Poly(4-vinylimidazolium)s/Diazabicyclo[5.4.0]undec-7-ene/ Zinc(II) Bromide-Catalyzed Cycloaddition of Carbon Dioxide to Epoxides

Ue Ryung Seo^a and Young Keun Chung^{a,*}

^a Intelligent Textile System Research Center, and Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea Fax: (+82)-2-889-0310; phone: (+82)-2-880-6662; e-mail: ykchung@snu.ac.kr

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Abstract: Poly(4-vinylimidazolium)s, derived from the self-immobilization of 4-vinylimidazoliums, with diazabicyclo[5.4.0]undec-7-ene (DBU) and zinc bromide $(ZnBr_2)$ are used as a highly efficient catalyst for the chemical fixation of carbon dioxide. This catalytic system has been applied for the preparation of cyclic carbonates from terminal epoxides and carbon dioxide. Many functional groups, including chloro, vinyl, ether, and hydroxy groups are well tolerated in the reactions. Moreover, the catalytic system was found to catalyze the conversion of more sterically congested epoxides which are generally considered to be challenging substrates for fabricating the cyclic organic carbonates. In addition, the disubstituted epoxides are found to react with retention of configuration. The polymer precatalyst is easily recovered and reused. A plausible reaction mechanism is proposed.

Keywords: carbon dioxide fixation; cyclic carbonates; cycloaddition; organocatalysis; polymers

Carbon dioxide (CO₂) has been attracting much attention as it is considered to a major cause of climate change, because of its greenhouse effect.^[1] To reduce the continuous accumulation of CO₂ in the atmosphere, the scientific and industrial initiatives have, in the recent decades, been focused on the chemical conversion of CO₂ to useful chemicals.^[2] However, the chemistry of CO₂ is limited because of its high stability. One of the potentially useful ways of reducing CO₂ is its reaction with epoxides to form cyclic carbonates.^[3] This reaction has tremendous potential because cyclic carbonates are widely used as the precursors of polycarbonates and other polymers, serve as excellent aprotic polar solvents, electrolytes in rechargeable batteries, and intermediates in the production of pharmaceuticals and fine chemicals.^[4] Therefore, a variety of diverse homogeneous and heterogeneous catalyst systems^[5] has been developed for catalyzing the reactions of CO₂ with epoxides. However, most of them suffer from low catalytic activity, wateror air-sensitivity of catalyst, and harsh reaction conditions.

Organocatalysts are usually robust, inexpensive, readily available, and non-toxic. Most of them are also inert towards moisture and oxygen. 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. Recently, the polymerization of catalysts has been developed as one of the heterogenization methods.^[6] In catalyst polymerization, the active centres of a catalyst are distributed over the polymer chain, which helps to prevent the loss of activity; therefore, polymerized catalysts show high activities in certain reactions. The structure of 4-vinylimidazolium is similar to that of styrene, and its polymer product, poly(4-vinylimidazolium)s, seems to be similar to that of polystyrenes. However, reports on the synthesis and use of poly(4-vinylimidazolium)s are rare.^[7] Very recently, we found that poly(4-vinylimidazolium)s derived from the self-immobilization of 4-vinylimidazoliums acted as a precatalyst in the carboxylation of epoxides with CO₂. Herein we communicate a very active, stable, recyclable and cost-effective organic precatalyst, poly(4-vinylimidazolium)s, for the carboxylation of epoxides with CO_2 . The use of 1-vinyl- and 1,3-divinylimidazole-based crosslinked polymers as the catalyst in the carboxylation of epoxides with CO₂ has been reported.^[8] Moreover, the use of poly[1,3-bis(4-vinylbenzyl)imidazolium]Clbased cross-linked polymers as the catalyst in carboxylation of epoxides with CO₂ has also been report-

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Scheme 1. Synthesis of 2 from histamine.

ed.^[9] However, all the reactions were carried out at high temperatures and high pressures of CO_2 .

Previously, the 4-vinylimidazolium salt was produced by the decarboxylation of urocanic acid.^[7] However, histidine can also be used to obtain 4-vinylimidazolium as shown in Scheme 1.

