Development of efficient polymer-supported catalytic systems for the synthesis of cyclic carbonates

環状カーボネート合成のための効率的なポリマー担持触媒系の開発

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Abstract

Chapter 1 is the introduction of carbon dioxide (CO_2) and cyclic organic carbonate. Considering CO_2 is a renewable carbon feed stock, the catalytic conversion of CO_2 and epoxides to cyclic organic carbonates is a highly attractive 100% atom economic reaction. It represents a greener and safer alternative to the conventional synthesis of cyclic carbonates from diols and toxic phosgene. Today, cyclic carbonates show many applications as intermediates for fine chemical synthesis, as electrolytes in Li-ion batteries, and as polar aprotic solvents, and also serve for the synthesis of important polymers such as polycarbonates and polyurethanes. However, CO_2 is a thermodynamically stable molecule, and the use of catalysts is therefore mandatory for activating and facilitating the CO_2/epoxide coupling reaction in a selective manner and under mild conditions. The development of new catalysts and catalytic systems for this atom-economic, scalable, and industrially relevant reaction is a highly active research field. Recently organocatalysts have attracted more and more interest in this field and are viewed as alternatives to metal-based ones. Enormous progress has been made these past few years to boost their performances, and some organocatalysts are now very competitive, cheap, readily available and exhibit good chemical stability. Hence, metal-free, active and easy-to-handle catalytic systems for the cycloaddition reaction of CO_2 and epoxides at a low reaction temperature and pressure remain to be developed. We focused on developing polymer-supported organocatalytic systems using inexpensive and commercially available epoxides to get the cyclic carbonates under solvent-free, atmospheric pressure of CO_2 and moderate temperature conditions.

Herein, four different type of organocatalytic systems with good activity for the chemical fixation of CO_2 into cyclic carbonates were developed. Firstly, in chapter 2, two polymer having benzyl bromide or chloride unit catalysts poly(4-vinylbenzylchloride) (PVBC) and poly(4-vinylbenzylbromide) (PVBB) were prepared, and we have examined PVBC or PVBB/DMF and PVBC or PVBB/DBU systems catalytic activity for the synthesis of cyclic carbonates by reacting styrene oxide or 1,2-epoxyhexane with CO_2 under mild condition (1 atm CO_2, 70-120 ^{o}C).

Secondly, in chapter 3, a novel polymer-supported catalyst **P1** with 2-pyridinemethanol moiety for the cycloaddition of CO_2 and epoxides using tetra-*n*-butylammonium iodide (TBAI) as a co-catalyst was developed for the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions (1 atm CO_2, 40-60 ^{o}C). The effects of the reaction conditions such as reaction temperature, time, and the amount of catalyst used, were systematically investigated. The reactivity of catalytic system was investigated and showed moderate activity for most of epoxides.

Thirdly, in chapter 4, an efficient and practical organocatalytic system comprising 3-hydroxypyridine and TBAI was developed for the synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions (1 atm CO_2, 25-60 ^{o}C) without organic solvent. By comparing with related hydroxypyridine derivatives, the effects of the hydroxyl group, the acidity and the steric factor, were discussed. Study on the mixtures of CO_2 and N_2 in various ratios indicated that the yield depends on CO_2 content, due to the solubility of CO_2 in the reaction mixture. The system was also shown not to be deteriorated by the presence of H_2O, air or O_2.

Fourthly, in chapter 5, an efficient polymer-based catalytic system of poly(4-vinylphenol) (PVP) and TBAI was developed for the synthesis of cyclic carbonates from epoxides and CO_2. Owing to the synergistic effects of hydroxyl groups and iodide anions, this commercially available and metal-free system was highly active for the reaction of various terminal epoxides under environmentally benign conditions, at 25-60 ^{o}C and atmospheric pressure of CO_2, without the use of any organic solvents. The catalytic system can be easily separated by adding ether, and its ability was recovered by treating it with 40% CH_3CO_2H *aq*. The recyclability was investigated in detail for three substrates, epichlorohydrin, 1,2-epoxyhexane and styrene oxide, using ^{1}H nuclear magnetic resonance (NMR) analysis.

Keywords: carbon dioxide, terminal epoxide, cyclic carbonate, organocatalytic system, polymer, hydroxy bond, recyclability.

Abbreviations

AIBN	Azobisisobutyronitrile
Bn	Benzyl
Bu	Butyl
CCS	Carbon capture and storage
COCs	Cyclic organic carbonates
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	4-Dimethylaminopyridine
DMF	*N,N*-Dimethylformamide
DMSO	Dimethylsulfoxide
EC	Ethylene carbonate
EO	Ethylene oxide
HBD	Hydrogen bond donating
ILs	Ionic liquids
Me	Methyl
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMI	*N*-Methylimidazole
PC	Propylene carbonate
Ph	Phenyl
PO	Propylene oxide
PPNCl	Bis(triphenylphosphine)iminium chloride
PVBB	Poly(4-vinylbenzylbromide)
PVBC	Poly(4-vinylbenzylchloride)
PVP	Poly(4-vinylphenol)
SC	Styrene carbonate
SO	Styrene oxide
TBAB	Tetrabutylammonium bromide
TBAC	Tetrabutylammonium chloride
TBAI	Tetrabutylammonium iodide
TEA	Triethylamine
THF	Tetrahydrofuran

Publication List

This thesis based on the paper below and is also related to the oral presentation. The published articles are reproduced here with the permission of the publishers.

1. Efficient and practical organocatalytic system for the synthesis of cyclic carbonates from carbon dioxide and epoxides: 3-hydroxypyridine/tetra-n-butylammonium iodide
Xiangyong Wang, Lin Wang, Yingying Zhao, Koichi Kodama, Takuji Hirose
Tetrahedron, **2017**, 73, 1190-1195.

2. Poly(4-vinylphenol)/tetra-n-butylammonium iodide: efficient organocatalytic system for synthesis of cyclic carbonates from CO_2 and epoxides
Xiangyong Wang, Yingying Zhao, Koichi Kodama, Takuji Hirose
J. Appl. Polym. Sci., **2017**, *134*, 45189.

3. Organocatalytic system for disubstituted carbonates from cycloaddition between CO_2 and internal epoxides
Takuji Hirose, Shujie Qu, Koichi Kodama, Xiangyong Wang
J of CO_2 utilization, accepted.

Oral Presentations

1. Highly efficient synthesis of carbonates from epoxides and CO_2 using poly(4-vinylphenol)/tetra-n-butylammonium iodide as catalyst
Xiangyong Wang, Koichi Kodama, Takuji Hirose
97th CSJ Annual Meeting, 2PC-206, **2017**.03.

2. Synthesis of carbonates from epoxides and CO_2 using polymer anchored hydroxyl as catalyst
王 相勇, 王 林, 張 廣友, 小玉 康一, 廣瀬 卓司
5th CSJ Chemistry Festa, P5-019, **2015**.10.

3. Development of a polymer-based catalytic system for the synthesis of cyclic carbonates from carbon dioxide and epoxides
王 相勇, 趙 盈盈, 小玉 康一, 廣瀬 卓司
高分子学会関東支部 第29回 埼玉地区懇話会, P-4, **2018**.01.24.

Contents

Chapter 1 Introduction

1.1. Emission of CO_2

Climate scientists have observed that carbon dioxide (CO_2) concentration~~s~~ in the atmosphere has been increasing significantly over the past century and it is the primary greenhouse gas emitted through human activities. Human activities such as the burning of coal, petroleum and natural gas, as well as deforestation are the primary causes of the increased CO_2 concentration~~s~~ in the atmosphere.[1] Since the Industrial Revolution (1970's), human activities of CO_2 emissions have been growing.

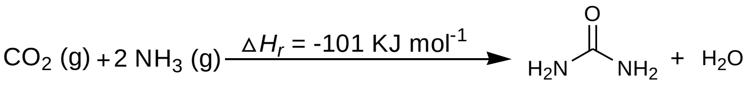
Global carbon emissions from fossil fuels have significantly increased since 1900. Since 1970, CO_2 emissions have increased by about 90%, with emissions from fossil fuel combustion and industrial processes contributing about 78% of the total greenhouse gas emissions increase from 1970 to 2011. Agriculture, deforestation, and other land-use changes have been the second-largest contributors.[2]

Several strategies are under assessment for the reduction of fossil-C consumption and CO_2 emission, such as (i) higher efficiency in electric energy production can contribute to reducing CO_2 emissions (but this cannot solve the problem easily as it has a high cost and long implementation time), (ii) new plants should be built using low-emission technologies (but this is also difficult for economic reasons), (iii) a better efficiency in energy utilization would help to save fossil fuels and reduce the emissions of CO_2, (iv) fuel shift (from coal to gas) is another technology that reduces the emissions of CO_2, (v) carbon capture and storage (CCS) has been considered for its large potential in CO_2 storage in natural fields.[3] Today, many CO_2 utilization methods are being considered by many countries with much attention.

1.2. CO_2 as chemical feedstock

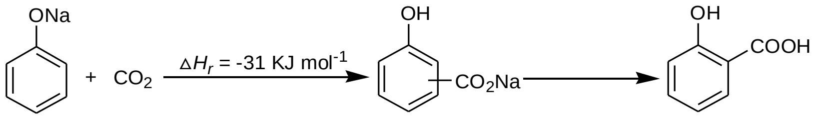
Over 90% of commercially available organic chemicals are sourced from crude oil. This is an unsustainable feedstock, which will be exhausted at some day in the future. The basis of worldwide primary energy production: 85% of the global energy production comprises oil, coal and natural gas, whilst the remaining 15% includes nuclear power and alternative renewable sources, such as solar heat, wind and biomass.[4] Thus, the present reserves will not sustain future demand, and it is therefore desirable to develop novel technologies based on renewable energy sources, to help to prevent any further increase in the atmospheric level of CO_2.

As a renewable, nontoxic, economical, and abundant C1 feedstock, CO_2 has attracted great attention from organic chemists for conversion to valuable chemicals.[5] Therefore, the chemical fixation of CO_2 into valuable organic chemicals has attracted much attention as a goal of environmental protection and sustainable development. Concerns about anthropogenic emissions have recently sparked interest in the chemical transformation of CO_2, although the excessive cost and a lack of effective and feasible processes often limit commercial applicability. At present, industrial transformations utilize around 300 Mt of CO_2 per year as a synthetic building block, which is less than 1% of global emissions.[6] For example, the chemical synthesis of urea is the largest-scale chemical process operated by humankind (Scheme 1-1). Around 157 Mt of urea is prepared from CO_2 and ammonia each year,[7] directly utilizing 115 Mt of CO_2. The synthesis of urea in this way is a highly exothermic process. However, the ammonia needed for urea synthesis is prepared from nitrogen and hydrogen and the hydrogen is obtained by steam reforming of methane in a highly endothermic process, which requires large amounts of energy and generates large amounts of waste CO_2.[8]

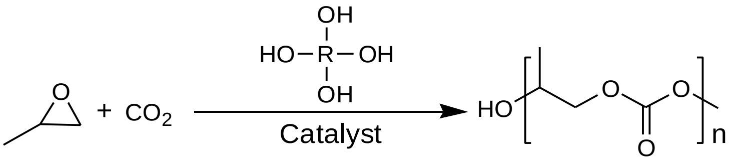


Scheme 1-1. The synthesis of urea.

The synthesis of salicylic acid from carbon dioxide and sodium phenolate is an even older industrial process (Scheme 1-2) dating back to the 19th century.[9] This is still an important process, as it is the first step in the industrial synthesis of aspirin, but only about 90 kt of salicylic acid are prepared by this way each year, directly consuming just 29 kt of CO_2.[8]



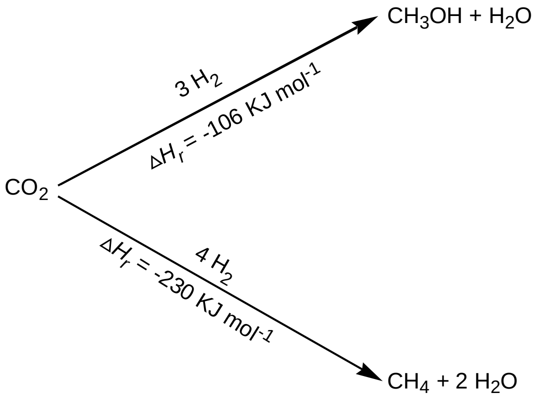
Scheme 1-2. The synthesis of salicylic acid.



Scheme 1-3. The synthesis of polyether-polycarbonate-polyol.

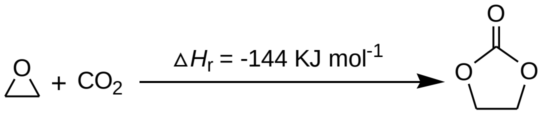
Polyurethanes are produced by the reaction between bis-isocyanate and polyol. In Bayer's (now Covestro's) implementation of this process, the polyol is a polyether-polycarbonate prepared by the polymerization of propylene oxide and CO_2 using an initiator with multiple OH groups (Scheme 1-3).[10] The global market for polyurethanes is around 18 mt per year and 10% CO_2 in the polyol corresponds to around 4% CO_2 in the polyurethane, giving the technology the potential to directly utilize 0.7 Mt of CO_2 each year. Importantly, each CO_2 incorporated into the polymer replaces a propylene oxide molecule which no longer needs to be manufactured from crude oil.[8]

The reduction of CO_2 to methanol or methane (Scheme 1-4) for use as fuels has almost unlimited potential scale due to their ability to provide replacements for existing liquid and gaseous fossil fuels. Both are apparently exothermic processes, but large amounts of hydrogen are required and these reactions are very unfavorable from a thermodynamic point of view, and the energy barriers can only be overcome with catalysts.[8]



Scheme 1-4. The synthesis of methanol and methane.

The synthesis of cyclic carbonate from CO_2 and ethylene oxide (EO) has been a commercial process since the 1950s (Scheme 1-5), although the scale of production has been around just 80 kt per annum,[7,9] directly utilizing 40 kt of CO_2 each year. However, the market for cyclic carbonates is experiencing rapid growth, owing to their use as electrolytes in lithium ion batteries for powering the portable electronic devices that are so essential to modern life.[8]



Scheme 1-5. The synthesis of cyclic carbonate.

Other applications of CO_2 are as refrigerants,[11] fire-extinguishers,[12] supercritical solvents[13,14] and extraction media, though their contribution to reducing CO_2 emissions is still negligible. However, developing new chemical reutilization technologies of CO_2 could accomplish decrease in carbon emissions and would also lead to economic benefits and sustainable development of humankind in future.

1.3. Synthesis of cyclic carbonate from CO_2

The synthesis of cyclic carbonates from CO_2 and epoxides is a 100% atom economic reaction and very attractive as it represents a greener and safer approach. This approach has the characteristics of eliminating phosgene as a reagent and making it a highly desirable transformation. Cyclic carbonates are valuable industrial products since their commercialization in the mid-1950s, and they have found applications as polar aprotic solvents, electrolytes for lithium secondary batteries, and synthetic intermediates for pharmaceuticals and polymers.[15-19]

This reaction does not occur spontaneously even though it is highly exothermic as non-catalytic reaction is calculated to have a rather high activation energy.[20] Thus far, numerous metal-based and metal-free catalytic systems have been developed for the synthesis of five-membered cyclic carbonates.[21-27] From the perspectives of "green chemistry" and "sustainable society", high pressure/temperature, organic solvent, and metal waste should be reduced by applying benign reaction conditions.[28]

1.4. Cyclic carbonate synthesis catalyzed by metal-based catalytic systems

Some metal complexes were the first catalysts enabling the conversion of CO_2 into cyclic carbonates under atmospheric pressure and ambient temperature.[29] And some representative metal-based catalysts were summarized in Figure 1-1. In 1978, Inoue *et al*. reported the synthesis of propylene carbonate (PC) from propylene oxide (PO) catalyzed by aluminium porphyrin complex **1** in the presence of *N*-methylimidazole (NMI) as a co-catalyst.[30] Spectroscopic methods were also used to study the reaction mechanism using aluminium phorphyrin **2** as a postulated active species.[31] Later, Kasuga *et al*. developed aluminium phthalocyanine complexes **3** and **4** for the transformation of PO to PC, in conjugation with quaternary ammonium salt **5** or NMI.[32] Disappointingly, these systems do not exhibit high catalytic activity and the conversion to the desired product is typically only 2%. Kleij *et al*. have investigated the catalytic potential of hexachlorinated aluminium(III)-aminotris (phenolate) complex **6a** for the preparation of organic carbonates using 1,2-epoxyhexane as substrate and tetrabutylammonium iodide (TBAI) as co-catalyst.[23,33] To further improve the catalyst activity, a number of Al(III)-aminotris (phenolate) analogues **6b-d** as well as a nonsymmetrical aluminium complex **7** were synthesized and their activities were tested under the same conditions. Amongst these catalysts, **6a** was found to be the most active. Williams *et al.* have used a bimetallic iron(III) complex **8** in the presence of bis(triphenylphosphine)iminium chloride (PPNCl) as a co-catalyst to form cyclic carbonates from epoxides and CO_2.[34] As this group showed that the catalytic system was capable of inducing 90% conversion of cyclohexene oxide to cyclohexene carbonate under mild conditions and focused primarily on the production of polycarbonates, the cyclic carbonate chemistry or substrate range was not fully explored. Srinivas *et al.* reported copper phthalocyanine complex **9** provided the highest TOF (502 h^{-1}) for the addition of CO_2 to epichlorohydrin using a series of copper and manganese macrocycles and Schiff base complexes.[35] The reactions were carried out at 120 ^{o}C for four hours under 6.9 atmospheres CO_2 pressure using 0.04 mol% of catalyst and DMAP as co-catalyst with dichloromethane as solvent. Tang *et al.* introduced 2-hydroxyisophthaldehydeoxime ligand **10** to form a dimeric cobalt(III) complex [Co(III)$L_2(C_2H_5OH)_2Cl_2$] **11** which catalyzed the synthesis of cyclic carbonates.[36]

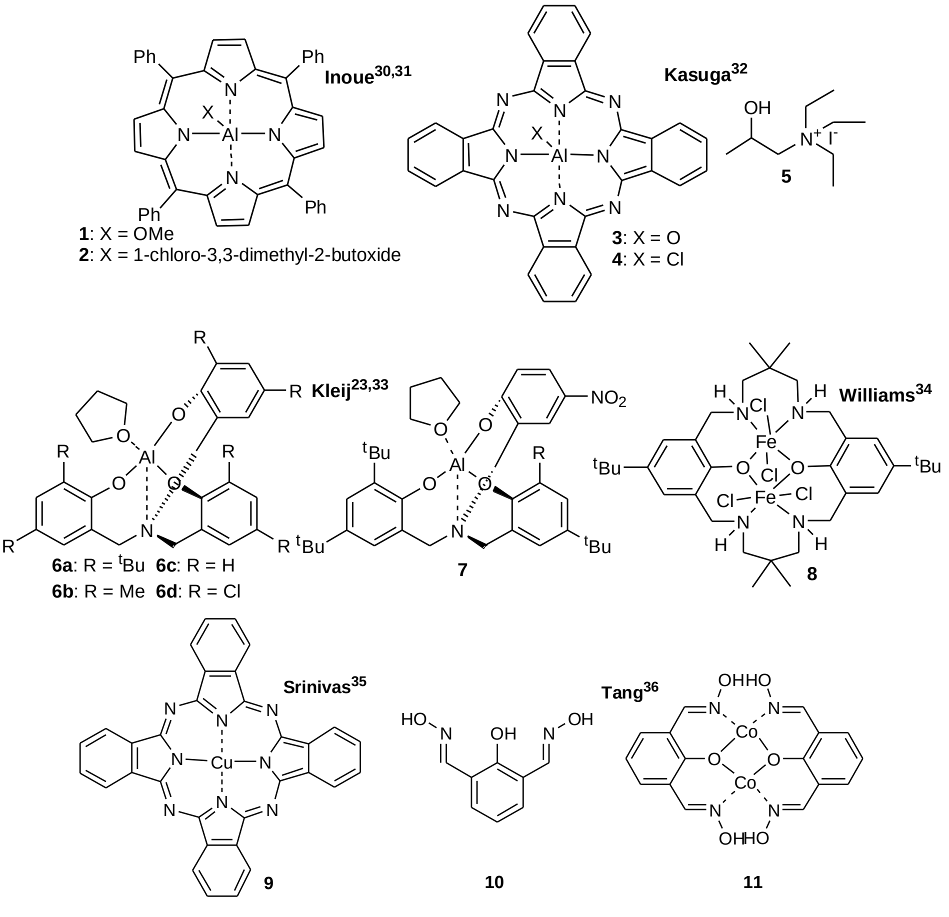


Figure 1-1. Representative metal-based catalysts for synthesis of cyclic carbonates.

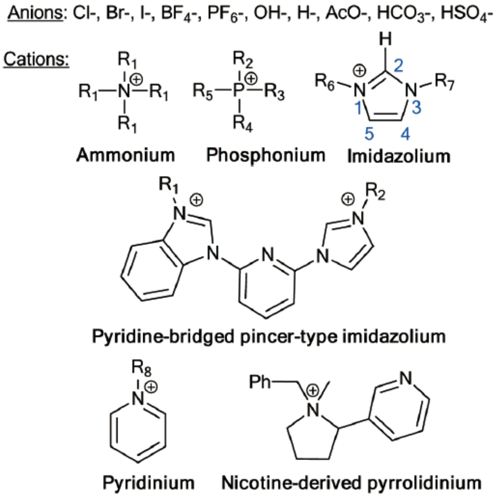
However, many metal catalysts are poorly selective, sensitive to hydrolysis and/or oxidation and/or are toxic. Based on the “green chemistry” and “sustainable society”, high pressure/temperature, organic solvent, and metal waste should be reduced by applying benign reaction conditions.[28] Currently, metal-free organocatalysts deserve more and more interest in this field and are tested as alternatives to metal-based ones.

1.5. Cyclic carbonate synthesis catalyzed by homogeneous metal-free organocatalysts

Homogeneous catalysts have far more efficient than heterogeneous analogues, which allow the conversion of CO_2 into cyclic carbonates with lower catalyst loadings at lower temperatures and reduced reaction times. On the other hand, the lower activity of heterogeneous catalysts originates from diffusion limitations of the reactant to the catalytic sites.[37] Due to the perspectives of “green chemistry” and “sustainable society”, the global trend is now to develop catalysts that are very active and selective under conditions as mild as possible.

Abundant, inexpensive and nontoxic alkali metal salts of sodium, lithium or potassium[38-40] were found to catalyze the coupling of CO_2 with epoxides. For example, Union Carbide (now Dow), Shell and a Japanese research group patented the use of KI as catalyst for the synthesis of ethylene carbonate (EC) from CO_2 and ethylene oxide (EO) under harsh experimental conditions, *i.e.* T = 190 °C and P = 1.3 MPa.[40]

Organic salts and ionic liquids (ILs) salts with melting point lower than 100 °C, in which ions are poorly coordinated,[41] are the most widely studied catalysts for the coupling of CO_2 with epoxides.[42,43] Organic salts and ILs can be classified according to their cation structure, *i.e.* ammonium, phosphonium, imidazolium or pyridinium and so on (Scheme 1-6).[44]



Scheme 1-6. Structures of the organic salts and ionic liquid catalysts.[44]

Most metal-free catalysts were initially efficient only under high pressure and temperature causing their thermal degradation. To overcome these limitations, functionalized organocatalysts and binary or ternary catalysts were successfully developed in the past few years and some of them were reported to be as competitive as metal-based catalysts. Additionally, many organocatalytic systems are composed of cheap, readily available and sometimes non-toxic compounds exhibiting good chemical stability towards moisture and air.[44] Some representative metal-free catalysts are summarized in Figure 1-2.

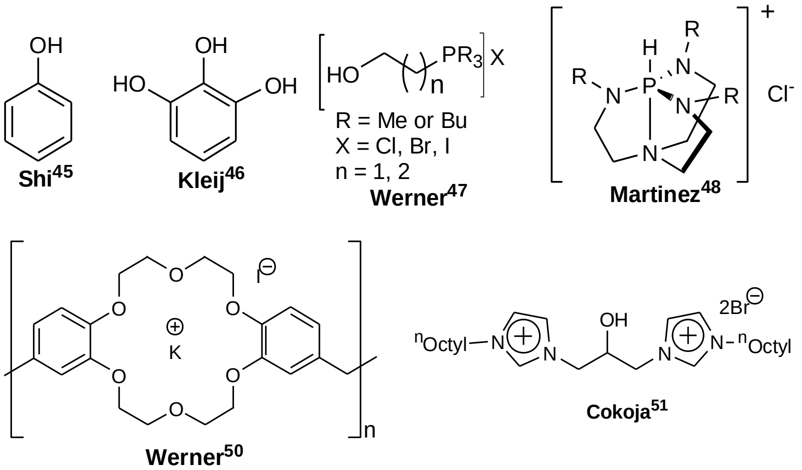


Figure 1-2. Representative metal-free catalysts for synthesis of cyclic carbonates.

