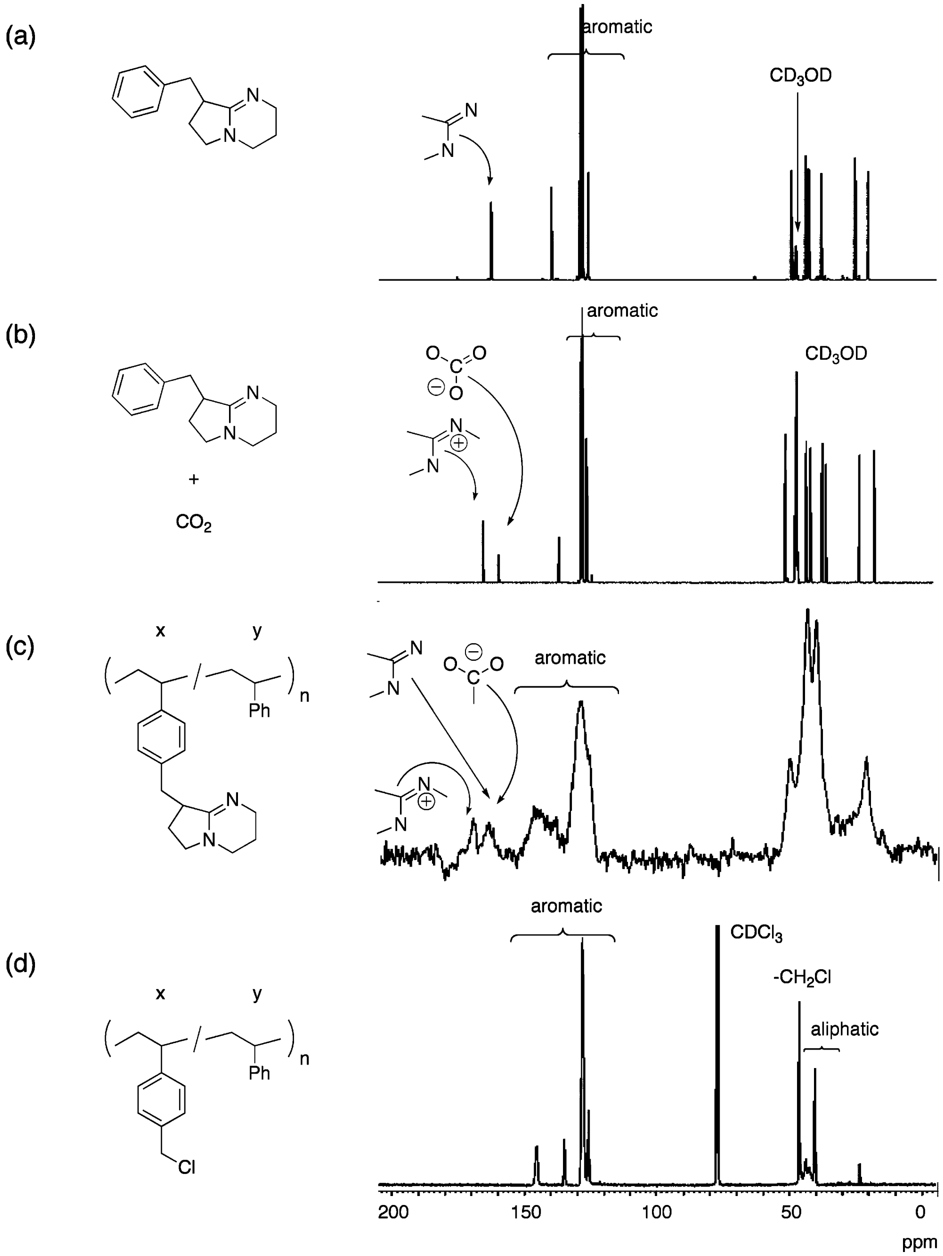


Figure 1. ^{13}C NMR spectra of (a) BDBN (CD_3OD), (b) BDBN−CO_2 (CD_3OD), (c) the polymer bearing DBN moieties prepared from **P2** (**P2DBN**) (CP-MAS with TOSS technique), and (d) poly(chloromethylstyrene-*co*-styrene) (**P2**) ($CDCl_3$).