Both histidine and histamine are commercially available. We chose histamine as the starting material. The reaction of histamine with NaNO₂, followed by chlorination reaction with SOCl₂, afforded 4-(2-chloroethyl)imidazole in 74% yield.^[10] Dehydrochlorination and dimethylation of 4-(2-chloroethyl)imidazole in the presence of NaHCO₃, K₂CO₃ and MeI in acetonitrile afforded an 4-vinylimidazolium salt, 1, in 70% yield.^[11] Polymerization of $\mathbf{1}$ in the presence of AIBN afforded poly(4-vinylimidazolium)s, 2, the precursor of an organocatalyst, in high yield.^[12] Broad ¹H NMR signals were observed, as expected for a high molecular weight polymer. The polymer was soluble in DMSO and DMF, and freely soluble in water, but insoluble in chloroform, dichloromethane, and acetone. The weight average molecular weight (MW) of 2 was found to be ~30000 from light scattering experiments.^[13] The polymer decomposed at 350 °C. The abilities of 1 and 2 to catalyze the carboxylation of epoxides with CO₂ in the presence of a base were examined [Eq. (1)].



First, the reaction conditions were screened, including the CO_2 pressure, reaction temperature, reaction time, solvent, base, and the catalyst amount to optimize the yield of the cyclic carbonate (Table 1). Initially, the study was performed under the reaction conditions (2 mol% catalyst, ZnI_2 as the Lewis acid, K₂CO₃ as the base, DMSO as the solvent, at 80 °C reaction temperature, and 24 h of reaction time) adopted from the previous work^[14] on the NHC-catalyzed carboxylation of epoxides. The coupling of styrene oxide (SO) with CO₂ to afford styrene carbonate (SC) was chosen as the model reaction. When the reaction

Table 1. Screening for the reaction conditions.^[a]

Ph
$$2$$
, Lewis acid, base 7 , solvent, 1 atm CO₂ Ph

Entry	$2(mo^{10/})$	Solvent	Base (mol ⁹ ()	Lewis	Yield
	(1101 /0)		(1101 /8)	aciu	[/0]: }
1	2	DMSO	$K_{2}CO_{3}(2)$	ZnI_2	86
2	2	DMF	$K_2CO_3(2)$	ZnI_2	88
3	2	DMF	DBU (2)	ZnI_2	95
4	2	DMF	DBU (4)	ZnI_2	99
5	1	DMF	DBU (2)	ZnI_2	90
6	1	DMF	DBU (2)	ZnBr ₂	94
7	1	DMF	DBU (2)	$ZnCl_2$	76
8	1	DMF	DBU (2)	CrCl ₃	72
9	1	DMF	DBU (2)	LiI	77
10	1	DMF	DBU (2)	FeCl ₃	77
11 ^[c]	1	DMF	DBU (2)	ZnBr ₂	50
12 ^[d]	1	DMF	DBU (2)	ZnBr ₂	87
13 ^[e]	1	DMF	DBU (2)	ZnBr ₂	94
14	1	DMF	_	_	4
15	-	DMF	DBU (2)	_	N.R
16	_	DMF	-	$ZnBr_2$	11

^[a] Reaction conditions: Styrene oxide (SO) (5 mmol), 2, Lewis acid (the same equiv. of 2), solvent (3 mL), base, and CO₂ (1 atm) at 80 °C for 24 h.

^[b] Isolated yield.

- ^[c] Reaction was performed at 60°C.
- ^[d] Reaction was performed at 100 °C.

^[e] Reaction time: 10 h.

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was carried out under the adopted reaction conditions, the SC yield was 86% (Table 1, entry 1). Changing the solvent to DMF afforded a slightly higher SC yield (entry 2: 88% yield). When diazabicyclo-[5.4.0]undec-7-ene (DBU) was used instead of K_2CO_3 in DMF, SC was obtained quantitatively (entries 3 and 4). When the amount of catalyst **2** was reduced to 1 mol%, the yield was still high (entry 5, 90% yield).