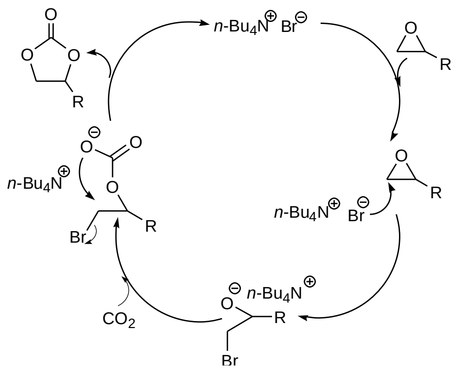
Shi and co-workers in 2003 have shown that phenolic compounds in combination with organic bases provide a two-component catalytic system that can be used to catalyze cyclic organic carbonate formation from epoxides and CO_2, albeit under elevated reaction conditions (T = 100-120 °C, P_{CO2} = 35 bar, 48 h) as a result of the low efficiency of this catalytic system.[45] Then, Kleij team reported a binary catalytic system comprising of commercially available (substituted) phenolic compounds combined with n-Bu_4NI as a co-catalyst required for the epoxide ring-opening step under very mild reaction conditions (T = 25-45 °C, P_{CO2} = 10 bar, 2-5 mol% catalyst and no need for a solvent).[46] Bifunctional phosphonium salts were also synthesized and employed as organocatalysts for the atom efficient synthesis of cyclic carbonates from CO_2 and epoxides by Werner *et al.* under harsh reaction conditions (T = 90-120 °C, P_{CO2} = 10-40 bar, 3-6 h).[47] Despite their potential effectiveness, disadvantage such as the requirement of high pressure is required. More recently, much milder reaction conditions were realized by developing efficient organocatalysts. For example, in 2013, Martinez *et al.* employed azaphosphatranes as organocatalysts for the synthesis of cyclic carbonates under 1 atm CO_2 and 100 °C.[48] Mattson *et al.* reported a silanediol-catalyzed system under ambient conditions (P_{CO2} = 1 atm, room temperature) in 2014.[49] However, one disadvantage of these catalytic systems is that they can't be recycled.

Homogeneous organocatalysts are often difficult to isolate from the reaction mixture due to the good catalyst solubility, which have complicated recycling process. Thus, a very promising approach is to immobilize these homogeneous organocatalysts. For example, Werner *el at*. reported polydibenzo-18-crown-6 could be utilized as a co-catalyst and polymeric support in combination with potassium iodide (KI) for the synthesis of cyclic carbonates from CO_2 and epoxides under mild and solvent-free conditions. This catalytic system could be successfully recovered and reused more than 20 times with excellent yields.[50] Cokoja *et al*. also reported hydroxy-functionalized imidazolium bromides as catalyst for the coupling of CO_2 with epoxides under relatively mild conditions (T = 70 ^{o}C, P_{CO2} = 4 atm), which can be easily recycled ten times without loss of activity.[51]

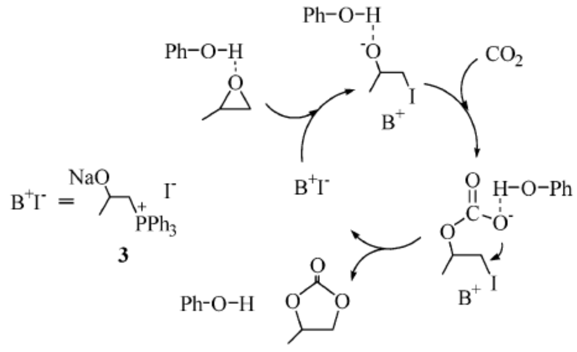
1.6. Mechanism of cyclic carbonates synthesis from epoxides and CO_2

Although the cycloaddition reaction has been widely studied and can be mediated by a variety of catalysts, there are still some disadvantages to overcome, such as low catalyst reactivity/stability, use of high pressures and/or temperatures, high catalyst loadings required for efficient turnover, availability of the catalytic system. Hence, it is crucial to know how the performance of any given catalyst can be improved, and mechanistic understanding provides a means to unravel the obstacles associated with the observation of low reactivity and/or selectivity.[52]

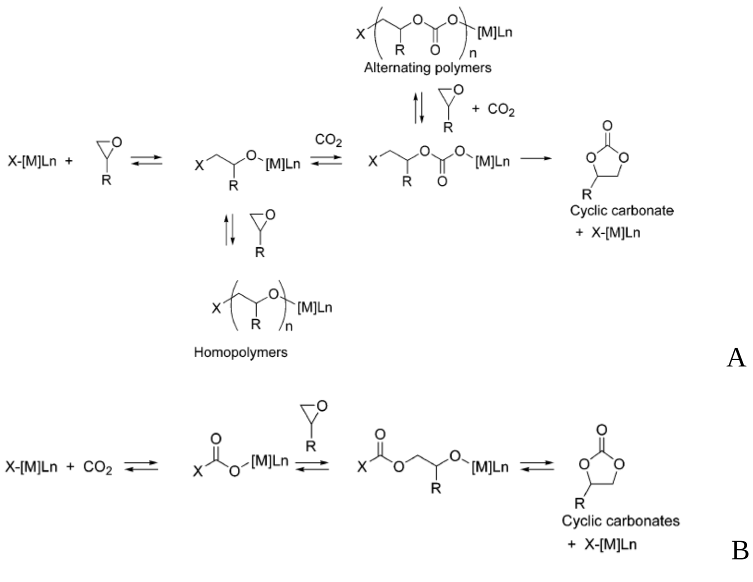
To date, a limited series of theoretical studies on the mechanism of the catalytic cycloaddition of CO_2 to epoxides have been reported.[53-61] Such as Caló *et al*. reported a mechanism for fixation of CO_2 with epoxides catalyzed by quaternary onium salts.[53] The ring of the epoxide first opened by a nucleophilic attack by the bromide ion, which led to an oxy anion species, and then afforded the corresponding cyclic carbonate after reaction with CO_2 (Scheme 1-7). And in 2003, Shim *et al*. reported a mechanism in the presence of catalytic amounts of sodium iodide (NaI), triphenylphosphine (PPh_3) and phenol (PhOH) for fixation of CO_2 with epoxides.[54] The initially formed phosphonium salt **3** (B^+I^-) in the catalytic system of NaI/PPh_3/PhOH catalyzes the reaction of epoxide with CO_2 by ring opening reaction of epoxide with iodide ion in **3**, which further reacts with CO_2 to produce cyclic carbonate and regenerate the catalyst (B^+I^-). The strong intramolecular hydrogen-bond patterns lead to large stabilization effects in catalytic processes (Scheme 1-8).



Scheme 1-7. Possible mechanism for fixation of CO_2 with epoxide catalyzed by tetra-*n*-butylammonium bromide (*n*-Bu_4NBr).



Scheme 1-8. Possible mechanism for fixation of CO_2 with propylene oxide catalyzed by NaI/PPh_3/PhOH.[54]



Scheme 1-9. Possible mechanism for fixation of CO_2 with epoxide catalyzed by metal halide (MX).[55]

Next, Sakakura *et al*. reported a cycloaddition of monosubstituted oxirane catalyzed by a metal halide (MX).[55] First, anion X attacks the less hindered side of oxirane to open the ring. Then, the resulting alkoxide part attacks CO_2 to give the carbonate anion. Then, the carbonate anion undergoes a S_N2 reaction, which simultaneously forms a five-membered ring and releases anion X (Scheme 1-9A). Another possible mechanism is for anion X to initially attack CO_2, followed by a nucleophilic attack of the resulting anion to form oxirane (Scheme 1-9B).

The above mechanisms showed binary catalytic system usually combines a Lewis acid and a suitable nucleophile (most often a halide), which make the ring-opening procedure less energetically demanding and the subsequent CO_2 insertion easier.

1.7. Our previous catalytic systems

We reported three different organocatalytic systems under atmospheric pressure of CO_2 in our previous works. First one is benzyl bromide/*N*,*N*-dimethylformamide (DMF) system that is an efficient, metal-free catalytic system for the conversion of CO_2 and epoxides to cyclic carbonates under mild conditions (T = 120 ^{o}C, 1 atm CO_2) with good-to-excellent yields (57-99%).[24] Second one is benzyl bromide/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) system that is a simple, inexpensive and efficient binary organocatalytic system for the synthesis of cyclic carbonates with excellent yields (81-95%) from epoxides and CO_2 under metal- and solvent-free conditions (T = 45-95 ^{o}C, 1 atm CO_2).[25] Last one is 2-pyridinemethanol or 2,6-pyridinedimethanol/*n*-Bu_4NI system that is an efficient, metal- and solvent-free catalytic system for the conversion of CO_2 and epoxides to the corresponding cyclic carbonates under mild conditions (T = 25-45 ^{o}C, 1 atm CO_2) in high-to-excellent yields (85-97%).[62] These three catalytic systems are organic catalytic system for the synthesis of cyclic carbonates at atmospheric pressure of CO_2. The last system allows chemical fixation of CO_2 into value-added chemicals under low reaction temperature (25-45 ^{o}C) that is near room temperature.

1.8. Aim of the thesis

Along with the rapid development of highly selective and reactive catalysts, various types of efficient CO_2 transformations in organic synthesis have been discovered in the past decades, greatly improving its efficiency and applicability. However, the chemical reactions involving CO_2 are commonly carried out at high pressure/temperature and using pure CO_2, which may not be the perspectives of “green chemistry” and “sustainable society”. The challenge is to develop efficient catalysts that are capable of activating CO_2 into organic chemicals under room temperature and atmospheric pressure. Hence, metal-free, active and easy-to-handle catalytic systems for the cycloaddition reaction of CO_2 and epoxides at a low reaction temperature and pressure remain to be developed. We focused on developing polymer-supported catalytic systems using inexpensive and commercially available epoxides to get the cyclic carbonates under solvent-free, atmospheric pressure of CO_2 and moderate temperature conditions.

1.9. References

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Chapter 2 Development of a polymer catalyst having benzyl bromide or chloride unit for the synthesis of cyclic carbonates from carbon dioxide and epoxides

2.1. Introduction

In general, organocatalysts are usually robust, inexpensive, readily available, and non-toxic.[1] From an environmental point of view, avoiding the usage of potentially toxic or costly metals in the synthesis of cyclic carbonates, employing organocatalysts have been expected to be a good alternative.[2] Several types of metal-free catalysts have so far been presented, such as halides containing weakly interacting cations (e.g., ammonium, imidazolium),[3] and nitrogen donor bases.[4] Although a catalyst is not consumed during the process, its separation from the final products may sometimes be difficult. Therefore, the recovery and reuse of the catalyst molecules can be a scientific challenge due to economic and environmental relevance. Polymer-supported catalysts can be easily separated from reaction mixtures and can be reused, or they can be used in flow systems such as fixed-bed and fluidized-bed reactors.

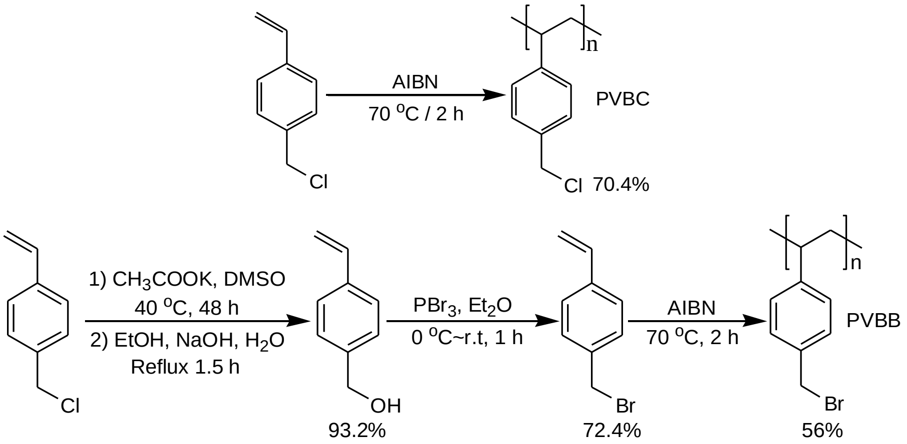
In our previous works, we reported the use of benzyl bromide (1 mol%) in combination with *N*,*N*-dimethylformamide (DMF) (500 mol%) as a very simple catalytic system at low CO_2 pressure (1 atm).[5] Subsequently, we reported the use of benzyl bromide (5 mol%) in combination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5 mol%) to catalyze the addition of CO_2 (1 atm) to various epoxides under similar conditions.[6] The benzyl bromide as effective organocatalyst for the synthesis of cyclic carbonates from the coupling of CO_2 with epoxides has exhibited excellent catalytic activity and selectivity in these two different catalytic systems.

Considering the results mentioned above, it seemed effective and important to apply the organocatalytic systems for an efficient polymer system: benzyl bromide or chloride unit in a polymer could be an active and the polymer could be recyclable for the coupling of CO_2 and epoxides. Herein, we have easily developed two new polymer catalysts: poly(4-vinylbenzylbromide) (PVBB) and poly(4-vinylbenzylchloride) (PVBC).

2.2. Results and discussion

2.2.1. The synthesis of polymer

The PVBC was easily prepared by radical polymerization of commercial 4-vinylbenzlychloride in the presence of 1 mol% azobis(isobutyronitrile) (AIBN) under nitrogen atmosphere (Scheme 2-1).[7] The PVBC was characterized by number-average molecular weight (M_n) and polymerization dispersity (M_w/M_n) of 3.4×10^4 and 2.4, respectively. The PVBB was synthesized by three steps reaction (Scheme 2-1).[7,8] Firstly, 4-vinylbenzyl alcohol was obtained by hydrolysis of the 4-vinylbenzylchloride. Then the 4-vinylbenzyl alcohol was brominated with phosphorus tribromide to afford monomer 4-vinylbenzylbromide. Finally, the PVBB was synthesized by radical polymerization of the 4-vinlybenzlybromide in the presence of the 1 mol% AIBN under nitrogen atmosphere. The PVBB was also characterized by number-average molecular weight (M_n) and polymerization dispersity (M_w/M_n) of 4.0×10^4 and 5.4, respectively.



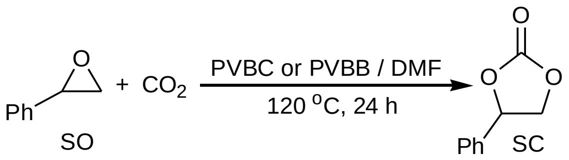
Scheme 2-1. The synthesis of PVBC and PVBB.

2.2.2. The application of PVBB and PVBC

Based on our previous reported results and reaction conditions,[5] the activity of the two polymers with DMF was tested at 120 °C and CO_2 pressure of 1 atm using the reaction of styrene oxide (SO) and CO_2 to produce styrene carbonate (SC), and the results were summarized in Table 2-1. The activity of the two polymers with DMF depends strongly on the structure of benzyl halide as nucleophilic catalyst on the PS support and DMF as activator. The two polymers with DMF as catalysts showed moderate catalytic activities (Table 2-1, entries 1 and 2) that were not good compared with the 4-vinylbenzylchloride or

4-vinylbenzylbromide with DMF as catalyst.[5] When we increased the amount of PVBB, the yield reached to 78.3% (Table 2-1, entry 3). The catalyst PVBB was then recovered by adding excess ethyl acetate to the reaction mixture to precipitate the PVBB and a simple filtration technique. The filtered PVBB was washed vigorously with ethyl acetate to remove all traces of the product or reactant if present. Then the PVBB was dried and reused in entry 4 and entry 5, gradually. The yield of SC decreased gradually. This means that decrease of catalytic activity from 3rd cycle in recyclability tests of PVBB might be due to the leaching of bromine from supported material.[9]

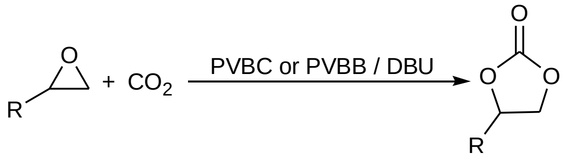
Table 2-1. Cycloaddition of CO_2 to styrene oxide catalyzed by PVBC or PVBB/DMF.



Entry	Polymer (mmol)	DMF (mmol)	Conditions	Yield[c] (%)
1	0.05 (PVBC)	25.0	120 °C, 24 h	57.2
2	0.05 (PVBB)	25.0	120 °C, 24 h	64.6
3	0.1 (PVBB)	25.0	120 °C, 24 h	78.3
4[a]	0.1 (PVBB)	25.0	120 °C, 24 h	60.0
5[b]	0.1 (PVBB)	25.0	120 °C, 24 h	56.1

Reaction conditions: SO (5.0 mmol, 0.62 g), CO_2 (1 atm). [a]The PVBB used in entry 4 was recycled from entry 3. [b]The PVBB used in entry 5 was recycled from entry 4. [c]Isolated product obtained after chromatographic purification.

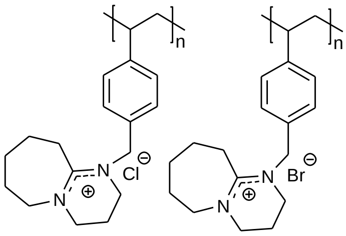
Table 2-2. Cycloaddition of CO_2 to epoxides catalyzed by PVBC or PVBB/DBU.



Entry	Substrate	Polymer (mmol)	DBU (mmol)	Conditions	Yield[a] (%)
1	SO	0.05 (PVBC)	0.25	70 °C, 24 h	10.2
2		0.05 (PVBC)	0.25	90 °C, 24 h	47.6
3		0.05 (PVBB)	0.25	90 °C, 24 h	48.8
4	1,2-epoxyhexane	0.25 (PVBC)	0.25	80 °C, 24 h	54.2
5		0.25 (PVBB)	0.25	80 °C, 24 h	54.2
6		0.25 (PVBB)	0.25	100 °C, 24 h	59.7

Reaction conditions: Substrate (5.0 mmol), CO_2 (1 atm). [a]Isolated product obtained after chromatographic purification.

We reported an efficient DBU and benzyl bromide catalytic system for the synthesis of cyclic carbonates from epoxides and CO_2 in our previous works.[6] Based on the previous research, we firstly did the reaction of CO_2 with SO that was conducted using PVBC with DBU as catalysts under the same reaction conditions as before. This reaction was very sluggish and did not give efficient yield of carbonate even under increased reaction temperature from 70 °C to 90 °C (Table 2-2, entries 1 and 2). When changed PVBC to PVBB as catalyst, the yield of carbonate showed almost no change (Table 2-2, entry 3). For SO, due to the presence of the aromatic ring, which makes the ring opening step more favorable on C_α (most substituted carbon), unlike the apparent preference for C_β (least substituted carbon) observed for aliphatic epoxides, resulting in a less nucleophilic alkoxide intermediate, which causes CO_2 activation (insertion) to be kinetically more difficult than for aliphatic epoxides.[10] Next, we used 1,2-epoxyhexane as substrate that has higher activity than SO. When 1,2-epoxyhexane was reacted with CO_2 and increased ~~the~~ catalytic amount of PVBC or PVBB, the yield of 4-butyl-1,3-dioxolan-2-one didn't show significant change (Table 2-2, entries 4 and 5). Even increased the reaction temperature to 100 °C, PVBB also showed significantly lower activity (Table 2-2, entry 6).



Scheme 2-2. PVBC and PVBB reacted with DBU.

PVBC and PVBB can dissolve in SO and 1,2-epoxyhexane. But when DBU was added to the mixture liquid of substrate with polymer, there was solid precipitation that was salt of DBU reacted with polymer (Scheme 2-2). Therefore, these are heterogeneous catalytic systems which lead to lower catalytic activity under the present reaction conditions.

2.3. Conclusion

Two polymer catalysts having benzyl bromide or chloride unit, PVBC and PVBB, were prepared, and we have examined PVBC or PVBB/DMF and PVBC or PVBB/DBU systems' catalytic activities for the synthesis of cyclic carbonates by reacting SO or 1,2-epoxyhexane with CO_2 under mild conditions. The PVBB showed poor recyclability tests which might be due to the leaching of bromine from the supported material in PVBB/DMF system. PVBC or

PVBB with DBU is a heterogeneous catalytic system which reduces the catalytic activity. These disadvantageous aspects are technically striking us to develop a new polymer supported catalyst for the fixation of CO_2 into epoxides to obtain cyclic carbonates in high yield and good recyclability in the future works.

2.4. Experimental

All commercially available starting materials and solvents were purchased and used as received unless indicated otherwise. 4-Vinylbenzylchloride was purchased from Aldrich. Carbon dioxide (99.99% pure) was used as received without further purification and dried prior to use (Tokyo Koatsu Yamazaki Co. Ltd.).

The number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the self-synthesis polymer were measured by gel permeation chromatography (GPC) in THF at 40 °C with a Shodex GPC KF-806 L column (flow rate: 1.0 mL/min). The M_n was calibrated with polystyrene standards (TSK: 945-7.1 × 10^5, $M_w/M_n \leq 1.1$).

^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. The chemical shifts of the products were reported in ppm with reference to Me_4Si as an internal standard in CD_3OD, $CDCl_3$, and DMSO-d_6.

2.4.1. General procedure for synthesis of polymer

1. Synthesis of PVBC

Poly(4-vinylbenzylchloride) (PVBC) was prepared by radical polymerization of 4-vinylbenzylchloride (7.6 g, 50 mmol) in the presence of 1% mol of AIBN (0.082 g, 0.5 mmol). A two-necked 50 mL round bottom flask was charged with the solution that was stirred at 70 ^oC for two hours under nitrogen atmosphere. The crude product was then purified twice by reprecipitation in methanol from a chloroform solution and then recovered after drying under reduced pressure. The polymer was obtained in 70.4% yield and the molecular weight of the polymer was evaluated by gel permeation chromatography (GPC).[7]

^1H NMR (500 MHz, $CDCl_3$) δ 1.37 (m, 2H), 1.67-1.69 (m, 2H), 4.50-4.53 (s, 2H), 6.27-6.67 (m, 2H), 6.91-7.05 (m, 2H). IR (neat): ν (cm^{-1}) 1509, 1447, 1422, 1266, 840, 826, 674 (C-Cl).

2. The procedure for synthesis of PVBB

① Synthesis of 4-vinylbenzyl alcohol

A two-necked 100 mL round bottom flask was equipped with a mixture of 4-vinylbenzyl chloride (10.7 g, 0.07 mol) and potassium acetate (8 g, 0.08 mol) in DMSO (30 mL) and stirred at 40 ^oC for 48 h. The reaction mixture was poured into water (100 mL) and extracted three times with ethyl acetate (30 mL × 3). The collected ethyl acetate layer was dried with Na_2SO_4. The ethyl acetate was evaporated to afford 4-vinylbenzyl acetate, which was used without further purification. Sodium hydroxide (5 g, 0.13 mol) was added to the crude 4-vinylbenzyl acetate in EtOH (30 mL)/water (5 mL) and refluxed for 1.5 h. The reaction mixture was poured into water and extracted with ethyl acetate, dried with $MgSO_4$. The ethyl acetate layer was evaporated and distilled under vacuum to obtain 4-vinylbenzyl alcohol (8.75 g, 93.2% yield).[8]

^1H NMR (300 MHz, DMSO-d6) δ 4.56 (s, 2H), 5.24 (d, 1H), 5.76 (d, 1H), 6.67-6.73 (dd, 1H), 7.35 (d, 2H), 7.42 (d, 2H); ^{13}C NMR (75 MHz, DMSO-d6) δ 62.7, 113.4, 125.8, 126.6, 135.6, 136.5, 142.3.

② Synthesis of 4-vinylbenzyl bromide

A three-necked 500 mL round bottom flask equipped with 4-vinylbenzyl alcohol (7.3 g, 0.054 mol) in Et_2O (200 mL) at 0 ^oC under N_2. After 1 h, PBr_3 (17.56 g, 0.064 mol) in Et_2O (10 mL) was added and the reaction mixture was stirred for 1 h at room temperature. After the reaction mixture was cooled to 0 ^oC and water (100 mL) was added slowly to control the temperature. The solution was extracted with Et_2O, and the Et_2O layer was washed with aqueous $NaHCO_3$, brine and dried with $MgSO_4$. The crude product was purified by vacuum distillation to obtain 4-vinlybenzylbromide (7.7 g, 72.4% yield).[8]

^1H NMR (500 MHz, $CDCl_3$) δ 4.48 (s, 2H), 5.28 (dd, 1H), 5.75 (dd, 1H), 6.69 (dd, 1H,), 7.36 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.7, 114.6, 127.5, 129.0, 135.1, 137.2, 137.7.

③ Synthesis of PVBB

Poly(4-vinylbenzylbromide) (PVBB) was prepared by radical polymerization of 4-vinylbenzylbromide (2.0 g, 10 mmol) in the presence of 1% mol of AIBN (0.016 g, 0.1 mmol). A two-necked 50 mL round bottom flask was charged with the solution that was stirred at 70 ^oC for two hours under nitrogen atmosphere. The crude product was then purified twice by reprecipitation in methanol from a chloroform solution and recovered after drying at reduced pressure. The polymer was obtained in 56.0% yield and the molecular weight of the polymer was evaluated by gel permeation chromatography (GPC).[7]

^1H NMR (500 MHz, $CDCl_3$) δ 1.25-1.52 (m, 2H), 1.67-1.71 (m, 2H), 4.43-4.50 (s, 2H), 6.62-6.64 (m, 2H), 6.93-7.11 (m, 2H). IR (neat): ν (cm^{-1}) 1509, 1444, 1421, 1266, 837, 826, 610 (C-Br).