The IR absorption of the free amidine at 1650 cm^{-1} disappeared after the reaction with CO_2 described later, and the IR absorption of the amidinium structure at 1678 cm^{-1} appeared instead (Figure 2c). The negligible IR absorption around 677 cm^{-1} suggests that efficient conversion of the chloromethyl group to the cyclic amidine structures (Figure 2). The other polymers bearing DBN moieties exhibit similar spectral features, and the IR spectrum of **P2DBU** shows an absorption at 1635 cm^{-1}, which is closer to the absorption observed in the IR spectrum of BDBU−CO_2 (1632 cm^{-1}) than that in the spectrum of BDBU (1617 cm^{-1}) (see Supporting Information). Specifically, the IR spectra of other polymers with amidine moieties also show negligible IR absorption of the chloromethyl group. Accordingly, we postulated that the copolymer compositions of the resulting copolymers bearing amidine moieties are same as those of the original copolymers.

CO_2 Fixation of Low Molecular Weight Amidines (Model Reaction). As model reactions for the CO_2 fixation with the polymers, CO_2 fixation behavior was examined using *n*-butyl benzene and DMF solutions (1.0 M) of DBU at 25 °C under a CO_2 flow (200 mL/min) (Figure 3). All the reaction mixtures were homogeneous without precipitates under a nitrogen atmosphere before the CO_2 flow, indicating that the amidines and the solvents did not contain enough amounts of water and CO_2 to produce detectable amounts of bicarbonate salts.[5] Namely, the amounts CO_2 in the amidines and the solvents are ignorable enough toward the CO_2 absorbed in these CO_2 fixation experiments. The mixtures became heterogeneous by the CO_2 flow. The reactions in *n*-butyl benzene are faster than those in DMF, and it suggests that polarity plays an important role in the reaction of the amidines with CO_2 (discussed later). When *n*-butyl benzene without distillation was used, precipitate formed instantaneously before introducing CO_2 to the mixtures in a nitrogen atmosphere. This precipitate formation is assumed to originate from the CO_2 and water dissolved from air while storing to accelerate the complexation of the amidines and CO_2. The reactions of the benzylated derivatives of DBU and DBU (BDBU and BDBN, respectively) were also carried out in DMF

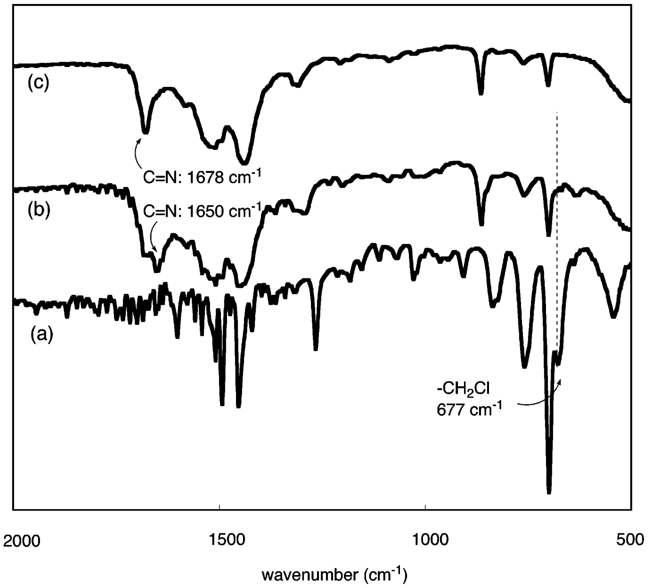


Figure 2. IR spectra of (a) poly(chloromethylstyrene-*co*-styrene) (**P2**), (b) the polymer bearing DBN moieties (**P2DBN**), and (c) **P2DBN** after reaction with CO_2.

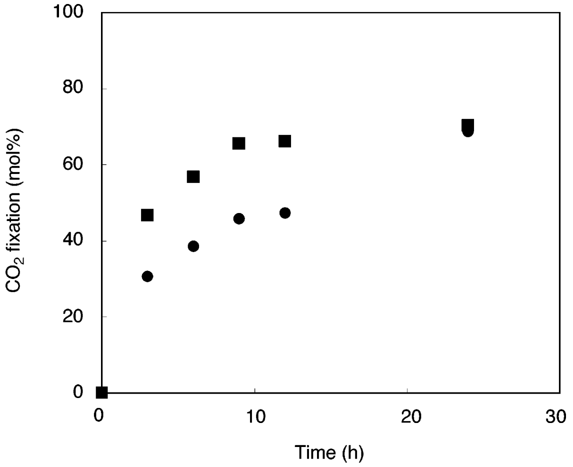


Figure 3. CO_2 fixation behavior of DBU in *n*-butyl benzene (square) and DMF (circle) (1.0 M) at 25 °C under a CO_2 flow (200 mL/min).