Thus, in the presence of 1 mol% of 2, the effect of metal ions, such as ZnX_2 (X = Cl, Br, and I), CrCl₃, LiI, and FeCl₃, on the reaction was also examined (entries 5–10). The SC yield was greatly affected by the different metal ions. Among them, the use of ZnBr₂ afforded the best result (entry 6, 94% yield), because of its strong Lewis acidity. The reactivity of different anions in the zinc salts decreased in the following order: $Br^- > I^- > Cl^{-}$.^[15] The different reactivity may be due to the different electrophilicity of Zn depending upon the anion.^[13] The effect of the reaction temperature on the product yield was also examined (entries 6, 11, and 12). In the lower temperature range, the yield increased with the increasing temperature (entry 6 vs 11); however, this trend was not observed at higher temperatures. The yield decreased to 87% at 100 °C (entry 6 vs. 12). The reaction proceeded well with 1 mol% of catalyst at 80°C. When the reaction time was reduced to 10 h, the excellent yield was maintained (entry 13, 94% yield). The necessity of a combination of 2, DBU, and a Lewis acid in the reaction was confirmed by the observation that in the presence of solely 2, DBU, or ZnBr₂ a negligible reaction was observed (entries 14–16).

Thus, the optimum reaction conditions were established as follows: 1 mol% catalyst, 2 mol% DBU, and 1 mol% ZnBr₂ in DMF at 80 °C under 1 atm CO₂ for 10 h. Under the optimized reaction conditions, the maximum turnover number was 320 (see the Supporting Information). When 1 was used as the precatalyst under the optimized reaction conditions, SC was obtained in 88% yield. The experiments were also carried out to examine the recyclability of the catalyst using SO as the substrate. The amount of 2 was too small to confirm the recycling test; therefore, twice the amounts of 2, ZnBr₂, and DBU as those used during optimization were used. After performing the reaction in DMF, excess MeOH was added to the reaction mixture to precipitate the polymer catalyst. The recovered polymer catalyst was dried and reused for the next run. The SC yields for the eight consecutive runs were 99%, 98%, 91%, 97%, 97%, 94%, 94%, and 91%. Considering the weight loss in the catalyst purification process, no considerable decrease in the SC yield was observed (Figure 1).

To show the catalytic activity of **3** [**3**=poly(NHC)s; NHC=1,3-dimethyl-4-vinylimidazol-2-ylidene], the coupling reactions of CO₂ to various substituted epoxides were also conducted at 80 °C and 1 atm CO₂



Figure 1. Recycling of poly(NHC-Zn) complex in the cycloaddition of CO_2 to SC.

(Table 2). To our delight, many functional groups, including chloro, vinyl, ether, and hydroxy groups were well tolerated in the reactions. Thus, all the epoxides used except propylene oxide (entry 6) could be transformed to the corresponding carbonates in almost quantitative yields. In the case of propylene oxide, a slightly lower yield (56%) was observed because of its low boiling point (33 °C).

Notably, most of the substrates afforded the desired products under mild reaction conditions, and the functional groups were stable in the reactions, indicating the outstanding efficiency of the catalyst. This catalytic reaction may be a good method for preparing functional monomers.

Owing to the steric hindrance and electronic effect, 1,1-disubstituted and internal disubstituted epoxides are often considered to be more challenging substrates for fabricating the cyclic organic carbonates.^[16] A series of these substrates (Table 3) was investigated using the catalyst system. The amounts of 2, ZnBr₂, and DBU were used four times more than those used for the cycloaddition of CO₂ with terminal epoxides (see the Supporting Information). As expected, higher pressures and temperatures were needed to convert the substrates to the corresponding organic carbonates; e.g., the cycloaddition of 1,1-dimethyloxirane with CO2 at 90°C and 1 atm of CO2 was unsuccessful. However, under 5 atm of CO₂ pressure, 1,1-dimethyloxirane was converted into 4,4-dimethyl-1,3-dioxolan-2-one in 46% yield after 24 h of reaction time. When the CO_2 pressure was increased to 7 atm and 10 atm, the yields of 4,4-dimethyl-1,3-dioxolan-2-one increased to 53% and 83% yields, respectively. Thus, the reactions of other substrates with CO2 were carried out at 90°C under 10 atm of CO₂. When the CO₂ pressure was increased, most of the substrates afforded the corresponding cyclic carbonates in 68-87% yields. In the case of stilbene oxide (entry 5), a relatively low yield (35%) was observed after 24 h of reaction time. The yield increased to 55% when the re-