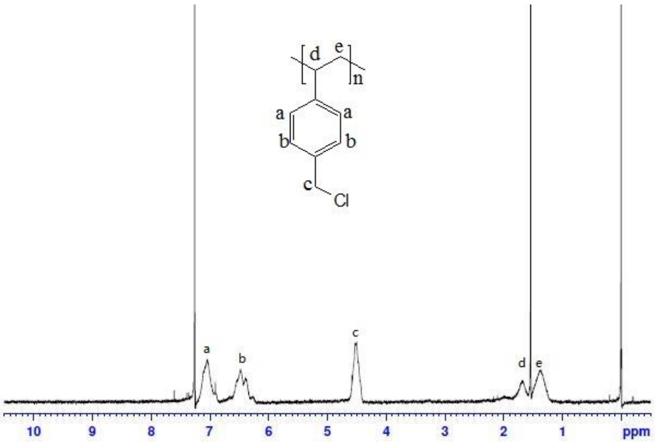
2.4.2. General procedure for synthesis of cyclic carbonates from CO_2 and epoxides

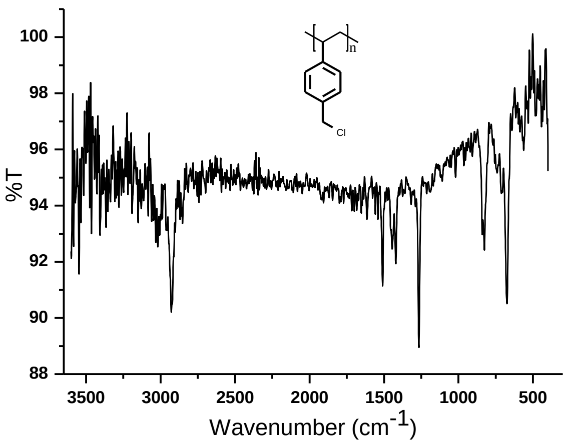
A 30 mL Schlenk tube was charged with epoxide (5.0 mmol), PVBC or PVBB (0.05-0.25 mmol), DMF (1.86 g, 25.0 mmol), or DBU (0.038 g, 0.25 mmol). The Schlenk tube was then subjected to three cycles of pressurization and depressurization with CO_2 through a balloon (1 atm, 20 cm in diameter). The reaction mixture was heated at a given temperature and stirred for 24 h. The reaction mixture was allowed to cool to room temperature, and then 20 mL of ethyl acetate was added slowly to extract the product and the remaining reactant and to precipitate the catalysts. After removing the solvent and the unreacted epoxide under reduced pressure, the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (2:1, v/v) as an eluent to afford the carbonate.

2.4.3. Recyclability study

The reaction was carried out as mentioned above using a typical experimental procedure. After completion of the reaction, the reactor was cooled to room temperature and then CO_2 was released slowly. The catalyst was then recovered by adding excess ethyl acetate to the reaction mixture to precipitate the PVBB and a simple filtration technique. The filtered catalyst was washed vigorously with ethyl acetate to remove all traces of the product and the reactant if present. The filtered catalyst was then dried (in vacuo or under reduced pressure) at 70-80 ^{o}C for 3 h. The dried catalyst was then further used for further recyclability study.

2.4.4. ^{1}H and ^{13}C NMR spectra for PVBC and PVBB

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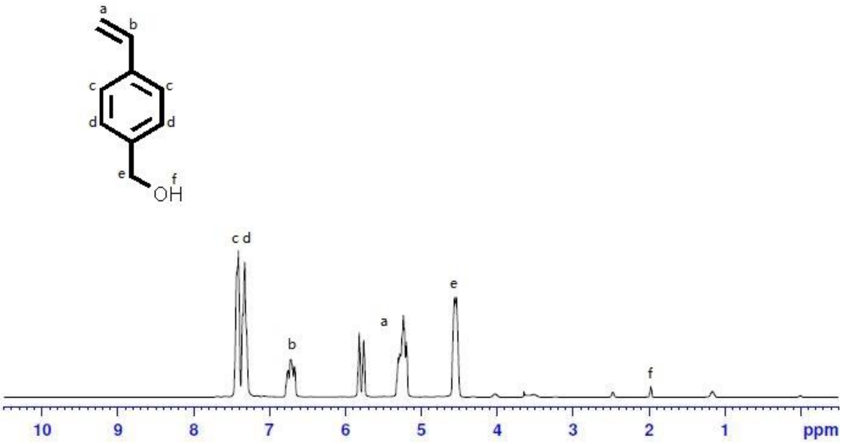
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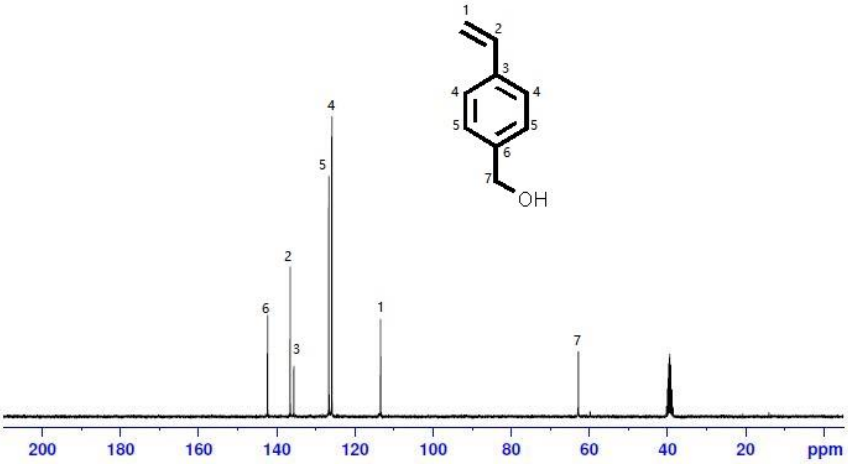
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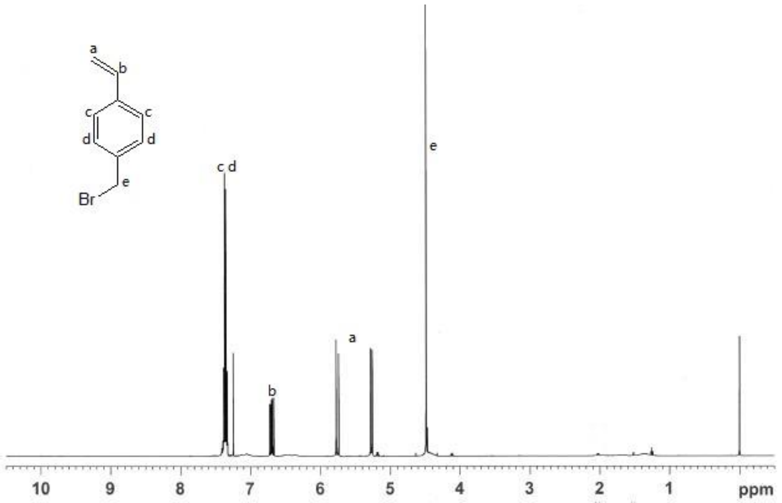
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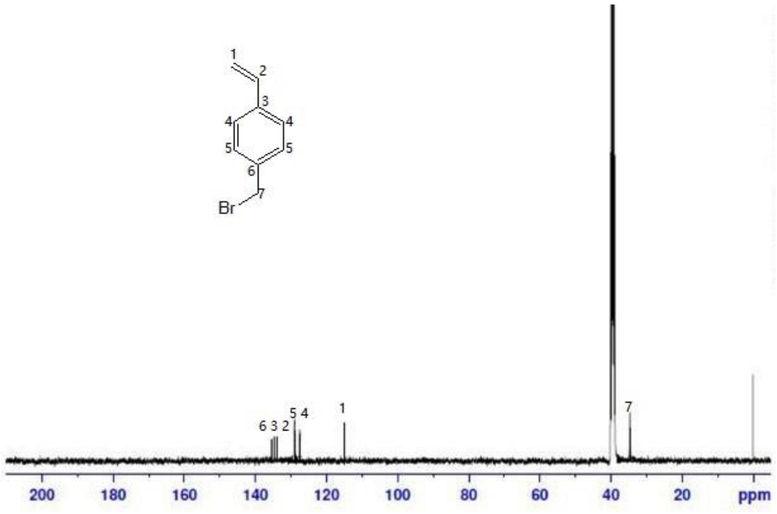
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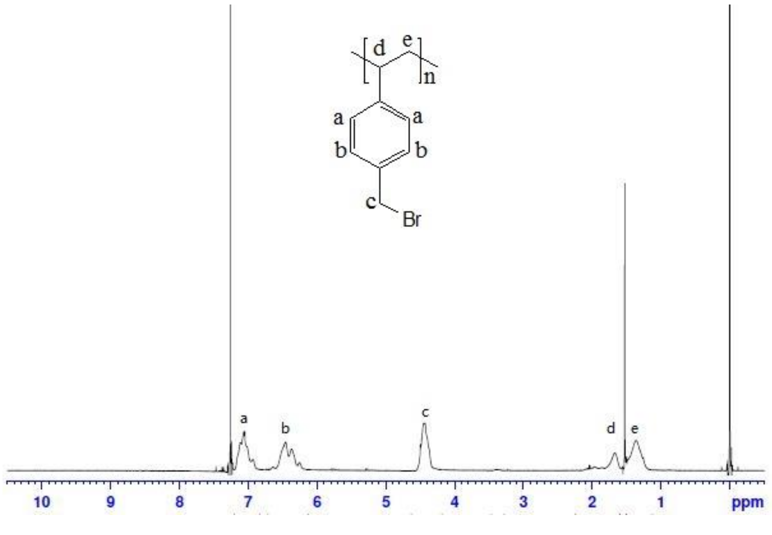
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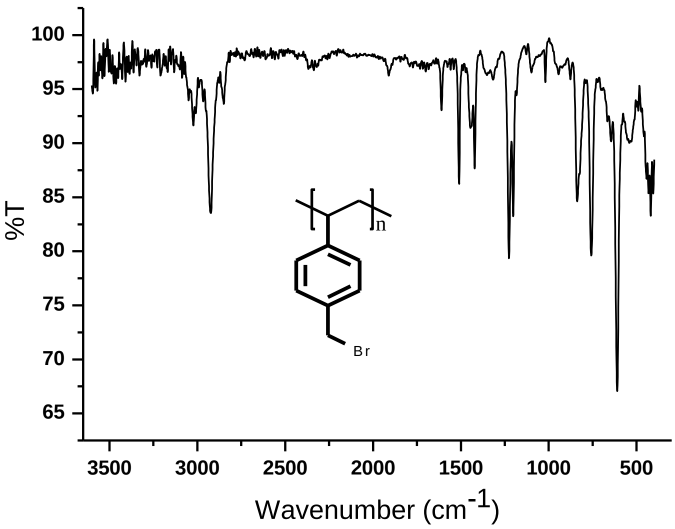

2.5. References

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Chapter 3 Development of a polymer having 2-pyridinemethanol unit for the synthesis of cyclic carbonates from carbon dioxide and epoxides

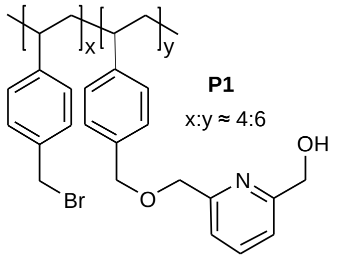
3.1. Introduction

Recently, many polymer-supported catalysts[1-7] have been reported for the cycloaddition of epoxides with CO_2 due to their attractiveness for technological applications and manufacturing processes with simplified product recovery. Jiang *et al*. reported polystyrene-supported threonine (PS-Thr) and polystyrene-supported tyrosine (PS-Tyr) as catalyst for the carboxylation of various epoxides and aziridines with CO_2.[4] Polymer-supported catalysts with carboxyl and hydroxyl functional groups have been demonstrated as effective catalyst for the synthesis of ethylene carbonate (EC) *via* the cycloaddition of ethylene oxide (EO) with CO_2 by Ren *et al*.[5] Bhanage *et al.* reported a polymer supported diol functionalized ionic liquids (PS-DFILX) for cyclic carbonates synthesis from CO_2 and epoxide providing remarkable yields of desired products under solvent free conditions.[6] Kleij and Pericàs reported a polystyrene supported pyrogallol for the conversion of CO_2 and oxiranes into cyclic organic carbonates under attractive conditions.[7] As a result, the polymer-supported catalytic system has been attracting much attention as an efficient catalyst.

It is widely accepted that the presence of a hydrogen bond donating group (HBD) activates the epoxide ring owing to the acidic nature of the oxygen atom.[8-16] The hydroxyl functional group coordinates to the epoxide ring and further polarizes the C-O bond, facilitating ring opening. Catalysts with HBDs also stabilize intermediates and transition states through inter- and intra-molecular hydrogen bonding. Recently, we reported a metal- and solvent-free, binary catalytic system consisting of commercially available 2-pyridinemethanol or 2,6-pyridinedimethanol (8.0 mol%) as the HBD (hydroxymethyl) containing an organonitrogen component (or basic nitrogen atom) (pyridine unit) and tetra-*n*-butylammonium iodide (TBAI) (8.0 mol%) as the co-catalyst for the cycloaddition of epoxides.[17] Those excellent binary organocatalytic systems were metal-free systems that allowed less energy-demanding and more environmentally friendly chemical fixation of CO_2 into value-added chemicals with high-to-excellent yields under rather mild reaction conditions (T = 25-45 °C, 1 atm CO_2). Based on this system, we focused on investigating the reactivity and recyclability of polymer-supported catalyst with 2-pyridinemethanol moiety.

Herein we synthesized a novel polymer-supported catalyst **P1** (Scheme 3-1) with

2-pyridinemethanol moiety *via* the reaction with poly(4-vinylbenzyl bromide) (PVBB) and 2,6-pyridinedimethanol. TBAI was used as a co-catalyst together with the new polymer for the cycloaddition of epoxides to ambient CO_2, affording five membered cyclic carbonates under ambient conditions.

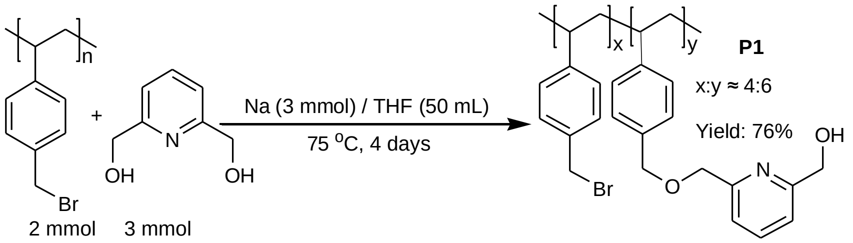


Scheme 3-1. The structure of **P1**.

3.2. Results and discussion

3.2.1. Synthesis and structure characterization

The polymeric catalyst **P1** was synthesized by Williamson ether synthesis reaction of PVBB (prepared in chapter 2) with 2,6-pyridinedimethanol and sodium in tetrahydrofuran (THF) as solvent (Scheme 3-2). As shown in Scheme 3-2, **P1** contains benzyl bromide and [6-(benzyloxymethyl)pyridin-2-yl]methanol units. According to ^{1}H NMR data of **P1**, the ratio of the two units was determined as 4:6. Fourier transform infrared (FT-IR) spectra of **P1** displayed a typical strong peak corresponding to OH stretching frequency centered at about 3380 cm^{-1}.



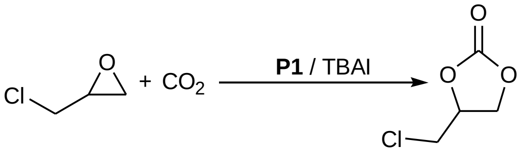
Scheme 3-2. The synthesis of **P1**.

3.2.2. Variation of reaction parameters

We optimized various reaction parameters such as the effect of reaction temperature, time and catalyst amount using **P1**/TBAI as the catalyst of choice for the synthesis of

4-(chloromethyl)-1,3-dioxolan-2-one from epichlorohydrin and CO_2 as a model reaction. Firstly, the temperature effect was tested under the conditions closely related to those tested previously for a 2-pyridinemethanol/TBAI system (Table 3-1, entry 1). At 25 °C, a yield of 57.4% was achieved, and an increase of the temperature to 40 °C increased the yield to 92.0% (Table 3-1, entry 2). Whereas further increase of the temperature resulted in a slight decrease in the product yield that may be due to formation of small amount of by-products or side reaction happened. Next, the effect of the reaction time from 12 h to 24 h on the reaction was examined. The yield increased with the prolonged reaction time and the yield reached to 92.0% at 24 h (Table 3-1, entry 5). Finally, the influence of the catalyst amount on the reaction was examined. The yield improved with the increase of the amount of **P1**/TBAI. When the amount of **P1** was 0.13 mmol and TBAI was 0.25 mmol, the yield reached to 92.0% (Table 3-1, entry 7).

Table 3-1. Screening of conditions using **P1**/TBAI as catalyst in the coupling of epichlorohydrin and CO_2 to afford 4-(chloromethyl)-1,3-dioxolan-2-one.

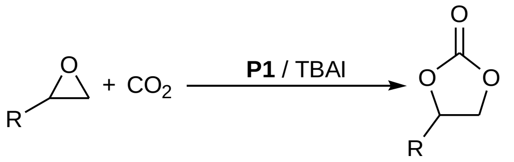


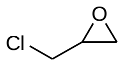
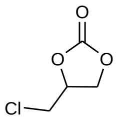
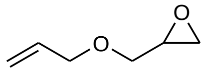
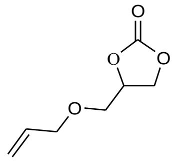
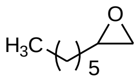
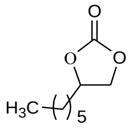
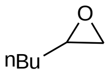
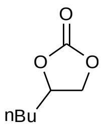
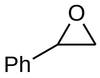
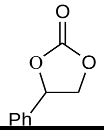
Entry	Temp / °C	T / h	**P1** (mg / mmol)	TBAI (mg / mmol)	Yield[a] (%)
I. Effect of temperature					
1	25	24	64.0 / 0.13	92.0 / 0.25	57.4
2	40	24	64.0 / 0.13	92.0 / 0.25	92.0
3	60	24	64.0 / 0.13	92.0 / 0.25	86.8
II. Effect of time					
4	40	12	64.0 / 0.13	92.0 / 0.25	74.2
5	40	24	64.0 / 0.13	92.0 / 0.25	92.0
III. Effect of catalyst amount					
6	40	24	31.0 / 0.07	47.0 / 0.13	87.0
7	40	24	64.0 / 0.13	92.0 / 0.25	92.0

Reaction conditions: Epichlorohydrin (5.0 mmol), CO_2 (1 atm), Catalyst: **P1**/TBAI, Solvent-free. [a]Isolated product obtained after chromatographic purification.

In order to study the efficiency and general applicability of the polymer-supported catalytic system, we studied the cycloaddition of CO_2 with different epoxides under optimized reaction conditions (Table 3-2). It was observed that all reactions proceeded smoothly providing desired products, but it is noteworthy to mention that only the epichlorohydrin as substrate provided the desired product in appreciable yield (Table 3-2, entry 1). Even we raised the reaction temperature to 60 °C in entries 3-5, lower product yields were obtained. The polymer-supported catalytic system showed low catalytic activity for most of substrates due to the higher molecular weight (The molecular weight (M_n) of PVBB is 4.0×10^4). So, this catalytic system is heterogeneous system that usually needs harsh reaction conditions to get high catalyst activity,[2,5] but our purpose is developing efficient catalysts that are capable of activating CO_2 into organic chemicals under mild reaction conditions.

Table 3-2. Reaction of various epoxides with CO_2 using **P1** as catalyst, TBAI as co-catalyst.



Entry	Epoxide	Product	Yield[a] (%)
1			92.0
2			43.5
3			13.4 36.2[b]
4			19.6 40.1[b]
5			28.0 78.6[b]

Reaction conditions: Epoxide (5.0 mmol), CO_2 (1 atm), Time (24 h), **P1** (5.0 mol%), TBAI (5.0 mol%), 40 °C, Solvent-free. [a] Isolated product obtained after chromatographic purification. [b] 60 °C.

3.3. Conclusion

We develop a novel polymer-supported catalyst **P1** with 2-pyridinemethanol moiety for the cycloaddition of CO_2 and epoxides using TBAI as a co-catalyst. The catalytic system was heterogeneous system and showed moderate activity for most of epoxides because **P1** has higher molecular weight or stronger polarity. Usually, heterogeneous systems need harsh reaction conditions.[2,5] As a result, unfortunately, the present system was shown to be unsatisfactory since our purpose is developing efficient catalytic systems that are capable of activating CO_2 into organic chemicals under mild reaction conditions.

3.4. Experimental

All commercially available starting materials and solvents were purchased and used as received unless indicated otherwise. 2,6-Pyridinedimethanol was purchased from Aldrich. The poly(4-vinylbeznly bromide) is the same as used in Chapter 2 one. Carbon dioxide (99.99% pure) was used as received without further purification and dried prior to use (Tokyo Koatsu Yamazaki Co. Ltd.).

^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. The chemical shifts of the products were reported in ppm with reference to Me_4Si as an internal standard in $CDCl_3$ and DMSO-d_6. FT-IR spectra was obtained as potassium bromide pellets with a JASCO FT/IR-460 spectrometer.

3.4.1. Procedure for synthesis of P1

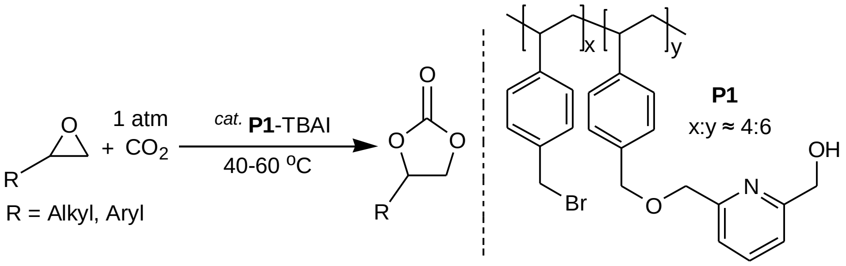
2,6-Pyridinedimethanol (0.42 g, 3.0 mmol) and dry THF (30 mL) were added to a three-necked flask equipped with a magnetic stirrer. Sodium (0.06 g, 3.0 mmol) is added piece by piece to the reaction mixture under a nitrogen atmosphere. The mixture was heated slowly from room temperature to 75 ^oC and reaction of sodium was accompanied by an increase in the temperature of the reaction mixture. After all sodium was dissolved, a dropping funnel with the solution of the corresponding poly(4-vinlybenzyl bromide) (0.39 g, 2.0 mmol) in dry THF (20 mL) was added to the reaction flask drop-by-drop. The temperature of the reaction mixture was kept at 75 ^oC. The precipitate of sodium bromide gradually appears and increases in quantity in the course of the reaction. After 4 days the reaction mixture was cooled to room temperature and about 50 mL of water was added to the organic solution. The product was extracted by ethyl acetate (50 mL) three times and dried with sodium sulfate. Then the solvent was evaporated and the residue was washed by methanol (2 x 10 mL). The product was obtained after drying under vacuum pressure.

^{1}H NMR (300 MHz, DMSO-d$_6$) δ ppm: 6.43-7.82 (m, 11H), 5.43 (s, OH), 5.1 (s, 2H), 4.2-4.8 (m, 8H), 1.24-1.95 (br, 3H). IR (neat): *ν* (cm^{-1}) = 3433 (OH), 1610, 1593, 1578, 1510, 1453, 1421, 1101 (C-O-C), 818, 609 (C-Br).

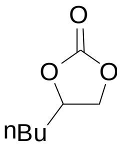
3.4.2. General procedure for synthesis of cyclic carbonates from CO2 and epoxides

A 30 mL Schlenk tube was charged with epoxide (5.0 mmol), **P1** (64.0 mg, 0.13 mmol), TBAI (92.0 mg, 0.25 mmol). The Schlenk tube was then subjected to three cycles of pressurization and depressurization with CO_2 through a balloon (1 atm, 20 cm in diameter). The reaction mixture was heated at a given temperature and stirred for 24 h. The reaction mixture was allowed to cool to room temperature, and then 20 mL of ethyl ether was added slowly to extract the product and the remaining reactant and to precipitate the catalysts. After removing the solvent and the unreacted epoxide under reduced pressure, the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (1:1-2:1, v/v) as an eluent to afford the carbonate.

3.4.3. Representative procedure for the cyclic carbonate formation



All cyclic organic carbonate products have been reported previously and the data given below are in agreement with the literature data.

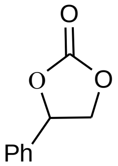


4-Butyl-1,3-dioxolan-2-one[17-19]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxyhexane (5 mmol, 0.51 g), **P1**

(0.13 mmol, 0.064 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.29 g (yield: 40.1%) as a colorless oil.

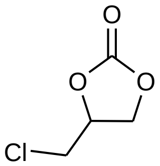
^1H NMR (300 MHz, $CDCl_3$) δ ppm: 4.77-4.68 (m, 1H), 4.57-4.52 (m, 1H), 4.11-4.05 (m, 1H), 1.82-1.68 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 77.3, 69.4, 33.4, 26.4, 22.2, 13.7.