(1.0 M) at 25 °C under a carbon dioxide flow (200 mL/min) (Figure 3). The DBN derivatives fixed faster than the DBU derivatives owing to the lower steric hindrance around the imine groups, which was supported by *ab initio* calculations (discussed later). The benzylated derivatives also fixed CO_2, and it suggests that the aforementioned polymers also fix CO_2. The CO_2 fixation rates are slower than their raw amidines (i.e., DBN and DBU), whereas this tendency is significant in the case of DBU and BDBU. We attributed the low CO_2 trapping efficiency of BDBU to the benzyl group in BDBU sterically demanding more than that in BDBN due to the lower dihedral angle of the benzyl−amidine bond and the imine bond. The CO_2 fixation with these fused bicyclic amidines are slower than that with MTHP bearing no substituents sterically demanding to the amidine moiety.[2] This fact also supports the assumption mentioned above.

Computational Calculation on Amidine−CO_2 Complexes. The effect of the amidine structures on the CO_2 fixation behaviors was elucidated by computational calculation. We calculated the geometries of the zwitter ionic adduct for simplicity, based on the postulation that the calculation conducted for the zwitter ionic adducts is also informative for bicarbonate or carbonate salts. Both the salts and the adducts are stabilized by conjugation when the O−C−O bonds and the amidine moieties are in the same plane.

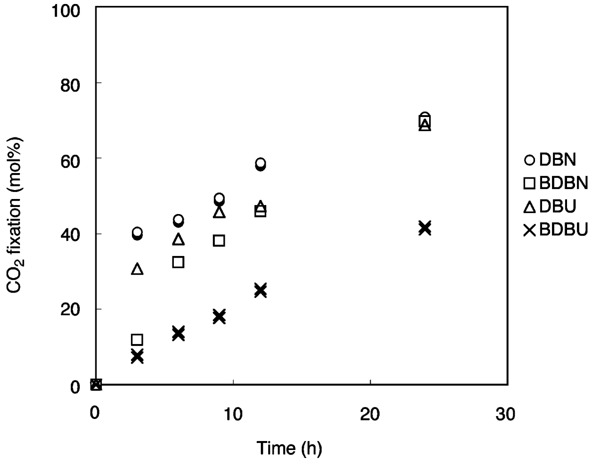


Figure 4. CO_2 fixation behavior of DBN, BDBN, DBU, and BDBU in DMF (1.0 M) at 25 °C under a CO_2 flow (200 mL/min).

Table 2. CO_2−Imine Nitrogen Bond Lengths and Angles and O−C−O Bond Angles of Amidine−CO_2 Complexes Calculated by DFT/B3LYP 6-31G* Calculations

amidine−CO_2	CO_2−imine nitrogen bond length (Å)	O−C−O bond angle (deg)	CO_2−imine bond angle (deg)
DBN−CO_2	2.718	173.64	127.10
BDBN−CO_2	2.713	173.60	129.77
DBU−CO_2	2.812	174.28	130.82
BDBU−CO_2	2.983	178.00	139.84

Pérez et al. evaluated the reactivity of DBU and 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene with CO_2 by theoretical calculation of hardness performed at the B3LYP/cc-pVTZ level of density functional theory (DFT). Their calculation constrained the angles of the O−C−O bonds in the complexes to 130 °. We optimized the geometries of the hypothetical amidine−CO_2 complexes without any constraints by HF/6-31G* and DFT B3LYP/6-31G* calculations.[31] Although the HF/6-31G* calculation suggested the formation of the zwitter ionic compounds by the bent O−C−O bonds, the DFT calculation suggested the very weak interactions by the almost straight O−C−O bonds (Table 2, Figure 5, and Supporting Information). We postulated that the DFT calculation provided better results than the HF calculation, by considering the facts that the amidine−CO_2 complexes or the amidinium salts exist stably only under CO_2 atmospheres and release CO_2 under the atmospheres of other gases. Namely, the stable complexes or the salts produce only in the presence of excess amounts of CO_2. The geometric features of the complexes differ with the amidines. The complexes from the DBN derivatives were calculated to have stronger interactions between CO_2 and the amidines, confirmed by the shorter CO_2−imine nitrogen bond lengths and the bent O−C−O bond angles of the trapped CO_2. Specifically, the geometry of the BDBU−CO_2 complex was calculated to have the longest CO_2−imine nitrogen bond length and the flattest O−C−O bond angle, and it implies that the interaction between BDBU and CO_2 is very weak. The reason for the differing amidine−CO_2 interaction is the steric hindrance, which can be estimated by the CO_2−imine bond angles. The sterically demanding structures around the amidine structures (i.e., the benzyl group in BDBN and BDBU and the cycloheptyl ring in DBU and BDBU) are assumed to prevent the strong donation of the lone pairs of the amidines to CO_2.

