

Effective Fixation of Carbon Dioxide and Its Application to Polymer Synthesis

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Introduction

Recently, the chemistry of carbon dioxide has much attention, since carbon dioxide is the most inexpensive and infinite carbon resources. Furthermore, greenhouse effect due to carbon dioxide has gained much attention and decreasing atmospheric carbon dioxide is a critical problem.¹ From these viewpoints, many chemists have studied on development of efficient methods for CO₂ recovery. Among them, chemical CO₂ fixation by primary or secondary amines have been most intensively studied and have become one of the most promising methods for CO₂ recovery.² However, detailed study concerning CO₂ fixation by tertiary amines. Reaction of epoxide with CO₂ is also attractive candidate for efficient CO₂ fixation; however, high pressure of CO₂ has been generally necessary.³ In the course of our works on chemical CO₂ fixation, we present the reversible CO₂ fixation by amidine derivatives and the reaction of epoxides with CO₂ under atmospheric pressure leading to the cyclic carbonate.

Experimental

Materials. *N*-Methyltetrahydropyrimidine (MTHP) was synthesized according to the reported procedure.⁴ Epoxides were distilled from CaH₂ and stored under nitrogen. *N,N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) were dried and distilled from CaH₂.

Instruments. ¹H-NMR and ¹³C-NMR spectra were recorded with JEOL JNM-270EX or JEOL JNM-GX500 spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded with a Jasco FT/IR-5300 spectrometer. Size exclusion chromatography (SEC) was used to determine number average molecular weight (*M*_n) and molecular weight distribution (*M*_w/*M*_n) of polymer samples with respect to polystyrene standards (Tosoh).

Reversible CO₂ fixation by MTHP. CO₂ was bubbled into anhydrous DMF solution (10 mL) of MTHP (982 mg, 10 mmol) at 25 °C for 3 h to afford MTHP-CO₂ in quantitative fixing efficiency (weight increase in the reaction mixture was 440 mg). Subsequently, a DMF solution of MTHP-CO₂ was heated to 65 °C for 2 h to regenerate MTHP quantitatively. The cycle was repeated two times. The structure of MTHP-CO₂ was confirmed by ¹H NMR, ¹³C NMR, and IR spectra.

Reaction of epoxide with CO₂. A mixture of epoxide (10 mmol), catalyst (5.0 mmol), and naphthalene (0.128 g) was introduced in a two-necked flask equipped with a rubber septum. After the atmosphere was replaced with CO₂, 10.0 mL of NMP was introduced using a syringe through a rubber septum to dissolve the mixture. The solution was allowed to stand at 100 °C with continuous stirring. Periodically, a small portion of the reaction mixture was removed out through rubber septum, diluted with dichloromethane, and washed with water. The organic extract was analyzed by HPLC to estimate the conversion of epoxide and yield of carbonate using naphthalene as an internal standard.

Results and Discussion

1. Reversible CO₂ Fixation by Amidines

The CO₂ fixation by primary or secondary amines to afford the corresponding ammonium carbamates have been already reported,² however, detailed study concerning CO₂ fixation by tertiary amines have not been carried out. Recently, we have found

that *N,N,N'*-trialkylamidines, such as *N*-methyltetrahydropyrimidine (MTHP) can construct reversible CO₂ fixation, where CO₂ was fixed at 25 °C and was released at 65 °C quantitatively (Figure 1).⁵

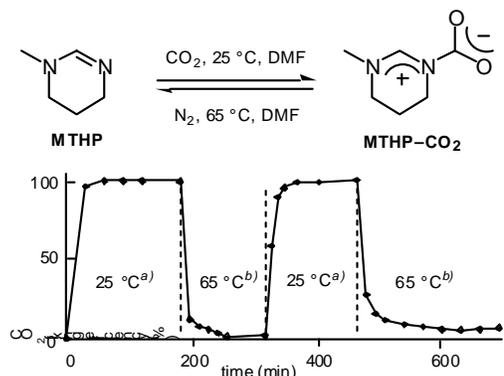
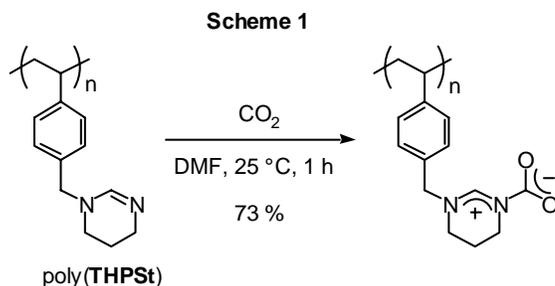


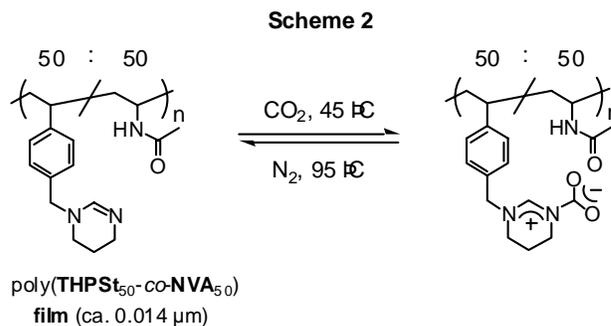
Figure 1. Reversible CO₂ fixation and release by MTHP in DMF. Conditions: *a*) under CO₂ flow (200 mL/min). *b*) under N₂ flow (200 mL/min).