4-Phenyl-1,3-dioxolan-2-one[17-19]

In a 30 mL single-necked round-bottomed flask, styrene oxide (5 mmol, 0.60 g), **P1** (0.13 mmol, 0.064 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.63 g (yield: 78.6%) as a white solid.

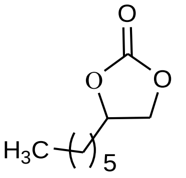
^1H NMR (500 MHz, $CDCl_3$) δ ppm: 7.44-7.38 (m, 3H), 7.36-7.34 (m, 2H), 5.68-5.65 (m, 1H), 4.80-4.77 (m, 1H), 4.33-4.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.1, 135.8, 129.7, 129.2, 120.0, 77.6, 71.2.



4-(Chloromethyl)-1,3-dioxolan-2-one[17,18]

In a 30 mL single-necked round-bottomed flask, epichlorohydrin (5 mmol, 0.46 g), **P1** (0.13 mmol, 0.064 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.62 g (yield: 92.0%) as a colorless oil.

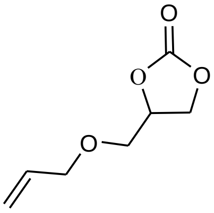
^1H NMR (500 MHz, $CDCl_3$) δ ppm: 5.12-5.01 (m, 1H), 4.69-4.55 (m, 1H), 4.48-4.35 (m, 1H), 3.89 (dd, 1H), 3.77 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.8, 74.7, 67.0, 44.6.



4-Hexyl-1,3-dioxolan-2-one[17,18]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxyoctane (5 mmol, 0.64 g), **P1** (0.13 mmol, 0.064 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.31 g (yield: 36.2%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 4.79-4.68 (m, 1H), 4.61-4.50 (m, 1H), 4.15-4.02 (m, 1H), 1.85-1.62 (m, 2H), 1.55-1.21 (m, 8H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.4, 22.4, 13.9.

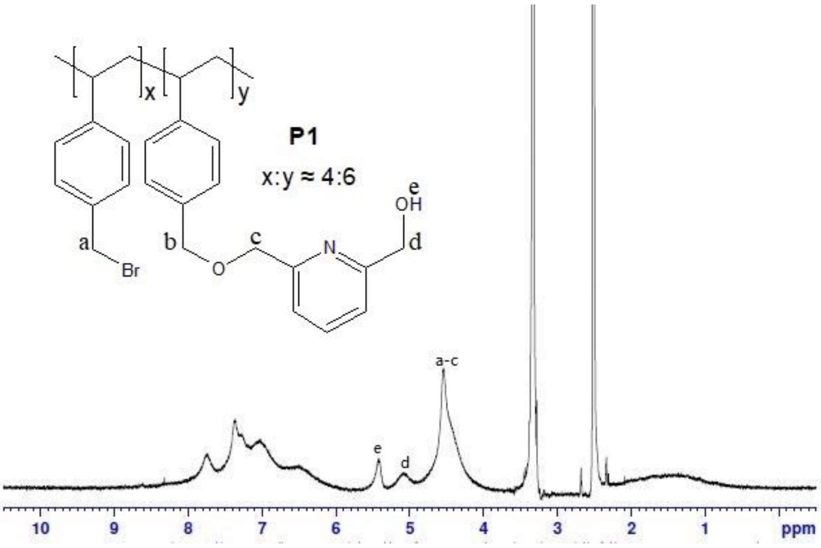


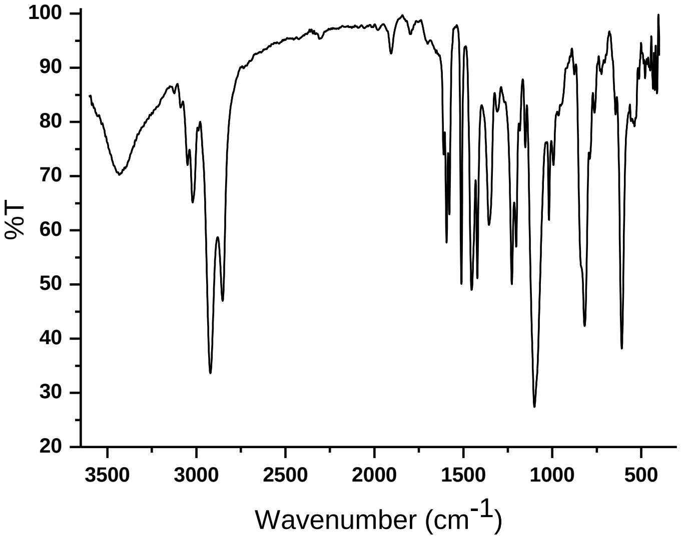
4-Allyloxymethyl-1,3-dioxolan-2-one[17,18]

In a 30 mL single-necked round-bottomed flask, allyl glycidyl ether (5 mmol, 0.57 g), **P1** (0.13 mmol, 0.064 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.34 g (yield: 43.5%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 5.95-5.80 (m, 1H), 5.35-5.12 (m, 2H), 4.93-4.80 (m, 1H), 4.60-4.45 (m, 1H), 4.44-4.30 (m, 1H), 4.11-3.99 (m, 2H), 3.75-3.65 (m, 1H), 3.64-3.52 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.1, 133.8, 117.3, 75.4, 72.2, 68.9, 66.2.

3.4.4. ^{1}H NMR and IR spectra of P1





3.5. References

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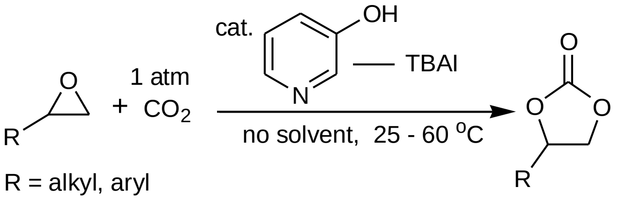
Chapter 4 Development of an efficient and practical organocatalytic system 3-hydroxypyridine/TBAI for the synthesis of cyclic carbonates from CO_2 and epoxides

4.1. Introduction

In the past decades, various homogeneous and heterogeneous catalysts have been developed for coupling reactions between CO_2 and epoxides, including metal oxides,[1,2] modified molecular sieves,[3,4] alkali metal salts,[5] organometallic complexes,[6,7] and ionic liquids.[8-13] However, many of these catalytic systems require high temperatures, high CO_2 pressures, or toxic polar solvents and the reaction under milder conditions is still an active research topic.



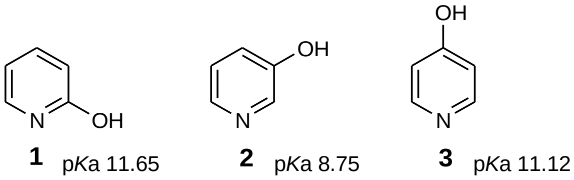
Scheme 4-1. Synthesis of cyclic carbonates from CO_2 and epoxides.

Many metal-based catalytic systems have been developed for the synthesis of cyclic carbonates. In recent years, on the other hand, the number of organocatalytic systems has been drastically increasing because organocatalysts offer several advantages, being inexpensive, robust, nontoxic, and bench-stable.[14] Until now, several organocatalysts that contain functionality such as hydroxy groups,[15-20] amino groups,[21] and carboxy groups[22] have been well recognized for playing important roles frequently combined with a halide salt as a co-catalyst. Such organocatalysts activate an epoxide and/or CO_2 to facilitate the nucleophilic ring-opening of the epoxide by the halide ion and/or following addition reaction with CO_2. Recently, we developed an organocatalytic system composed of 2-hydroxymethylpyridine and tetra-*n*-butylammonium iodide (TBAI).[23] We proposed that 2-hydroxymethylpyridine serves as a bifunctional catalyst and its hydroxyl group (hydrogen-bonding donor) and nitrogen atom (Lewis base) activate the epoxide and coordinate to CO_2, respectively.[24,25] As a new organocatalyst with a stronger hydrogen-bonding donor group, herein, we report 3-hydroxypyridine/TBAI as a new catalytic system for the synthesis of cyclic carbonates under mild and economical conditions such as solvent-free, atmospheric pressure of CO_2, moderate temperature (Scheme 4-1).

4.2. Results and discussion

4.2.1. Reaction with hydroxypyridine-TBAI systems

Although the application of various organic bases to CO_2 activation or absorption has been reported,[26-31] we have shown that pyridine is not a good catalyst for the cycloaddition of CO_2 and epoxides in the presence of TBAI at ambient pressure.[23] However, as mentioned above, hydroxy groups are good activators of epoxides due to hydrogen bond formation.[15-20,23] Therefore, hydroxypyridines were expected to be alternative catalysts for the cycloaddition of CO_2 and epoxides. We studied three hydroxypyridine isomers **1-3** (Scheme 4-2) as simple and easily available organocatalysts, in combination with tetra-*n*-butylammonium halide as a co-catalyst, to form a new catalytic system for the synthesis of cyclic carbonate from CO_2 and epoxides.

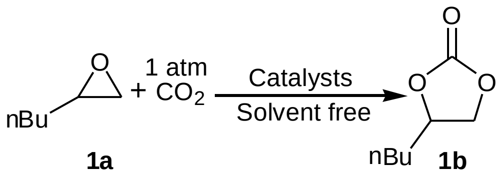


Scheme 4-2. Structures of hydroxypyridines and p*K*a values of the hydroxy groups.

Catalysts **1-3** were screened with the same amount of TBAI as a co-catalyst using 1,2-epoxyhexane (**1a**) as a substrate at 40 °C under atmospheric pressure of CO_2 for 24 h. The results are summarized in Table 4-1. Good to excellent yields of 4-butyl-1,3-dioxolan-2-one (**1b**) were obtained, with no by-products detected in the experiments (Table 4-1, entries 1-3). As reported previously,[23] pyridine was ineffective under the same conditions (Table 4-1, entry 4). The effect of the hydroxyl group, therefore the hydrogen bonding ability, is evident in the reaction between CO_2 and an epoxide, as mentioned previously.[15-20,23] When **2** and TBAI were used individually, both gave poor yields (Table 4-1, entries 5 and 6). Thus, the high catalytic activity was realized by the cooperative effect of hydroxypyridines and TBAI.[15,16,18,23]

Kleij *et al.* worked on the combinations of various phenols and TBAI for the cycloaddition of CO_2 and epoxides in methyl ethyl ketone.[16] In their work, simple phenol afforded only 15% yield from **1a** under 10 bar at 45 °C while pyrogallol gave 100% yield (93% isolated yield) under the same condition and 54% yield under 2 bar. Phenol, pyrocatechol or pyrogallol as catalyst combined with TBAI as a co-catalyst was studied (Table 4-1, entries 7-9). Comparing with the present result of **2** (95% isolated yield under 1 atm and 40 °C; Table 4-1, entry 2), the solvent-free system seems effective for the phenol-TBAI system. On the other hand, Shi *et al.* studied the effect of *p*-methoxyphenol combined with several bases and found that high yield of 98% is achieved with *N*,*N*-dimethylaminopyridine (DMAP) under high CO_2 pressure and temperature (3.57 MPa, 120 °C) but only 20% is obtained using pyridine.[20] It is also interesting that they observed *p*-toluenesulfonic acid, much stronger acid, and DMAP gave poor yield of 10% under the same condition. We tried the combination of **2** and DMAP to obtain almost no carbonate (Table 4-1, entry 10). Under the present reaction conditions (1 atm CO_2, 40 °C), **2** works very efficiently in combination with TBAI.

Table 4-1. Reaction of 1,2-epoxyhexane with CO_2 using various catalysts[a].



Entry	Catalyst	Co-catalyst	Yield[b] (%)
1	**1**	*n*-Bu_4NI	67
2	**2**	*n*-Bu_4NI	95
3	**3**	*n*-Bu_4NI	86
4	pyridine	*n*-Bu_4NI	10
5	**2**	-	6
6	-	*n*-Bu_4NI	9
7	phenol	*n*-Bu_4NI	97
8	pyrocatechol	*n*-Bu_4NI	97
9	pyrogallol	*n*-Bu_4NI	97
10	**2**	DMAP	0
11	2-methyl-3-hydroxypyridine	*n*-Bu_4NI	95
12	2,4-dimethyl-3-hydroxypyridine	*n*-Bu_4NI	83
13	**2**	*n*-Bu_4NBr	82
14	**2**	*n*-Bu_4NCl	36

[a] Reaction conditions: **1a** (5.0 mmol), Catalyst (5.0 mol%), Tetrabutylammonium halide (5.0 mol%), Solvent-free, CO_2 (1 atm), 40 °C, 24 h. [b] Isolated product obtained after chromatographic purification.

Interestingly, the reaction yield varied depending on the structure of the hydroxypyridine: **2** afforded the best result, followed by **3** and then **1** (Table 4-1, entries 1-3). To study the intrinsic catalytic activity in detail, kinetic studies of the catalytic conversion of CO_2 and **1a** to **1b** were carried out using **1**, **2**, or **3** and TBAI as co-catalysts for 4 h. The resulting kinetic curves of three different catalysts are shown in Figure 4-1 and summarized in Table 4-2. Catalyst **2** showed the highest catalytic activity, with reaction rates in the order **2** > **3** > **1**, affording the TON of 7.8 for **2** in the initial 2 h while those of **1** and **3** were 1.5 and 3.3, respectively. Such a difference can be explained from the acidity of their hydroxyl groups. Shi *et al.* reported that this reaction was catalyzed well by phenols with pK_as between 7.15 and

10.64.[20] The pK_a of **2** meets this acidity requirement (Scheme 4-2),[32] which is a principal reason that **2** afforded the highest yield. It is known that **1** and **3** tautomerize to the corresponding pyridones **1'** and **3'** (Scheme 4-3),[33] which lowers their acidity and therefore the catalytic ability of the hydroxyl groups.[19] It is still interesting that weaker acids, **1** and **3** with pK_a values higher than 11, have good catalytic activities. The tautomer forms containing the NH structure might contribute the reaction more or less.

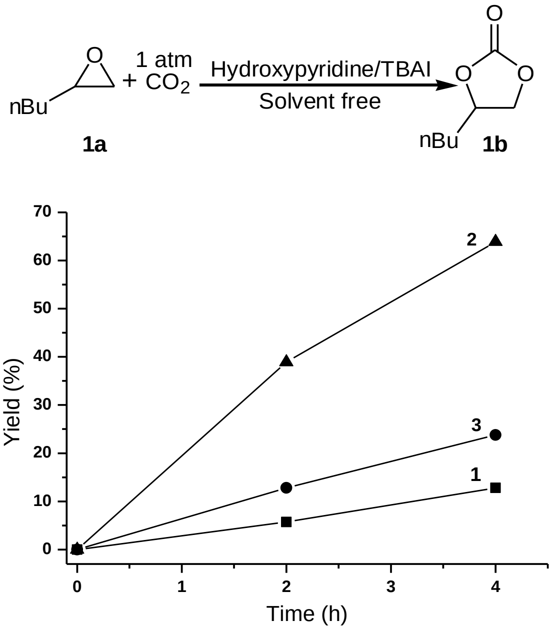
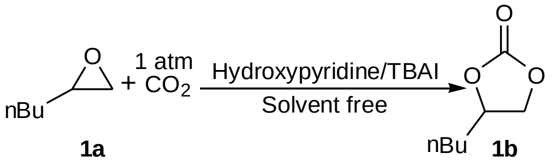


Figure 4-1. Comparative kinetics in the formation of **1b** from **1a** and CO_2 using **1-3** as catalysts. Reaction conditions: **1a** (5.0 mmol), catalyst (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), 40 °C.

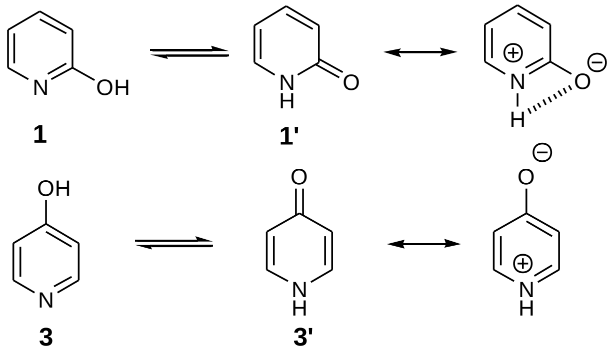
Table 4-2. Time dependence of the synthesis of **1b** using **1**, **2** and **3** as a catalyst in the coupling of **1a** and CO_2[a].



Catalyst	Time (h)	Yield of **1b** (%)	TON
1	2	5.7	1.5
	4	12.8	3.3
2	2	38.9	7.8
	4	63.9	12.8
3	2	12.8	3.3
	4	23.8	6.1

[a] Reaction conditions: **1a** (5.0 mmol), catalyst (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), 40 °C.

Two kinds of methylated 3-hydroxypyridines were studied to further study the effect of hydroxyl group. While 2-methyl-3-hydroxypyridine afforded the same high yield (95%) as **2** (Table 4-1, entry 11), the yield of the product (83%) became lower more than 10% by 2,4-dimethyl-3-hydroxypyridine (Table 4-1, entry 12). The results clearly suggest the importance of hydrogen bonding of the hydroxy group; steric hindrance of the methyl groups introduced at 2- and 4-positions of **2** disturbs the hydroxy group in formation of a hydrogen bond with the epoxide.



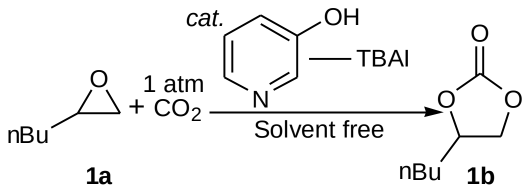
Scheme 4-3. The tautomerization of 2-hydroxypyridine (**1**) and 4-hydroxypyridine (**3**).

4.2.2. Optimization of the reaction conditions

In the synthesis of cyclic carbonates from CO_2 and epoxides, it has often been proposed that the halide ion opens the activated epoxide ring through a nucleophilic reaction.[17,21-23,34,35] In order to study the effect of the halide ion, tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium chloride (TBAC) were used in combination with **2**; the results were also summarized in Table 4-1. The activity of the catalysts increased in the order: TBAC < TBAB < TBAI (Table 4-1, entries 2, 13 and 14), however this is inconsistent with the order of nucleophilicity of halide anions ($Cl^- > Br^- > I^-$), which has been observed in some systems.[17,34] It is probable that the activity is corresponding with leaving ability of the halide ions ($Cl^- < Br^- < I^-$), as noted previously.[17,21-23,35]

The effect of amount of the binary catalyst **2** and TBAI (1:1) was evaluated, and the results were shown in Figure 4-2. Even when the catalyst loading was reduced to 1 mol%, the yield of **1b** was as high as 71%, demonstrating the high capability of this catalytic system. Catalytic activity gradually increased with the catalyst amount, and the yield increased to 94% using 4 mol% catalyst loading.

The reaction time course was also examined at 40 °C with 5 mol% loading of **2**/TBAI, with the results shown in Figure 4-3 (I). The reaction proceeded quickly in the first few hours, then gradually slowed, to afford 95% yield after 24 h.



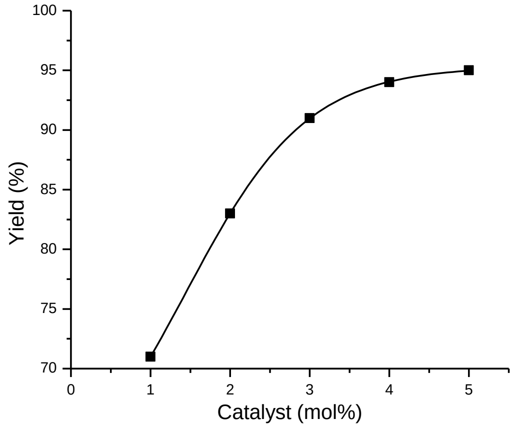


Figure 4-2. Effect of the amount of **2**/TBAI (1:1) on the yield of **1b**. Reaction conditions: **1a** (5.0 mmol), **2** (1.0-5.0 mol%), TBAI (1.0-5.0 mol%), CO_2 (1 atm), 24 h, 40 °C.

It has been verified that the synthesis of cyclic carbonates from CO_2 and epoxides obey the first order kinetics according to previous study.[36] Therefore, the rate equation for the reaction catalyzed by **2** and Bu_4NI can be written as Eq. (1).

$$r = \mathrm{k[epoxide]}[\mathit{Cat.}][\mathrm{CO_2}] \qquad (1)$$

The catalyst concentration did not change, and the CO_2 concentration change was negligible during the reaction, so the pseudo first-order rate equation can be applied as Eq. (2). Taking the logarithm of Eq. (2) leads to Eq. (3).

$$r = \mathrm{-d[epoxide]/dt = k[epoxide]} \qquad (2)$$

$$\mathrm{ln[epoxide]_{t\,=\,0} - ln\,[epoxide] = kt} \quad \text{or} \quad \mathrm{ln[1/(1 - x)] = kt} \qquad (3)$$

where x is the conversion rate of epoxide, t is the reaction time, k is the reaction rate constant. Under the optimal reaction conditions, the conversion rate of **1a** was calculated at 40 °C, to get the values of ln[1/(1-x)] and a plot of ln[1/(1-x)] against reaction time in Figure 4-3 (II), where x was conversion rate of **1a**. A linear relationship was observed in this case. Therefore, the **1a**-CO_2 reaction was confirmed to be the first order one with respect to the concentration of **1a**.

The effect of reaction temperature was studied and summarized in Table 4-3. It was shown that the yield substantially increased with increase of the reaction temperature from 25 to 40 °C, whereas there seemed minor increase in catalytic activity at 60 °C.

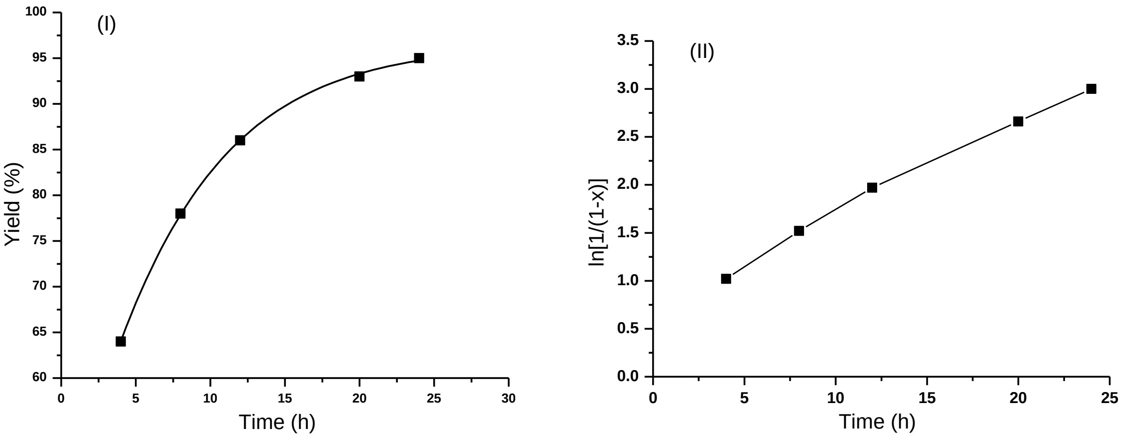
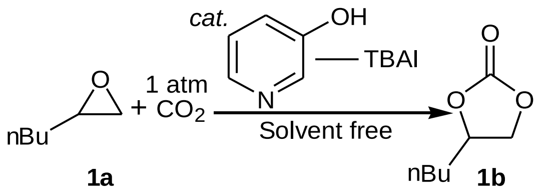


Figure 4-3. (I) Time dependence of the synthesis of **1b** and (II) rate of the reaction **1a** with CO_2 by **2**/TBAI, x is conversion rate of **1a**. Reaction conditions: **1a** (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), 40 °C.

Table 4-3. Effect of reaction temperature on the synthesis of **1b** by **2**/TBAI.[a]



Entry	Catalyst	Co-catalyst	Temperature (°C)	Yield[b] (%)
1	**2**	TBAI	25	78
2	**2**	TBAI	40	95
3	**2**	TBAI	60	97

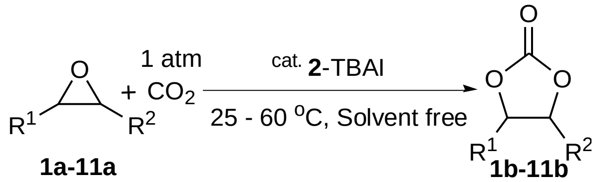
[a] Reaction conditions: **1a** (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), Solvent-free, CO_2 (1 atm), 24 h. [b] Isolated product obtained after chromatographic purification.