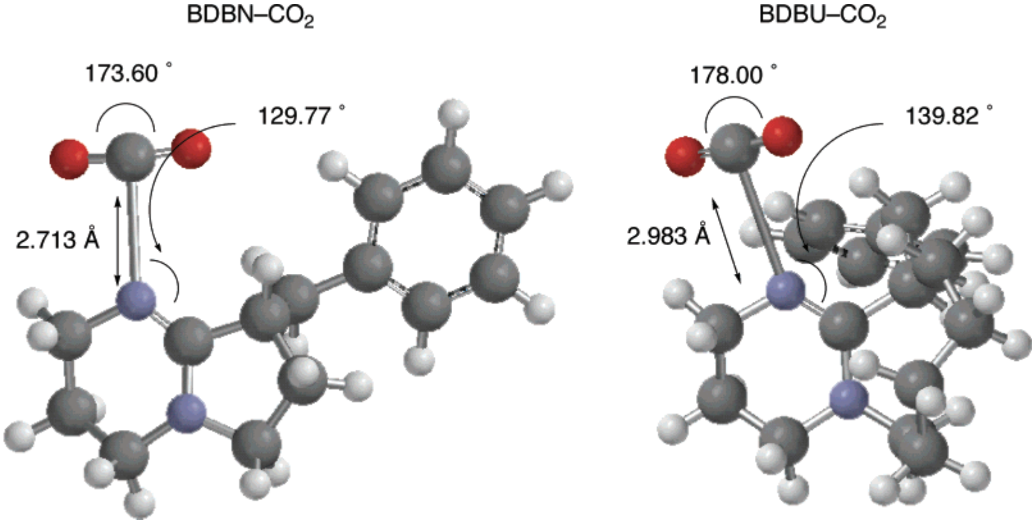


Figure 5. Optimized geometries of BDBN−CO_2 complex and BDBU−CO_2 complex (DFT/6-31G*).

