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A Novel Construction of a Reversible Fixation−Release System of Carbon Dioxide by Amidines and Their Polymers

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Development of efficient methods for CO_2 recovery from industrial waste gases etc. is extremely important in relation to both reutilization of CO_2 as carbon resources[1] and environmental issue concerned with the greenhouse effect.[2] One of the most commonly used processes for CO_2 recovery is chemically reversible CO_2 fixation by primary or secondary amines based on CO_2 fixation by amines at room temperature to give ammonium carbamates, and CO_2 release from ammonium carbamates upon heating.[3] Application of CO_2 fixation in functional polymers has been also examined,[4] for instance, copolymers of styrene bearing pendant amino groups fixed CO_2 under ambient conditions.[4b]

A more attractive process may be CO_2 fixation by tertiary amines giving zwitterion adducts that may provide a more easily handled fixation−release treatment, since these zwitterions could release CO_2 at reduced temperatures owing to their lability (primary-(secondary) amines; at >100 °C). Furthermore, this process can provide zwitterions having a unique reactivity. However, detailed studies concerning CO_2 fixation by tertiary amines and its application to functional polymers have not been carried out. Here we report a new type of reversible CO_2 fixation by amidine derivatives and by polymers bearing an amidine moiety both in solution and solid state.

In the course of the study of CO_2 fixation by tertiary amines, there has been one example of CO_2 fixation by 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) to afford the zwitterion adduct.[5] Assuming the reasons why DBU can react with CO_2 are its high nucleophilicity and stabilization of the cation species by delocalization in the amidine moiety, we constructed the idea that amidine derivatives with higher nucleophilicity may provide a success of CO_2 fixation. *N*-Methyltetrahydropyrimidine (**MTHP**) containing an amidine structure was synthesized,[6] since it would have higher nucleophilicity due to decrease in the steric hindrance around the nitrogen atom of imine moiety. CO_2 fixation using **MTHP** was performed in *N*,*N*-dimethylformamide (DMF) at 25 °C under atmospheric pressure.[7] Fixing efficiency (%, mmol of CO_2/mmol of **MTHP**) was estimated from the weight increase in the reaction mixture. When CO_2 was bubbled into a DMF solution of **MTHP**, a white precipitate was formed immediately, and the weight increase in the reaction mixture ceased after 1 h to afford the corresponding zwitterion adduct (**MTHP—CO₂**) in quantitative fixing efficiency. On the other hand, DBU needed 100 h to fix CO_2 in 89% fixing efficiency,[8] thus, **MTHP** proved to be an excellent agent for CO_2 fixation. The IR spectrum of **MTHP—CO₂** showed two absorption bands assignable to the CO_2 moiety at 1689 and 1389 cm^{-1}. The ^1H NMR spectrum of **MTHP—CO₂** showed that the signal of the imine proton was shifted to lower field (0.57 ppm) compared with **MTHP** and the ^{13}C NMR spectrum showed a signal attributable to the carbonyl group at 161.3 ppm.

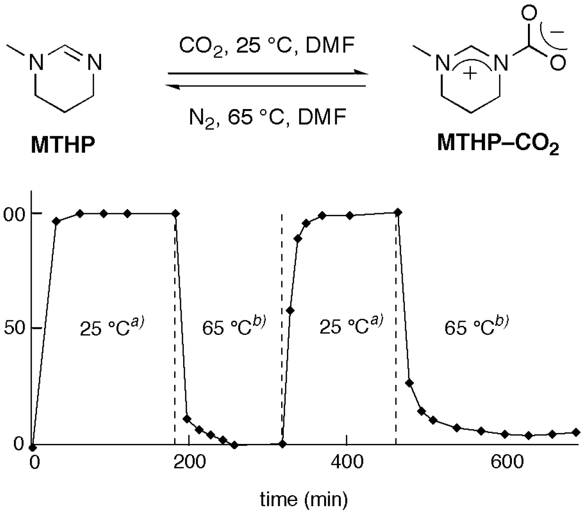
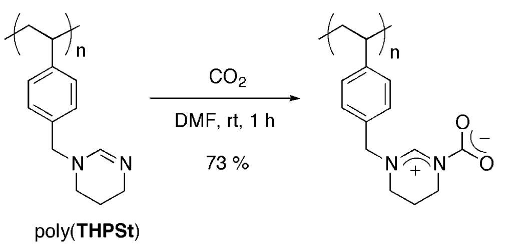


Figure 1. Reversible CO_2 fixation and release by **MTHP** in DMF. Conditions: (a) under CO_2 flow (200 mL/min); (b) under N_2 flow(200 mL/min).