4.2.3. Cycloaddition of CO_2 to various epoxides

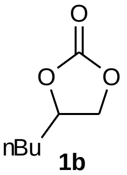
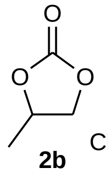
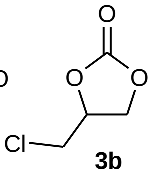
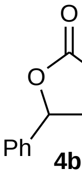
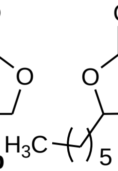
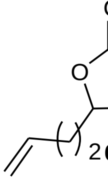
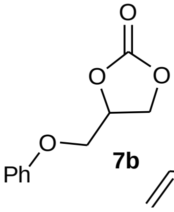
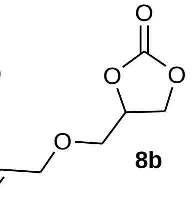
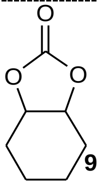
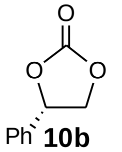
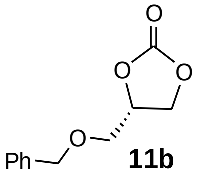
According to the results mentioned above, cycloaddition reactions of CO_2 with various epoxides in the presence of **2**/TBAI (5 mol%) were studied under atmospheric pressure and at 25-60 °C depending on the reactivity of the epoxide; the results are summarized in Table 4-4. The catalytic system effectively converted mono-substituted aliphatic epoxides into the corresponding cyclic carbonates in yields of 82-96% at 25 °C without solvent (Table 4-4, **1b**-**3b** and **5b**-**8b**). For **7b**, product precipitation lowered the yield by preventing continuous stirring of the reaction mixture. Epoxides with longer alkyl groups gave slightly lower yields (Table 4-4, **1b** and **5b**), which could be improved (>90%) at higher temperatures (40 °C). The relatively low yield using styrene oxide at 40 °C was probably due to the presence of the aromatic ring, which makes the ring-opening step more favorable on C_α (most substituted carbon), unlike the apparent preference for C_β (least substituted carbon) observed for other epoxides (Table 4-4, **1a**-**3a** and **5a**-**8a**), resulting in a less nucleophilic alkoxide intermediate, which causes CO_2 activation (insertion) to be kinetically more difficult than for aliphatic epoxides.[37] Thus, a higher temperature (60 °C) was necessary to achieve a 95% yield. Cyclohexene oxide exhibited the lowest reactivity, even at 60 °C (Table 4-4, **9a**), probably owing to the greater steric hindrance compared with monosubstituted epoxides.[15]

This catalytic system was also applied for the coupling reaction of enantiomerically pure epoxides and CO_2. When (*R*)-styrene oxide was transformed to the corresponding carbonates, the ee value of the carbonate was 92% ee at 40 °C and it lowered to 84% ee at 60 °C (Table 4-4, **10b**). On the other hand, unexpectedly, further decrease to 64% ee was observed for (*R*)-glycidyl benzyl ether even at 40 °C (Table 4-4, **11b**), which demands further refinement of the present system in the next stage.

Table 4-4. Reactions of various epoxides with CO_2 using **2** as catalyst and TBAI as co-catalyst[a].



1a-11a **1b-11b**

 **1b**	 **2b**	 **3b**	 **4b**	 **5b**
78 95^{c}	86	96	86^{c} 95^{d}	82 91^{c}
 **6b**	 **7b**	 **8b**	 **9b**	
93	82	91	14^{d}	
 **10b**		 **11b**		
84^{c} (92% *ee*) 93^{d} (84% *ee*)		89^{c} (64% *ee*)		

[a] Reaction conditions: Epoxide (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), solvent-free, CO_2 (1 atm), 24 h, 25 °C. [b] Isolated product obtained after chromatographic purification. [c] 40 °C. [d] 60 °C.

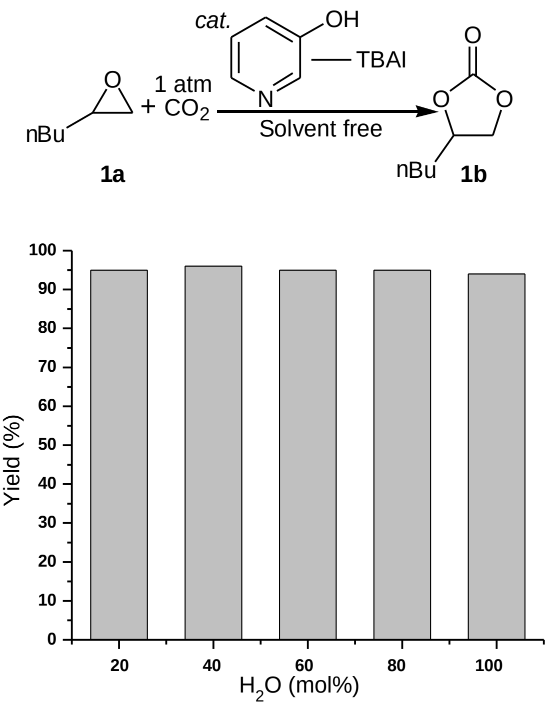


Figure 4-4. Effect of water on the catalytic activity of **2**/TBAI for the synthesis of **1b**. Reaction conditions: **1a** (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), H_2O (20%-100%), CO_2 (1 atm), 24 h, 40 °C.

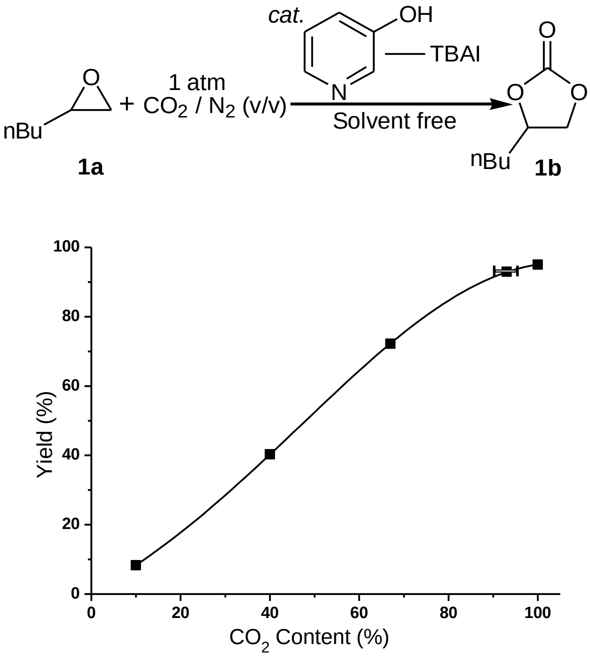


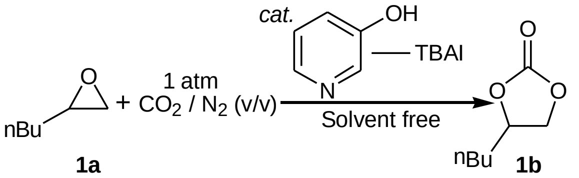
Figure 4-5. Effect of CO_2 content in feed gas (CO_2/N_2) on yield for the synthesis of **1b**. Reaction conditions: **1a** (5.0 mmol), gas mixture (1 atm), **2** (5.0 mol%), TBAI (5.0 mol%), 24 h, 40 °C. CO_2 purities were 9.93%, 39.9%, 67.1%, and >99.99% (CO_2/N_2, vol%). See text for data of 93% pure CO_2.

4.2.4. Effect of water and other gas components in CO_2

The ultimate goal of this research was the direct fixation of CO_2 in combustion gases, which can contain other gas components, including water. Under such conditions, other gas components could affect the reaction and/or catalytic system. For practical applications, it is important to study the effect of water and other gas components on the present system.

First, the effect of H_2O on the **2**/TBAI catalytic system was studied using **1a** in the presence of H_2O (20-100 mol%). As shown in Figure 4-4, the yield was unaffected by addition of a small amount of water up to the same amount of the substrate and 20 times more than the catalyst. Moisture in the feed gas, therefore, does not appear to impair the application of this catalytic system to fix CO_2 at 40 ^{o}C under 1 atm of CO_2.

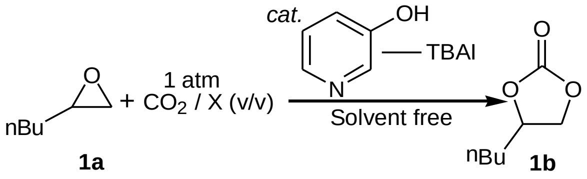
Table 4-5. Effect of minor gas component in CO_2 for the synthesis of **1b**[a].



Entry	Gas composition (v/v)	Time (h)	Yield[b] (%)
1	CO_2/N_2 = 10/90	24	8.3
2	CO_2/N_2 = 10/90	48	11.1
3[c]	CO_2/N_2 = 10/90	48	16.7
4	CO_2/N_2 = 40/60	24	40.3
5	CO_2/N_2 = 67/33	24	72.2
6	CO_2/N_2 = 67/33	48	82.0
7[c]	CO_2/N_2 = 67/33	48	86.1
8	CO_2/N_2 = 93/7	24	93.0
9	CO_2/O_2 = 93/7	24	92.0
10	CO_2/Air = 93/7	24	93.0

[a] Reaction conditions: **1a** (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), Solvent-free, Mixed gas (1 atm), 40 ^{o}C. [b] Isolated product obtained after chromatographic purification. [c] The reaction was conducted in the dark.

In most studies, highly pure CO_2 (>99%) was used for the cycloaddition reaction with epoxides. The content of CO_2 in the feed gas is an important factor in practical applications, and the effect of a second gas component was investigated using CO_2/N_2 mixtures with various CO_2 volume fractions (9.93%, 39.9%, 67.1%, and >99%). As shown in Figure 4-5 and Table 4-5, the yield of carbonate increased with the increase of CO_2 content. In order to gain a deeper insight into the effect of a second gas component, O_2 or air (7%, vol%) was added to CO_2. Figure 4-6 shows that the yields were not affected by O_2 or air, indicating that these minor components do not deteriorate the reaction. These results mean that the catalytic system has good resistance to oxidation in the presence of up to 7% O_2. To check the reliability of the manual mixing method for air and O_2, the same procedure was also applied to N_2 (7%, vol%; Figures 4-5 and 4-6).



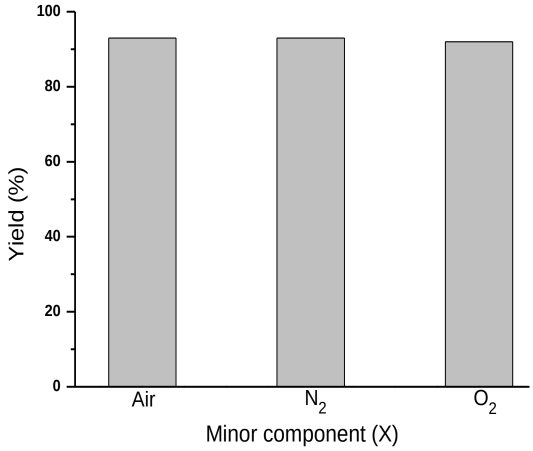


Figure 4-6. Effect of air, N_2 and O_2 in CO_2 on the catalytic activity of **2**/TBAI for **1b** synthesis. Reaction conditions: **1a** (5.0 mmol), **2** (5.0 mol%), TBAI (5.0 mol%), CO_2/minor gas (93/7 (vol%); 1 atm), 24 h, 40 °C; the minor gas is air, N_2 or O_2.

4.3. Conclusions

A new efficient catalytic system (3-hydroxypyridine, **2**/tetra-*n*-butylammonium iodide) was presented for the synthesis of cyclic carbonates by coupling CO_2 with epoxides without solvent, under atmospheric pressure, and at low to moderate temperatures, 25-60 ^{o}C. The effects of hydroxyl group, the pK_a and hydrogen bonding ability, were discussed by comparing with 2-hydroxypyridine, 4-hydroxypyridine, and 2,4-dimethyl-3-hydroxypyridine: catalytic activity was significantly influenced by the acidity of hydroxy group and the steric environment of its vicinity. Moreover, the organocatalytic system exhibited excellent stability in the cycloaddition reaction of CO_2 with epoxides, even in the presence of minor non-toxic components such as water, air and O_2. This highly active and stable organocatalytic system is expected to provide practical applications for CO_2 fixation.

4.4. Experimental

All commercially available starting materials and solvents were purchased and used as received, unless stated otherwise. Carbon dioxide (99.99% pure) and CO_2-N_2 mixtures (CO_2 purities: 67.1%, 39.9%, and 9.93%) were used as received without further purification and drying prior to use (Tokyo Koatsu Yamazaki Co. Ltd.). The purities of N_2 and O_2 were 99.9% and 99.5%, respectively.

In order to prepare the mixtures of CO_2 (93 ± 2%, vol%) with N_2, O_2 or air (7 ± 2%, vol%), the minor gas component was introduced into the balloon *via* syringe, as follows: pure CO_2, N_2 and O_2 were introduced into separate balloons (~4.2 L). Then, 300 mL of CO_2 was removed from the CO_2 balloon and 300 mL of N_2 or O_2 taken from the corresponding balloon were introduced into the CO_2 balloon *via* syringe. Ambient air was also introduced into the CO_2 balloon in the same way.

Reactions were monitored using thin-layer chromatography using 0.25-mm E. Merck silica gel coated on aluminum plates (60F-254). Chemical yields refer to the pure isolated carbonate.

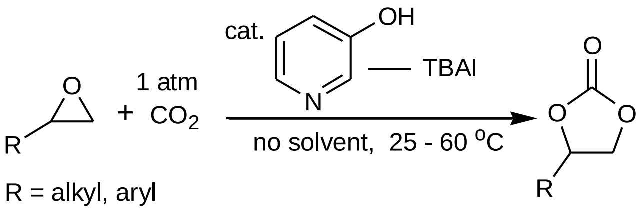
^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 or AV-500 spectrometers. The chemical shifts of the products were reported in ppm with reference to Me_4Si as the internal standard in CD_3OD and $CDCl_3$.

4.4.1. General procedure for the synthesis of cyclic carbonates from CO_2 and epoxides

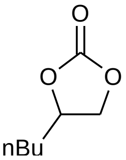
A 5 mL Schlenk flask was charged with epoxide (5 mmol), hydroxypyridine (0.25 mmol), and tetrabutylammonium halide (0.25 mmol), and a CO_2 balloon (20 cm of diameter) was connected to the flask (1 atm). The total volume of the gas phase, including the connection, was approx. 4.2 L. The reaction mixture was set to the relevant temperature and stirred for 24 h. The reaction mixture was allowed to cool to room temperature and the product was isolated by silica gel column chromatography using a mixture of hexane and ethyl acetate (1:1-2:1, v/v) as an eluent.

In order to examine the effect of water on catalytic activity, the above procedure was used, but with the known amounts of distilled water added into the reactor.

4.4.2. Representative procedure for the cyclic carbonate formation



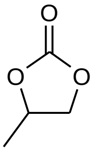
All cyclic organic carbonate products have been reported previously and the data given below are in agreement with the literature data.



4-Butyl-1,3-dioxolan-2-one[23,27,38]

In a 5 mL Schlenk flask, 1,2-epoxyhexane (5 mmol, 0.51 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.69 g (yield: 95.0%) as a colorless oil.

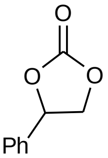
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 4.77-4.68 (m, 1H), 4.57-4.52 (m, 1H), 4.11-4.05 (m, 1H), 1.82-1.68 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 77.3, 69.4, 33.4, 26.4, 22.2, 13.7.



Propylene carbonate[23,27,38]

In a 5 mL Schlenk flask, propylene oxide (5 mmol, 0.29 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.44 g (yield: 86.3%) as a colorless oil.

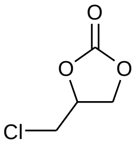
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 4.92-4.80 (m, 1H), 4.62-4.51 (m, 1H), 4.10-3.95 (m, 1H), 1.55-1.40 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 73.7, 70.7, 19.3.



4-Phenyl-1,3-dioxolan-2-one[23,27,38]

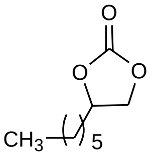
In a 5 mL Schlenk flask, styrene oxide (5 mmol, 0.60 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.78 g (yield: 95.0%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.44-7.38 (m, 3H), 7.36-7.34 (m, 2H), 5.68-5.65 (m, 1H), 4.80-4.77 (m, 1H), 4.33-4.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.1, 135.8, 129.7, 129.2, 120.0, 77.6, 71.2. Mp 50-52 °C.[39]



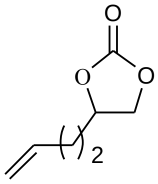
4-(Chloromethyl)-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, epichlorohydrin (5 mmol, 0.46 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.65 g (yield: 96.0%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 5.12-5.01 (m, 1H), 4.69-4.55 (m, 1H), 4.48-4.35 (m, 1H), 3.89 (dd, 1H), 3.77 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.8, 74.7, 67.0, 44.6.



4-Hexyl-1,3-dioxolan-2-one[23,27]

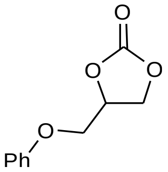
In a 5 mL Schlenk flask, 1,2-epoxyoctane (5 mmol, 0.64 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.78 g (yield: 91.0%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 4.79-4.68 (m, 1H), 4.61-4.50 (m, 1H), 4.15-4.02 (m, 1H), 1.85-1.62 (m, 2H), 1.55-1.21 (m, 8H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.4, 22.4, 13.9.



4-(But-3-en-1-yl)-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, 1,2-epoxy-5-hexene (5 mmol, 0.49 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.66 g (yield: 93.0%) as a colorless oil.

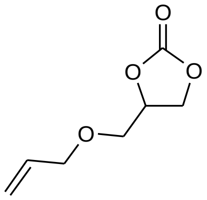
^{1}H NMR (500 MHz, CDCl$_3$) δ ppm: 5.87-5.61 (m, 1H), 5.18-4.91 (m, 2H), 4.76-4.61 (m, 1H), 4.59-4.42 (m, 1H), 4.15-3.95 (m, 1H), 2.30-2.01 (m, 2H), 1.95-1.65 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm: 155.1, 136.3, 116.0, 76.4, 69.4, 32.8, 28.5.



4-(Phenoxymethyl)-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, 1,2-epoxy-3-phenoxy propane (5 mmol, 0.75 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.83 g (yield: 86.0%) as a white solid.

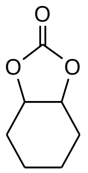
^{1}H NMR (500 MHz, CDCl$_3$) δ ppm: 7.36-7.22 (m, 2H), 7.06-6.92 (m, 1H), 6.91-6.85 (m, 2H), 5.06-4.95 (m, 1H), 4.65-4.56 (m, 1H), 4.55-4.46 (m, 1H), 4.22 (dd, 1H), 4.12 (dd, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm: 157.8, 154.7, 129.7, 122.0, 114.6, 74.2, 66.8, 66.2. Mp 98-99 °C.[40]



4-Allyloxymethyl-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, allyl glycidyl ether (5 mmol, 0.57 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.72 g (yield: 91.0%) as a colorless oil.

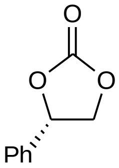
^{1}H NMR (CDCl$_3$, 500 MHz) δ ppm: 5.95-5.80 (m, 1H), 5.35-5.12 (m, 2H), 4.93-4.80 (m, 1H), 4.60-4.45 (m, 1H), 4.44-4.30 (m, 1H), 4.11-3.99 (m, 2H), 3.75-3.65 (m, 1H), 3.64-3.52 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ ppm: 155.1, 133.8, 117.3, 75.4, 72.2, 68.9, 66.2.



Hexahydro-benzo[1,3]dioxol-2-one[23,27]

In a 5 mL Schlenk flask, cyclohexene oxide (5 mmol, 0.49 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.1 g (yield: 14.0%) as a colorless oil.

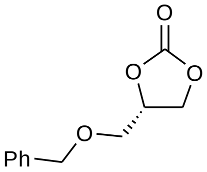
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 4.76-4.59 (m, 2H), 2.0-1.79 (m, 4H), 1.72-1.53 (m, 2H), 1.51-1.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 155.35, 75.73, 26.78, 19.17.



(*S*)-4-Phenyl-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, (*R*)-styrene oxide (5 mmol, 0.60 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C and 60 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.69 g (yield: 84.1%, 40 °C) and 0.76 g (yield: 93.0%, 60 °C) as a white solid. The *ee* of the product was determined by chiral HPLC measurement using Chiralcel IB-3, 10% IPA/hexane, 1 mL/min, 40 °C (t_R = 21.58 min, t_S = 24.96 min), 60 °C (t_R = 18.96 min, t_S = 21.52 min), 254 nm. Partial racemization of the product relative to the starting material was observed (*ee*: 92%, 40 °C) and (*ee*: 84%, 60 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.44-7.42 (m, 3H), 7.37-7.35 (m, 2H), 5.68-5.66 (m, 1H), 4.81-4.78 (m, 1H), 4.35-4.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.9, 135.8, 129.7, 129.2, 125.9, 77.3, 71.2.



(*R*)-4-Benzyloxymethyl-1,3-dioxolan-2-one[23,27]

In a 5 mL Schlenk flask, (*R*)-glycidyl benzyl ether (5 mmol, 0.81 g), 3-hydroxypyridine (0.25 mmol, 0.024 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 24 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.93 g (yield: 89.4 %) as a colorless oil. The *ee* of the product was determined by chiral HPLC measurement using Chiralcel IB-3, 10% IPA/hexanes, 1 mL/min, t_R =38.48 min, t_S = 51.72 min, 254 nm. Partial racemization of the product relative to the starting material was observed (*ee*: 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.35-7.30 (m, 5H), 4.81-4.78 (m, 1H), 4.59 (q, 2H), 4.46 (t, 1H), 4.38 (dd, 6.5 Hz, 1H), 3.69 (dd, 3.5 Hz, 1H), 3.61 (dd, 3.5 Hz, 1H) ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.96, 137.10, 128.57, 128.08, 127.75, 75.03, 73.68, 68.84, 66.28.

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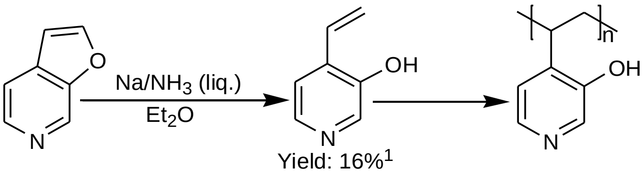
Chapter 5 Development of an efficient polymer organocatalytic system poly(4-vinylphenol)/TBAI for synthesis of cyclic carbonates from CO_2 and epoxides

5.1. Introduction

We reported an efficient organic system 3-hydroxypyridine/TBAI for the formation of cyclic carbonates under mild reaction conditions (25-60 ^{o}C, 1 atm CO_2). 3-Hydroxypyridine/TBAI system exhibited good activity and excellent stability even in the presence of a minor component such as water, air and O_2. From these results we planned to develop a polymer poly(4-vinyl-3-hydroxypyridine) base on the 3-hydroxypyridine structure (Scheme 5-1). Synthesis of 4-vinyl-3-hydroxypyridine, the monomer of poly(4-vinyl-3-hydroxypyridine), has been reported[1] but it was obtained in lower yield by Brich reduction of furo[2,3-c]pyridine. Therefore, it seemed apparent that the polymer synthesis has some difficulties and is not economical.



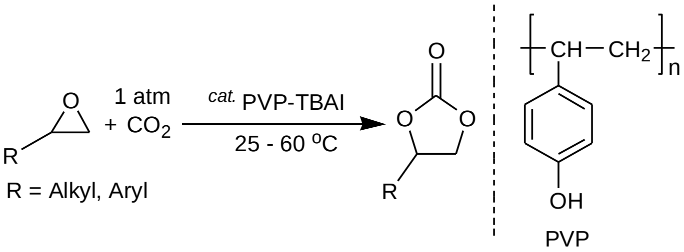
Scheme 5-1. A possible synthetic route for poly(4-vinyl-3-hydroxypridine).

It is widely accepted that hydrogen bond donors (HBDs) have the ability to accelerate the cycloaddition reaction of CO_2 and epoxides,[2-10] and some research groups have used phenol derivatives in combination with 4-dimethylaminopyridine (DMAP),[4] NaI/PPh_3,[5] n-Bu_4NI,[6,9,10] and n-Bu_4NBr.[7] Huang and Shi first applied phenol[4] and reported a combination with NaI/PPh_3.[5] However, high temperatures and/or pressures, often above 100 ^{o}C and 1 MPa, were necessary to achieve high conversions of epoxides. As the improved systems, Kleij *et al.* proposed efficient (multi)phenolic compound/n-Bu_4NI combinations, which have achieved a breakthrough in temperature condition but the pressure condition remained as a challenge of research.[6,10]

Recently, on the other hand, many functional polymers have been used as catalysts or catalyst supports for the conversion of CO_2 into cyclic carbonates.[11-16] In spite of their potential effectiveness, the requirements of high pressure, high temperature, and well-designed but tedious catalyst synthesis are disadvantages.

For the development of effective and practical polymer-based catalytic systems, two major problems need to be solved or addressed. One is how to easily separate a catalyst from the product or the reaction mixture and the other is how to lessen the use of solvents under mild conditions. Kleij and Pericàs reported that solvent-free polymer system based on polystyrene supported pyrogallol for the conversion of CO_2 and oxiranes into cyclic carbonates under attractive conditions,[14] but still the multi-step synthesis of the polymer and high pressure were required for reaction. It is important to develop an active and easy-to-handle catalytic system for the cycloaddition reaction of CO_2 and epoxides at a low reaction temperature and pressure.