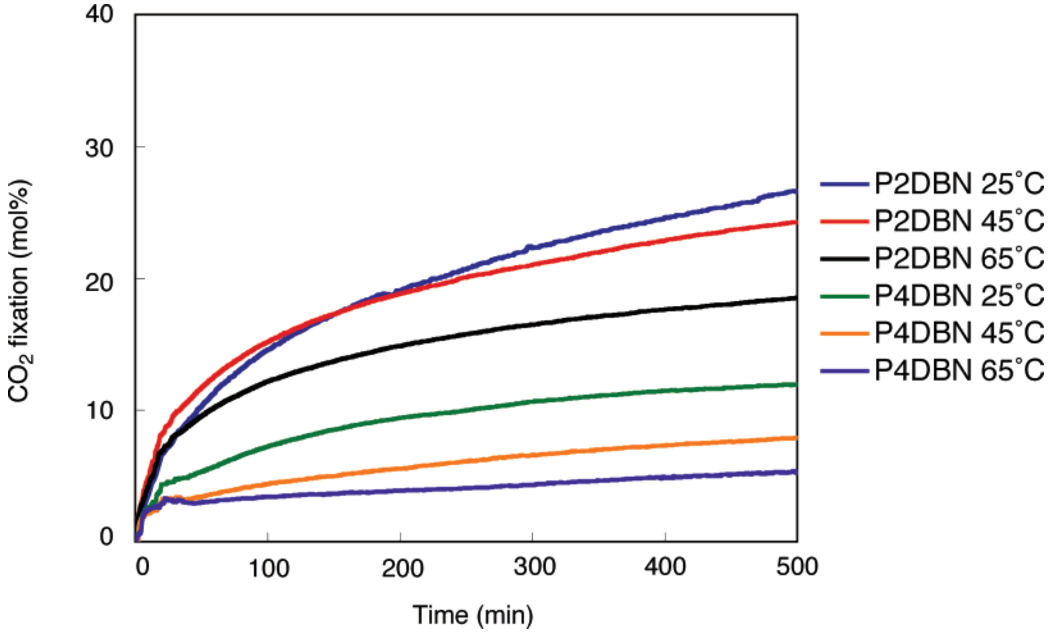


Figure 6. CO_2 fixation of **P2DBN**, and **P4DBN** under a CO_2 flow (200 mL/min) under various temperatures.

These calculated structures agree well with the aforementioned CO_2 fixation behaviors.

CO_2 Fixation of Copolymers Bearing Amidine Moieties. On the basis of the successful results of the model reactions, we conducted CO_2 fixation reaction of the polymers bearing amidine moieties (Scheme 1). The CO_2 fixation with the polymers was conducted in a TGA instrument under a CO_2 flow (200 mL/min) in a similar manner with the case of the polymers bearing tetrahydropyrimide-1-yl moieties previously reported.[2] The powders of the polymers were dried under reduced pressure, and then were placed on a sample pan in the TGA instrument. The samples were dried again in the TGA instrument under nitrogen flow (200 mL/min) at 120 °C until the weight decrease stopped. The IR spectra of the polymers after the reaction showed characteristic absorptions of imine moieties at 1650 and 1670 cm^{-1}, which is assignable to the amidinium salts and free amidines (Figure 2c). Figure 6 shows the CO_2 fixation behavior of **P2DBN** and **P4DBN** containing styrene and *N*,*N*-dimethyl acrylamide as the comonomer components. The CO_2 fixation efficiency with **P4DBN** is lower than that with **P2DBN** in spite of the identical copolymer compositions. This result can be correlated to the faster CO_2 fixation of DBU in less polar *n*-butyl benzene than in polar DMF. We attributed the better results in less polar environments to (a) the faster permeation of nonpolar CO_2 in low polar substances and (b) stronger nucleophilicity of the amidines in weakly polar environments. The CO_2 fixation ability of **P2DBN** is competitive with that of the polymer bearing tetrahydropyrimide-1-yl moieties previously reported (27% at 35 °C and 34% at 45 °C). We presume that the increased CO_2 fixation ability by the less polar comonomer component compensated for the weaker CO_2 ability of DBN than that of tetrahydropyrimide-1-yl structures. A lower temperature resulted in higher amounts of CO_2 fixation owing to the entropic advantage.

The CO_2 fixation with other polymers was also carried out at 25 °C (Figure 7). The CO_2 fixation rate of **P2DBU** is significantly lower than that of **P2DBN**. The lower efficiency of **P2DBU** is attributable to the steric hindrance of the BDBU structure, as confirmed by the model reaction. The CO_2 fixation with both **P1DBN** and **P3DBN** is also slower than that with **P2DBN**. Although the reason is unclear, this fact indicates that the CO_2 fixation efficiency does not correlate linearly with the

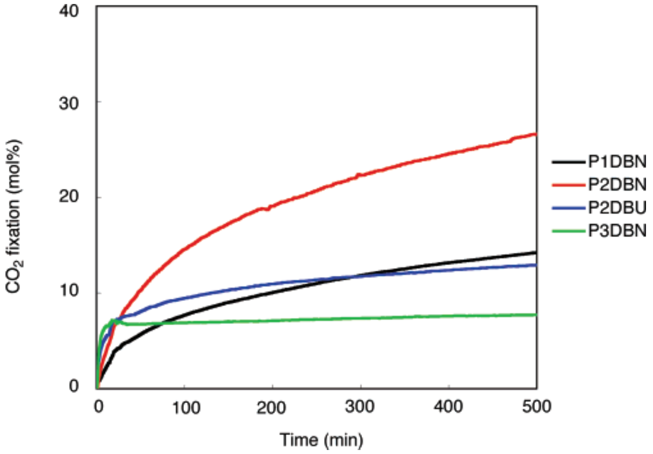


Figure 7. CO_2 fixation of **P1DBN**, **P2DBN**, **P2DBU**, and **P3DBN** under a CO_2 flow (200 mL/min) at 25 °C.