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Å	2 (1 mol%), DBU (2 m		
R Entry	Substrate	Product	R
1			98
2	Ph	O Ph	92
3	CI		98
4			98
5	° () s		99
6	گر		56
7			93
8	Остон	о сон	94
9	Br		93
10	Ph		94
11 4	O O O O O O O O O O O O O O O O O O O		-OMe ⁸⁹

Table 2. Cycloaddition	of	CO_2	with	various	terminal	epox-
ides. ^[a]						-

Table 3. Cycloaddition of CO₂ with various internal epoxides.^[a]

R ¹	2 (4 mol%), DBU (R ² DMF, CO ₂ (*	(8 mol%), ZnBr ₂ (4 mol% 10 atm), 90 °C, 24 h	$(a) \qquad (b) \qquad (c) $
Entry	Substrate	Product	Yield [%] ^[b]
1	4		83
2	Å		81
3	\bigcirc		80
4	\diamondsuit		87
5 ^[c]	Ph Ph	Ph Ph	55
6	Ph OEt		68
7	Å		N.R

^[a] The catalyst (4 mol%), ZnBr₂ (4 mol%), DBU (8 mol%), expoxide (5 mmol), DMF (4 mL), CO₂ (10 atm), 90 °C, 24 h.

^[b] Isolated yields.

^[c] 48 h

However, in the case of 2,2,3,3-tetramethyloxirane, no reaction was observed under the reaction conditions (90°C, 10 atm CO₂, 24 h). When the reaction time was prolonged to 72 h, no reaction was observed.

The internal epoxides provided an opportunity to study the stereochemistry of this cyclic carbonate synthesis. According to their ¹H and ¹³C NMR spectra,

[a]	1 mol% of 2, epoxide (5 mmol), ZnBr ₂ (1 mol%), DBU
	(2 mol%), CO ₂ (1 atm), 80 °C, 10 h.

^[b] Isolated yields.

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action time was increased to 48 h. Moreover, ethyl 2oxo-5-phenyl-1,3-dioxalane-4-carboxylate (entry 6) was found to be a good substrate.^[17]

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[a] Styrene oxide (SO) (5 mmol), DMF (3 mL), CO₂ (1 atm), 80°C, 10 h.

the cyclic carbonates, (\pm) -trans-4,5-dimethyl-1,3-dioxolan-2-one and (\pm) -trans-4,5-diphenyl-1,3-dioxolan-2one, had the same stereochemistry as that of the starting epoxides. Thus, the disubstituted epoxides were found to react with retention of configuration.

To better understand the reaction mechanism, various reaction conditions were tested (Table 4). The reaction of SO in the presence of ZnBr₂ alone afforded SC in 11% yield (entry 1). The same reaction in the presence of ZnBr₂ and DBU^[18] afforded SC in 43% isolated yield (entry 2). We expected that the reaction of 2 with DBU would afford 3; however, SC was obtained in 8% yield (entry 3). This observation suggested that 3 would not be generated in situ. The rapid CO₂ fixation by DBU and the coupling of aziridine to CO_2 in the presence of DBU have been well documented.^[19] However, DBU by itself did not catalyze the reaction (entry 4). The use of imidazolium-based polymeric ionic liquids as catalyst in the reaction of the coupling of CO₂ with epoxides has been reported.^[9,20] Thus, the reaction of SO with CO_2 in the presence of 2 and ZnBr₂ was examined; and SC was obtained in 45% yield (entry 5). The NHC-CO₂ adduct has been reported to be a potent organocatalyst at high temperatures and high pressures (100-120 °C and 20–100 atm of CO_2 and).^[9,20a,21] Thus, the 3- CO_2 adduct was prepared (see the Supporting Information) and used as the catalyst under the above-mentioned reaction conditions. However, no reaction was observed in the presence of $3-CO_2$ adduct (entry 6). Furthermore, the IR spectrum of the recovered poly-(NHC)-CO₂ adduct showed that almost all of the CO₂ was lost during the reaction. Thus, the poly(NHC)-CO₂ adduct itself did not play an important role in the catalytic reaction. Interestingly, when the same reaction was carried out in the presence of 3-CO₂ adduct and ZnBr₂ (entry 7), SC was obtained in 33%