We were interested in poly(4-vinylphenol) (PVP) that can be a homogeneous catalyst under certain conditions and can be separated as a solid from the products easily. In addition, polymeric phenols as catalysts are expected to be more stable and tolerant to oxidation than simple phenol derivatives. We started to work on a practical route for the synthesis of cyclic carbonates using an easily recyclable PVP and tetra-*n*-butylammonium iodide (TBAI) catalytic system (Scheme 5-2) that exhibits significant activity, providing good to excellent yields of the desired products under mild conditions, at a low temperature of 25-60 ^oC and atmospheric pressure of CO_2, and without using any solvents.

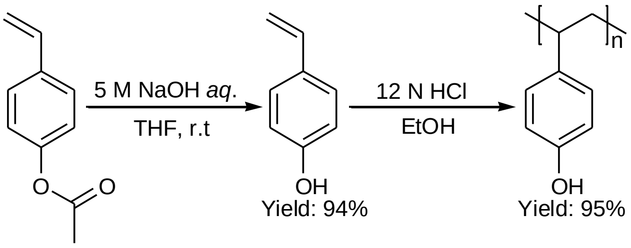


Scheme 5-2. Synthesis of cyclic carbonates from CO_2 and epoxides.

5.2. Results and discussion

5.2.1. The synthesis of PVP

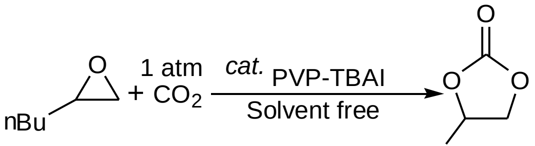
According to the literature method[17], the synthesis of the PVP could be achieved in two simple steps from commercially available starting materials and is shown in Scheme 5-3. Hydrolysis of 4-acetoxystyrene afforded 4-vinylphenol under basic condition. Polymerization of 4-vinylphenol in the presence of 12 N HCl afforded PVP with low M_n values (~ 4.9×10^3). However, we discovered PVP is commercially available that maybe convenient for our research. Therefore, commercially available PVP was chosen as a catalyst in the following research.



Scheme 5-3. Synthesis of poly(4-vinylphenol) (PVP).

5.2.2. Effect of reaction temperature

First, the effect of the reaction temperature on the cycloaddition reaction was studied for 1,2-epoxyhexane (**1a**) under 1 atm of CO_2. As is easily seen from Figure 5-1, the activity of the catalytic system was high and largely dependent on the reaction temperature, as the yield of 4-butyl-1,3-dioxolan-2-one (**1b**) increased from 81% at 25 °C to 99% at 40 °C. However, when the reaction temperature was raised to 50 °C, the conversion to **1b** slightly decreased to 96%. A further increase in temperature caused further decrease (90% yield at 60 °C). Probably it is due to the side reactions between PVP and TBAI and **1a**, as will be discussed later. Other conditions were further optimized at 40 °C and atmospheric pressure of CO_2.



1a **1b**

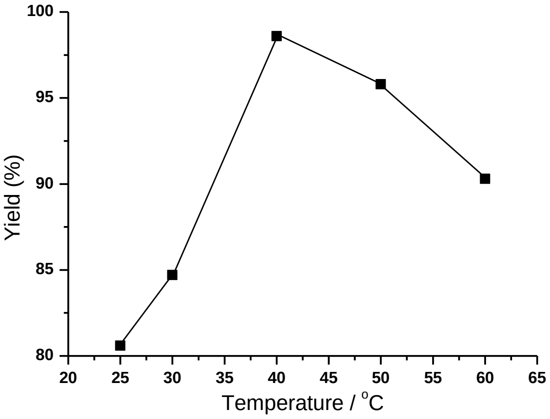
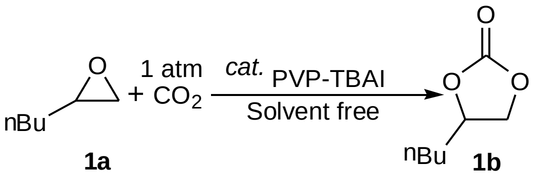


Figure 5-1. Effect of reaction temperature on the yield of **1b** by PVP-TBAI. Reaction conditions: **1a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), 22 h.

5.2.3. Effect of catalyst amount



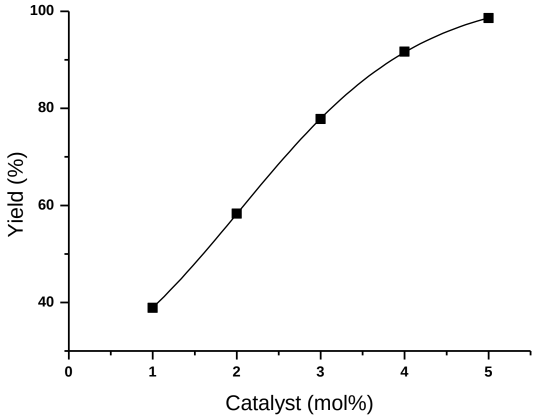


Figure 5-2. Effect of the amount of PVP-TBAI (1:1) on the yield of **1b**. Reaction conditions: **1a** (5.0 mmol), PVP-TBAI (1.0-5.0 mol%), CO_2 (1 atm), 22 h, 40 °C.

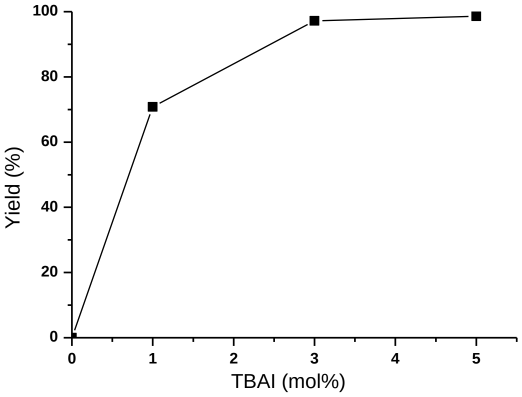
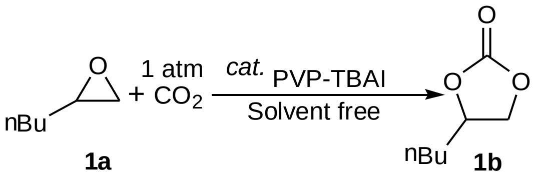


Figure 5-3. Effect of the catalyst activity of TBAI on the yield of **1b**. Reaction conditions: **1a** (5.0 mmol), PVP (5.0 mol%), CO_2 (1 atm), 40 °C, 22 h.

The effect of the amount of the catalysts, PVP and TBAI (1:1), was evaluated, and the results are shown in Figure 5-2. Even when the catalyst amount was as low as 1 mol% with respect to **1a**, the coupling reaction proceeded smoothly to give **1b** in 39% yield. It is clear that the catalytic system is active for the coupling reaction of an epoxide with CO_2. Above 3 mol%, the yield increase tends to lower gradually. However, when 5 mol% of the catalyst was used, the isolated yield reached to 99%, which was set as the optimum amount for the next recycling experiment study. The effect of the catalyst activity of TBAI was investigated in the presence of PVP (5.0 mol %) at 40 °C and 22 h, and the results were shown in Figure 5-3.

5.2.4. Effect of reaction time

The time dependence of the yield was investigated by a series of experiments that were identical except for the reaction time. As shown in Figure 5-4 (I), the reaction time also has a significant influence on the reaction yield. The reaction proceeded slowly in the first 4 h, probably because TBAI has poor solubility in **1a** while PVP has good solubility. This aspect was confirmed to be reproducible. Therefore, it takes some time for the catalytic system to exert its potential until TBAI dissolves in the reaction mixture as the production of **1b**. The yield increased to approximately 50% after 6 h and reached 89% after 12 h. Under the present static conditions (1 atm of CO_2), a reaction time of 22 h was necessary to achieve quantitative yield of **1b**.



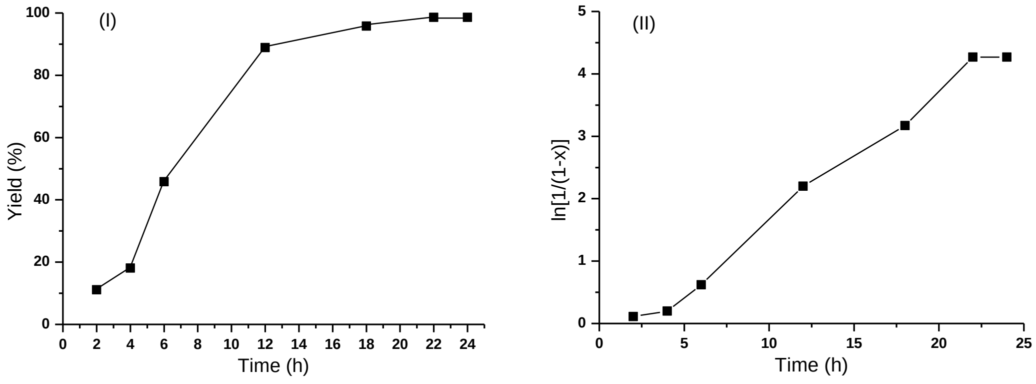


Figure 5-4. (I) Effect of reaction time on the yield of **1b** and (II) rate of the reaction of **1a** with CO_2 by PVP-TBAI. Reaction conditions: **1a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), 40 °C, CO_2 (1 atm).

It has been verified that the synthesis of cyclic carbonates from CO_2 and epoxides obey the first order kinetics according to previous study.[18] Therefore, the rate equation for the reaction catalyzed by PVP and Bu_4NI can be written as Eq. (1).

$$r = \mathrm{k}[\mathrm{epoxide}][\mathit{Cat.}][\mathrm{CO_2}] \qquad (1)$$

The catalyst concentration did not change, and the CO_2 concentration change was negligible during the reaction, so the pseudo first-order rate equation can be applied as Eq. (2). Taking the logarithm of Eq. (2) leads to Eq. (3).

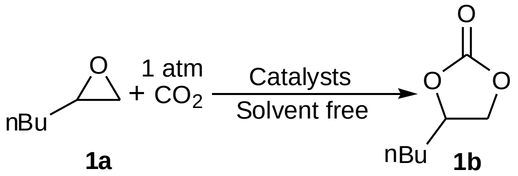
$$r = -\mathrm{d[epoxide]/dt} = \mathrm{k[epoxide]} \qquad (2)$$

$$\ln[\mathrm{epoxide}]_{t=0} - \ln[\mathrm{epoxide}] = \mathrm{kt} \quad \text{or} \quad \ln[1/(1-x)] = \mathrm{kt} \qquad (3)$$

where x is the conversion rate of epoxide, t is the reaction time, k is the reaction rate constant. Under the optimal reaction conditions, the conversion rate of **1a** was calculated at 40 °C, to get the values of ln[1/(1-x)] and a plot of ln[1/(1-x)] against reaction time in Figure 5-4 (II), where x was the conversion rate of **1a**. A linear relationship was observed in this case. Therefore, the **1a**-CO_2 reaction was confirmed to be the first order one with respect to the concentration of **1a**.

5.2.5. Effect of co-catalyst

Table 5-1. Reaction of 1,2-epoxyhexane with CO_2 using various catalysts[a].



Entry	Catalyst	Co-catalyst	T (°C)	Yield[c] (%)
1	PVP	*n*-Bu_4NI	25	81
2	PVP	*n*-Bu_4NI	40	99
3[b]	PVP	*n*-Bu_4NI	40	97
4	PVP	-	40	0
5	-	*n*-Bu_4NI	40	10
6	*p*-cresol	*n*-Bu_4NI	40	97
7	catechol	*n*-Bu_4NI	40	97
8	pyrogallol	*n*-Bu_4NI	40	97
9	PVP	*n*-Bu_4NBr	40	49
10	PVP	*n*-Bu_4NCl	40	25
11	PVP	Et_3N	60	Trace
12	PVP	DMAP	60	Trace
13	PVP	DBU	60	Trace

[a] Reaction conditions: **1a** (5.0 mmol), Catalyst (5.0 mol%), Co-catalyst (5.0 mol%), CO_2 (1 atm), 22 h, 40

°C, Solvent-free. [b] Self-synthesized PVP as catalyst. [c] Isolated product obtained after chromatographic purification.

In order to raise the reaction efficiency, various ammonium salts and organic bases were also studied as a co-catalyst of PVP, and the yields of **1b** are summarized in Table 5-1. As mentioned above, when PVP was combined with TBAI (*n*-Bu_4NI) as a binary catalytic system, a good yield was obtained at ambient temperature (Table 5-1, entry 1) and a nearly quantitative yield was obtained at 40 °C (Table 5-1, entry 2). Self-synthesized PVP also showed good activity comparable to with the commercially available PVP (Table 5-1, entry 3). When PVP was used as a single catalyst, no reaction occurred (Table 5-1, entry 4). On the other hand, a low yield of 10% was obtained when *n*-Bu_4NI was used as the sole catalyst (Table 5-1, entry 5). These results support the proposed mechanism[19] in which OH group and halide ion work synergistically, by activating the epoxide ring through hydrogen bonding and opening the ring nucleophilically, respectively. The combinations of phenolic compound-TBAI systems were examined using *p*-cresol, catechol and pyrogallol with no solvents (Table 5-1, entries 6-8). *p*-Cresol was chosen as a model of the repeating unit of PVP. These phenols afforded high yields of 97% and the results are comparable to that of entry 2. The results clearly indicate that the present polymeric system works just as the low-molecular weight phenolic compounds because PVP dissolves well in the reaction mixture.

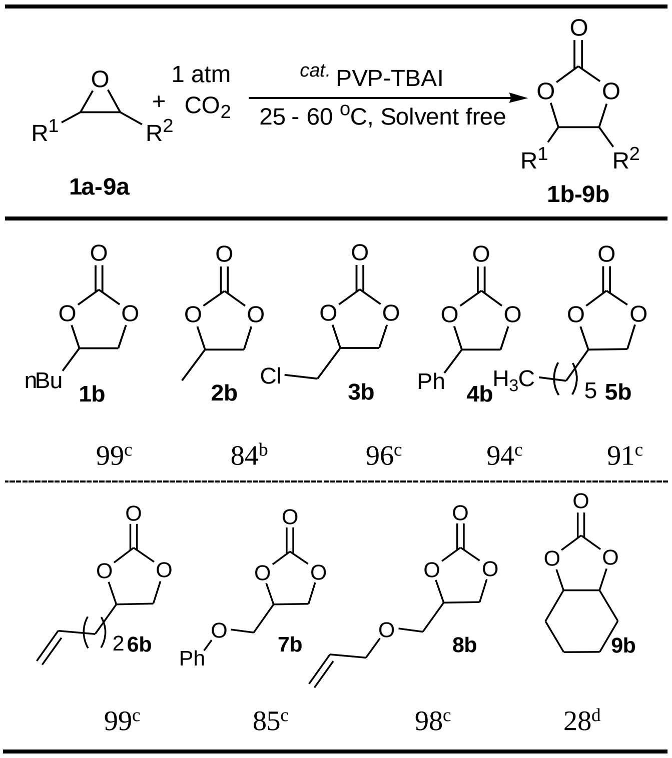
In order to study the effect of the halide ion, *n*-Bu_4NBr and *n*-Bu_4NCl were applied in combination with PVP (1:1). The yield decreased by a factor of 0.5 in the order I^- (99%) > Br^- (49%) > Cl^- (25%) when these binary catalytic systems were used (Table 5-1, entries 9 and 10 vs. entry 2), as has often been reported.[3,20-24] Considering that the intrinsic activity and nucleophilicity increase in the order Cl^- > Br^- > I^-,[3,24] the results are often interpreted based on the leaving ability of the halide ion, which decreases in the order I^- > Br^- > Cl^-. For hydroxyl group-halide ion systems, Büttner group[25] and Kühn group[26] have suggested that the effect of hydrogen bond interactions between the OH group and halide ion is stronger for Cl^- than for Br^-, and even stronger than for I^-, which may also affect the effect of halide ion.

Some reports have suggested that acids and/or bases also work together to activate an epoxide ring and CO_2 to give the corresponding cyclic carbonate.[8,27,28] Under the present screening conditions, triethylamine (Et_3N) was studied as a co-catalyst of PVP, but showed the lowest activity; it gave no product at 40 °C, and only a trace amount of **1b** was obtained at 60 °C (Table 5-1, entry 11). As organic bases, DMAP and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were studied in combination with PVP, and also showed the lowest activity, and only trace amount of **1b** was obtained at 60 °C, respectively (Table 5-1, entries 12 and 13).

5.2.6. Cycloaddition of CO_2 and various epoxides

In order to study the efficiency and applicability of the developed catalytic system, the cycloaddition of CO_2 and various epoxides was studied under the optimized reaction conditions using PVP and TBAI, and the results are summarized in Table 5-2. The catalytic system effectively converted terminal epoxides into the corresponding cyclic carbonates in yields of 84-99% without the use of any solvents. The lower yield of **2b** should be due to the low boiling point (34 °C) of **2a**, which makes the interaction with the catalysts less effective. For **7a**, precipitation of the product (**7b**) lowered the yield by disturbing efficient stirring of the reaction mixture. In addition, cyclohexene oxide (**9a**), a challenging 1,2-disubstituted epoxide, was converted to the corresponding carbonate (**9b**) in only 28% yield because of the steric hindrance from the substituents.[29,30]

Table 5-2. Reactions of various epoxides with CO_2 using the PVP-TBAI catalytic system[a].



[a] Reaction conditions: Epoxide (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), solvent-free, 22 h. [b] 25 °C. [c] 40 °C. [d] 60 °C. Isolated product obtained after chromatographic purification.

5.2.7. Early-stage kinetic comparison between 1,2-epoxyhexane (1a), epichlorohydrin (3a), and styrene oxide (4a)

To understand the characteristics of the present system, the kinetic profile was studied for three epoxides: **1a**, **3a**, and **4a**. The time dependence of the yields in the first 8 h was compared in Figure 5-5. Interestingly, the activity of **3a** was approximately four times higher than that of **1a** in the first hour. This is because **3a** has higher reactivity owing to its electron-withdrawing chloromethyl group and because TBAI has higher solubility in **3a** than in **1a**. However, the yield of **3b** was not as high as that of **1b** after 22 h (Table 5-2). As seen in Figure 5-5, the yield of **3b** increased slowly while that of **1b** increased quickly after 4 h as mentioned above for Figure 5-4.

On the other hand, the activity of **4a** was almost the same as that of **1a** on the first 4 h because the reactivity is lower than **3a** and **1a** and because TBAI is not very soluble in it, which led to a slightly lower yield of **4b** than of **1b** and **3b** (Table 5-2). It is known that **4a** is less reactive owing to not only the presence of a sterically bulky phenyl group but also the reduced preference for C_β (least-substituted carbon) compared to the benzylic position of C_α (most-substituted carbon).[31]

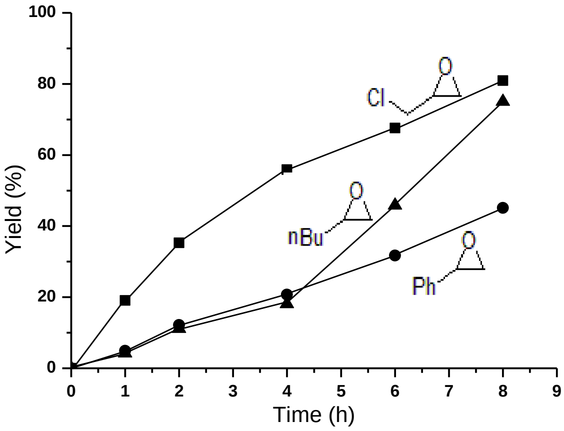


Figure 5-5. Comparative kinetics of **1a** (▲), **3a** (■) and **4a** (●) as the substrates for the PVP-TBAI system. Reaction conditions: Epoxide (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), CO_2 (1 atm), 40 °C.

5.2.8. Recyclability of PVP-TBAI catalytic system

Considering recyclability and stability are important features for practical application, the present PVP-TBAI system were investigated. The catalysts were recycled as described for each system in Experimental and applied to subsequent reactions after drying under reduced pressure.

5.2.8.1 1,2-Epoxyhexane (**1a**)

The recyclability of the PVP-TBAI system was first investigated using **1a** as the reactant, and the results are shown in Figure 5-6. There seemed to be no major damage to the system and yield higher than 90% was obtained in each of seven successive reaction cycles. In the eighth and ninth reactions, however, the yield became lower than 90%, and was only 74% in the tenth cycle.

In order to investigate the cause of the reduction in catalytic activity, the retrieved catalytic system was washed with H_2O and subjected to ^{1}H nuclear magnetic resonance (NMR) analysis. The spectrum clearly showed an increase in the intensity of signals attributed to protons on aliphatic (1.05-0.96, 1.43-1.37, 1.66-1.63, 3.27-3.16 ppm) and ethereal (3.86 ppm) carbons (Figure 5-7A vs. Figure 5-7B). This result suggests that PVP reacted with both TBAI and **1a** to yield ammonium phenolate salt and phenyl ether, respectively.

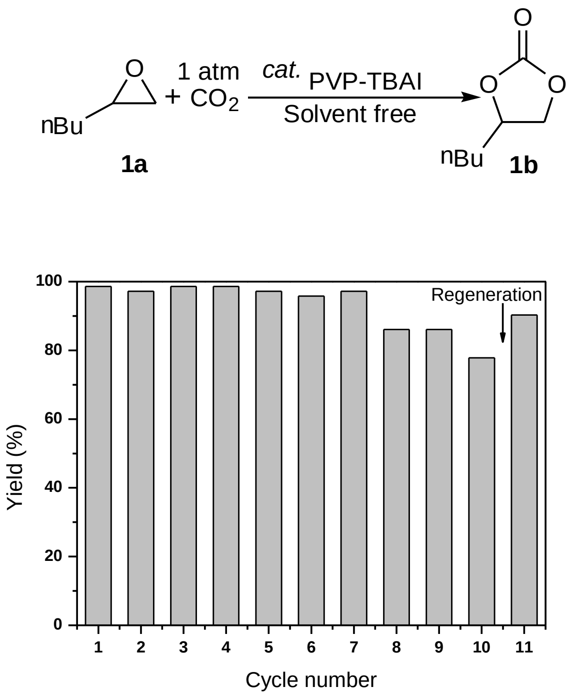


Figure 5-6. Recyclability study of the PVP-TBAI system for **1a** as a reactant. Reaction conditions: **1a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), 40 °C, CO_2 (1 atm), 22 h. The catalyst was regenerated after cycle 10.

In order to recycle a catalytic system, the catalysts need to be regenerated and some treatment methods have been reported.[9,14,16] For example, Kleij *et al.* reported the regeneration of tannic acid by concentrated HCl (37%) treatment of the isolated solid fraction separated from the recycling experiments.[9] Here, in this study, recovery of the catalytic ability of PVP was investigated by treating with some acids and H_2O. It was found that the activity was recovered most effectively when the precipitated solid was treated with 40% CH_3CO_2H *aq*. at 40 °C for 1 h. The ^{1}H NMR spectra of the treated PVP showed that the number of aliphatic protons relatively decreased (Figure 5-7C), although oxymethylene signals remained, as expected; that is, only tetra-*n*-butylammonium (TBA) cation was exchanged with a proton to regenerate phenolic OH, but the ether bond was not hydrolyzed significantly.

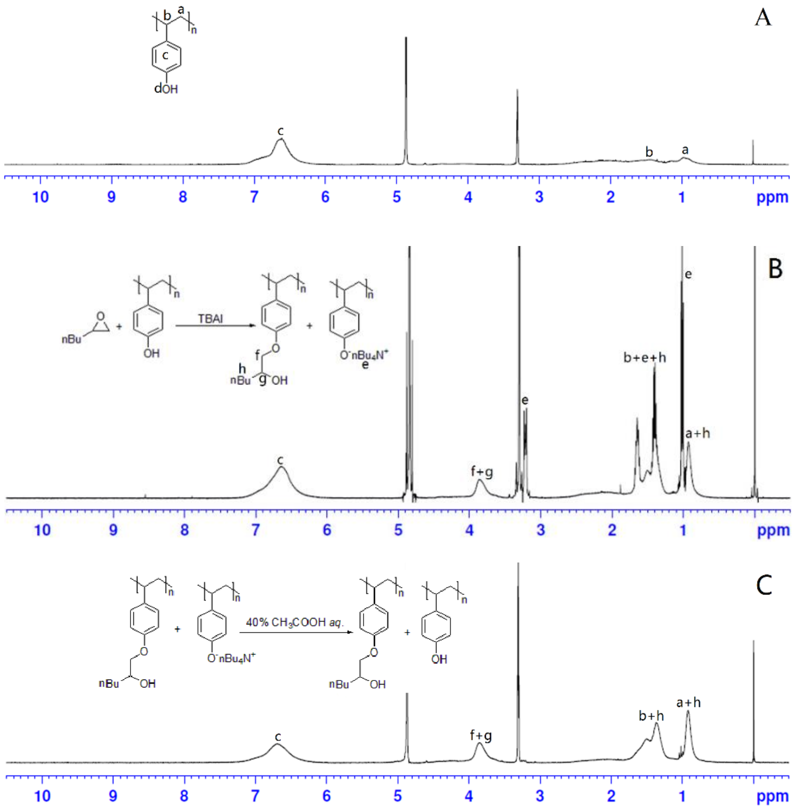


Figure 5-7. ^{1}H NMR spectra of PVP reacted with 1,2-epoxyhexane and TBAI (B), treatment of the catalytic system with acetic acid solution (C) and pure PVP (A) in CD_3OD.