Scheme 1



Reversibility of CO_2 fixation by **MTHP** was examined (Figure 1): The obtained zwitterion adduct (**MTHP—CO₂**) could release CO_2 at 65 °C to regenerate the original **MTHP**. It is noteworthy that **MTHP—CO₂** can release CO_2 at lower temperature than the ammonium carbamates from primary (secondary) amines (at >100 °C).[9] Subsequently, CO_2 was bubbled into a DMF solution of **MTHP** at 25 °C to regenerate **MTHP—CO₂**; any degradation in this system could not be observed throughout the fixation/release cycles.

Next, we synthesized a polystyrene derivative bearing an amidine moiety (poly(**THPSt**)) by the synthesis of 4-(1,4,5,6-tetrahydropyrimide-1-yl)methylstyrene (**THPSt**) and its radical polymerization.[10] When CO_2 was bubbled into the suspension of poly(**THPSt**) in DMF at 25 °C for 1 h under atmospheric pressure, the CO_2 fixation took place in 73% fixing efficiency (mmol of CO_2/mmol of amidine moiety) (Scheme 1).[11] The IR spectrum of the resulting polymer showed the absorption bands of carboxylate moieties at 1666 and 1403 cm^{-1}.

The CO_2 fixation in the solid-state by polymer bearing amidine moiety may be one of the most simple, eco-

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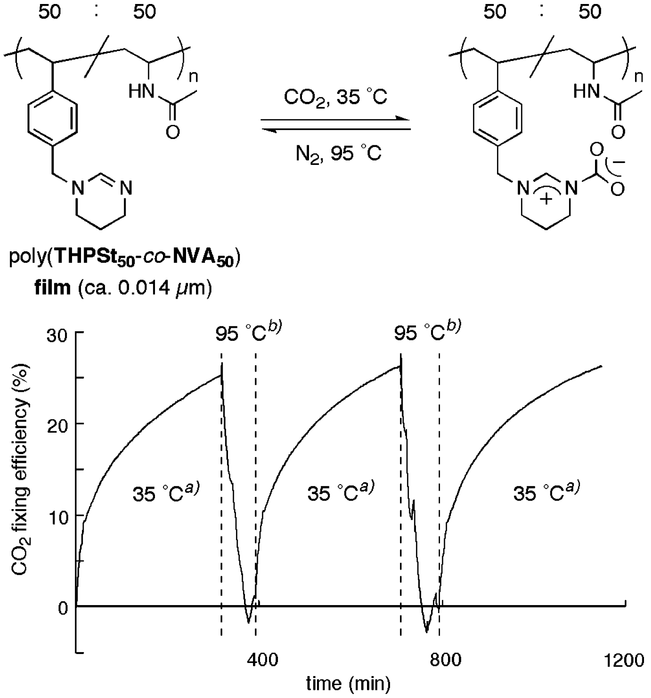

Figure 2. Reversible CO_2 fixation and release by the film in TGA. Conditions: polymer (ca. 5 mg), (a) under CO_2 flow (200 mL/min) and (b) under N_2 flow (200 mL/min).

nomical, and effective methods for CO_2 recovery. When the poly(**THPSt**) powder was exposed to CO_2 atmosphere at 25 °C for 500 min, 12% fixing efficiency could be found from the weight increase monitored by thermogravimetric analysis (TGA).[12] IR spectrum of the resulting polymer showed the absorption bands of carboxylate moieties at 1666 and 1403 cm^{-1}. The effect of the functional comonomer on CO_2 fixation was next examined; *N*-vinylacetamide (**NVA**) was chosen as the comonomer since its polymer might have high CO_2 permeability.[13] The copolymer of **THPSt** with **NVA**, poly(**THPSt**$_{50}$-*co*-**NVA**$_{50}$)[14] exhibited a remarkably higher fixing ability (48%).