nus, the presence of both ZnBr₂ and DBU is y for achieving good results similar to those obtained with other Lewis acid and Lewis base co-catalyzed coupling reactions of CO₂ with epoxides.^[3,22] Furthermore, the best result was obtained when the reaction was carried out in the presence of 2, DBU, and ZnBr₂ (2-DBU-ZnBr₂) catalyst system (entry 8, 94% yield). The ¹H NMR spectra of 2, 2/DBU, and 2/DBU/ZnBr₂ in [D₇]DMF were taken at room temperature and 80°C (see the Supporting Information), the imidazolium C–H peak of **2** appeared at $\delta = 9.15$ ppm and was observed in the presence of DBU even at 80°C. However, in the presence of DBU and ZnBr₂, it disappeared at 80 °C and reappeared at room temperature. Thus, we envision the formation of 3-ZrBr₂ at 80°C.

Although the exact mechanism of this transformation is not clear at the moment, a plausible reaction mechanism was proposed on the basis of the experimental observations (Figure 2).

We envision that the NHC-ZnBr₂ species may play a major role in the coupling reaction at 80 °C, i.e., the reaction may be co-catalyzed by a Lewis base, DBU, and Lewis acid, NHC-ZnBr₂ or ZnBr₂. The Lewis base and Lewis acid act together to open the epoxy ring and then react with CO₂ to afford the corresponding cyclic carbonates via a ring-opening and recyclization process. When a pre-synthesized polymer-NHC-ZnBr₂ complex was used as a catalyst, SC was obtained in 93% yield. This observation also supports the mechanism shown in Figure 2.

In conclusion, we have examined an efficient poly(4-vinylimidazolium)s-DBU-ZnBr₂ catalyst

2 + ZnBr₂ + DBU



Figure 2. Plausible mechanism of cycloaddition of epoxide to CO₂

Table 4.	Cycloaddition	under various	reaction	conditions. ^[a]
----------	---------------	---------------	----------	----------------------------

DMF, 80 °C, 10 h

DBU

0

2

2

2

0

0

0

2

(mol%)

CO

3-CO2

0

0

0

0

0

1

1

0

(mol%)

Entry 2

1

2

3

4

5

6

7

8

(mol%)

0

0

1

0

1

0

0

1

f able 4. Cycloadditi	on under various reaction	conditions. ^[a]	yield. Th
		0	necessary
0	catalytic conditions	人	obtained

ZnBr₂

1

1

0

0

1

0

1

1

(mol%)

Yield

[%]

11

43

8

N.R

N.R

45

33

94

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asc.wiley-vch.de These are not the final page numbers! 77 system for the synthesis of cyclic carbonates by reacting terminal epoxides and internal epoxides with CO_2 . Cyclic carbonate is the sole product in this reaction. Efforts are underway to elucidate the mechanistic details of the reaction and extend the applications of the catalyst system.