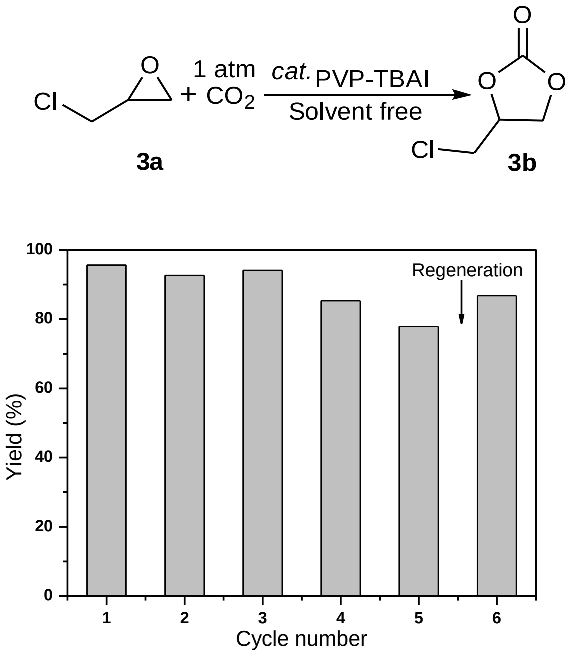


Figure 5-8. Recyclability study of the PVP-TBAI system for **3a** as a reactant. Reaction conditions: **3a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), 40 °C, CO_2 (1 atm), 22 h. The catalyst was regenerated after

cycle 5.

After treatment with CH_3CO_2H *aq*., PVP was applied to carbonate synthesis again with new TBAI (5 mol%). A greatly improved yield higher than 90% (from 74% yield in the tenth experiment) was obtained as seen in Figure 5-6. As a result, it was clearly shown that the reaction between PVP and TBAI was a major cause of the yield reduction, which can be addressed by treatment with CH_3CO_2H *aq*. and the reaction with the substrate seems to be a minor cause for **1a**, but its effect cannot be recovered easily.

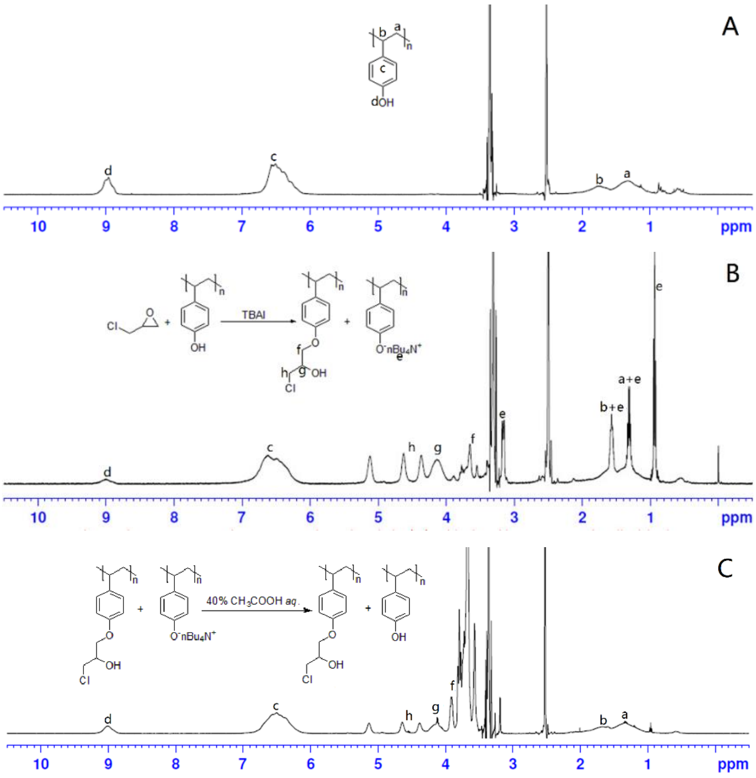


Figure 5-9. ^{1}H NMR spectra of PVP reacted with epichlorohydrin and TBAI (B), treatment of the catalytic system with acetic acid solution (C) and pure PVP (A) in DMSO-d_6.

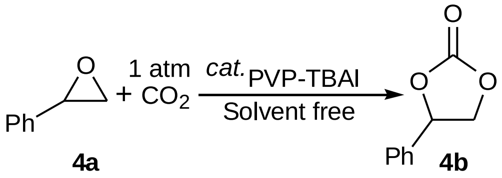
5.2.8.2. Epichlorohydrin (3a)

The recyclability of the catalytic system was studied for **3a**, which has higher reactivity than **1a**, and the result is shown in Figure 5-8. Reaction yields higher than 90% were obtained for three cycles, but the reactivity dropped much earlier compared to seven cycles for **1a**. As a result, the yield was 85% in the fourth run and a further reduction to 78% was observed in the fifth run.

The ^{1}H NMR analysis of the retrieved PVP revealed a similar but more complex spectral change at 3-5 ppm, suggesting some side reactions with **3a** (Figure 5-9B). After treatment with aqueous CH_3CO_2H, the aliphatic proton signals at 1-2 ppm were reduced, but those around 3-5 ppm mostly remained unchanged (Figure 5-9C). When the retrieved PVP was used for the carbonate synthesis reaction, the yield recovered to 87% (vs. 78% for the untreated retrieved PVP). As mentioned above, because of its higher reactivity due to the chloromethyl group, **3a** tends to react with the hydroxy group of PVP more easily and frequently than **1a** does. Therefore, the recyclability and recovery of the catalytic system were lower than those observed for **1a**.

5.2.8.3. Styrene oxide (**4a**)

In order to continue to prove the influence of the reactant, **4a** was also studied, as it gives a high yield of **4b**. As shown in Figure 5-10, the catalyst was recycled more than for **3a** and the yield remained higher than 90% for six cycles. After washing the retrieved precipitate with H_2O, the change in PVP was almost the same as that observed for **1a** (Figure 5-11B), and the TBA cation seemed to be removed after treatment with aqueous CH_3CO_2H (Figure 5-11C). As a result, the yield recovered to 88% in the ninth run from 81% after eight successive reaction cycles.



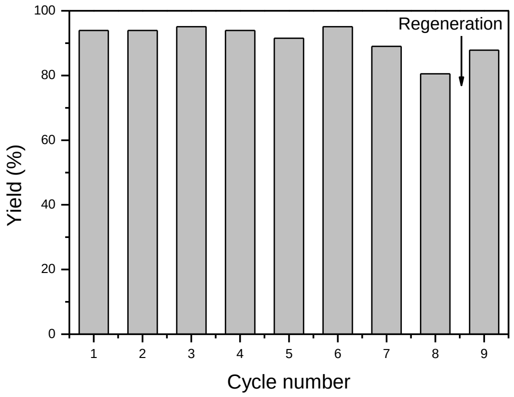


Figure 5-10. Recyclability study of the PVP-TBAI system for **4a** as a reactant. Reaction conditions: **4a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), 40 °C, CO_2 (1 atm), 22 h. The catalyst was regenerated after cycle 8.

5.2.9. Effect of CO_2 content

Although highly pure CO_2 (>99%) was used for the reaction with epoxides thus far, CO_2 purity in the feed gas is an important factor for practical applications. The effect of a second gas component was investigated using **1a** and CO_2/N_2 mixtures of various CO_2 volume fractions (9.93%, 39.9%, 67.1% and >99%). When the content of CO_2 was 9.93%, the yield of **1b** was 25%, while the reaction proceeded smoothly to give an 86% yield when the CO_2 content was increased to 67%. As shown in Figure 5-12, the yield of carbonate increased with the CO_2 content (or CO_2 partial pressure), showing that the present system has good practical applicability.

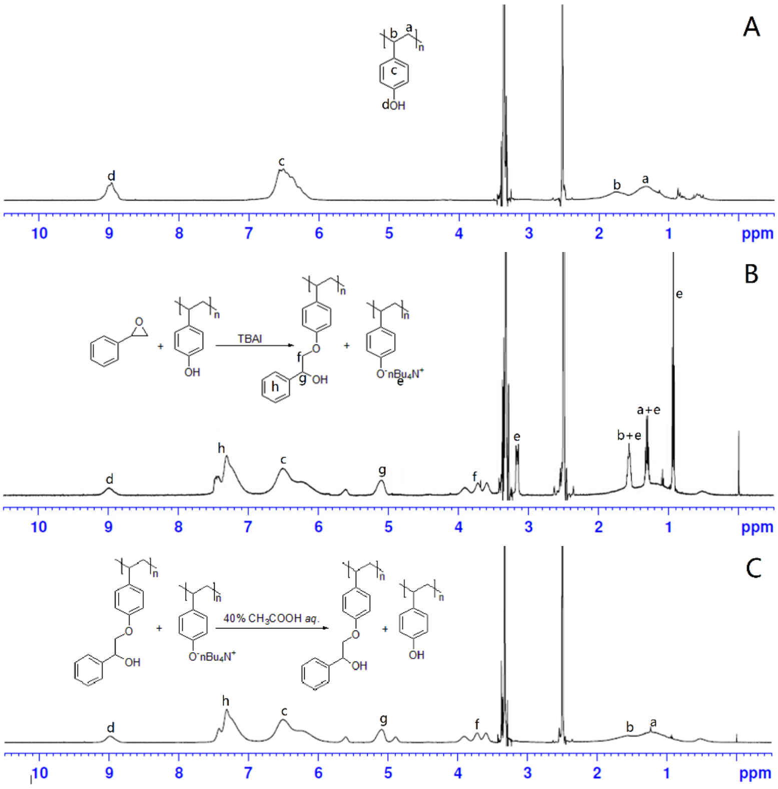


Figure 5-11. ^1H NMR spectra of PVP reacted with styrene oxide and TBAI (B), treatment of the catalytic system with acetic acid solution (C) and pure PVP (A) in DMSO-d_6.

5.3. Conclusions

We developed a facile protocol using highly active and recyclable PVP with TBAI for the catalytic synthesis of cyclic carbonates from CO_2 and terminal epoxides under solvent-free conditions. Various cyclic carbonates were obtained in high yields under mild conditions (25-60 ^oC and atmospheric pressure of CO_2). The present catalytic system has the advantages of being commercially available, environmentally benign, and metal-free, and can be applied under homogeneous conditions. So the reaction is expected to proceed smoothly by the attack of I^- to an epoxide activated by OH group of PVP and then by the reaction of alkoxide ion with CO_2 as proposed previously.[19]

It was also found that the catalytic system could be easily separated and recycled more than six times and give yields higher than 90% for 1,2-epoxyhexane and styrene oxide, while it was deactivated sooner for epichlorohydrin (three times) owing to more frequent and complex reactions with PVP, which was suggested by ^{1}H NMR analysis. Importantly, in addition, the catalyst activity was restored by treating with 40% aqueous CH_3CO_2H. Our future work will be focused on merging these concepts with the design of organocatalytic systems with improved reusability and stability that can still provide high yields of carbonate. Although additional feed of TBAI for the recycle use of the present system, it is worth to be mentioned that TBAI is less expensive than PVP.

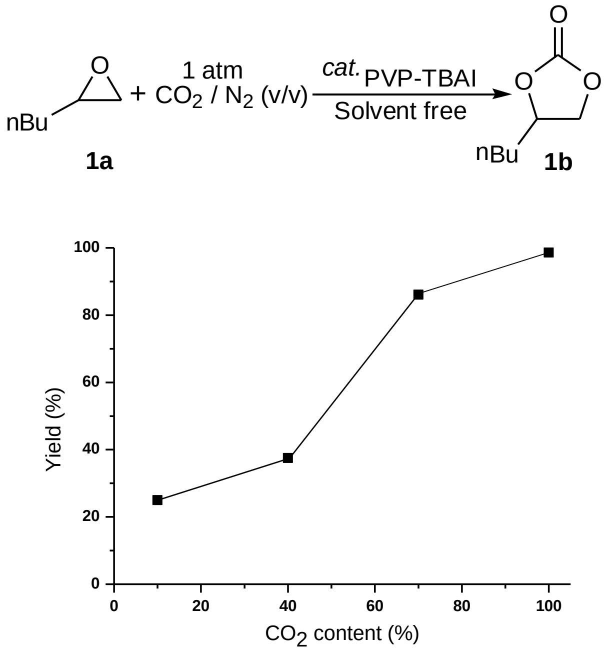


Figure 5-12. Effect of CO_2 content in the feed gas (CO_2/N_2) on the catalytic activity for the synthesis of **1b** by PVP-TBAI. Reaction conditions: **1a** (5.0 mmol), PVP (5.0 mol%), TBAI (5.0 mol%), gas mixture (1 atm), 22 h, 40 °C. CO_2 purities were 9.93%, 39.9%, 67.1%, and >99.99% (CO_2 / N_2, vol%).

5.4. Experimental

All commercially available starting materials and solvents were purchased and used as received unless indicated otherwise. Poly(4-vinylphenol) (PVP: Mw~11,000) was purchased from Aldrich. Carbon dioxide (99.99% pure) and CO_2/N_2 mixtures (CO_2 purities: 67.1%, 39.9%, and 9.93%) were used as received without further purification and dried prior to use (Tokyo Koatsu Yamazaki Co. Ltd.).

The number-average molecular weight (M_n) and molecular weight distribution (MWD, M_w/M_n) of the self-synthesis polymer were measured by gel permeation chromatography (GPC) in THF at 40 °C with a Shodex GPC KF-806 L column (flow rate: 1.0 mL/min). The

M_n was calibrated with polystyrene standards (TSK: 945-7.1 × 10^5, $M_w/M_n \leq 1.1$).

^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. The chemical shifts of the products were reported in ppm with reference to Me_4Si as an internal standard in CD_3OD, $CDCl_3$, and DMSO-d_6.

5.4.1. Synthesis of Poly(4-vinylphenol)

Poly(4-vinylphenol) (PVP) was prepared by slight modification of the reported method.[17] To a two-necked 100 mL round-bottom flask under nitrogen and fitted with a stir bar was added commercially available 4-acetoxystyrene (3.0 g, 18.5 mmol) and tetrahydrofuran (20 mL). After deoxygenation via the water vacuum air exhaust (ultrasonic vibration) method (3 times), the flask was backfilled with nitrogen, and a 5 M solution of aqueous sodium hydroxide (20 mL, sparged with nitrogen) was syringed into the reaction mixture. The reaction was stirred at room temperature for 1 h or until the reaction was complete as indicated by TLC (SiO_2: Rf = 0.7, 30% ethyl acetate/hexanes). The crude reaction mixture was chilled to 0 °C, at which time 4 N HCl (15 mL) was added slowly until a pH of neutral was reached. The product was extracted into ethyl acetate, washed with distilled water three times, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The resultant oily product was precipitated into cold hexanes, decanted, and dried under vacuum to yield 4-vinylphenol (2.1 g, 94.0%) as a white powder which was immediately polymerized as described in the literature. A two-necked 100 mL round-bottom flask under nitrogen fitted with a stir bar was charged with 4-vinylphenol (2.0 g, 16.7 mmol) and ethanol (20 mL) while a second flask, also under nitrogen, was charged with ethanol (10 mL) and 12 N HCl (5 mL). Both flasks were deoxygenated via the freeze-pump-thaw method (3 times) and backfilled with nitrogen, after which the HCl solution was syringed into the reaction mixture containing the 4-vinylphenol and stirred at room temperature for 4 days. Although this reaction was not optimized, it was confirmed by TLC (SiO_2: Rf = 0.7 for 4-vinylphenol, 30% ethyl acetate/hexanes) that consumption of the monomer was complete. The resultant polymer was precipitated into distilled water, filtered, and rinsed with distilled water until a pH of neural was reached. The crude materials were then redissolved in acetone, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. Further drying under vacuum yielded poly(4-vinylphenol) (1.9 g, 95.0%) as a white powder which was used without further purification.

4-Vinylphenol: ^1H NMR (500 MHz, CD_3OD) δ ppm: 7.25 (d, 2H), 6.72 (d, 2H), 6.60 (q, 1H), 5.57 (d, 1H), 5.03 (d, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ ppm: 155.5, 149.6, 134.3, 127.4, 115.7, 114.9.

Poly(4-vinylphenol): ^{1}H NMR (500 MHz, CD_3OD) δ ppm: 6.63 (br, 4H), 1.89-0.87 (m, 3H). IR (neat): *ν* (cm^{-1}) = 3399 (OH), 1511, 1450, 1446, 1372, 1227 (C-O), 833.

5.4.2. General procedure for synthesis of cyclic carbonates from CO_2 and epoxides

A 30 mL Schlenk tube was charged with epoxide (5 mmol), PVP (0.03 g, 0.25 mmol as vinylphenol unit), and tetra-*n*-butylammonium halide (0.25 mmol). The Schlenk tube was then subjected to three cycles of pressurization and depressurization with CO_2 through a balloon (1 atm, 20 cm in diameter). The reaction mixture was heated at a given temperature and stirred for 22 h. The reaction mixture was allowed to cool to room temperature, and then 20 mL of diethyl ether was added slowly to extract the product and the remaining reactant and to precipitate the catalysts. After removing the solvent and the unreacted epoxide under reduced pressure, the residue was purified by silica gel column chromatography using a mixture of hexane and ethyl acetate (1:1-2:1, v/v) as an eluent to afford the carbonate.

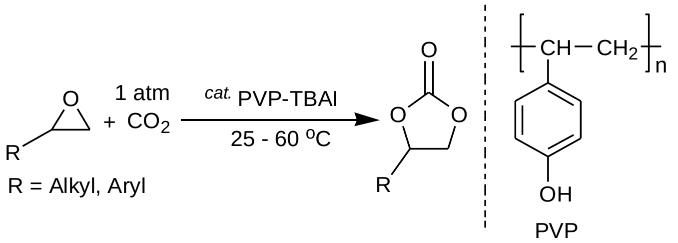
5.4.3. Recycling experiments

After the reaction as mentioned above, the retrieved catalysts were filtered or separated and washed thoroughly with diethyl ether to remove all product and the unreacted reactants present. After drying under reduced pressure for 1 h at room temperature, the catalyst was then reused in a subsequent reaction and the same procedure was followed.

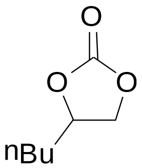
For epichlorohydrin, however, the reaction system separated into two liquid phases upon addition of diethyl ether. The catalysts were found to be in the lower phase and usable for a subsequent reaction.

When recovery of the activity is necessary for the carbonate synthesis, PVP can be treated with CH_3CO_2H and TBAI needs to be added as it is removed by the treatment.

5.4.4. Representative procedure for the cyclic carbonate formation



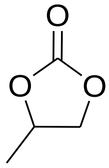
All cyclic organic carbonate products have been reported previously and the data given below are in agreement with the literature data.



4-Butyl-1,3-dioxolan-2-one[3,21,32]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxyhexane (5 mmol, 0.51 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 ^{o}C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.71 g (yield: 98.6%) as a colorless oil.

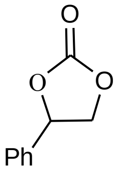
^{1}H NMR (300 MHz, $CDCl_3$): 4.77-4.68 (m, 1H), 4.57-4.52 (m, 1H), 4.11-4.05 (m, 1H), 1.82-1.68 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.2, 77.3, 69.4, 33.4, 26.4, 22.2, 13.7.



Propylene carbonate[3,21,32]

In a 30 mL single-necked round-bottomed flask, propylene oxide (5 mmol, 0.29 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 25 ^{o}C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.43 g (yield: 84.3%) as a colorless oil.

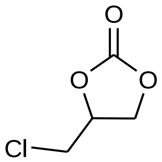
^{1}H NMR (500 MHz, $CDCl_3$): 4.92-4.80 (m, 1H), 4.62-4.51 (m, 1H), 4.10-3.95 (m, 1H), 1.55-1.40 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.2, 73.7, 70.7, 19.3.



4-Phenyl-1,3-dioxolan-2-one[3,21,32]

In a 30 mL single-necked round-bottomed flask, styrene oxide (5 mmol, 0.60 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 ^{o}C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.77 g (yield: 93.9%) as a white solid.

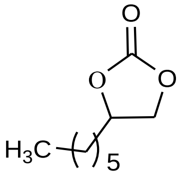
^{1}H NMR (500 MHz, $CDCl_3$): 7.44-7.38 (m, 3H), 7.36-7.34 (m, 2H), 5.68-5.65 (m, 1H), 4.80-4.77 (m, 1H), 4.33-4.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.1, 135.8, 129.7, 129.2, 120.0, 77.6, 71.2.



4-(Chloromethyl)-1,3-dioxolan-2-one[3,21]

In a 30 mL single-necked round-bottomed flask, epichlorohydrin (5 mmol, 0.46 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.65 g (yield: 95.6%) as a colorless oil.

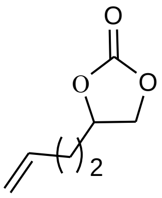
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 5.12-5.01 (m, 1H), 4.69-4.55 (m, 1H), 4.48-4.35 (m, 1H), 3.89 (dd, 1H), 3.77 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 154.8, 74.7, 67.0, 44.6.



4-Hexyl-1,3-dioxolan-2-one[3,21]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxyoctane (5 mmol, 0.64 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.78 g (yield: 90.7%) as a colorless oil.

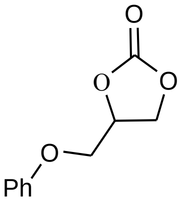
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 4.79-4.68 (m, 1H), 4.61-4.50 (m, 1H), 4.15-4.02 (m, 1H), 1.85-1.62 (m, 2H), 1.55-1.21 (m, 8H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.2, 77.2, 69.4, 33.7, 31.5, 28.7, 24.4, 22.4, 13.9.



4-(But-3-en-1-yl)-1,3-dioxolan-2-one[3,21]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxy-5-hexene (5 mmol, 0.49 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.7 g (yield: 98.6%) as a colorless oil.

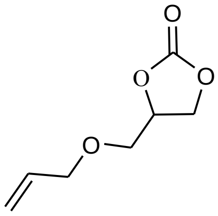
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 5.87-5.61 (m, 1H), 5.18-4.91 (m, 2H), 4.76-4.61 (m, 1H), 4.59-4.42 (m, 1H), 4.15-3.95 (m, 1H), 2.30-2.01 (m, 2H), 1.95-1.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.1, 136.3, 116.0, 76.4, 69.4, 32.8, 28.5.



4-(Phenoxymethyl)-1,3-dioxolan-2-one[3,21]

In a 30 mL single-necked round-bottomed flask, 1,2-epoxy-3-phenoxy propane (5 mmol, 0.75 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.82 g (yield: 84.5%) as a white solid.

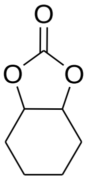
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.36-7.22 (m, 2H), 7.06-6.92 (m, 1H), 6.91-6.85 (m, 2H), 5.06-4.95 (m, 1H), 4.65-4.56 (m, 1H), 4.55-4.46 (m, 1H), 4.22 (dd, 1H), 4.12 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 157.8, 154.7, 129.7, 122.0, 114.6, 74.2, 66.8, 66.2.



4-Allyloxymethyl-1,3-dioxolan-2-one[3,21]

In a 30 mL single-necked round-bottomed flask, allyl glycidyl ether (5 mmol, 0.57 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 40 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 1 : 1) to afford the desired cyclic carbonate 0.77 g (yield: 97.5%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm: 5.95-5.80 (m, 1H), 5.35-5.12 (m, 2H), 4.93-4.80 (m, 1H), 4.60-4.45 (m, 1H), 4.44-4.30 (m, 1H), 4.11-3.99 (m, 2H), 3.75-3.65 (m, 1H), 3.64-3.52 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 155.1, 133.8, 117.3, 75.4, 72.2, 68.9, 66.2.