Poly(**THPSt**$_{50}$-*co*-**NVA**$_{50}$) was well soluble in MeOH, and it was cast from its MeOH solution to form ca. 0.014 μm thick film. To evaluate the CO_2 fixing ability, the film was exposed to CO_2 atmosphere in a TGA instrument at 25 °C for 500 min, where the CO_2 fixation took place in 25% fixing efficiency. The fixing ability was enhanced by raising reaction temperature (35 °C; 27%, 45 °C; 34%), presumably due to the increase in the degree of diffusion of CO_2 through the polymer film. In Figure 2, we showed the results of the reversible CO_2 fixation experiment. The film could conduct reversible CO_2 fixation, where CO_2 was fixed at 45 °C and was released at 95 °C. Interestingly, the CO_2 fixing efficiency did not change over three cycles, indicating the high recyclability of the solid-state CO_2 fixing system.

In summary, we developed the reversible fixing system of carbon dioxide by amidines. The *N*,*N*,*N′*-trialkylamidine derivative *N*-methyltetrahydropyrimidine was found to exhibit reversible fixation−release of CO_2. Polymers bearing an amidine moiety that can fix CO_2 both in solution and solid state were successfully synthesized. The polymer film containing the amidine moiety could fix and release CO_2 reversibly, and it might be applicable for CO_2 storage materials that can recover CO_2 from industrial waste gases and can provide a carbon source to synthesize useful substances.

Supporting Information Available: Text giving the experimental procedures for the preparation of the monomer and the polymer and their spectral data and a scheme showing the synthetic routs for th emonomer and polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Procedure for the reversible CO_2 fixation by **MTHP**: CO_2 was bubbled into anhydrous DMF solution (10 mL) of **MTHP** (982 mg, 10 mmol) at 25 °C for 3 h to afford **MTHP—CO$_2$** in quantitative fixing efficiency (weight increase in the reaction mixture was 440 mg). Subsequently, a DMF solution of **MTHP—CO$_2$** was heated to 65 °C for 2 h to regenerate **MTHP** quantitatively. The cycle was repeated two times. **MTHP—CO$_2$**: IR (NaCl) 1689, 1389 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, δ, ppm): 1.88 (2H, m), 3.18 (3H, s), 3.27 (2H, t, $J = 7.29$ Hz), 3.40 (2H, t, $J = 7.29$ Hz), 7.46 (1H, s). ^{13}C NMR (270 MHz, DMSO, δ, ppm): 19.81, 39.92, 40.62, 45.13, 152.37, 161.32.

(8) Pyridine, triethylamine, 4-(dimethylamino)pyridine, and 1,4-diazabicyclo[2,2,2]octane did not fix CO_2.

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(10) Experimental details are given in the Supporting Information.

(11) Since poly(**THPSt**) is less soluble in common organic solvents, the CO_2 fixation experiment was carried out in the suspension of poly(**THPSt**) in DMF.

(12) Representative procedure for the CO_2 fixation by polymer

in the solid state: The CO_2 fixing ability of the polymer powder or the film were evaluated by thermogravimetric analysis (TGA) (TG/DTA220). The sample was first regenerated (these polymers will fix CO_2 from the air) by a heat treatment at 95 °C for 2 h under a dry nitrogen purge (200 mL/min). The furnace was allowed to cool to 25 °C and maintained isothermal conditions. The radial purge was switched to CO_2 (200 mL/min) to contact the gas with the sample and the reaction was left to proceed to equilibrium.

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(14) Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(**THPSt**$_{50}$-*co*-**NVA**$_{50}$) were estimated to be 15500 and 1.39, respectively, by size exclusion chromatography (eluent: H_2O, poly(ethylene glycol) standards).

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