Experimental Section

Advanced 🥟

Catalysis

Synthesis &

General Procedure for the Synthesis of Mono-Subsitituted Cyclic Carbonates

Reactions were performed in a Schlenk tube equipped with a stirring bar and capped with a rubber cap and the following were placed in the tube in order: 1 mol% of catalyst (13 mg, 0.05 mmol), 1 mol% of ZnBr₂ (12 mg, 0.05 mmol), 2 mol% of DBU (15 μ L, 0.1 mmol) and 1 mL of DMF. while they were mixing together, tube was charged with CO₂ by balloon for 30 seconds. Then, mono-substituted epoxide (5 mmol) and 2 mL of DMF were put into the Schlenk tube. The mixture was stirred at 80 °C for 10 h and CO₂ was provided by a balloon (1 atm). The reaction mixture was taken up in methanol and catalysts were filtered and filtrate was concentrated under reduced pressure. Purification by flash chromatography on silica gel with *n*-hexane and ethyl acetate afford the cyclic carbonates.

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References

- [1] a) M. Aresta, A. Dibenedetto, *Dalton Trans.* 2007, 28, 2975; b) K. Huang, C.-L. Sun, Z.-J. Shi, *Chem. Soc. Rev.* 2011, 40, 2435.
- [2] a) C. J. Liu, R. Mallinson, M. Aresta (Eds.), Utilization of Green House Gases, American Chemical Society, Washington, DC, 2003; b) S. N. Riduan, Y. Zhang, Dalton Trans. 2010, 39, 3347; c) B.-L. Lu, L. Dai, M. Shi, Chem. Soc. Rev. 2012, 41, 3318; d) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, Chem. Rev. 2013, 113, 6621; e) M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. ASAP; DOI: 10.1021/cr4002758.
- [3] a) D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* 1996, 153, 155; b) T. Sakakura, K. Kohno, *Chem. Commun.* 2009, 1312; c) D. J. Darensbourg, S. J. Wilson, *Green Chem.* 2012, 14, 2665.

- [4] a) A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* 1996, 96, 951; b) J. H. Clements, *Ind. Eng. Chem. Res.* 2003, 42, 663; c) B. Schäffner, F. Schäffner, S. P. Verevkin, A. Bcrner, *Chem. Rev.* 2010, 110, 4554.
- [5] For reviews, see: a) A. Decortes, A. M. Castilla, A. W. Kleij, Angew. Chem. 2010, 122, 10016; Angew. Chem. Int. Ed. 2010, 49, 9822; b) X.-B. Liu, D. J. Darensbourg, Chem. Soc. Rev. 2012, 41, 1462; c) D. J. Darensbourg, Chem. Rev. 2007, 107, 2388; d) W.-L. Dai, S.-L. Luo, S. F. Yin, C.-T. Au, Appl. Catal. A: 2009, 366, 2.
- [6] a) H. G. Alt, J. Chem. Soc. Dalton Trans. 1999, 1703;
 b) J. Zhang, X. Wang, G.-X. Jin, Coord. Chem. Rev. 2006, 250, 95.
- [7] a) C. G. Overberger, N. Vorchheimer, J. Am. Chem. Soc. 1963, 85, 951; b) C. G. Overberger, R. C. Glowaky, T. J. Pacansky, K. N. Sannes, Macromol. Synth. 1974, 5, 43; c) J. Wang, T. W. Smith, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 2004, 45, 290; d) T. W. Smith, M. Zhao, F. Yang, D. Smith, P. Cebe, Macromolecules 2013, 46, 1133.
- [8] a) Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, Angew. Chem. 2007, 119, 7393; Angew. Chem. Int. Ed. 2007, 46, 7255; b) Y. Xiong, Y. Wang, H. Wang, R. Wang, Z. Cui, J. Appl. Polym. Sci. 2012, 123, 1486.
- [9] S. Ghazali-Esfahani, H. Song, E. Păunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yana, P. J. Dyson, *Green Chem.* 2013, 15, 1584.
- [10] Y. Takecuchi, S. Ozaki, M. Satoh, K.-i. Mimura, S.-i. Hara, H. Abe, H. Nishioka, T. Harayama, *Chem. Pharm. Bull.* **2010**, *58*, 1552.
- [11] A. Monney, G. Venkatachalam, M. Albrecht, *Dalton Trans.* 2011, 40, 2716.
- [12] H. Sellner, C. Faber, P. B. Rheiner, D. Seebach, *Chem. Eur. J.* 2000, *6*, 3692.
- [13] We tentatively assigned a molecular weight (ca. 30,000) of the polymer. An accurate molecular weight measurement was not possible because of aggregations and interactions among charged polymers. The 30,000 value was obtained from a Zimm plot of diluted DMF solutions of the polymer. For molecular weight determinations of charged polymers, see the following papers: a) M. D. Green, T. E. Long, J. Macromol. Sci. Part C: Polym. Rev. 2009, 49, 291; b) E. B. Anderson, T. E. Long, Polymer 2010, 51, 2447; c) J. Pinaud, J. Vignolle, Y. Gnanou, D. Taton, Macromolecules 2011, 44, 1900.
- [14] X. Liu, C. Cao, Y. Li, P. Guan, L. Yang, Y. Shi, Synlett 2012, 1343.
- [15] L. Xiao, D. Lv, W. Wu, Catal. Lett. 2011, 141, 1838.
- [16] a) D. P. Sanders, K. Fukushima, D. J. Coady, A. Nelson, M. Fujiwara, M. Yasumoto, J. L. Hedrick, J. Am. Chem. Soc. 2010, 132, 14724; b) C.-Y. Li, C.-R. Wu, Y.-C. Liu, B.-T. Ko, Chem. Commun. 2012, 48, 9628; c) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. Kleij, J. Am. Chem. Soc. 2013, 135, 1228; d) C. J. Whiteoak, E. Martin, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, Adv. Synth. Catal. 2012, 354, 469.
- [17] C. J. Whiteoak, E. Martin, E. Escudero-Adán, A. W. Kleij, Adv. Synth. Catal. 2013, 355, 2233.
- [18] Y.-M. Shen, W.-L. Duan, M. Shi, J. Org. Chem. 2003, 68, 1559–1562.