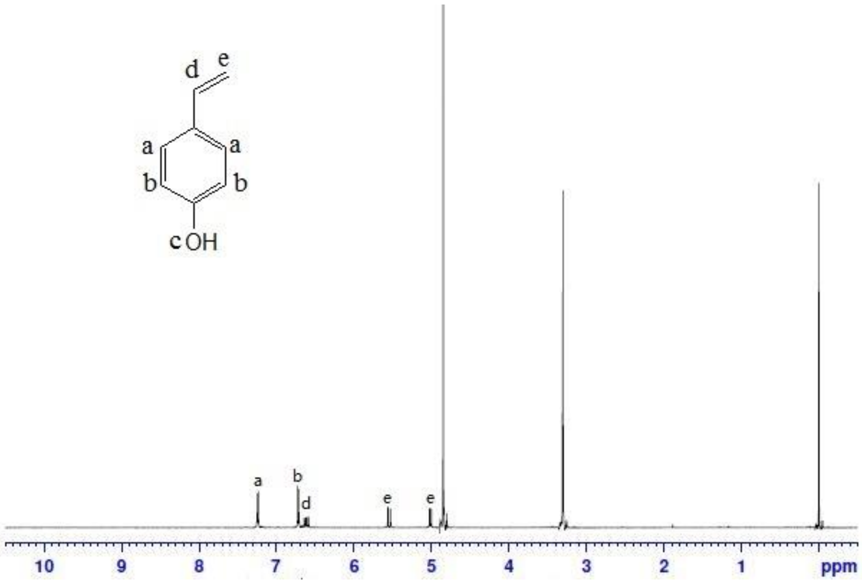


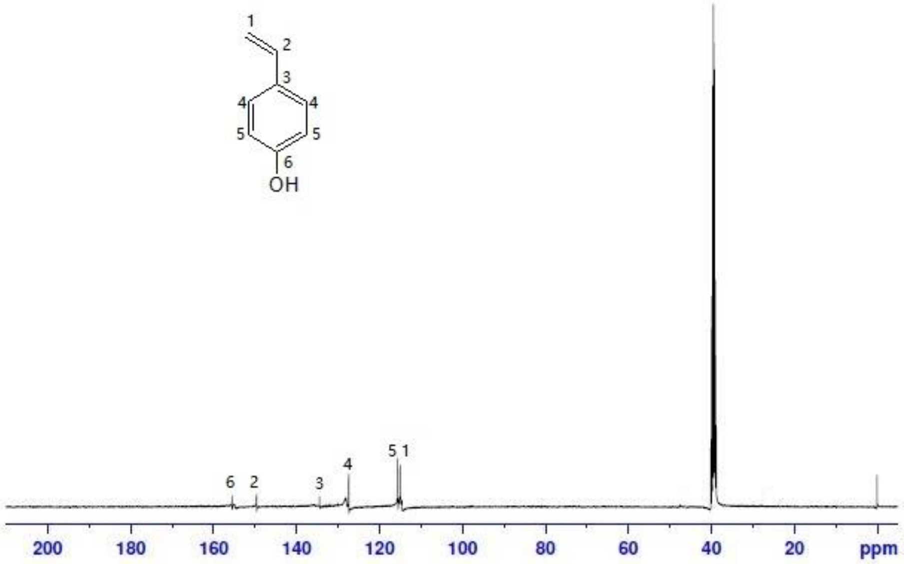
Hexahydro-benzo[1,3]dioxol-2-one[3,21]

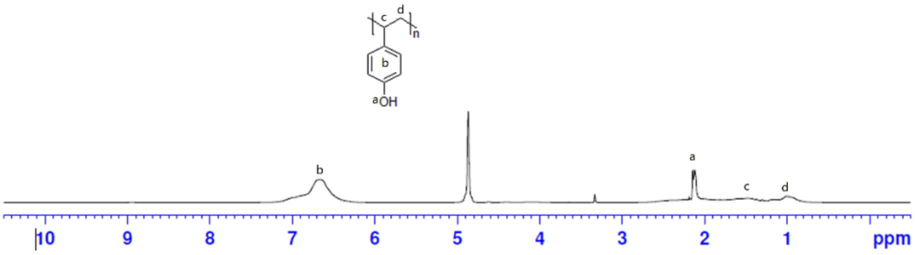
In a 30 mL single-necked round-bottomed flask, cyclohexene oxide (5 mmol, 0.49 g), PVP (0.25 mmol, 0.03 g) and TBAI (0.25 mmol, 0.092 g) were stirred at 60 °C for 22 h under an atmosphere of CO_2 (balloon). The crude product was purified by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the desired cyclic carbonate 0.2 g (yield: 28.2%) as a colorless oil.

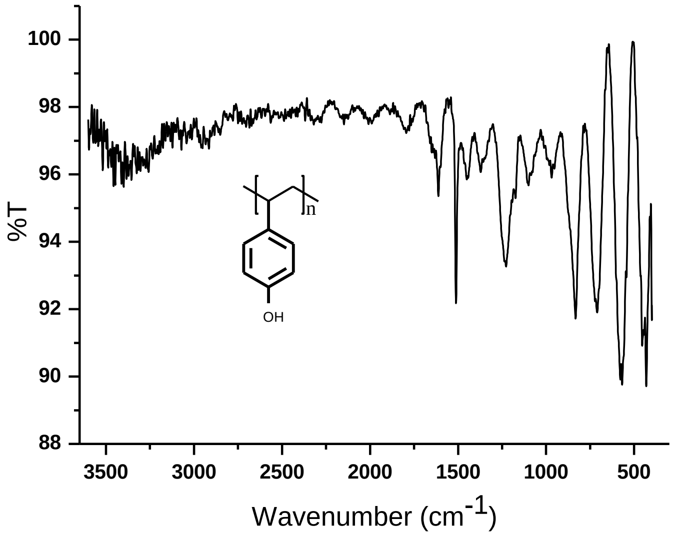
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 4.76-4.59 (m, 2H), 2.0-1.79 (m, 4H), 1.72-1.53 (m, 2H), 1.51-1.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 155.35, 75.73, 26.78, 19.17.

5.4.5. ^{1}H and ^{13}C NMR spectra of 4-vinylphenol and poly(4-vinylphenol)









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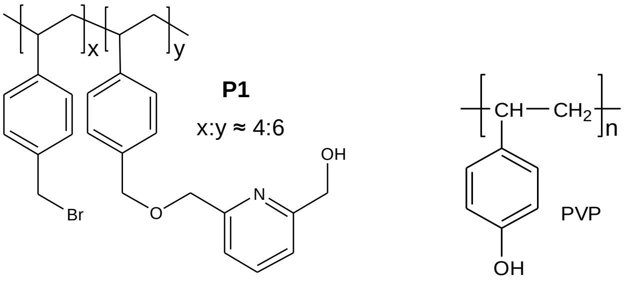
Chapter 6 Summary and outlook

Carbon dioxide (CO_2) as an abundant, typical renewable C1 source as well as the most significant greenhouse gas has been drawing more and more attention. As a renewable feedstock, the transformation of CO_2 into useful chemicals would be particularly important and deserves worldwide attention. The reaction of CO_2 with epoxides to produce cyclic carbonates has gained considerable attention over the past years. The 100% atom-economical reaction between epoxides and CO_2 to produce cyclic carbonates has great potential to be a key reaction in the future green chemical industry. The cyclic carbonate products already have numerous applications, and these will surely expand further as the importance of green and sustainable chemistry increases in coming decades. Notably, the synthesis of ethylene and propylene carbonates has already been industrialized.



Scheme 6-1. The structure of **P1** and PVP.

In this paper we have developed three polymers and hydroxypyridines as catalyst in cyclic carbonate synthesis starting from CO_2 and epoxides. Especially emphasized organocatalytic systems which were allowed this transformation under mild conditions. With respect to the employed catalyst types it can be shown that organocatalysts in contrast to metal complex catalysts are often commercially available and/or easily accessible, e.g. poly(4-vinylphenol) (PVP) (Scheme 6-1) and hydroxypyridines. The reaction of terminal epoxides with CO_2 is well established and can be performed at lower temperature and under atmosphere pressure of CO_2. In contrast the conversion of internal epoxide (for example, cyclohexene oxide) under mild conditions remains challenging. Moreover, the 3-hydroxypyridine/tetra-*n*-butylammonium iodide (TBAI) organocatalytic system exhibited excellent stability in the cycloaddition reaction of CO_2 with epoxides, even in the presence of minor non-toxic components such as water, air and O_2. The poly(4-vinylbenzylbromide) (PVBB) showed bad recyclability tests might be due to the leaching of bromine from supported material in PVBB/DMF system. Poly(4-vinylbenzylchloride) (PVBC) or PVBB combine with DBU is a heterogeneous catalytic system and might reduce the catalytic activity. The polymer-supported catalyst **P1** (Scheme 6-1) with 2-pyridinemethanol moiety with TBAI was a heterogeneous system and showed moderate activity for most of epoxides because **P1** has higher molecular weight or stronger polarity. And the PVP/TBAI system could be easily separated and recycled more than six times and give yields higher than 90% for 1,2-epoxyhexane and styrene oxide, while it was deactivated sooner for epichlorohydrin (three times) owing to more frequent and complex reactions with PVP, which was suggested by ^{1}H NMR analysis. These discovery of strengths and weaknesses will be applied and improved in our future works.

The quest for even more active and selective organocatalysts at low temperature, CO_2 concentrations and pressure (preferably at atmosphere pressure) still remains challenging and is a hot research topic in academic laboratories and industries. It is now recognized that the most effective catalysts combine a Lewis acid to activate the epoxide with a nucleophile to open the epoxide ring and subsequently act as a leaving group and a Lewis or Brønsted base to activate CO_2. And the halide ions (I^-, Br^- and Cl^-) usually acted as the nucleophile. Therefore, developing halide ion free catalytic systems are attracting important interest from the scientific community.

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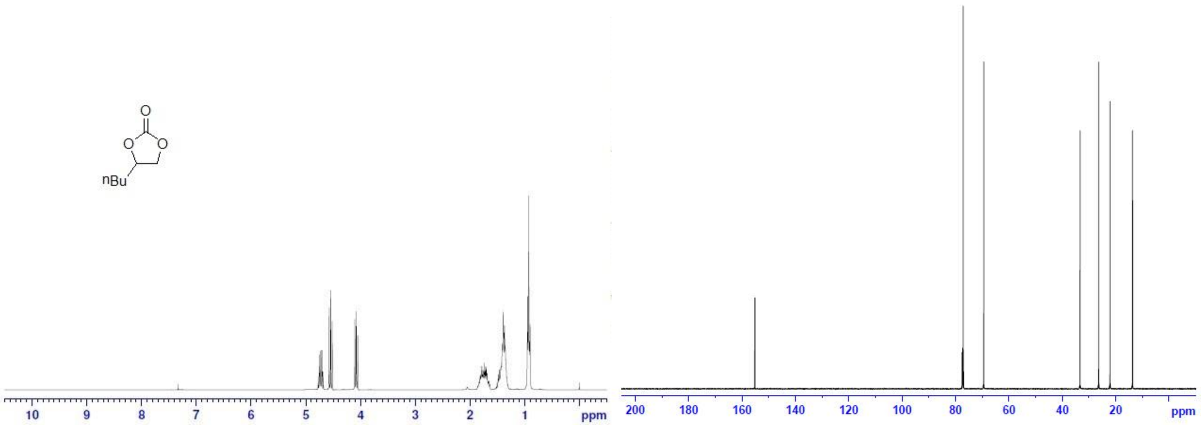
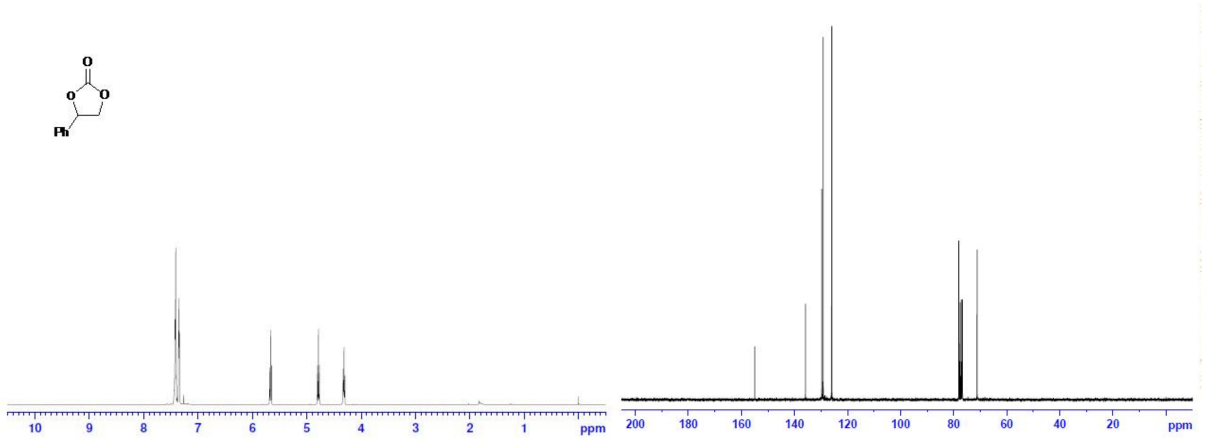
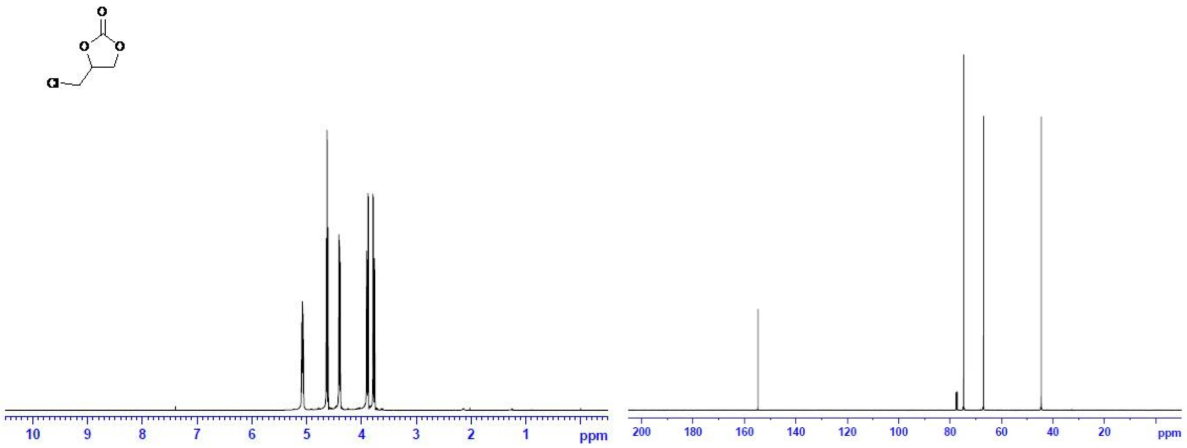
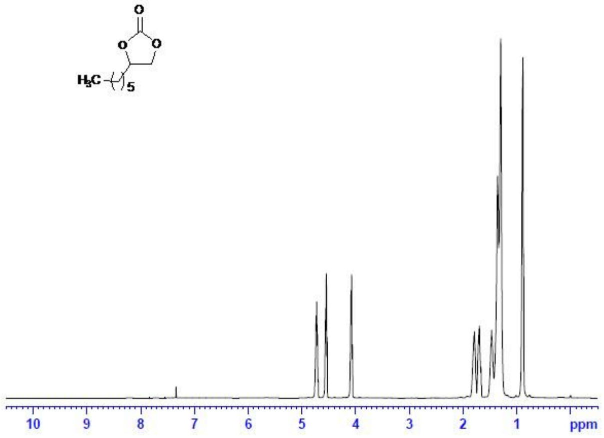
Supplementary data: ^1H and ^{13}C NMR spectra of cyclic carbonates





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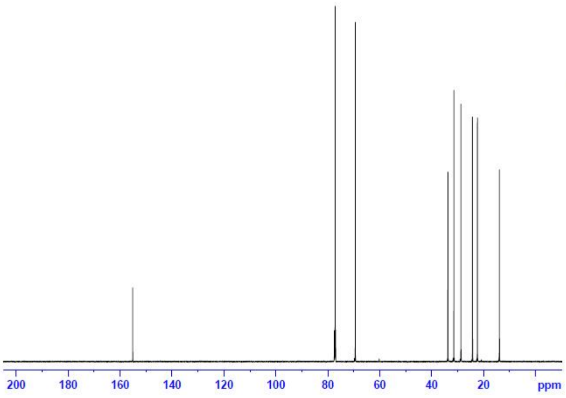
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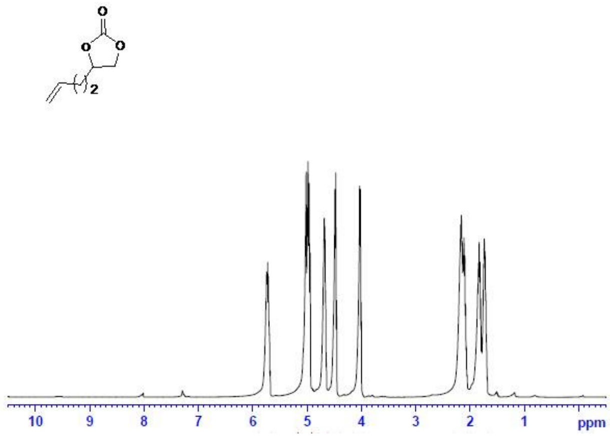
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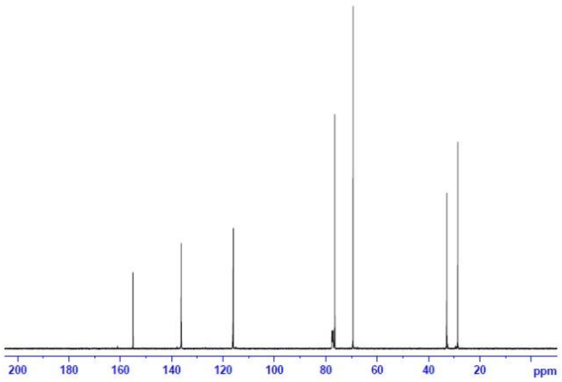
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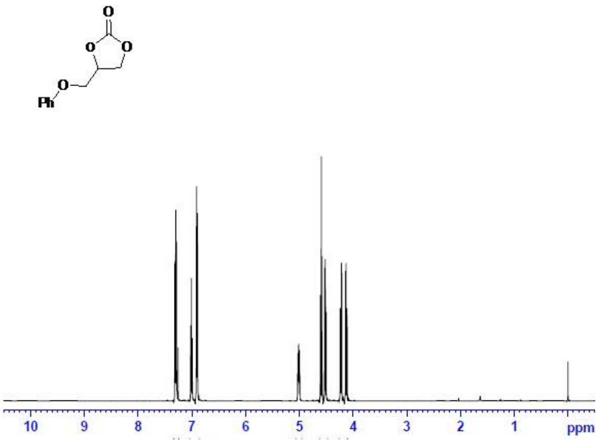
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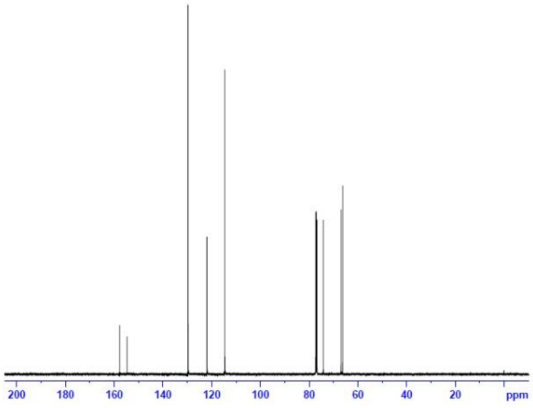
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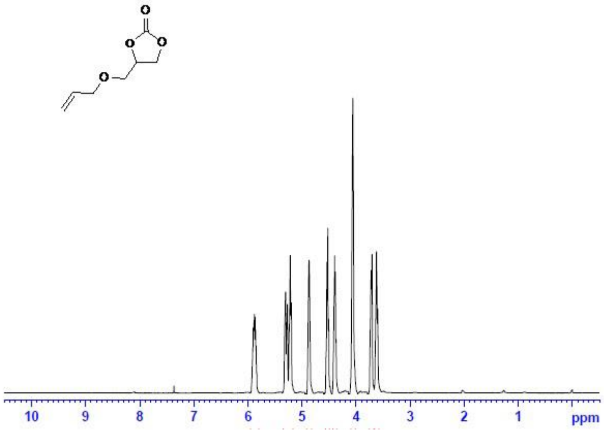
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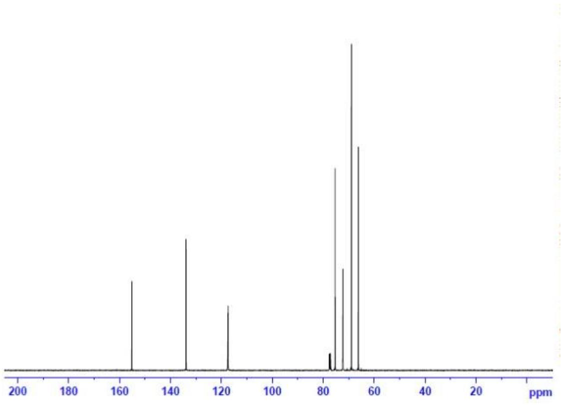
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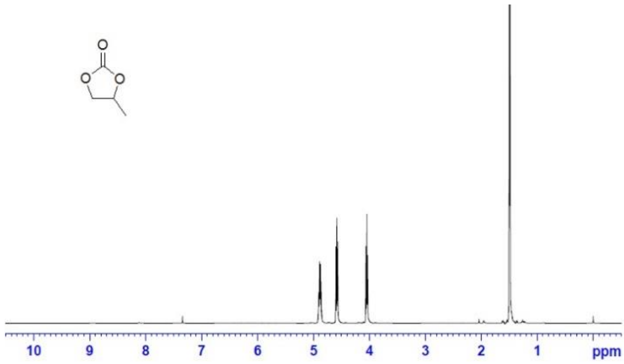
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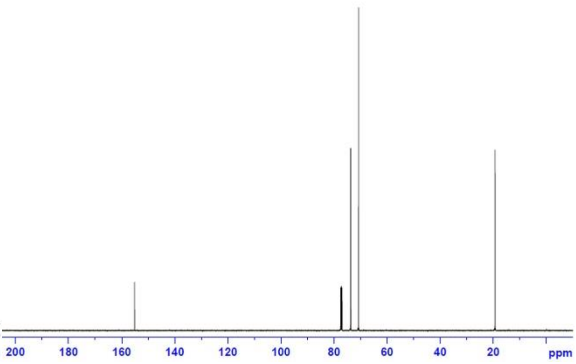
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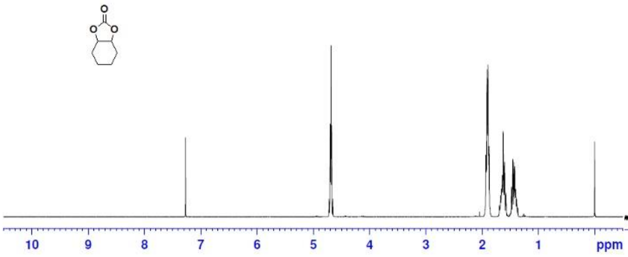
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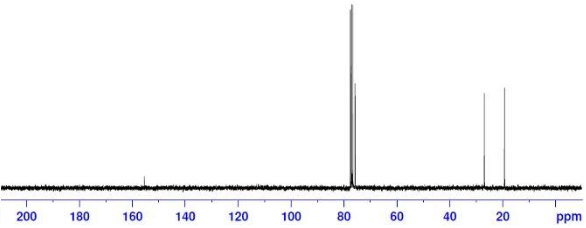
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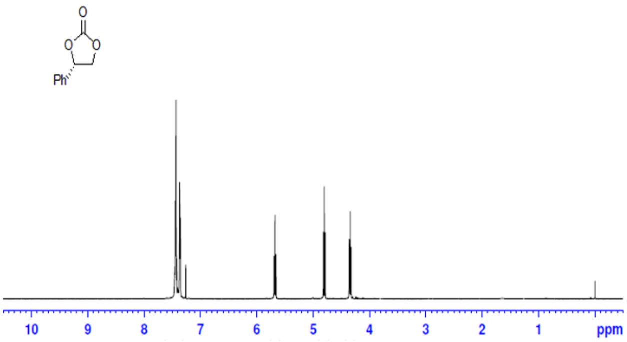
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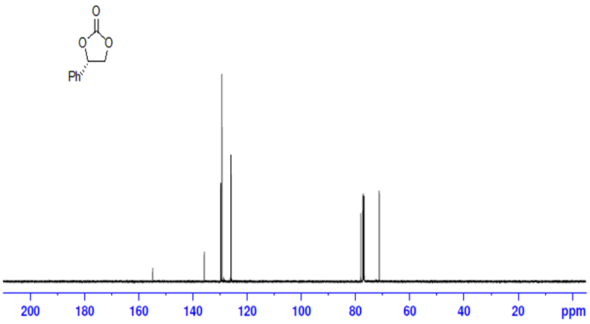
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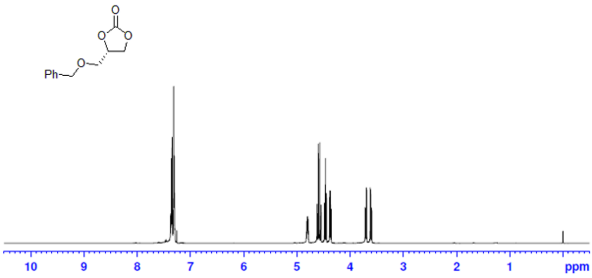
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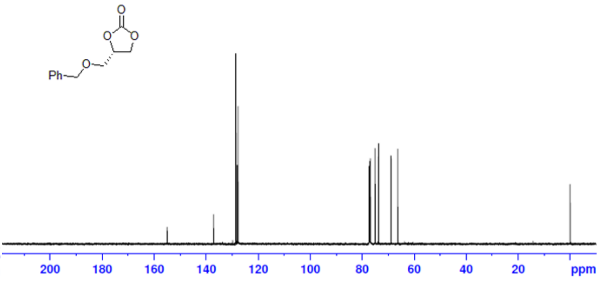
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