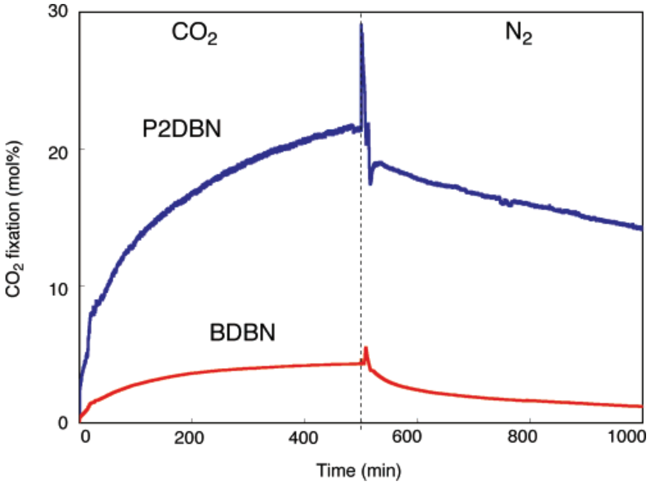


Figure 8. CO_2 fixation−release behaviors of (a) BDBN and (b) **P2DBN** under CO_2 (0−500 min) or N_2 (500−1000 min) flows (200 mL/min each) at 25 °C.

comonomer composition. A plausible reason for the insufficiency of **P1DBN** is the too high compositions of the amidine moieties are responsible to the lower mobility of the polymers and the slower permeation of CO_2 due to the high concentration of the polar ionic structures. Similarly, in the case of the polymers with tetrahydropyrimide-1-yl moieties, the fixation with a copolymer is more efficient than the corresponding homopolymer. We also attributed the lower fixation ability of **P3DBN** to the slower rate due to the diluted concentration of the DBN structure in the copolymer.

CO_2 Fixation—Release Behaviors of the Polymers Bearing Amidine Moieties and the Model Compounds. Amidines trapping CO_2 release CO_2 by thermal treatment or other gases.[2−6] In the cases of low-molecular weight amidines, the CO_2 trapping takes place only at ambient temperatures under CO_2 atmospheres, and the CO_2 releasing takes place by changing the atmospheres to inert gases.[5,6] This behavior is advantageous when the amidines are used as CO_2-responsive materials. However, too sensitive CO_2 releasing is not suitable for CO_2 absorption materials. We presumed that **P2DBN** absorbing CO_2 even at 65 °C would have good retain-ability of trapped CO_2. Accordingly, we evaluated the CO_2 fixation−release behaviors of BDBN and **P2DBN** under nitrogen or CO_2 flows (200 mL/min each) at 25 °C in a TGA instrument (Figure 8). First, the monomeric (BDBN) and polymeric (**P2DBN**) amidines were reacted with CO_2, and weight increases were observed. The weight increase with **P2DBN** is larger than that with BDBN, probably due to the reason described for the better CO_2 fixation ability of **P2DBN** than **P1DBN**. In a similar manner, BDBN and **P2DBN** fixed CO_2 even under diluted CO_2 flow (CO_2: 50 mL/min and N_2: 150 mL/min) (see Supporting Information). After 500 min of CO_2 flows, the flow gas was changed to N_2. A fast weight decrease was observed for BDBN in similar manners with other low-molecular weight amidines.[5,6] Contrary to this, the weight decrease was slow in the case of **P2DBN**, in spite of the faster CO_2 fixation. It indicates that **P2DBN** have an ability to retain trapped CO_2 under a nitrogen atmosphere, which is better than that of BDBN. Plausible reasons for the good CO_2 retainability of **P2DBN** are as follows: (a) entropic advantage over BDBN owing to the comonomer component and (b) the loss of mobility of the ionic structures originating from the trapped CO_2 by the hydrophobic comonomer components and the hard polystyrene backbone.