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KK These are not the final page numbers!

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- [19] a) B. Ochiai, K. Yokota, A. Fujii, D. Nagai, T. Endo, *Macromolecules* 2008, 41, 1229; b) D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert, C. L. Liotta, *J. Org. Chem.* 2005, 70, 5335; c) J. M. Hooker, A. T. Reibel, S. M. Hill, M. J. Schueller, J. S. Fowler, *Angew. Chem.* 2009, 121, 3534; *Angew. Chem. Int. Ed.* 2009, 48, 3482.
- [20] a) T.-Y. Shi, J.-Q. Wang, J. Sun, M.-H. Wang, W.-G. Cheng, S.-J. Zhang, *RSC Adv.* 2013, *3*, 3726; b) Y. Xiong, Y. Wang, H. Wang, R. Wang, Z. Cui, *J. Appl. Polym. Sci.* 2012, *123*, 1486; c) R. A. Watile, K. M. Deshmukh, K. P. Dhake, B. M. Bhanage, *Catal. Sci. Technol.* 2012, *2*, 1051; d) Z.-Z. Yang, Y.-N. Zhao, L.-N.

He, J. Gao, Z.-S. Yin, *Green Chem.* **2012**, *14*, 519; e) L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, *Green Chem.* **2011**, *13*, 1023.

- [21] a) H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu, X.-B. Lu, J. Org. Chem. 2008, 73, 8039; b) Y. Kayaki, M.; Yamamoto, T. Ikariya, Angew. Chem. 2009, 121, 4258; Angew. Chem. Int. Ed. 2009, 48, 4194.
- [22] a) T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* 1997, 1129; b) T. Chang, H. Jing, L. Jin, W. Qiu, *J. Mol. Catal. A: Chem.* 2007, 264, 241; c) Y.-M. Shen, W.-L. Duan, M. Shi, *J. Org. Chem.* 2003, 68, 1559.

COMMUNICATIONS

 8 Poly(4-vinylimidazolium)s/Diazabicyclo[5.4.0]undec-7-ene/ Zinc(II) Bromide-Catalyzed Cycloaddition of Carbon Dioxide to Epoxides

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Ue Ryung Seo, Young Keun Chung*



7 examples retention of the configuration up to 87% isolated yield

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