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. From these viewpoints, many chemists have studied on development of efficient methods for CO$_2$ recovery. Among them, chemical CO$_2$ fixation by primary or secondary amines has been most intensively studied and have become one of the most promising methods for CO$_2$ recovery. However, detailed study concerning CO$_2$ fixation by tertiary amines has been generally necessary. In the course of our works on chemical CO$_2$ fixation, we present the reversible CO$_2$ fixation by amidine derivatives and the reaction of epoxides with CO$_2$ under atmospheric pressure leading to the cyclic carbonate.

Experimental
Materials. N-Methyltetrahydropyrimidine (MTHP) was synthesized according to the reported procedure. Epoxides were distilled from CaH$_2$ and stored under nitrogen. N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) were dried and distilled from CaH$_2$.

Instruments. $^1$H-NMR and $^{13}$C-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 (Mn) and molecular weight distribution (Mw/Mn) of polymer samples with respect to polystyrene standards (Tosoh).

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 with nitrogen flow to regenerate MTHP quantitatively. The structure of MTHP-CO$_2$ was confirmed by $^1$H NMR, $^{13}$C NMR, and IR spectra.

Reaction of epoxide with CO$_2$. 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 CO$_2$, 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 CO$_2$ Fixation by Amidines
The CO$_2$ fixation by primary or secondary amines has been already reported, however, detailed study concerning CO$_2$ fixation by tertiary amines has not been carried out. Recently, we have found that N,N,N'-trialkylamidines, such as N-methyltetrahydropyrimidine (MTHP) can construct reversible CO$_2$ fixation, where CO$_2$ was fixed at 25 °C and was released at 65 °C quantitatively (Figure 1).
3. Reaction of Epoxide with CO$_2$

The reaction of epoxides with CO$_2$ have been already reported. However, high pressure of CO$_2$ is generally necessary. 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.

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. 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 $\beta$-haloalkoxide which reacts with CO$_2$ followed by cyclization (Scheme 4).

4. Polymer Reaction of Polymer Bearing Epoxide Moiety with CO$_2$

The incorporation of CO$_2$ into the polymers bearing epoxide moiety under atmospheric pressure is useful from the viewpoint of CO$_2$ fixation and the functionality of produced cyclic carbonate. Quantitative incorporation of CO$_2$ into poly(glycidyl methacrylate) was accomplished in the presence of NaI and Ph$_3$P as catalyst under atmospheric pressure of CO$_2$ (Scheme 5). 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 CO$_2$. 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.

Conclusion

In this paper, we described several examples for the CO$_2$ fixation by amidines and epoxides. The reversible fixation–release system of CO$_2$ by amide and the polystyrene derivatives having amide moiety were accomplished. The reaction of epoxide with CO$_2$ 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 CO$_2$ into poly(glycidyl methacrylate) and polyaddition of bis(cyclic carbonate)s and diamines to afford the poly(hydroxyurethane)s.

References