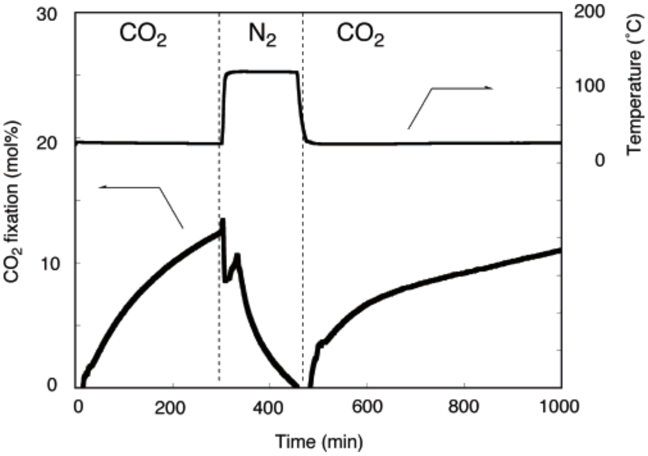


Figure 9. CO_2 fixation−release behaviors of **P2DBN** under a CO_2 atmosphere at 25 °C or a nitrogen atmosphere at 120 °C.

In order to evaluate the reversible CO_2 fixation-release ability of **P2DBN**, the CO_2 fixation−release behaviors of **P2DBN** was evaluated under a CO_2 atmosphere at 25 °C and then under a nitrogen atmosphere at 120 °C (Figure 9). The first CO_2 fixation at 25 °C for 300 min resulted in 17% of CO_2 fixation, and the trapped CO_2 was completely removed by a N_2 flow (200 mL) at 120 °C for 200 min. Then, the flow gas was changed to CO_2 and **P2DBN** fixed CO_2 again. This result demonstrates that **P2DBN** is a recyclable CO_2 fixation material. The potential application of **P2DBN** is emphasized by the fact that **P2DBN** absorbs CO_2 in air. For example, drying of **P2DBN** stored under air by a N_2 flow at 120 °C typically released approximately 60−70 mol % amounts of trapped CO_2 (i.e., longer exposure of **P2DBN** to CO_2 leads to more amounts of fixed CO_2) and dried **P2DBN** fixed CO_2 as aforementioned. The release of trapped CO_2 in **P2DBN** is slower than that in the polymer bearing tetrahydropyrimide-1-yl moieties, from which CO_2 is released quantitatively at 95 °C within 100 min. Although the higher temperature and the longer release time for **P2DBN** are responsible to the higher energy cost, these factors are reciprocal to the higher CO_2 retaining ability.

Conclusions

We prepared copolymers bearing DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) and DBN (1,5-diazabicyclo[4.3.0]non-5-ene) moieties for CO_2 fixation via an easier procedure than conventional polymers bearing amidine moieties.[2] The copolymers bearing DBN moieties fix carbon dioxide faster than those bearing DBU moieties owing to the lower steric hindrance around the imine structure. The copolymer has a better ability to retain trapped CO_2 under a N_2 flow at 25 °C, whereas the corresponding low-molecular weight amidine releases trapped CO_2 immediately under the same conditions. As a result, these copolymers can absorb CO_2 in air, whereas low molecular weight amidines fix negligibly in air. The trapped CO_2 in the copolymers was quantitatively released by a N_2 flow at 120 °C. This result demonstrates the potential application of the polymers bearing amidine moieties as recyclable CO_2 concentration materials, which can fix CO_2 at ambient conditions and release trapped CO_2 at higher temperature reversibly. Further exploration on the suitable comonomer components and compositions will find better CO_2 fixation polymers.

Supporting Information Available: Figures showing IR spectra of **P1DBN**, **P2DBU**, **P3DBN**, and **P4DBN**, and those after reactions with CO_2, ^1H NMR spectra of DBN, DBU, BDBN, and BDBU and those after reactions with CO_2, and CO_2 fixation with **P2DBN** and BDBN under diluted CO_2 flow (CO_2 (50 mL/min) and N_2 (150 mL/min)) and tables giving the geometry data of the computational calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) The degrees of CO_2 fixation were calculated based on the presumption that all the gravimetric increase originated from bicarbonate salt formation (i.e., the weight increase by addition of CO_2 and water in CO_2 gas). If the zwitter ionic adducts existed, the CO_2 fixation degrees may become as high as 1.4 times larger than those calculated based on the bicarbonate salts.
(31) The geometry of DBU−CO_2 complex was calculated without any constraint at the B3LYP/cc-pVTZ level of DFT, which was applied in the calculation with the constrained geometry of the trapped CO_2 conducted by Pérez et al. The geometry is almost identical to that calculated at the B3LYP/6−31G* level of DFT (e.g., CO_2−imine nitrogen bond length = 2.912 Å, CO_2−imine nitrogen bond angle = 133.49°, and O−C−O bond angle = 175.80°). The geometry data are indicated in the Supporting Information.

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