2. Reversible CO₂ Fixation by Polymer Bearing Amidine Moiety

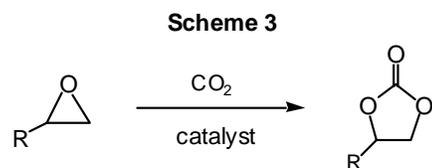
The polymer bearing amidine moiety (poly(THPSt)) was prepared by the synthesis of 4-(1,4,5,6-tetrahydropyrimidine-1-yl)methylstyrene (THPSt) and its radical polymerization. Poly(THPSt) could fix CO₂ in *N,N*-dimethylformamide (DMF) at 25 °C in 73 % fixing efficiency (Scheme 1).



The CO₂ fixation in the solid state using polymer bearing amidine moiety may be one of the most simple, economical, and effective methods for CO₂ recovery. Poly(THPSt) was found to fix CO₂ in the solid state (30 %). The copolymer of THPSt with *N*-vinylacetamide (NVA), poly(THPSt_{50-co-NVA}₅₀) exhibited the higher fixing ability (48 %) than poly(THPSt), presumably due to the decrease in steric hindrance between the adjacent pendant groups. Poly(THPSt_{50-co-NVA}₅₀) was cast from its MeOH solution to form a film that could fix CO₂ at 45 °C in 34 % fixing efficiency. As shown in Scheme 2, the film could conduct the reversible CO₂ fixation, where CO₂ was fixed at 45 °C and was released at 95 °C.

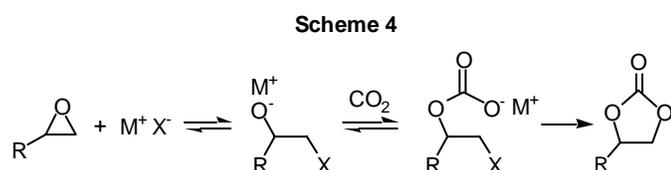


3. Reaction of Epoxide with CO₂



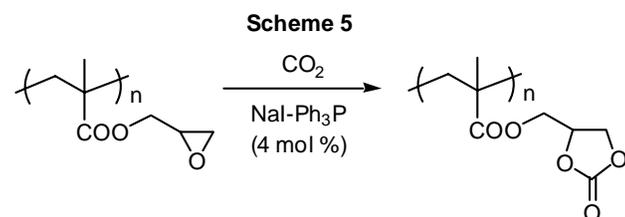
The reaction of epoxides with CO₂ have been already reported. However, high pressure of CO₂ is generally necessary.³ We have

found that alkali metal halides such as lithium bromide show high catalytic activity for this reaction to afford the five-membered cyclic carbonates under atmospheric pressure in excellent yield.⁶ The order of intrinsic activity is following order: chloride > bromide > iodide, which is the order of nucleophilicity of the anion, and lithium salt > sodium salt > benzylammonium salt, which is in accord with the order of Lewis acidity of the cation. The reaction may proceed via nucleophilic attack of halide to epoxide to form β-haloalkoxide which reacts with CO₂ followed by cyclization (Scheme 4).



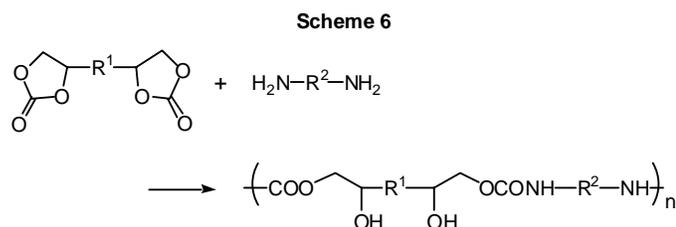
4. Polymer Reaction of Polymer Bearing Epoxide Moiety with CO₂

The incorporation of CO₂ into the polymers bearing epoxide moiety under atmospheric pressure is useful from the viewpoint of CO₂ fixation and the functionality of produced cyclic carbonate. Quantitative incorporation of CO₂ into poly(glycidyl methacrylate) was accomplished in the presence of NaI and Ph₃P as catalyst under atmospheric pressure of CO₂ (Scheme 5).⁷ The polymer could react with primary amines selectively at room temperature to afford the corresponding polymer containing 2-hydroxyethylurethane moiety quantitatively.



5. Synthesis of Bis(cyclic carbonate)s and Their Polyaddition with Diamines

Bis(cyclic carbonate)s were prepared by the reaction of the corresponding bis(epoxide)s with CO₂. Polyaddition of bis(cyclic carbonate)s and diamines afforded the corresponding poly(hydroxyurethane)s with *M_n* 20,000–30,000 in excellent yields (Scheme 6). The presence of water, methanol, or ethyl acetate in the solvent had little effect on *M_n* of the resulting polymer, indicating the high chemoselectivity of the polyaddition reaction.⁸



Conclusion

In this paper, we described several examples for the CO₂ fixation by amidines and epoxides. The reversible fixation–release system of CO₂ by amidine and the polystyrene derivatives having amidine moiety were accomplished. The reaction of epoxide with CO₂ in the presence of alkali metal halides proceeded under atmospheric pressure to afford the corresponding five-membered cyclic carbonate in excellent yield. Further, this reaction was applied to polymer system, i.e., quantitative incorporation of CO₂ into poly(glycidyl methacrylate) and polyaddition of bis(cyclic carbonate)s and diamines to afford the poly(hydroxyurethane)s.

References

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