View Online

# Selective production of cyclic carbonate over polycarbonate using a double metal cyanide–quaternary ammonium salt catalyst system†

**Manju Mamparambath Dharman, Jeong-In Yu, Ji-Yeon Ahn and Dae-Won Park***

***Received 25th May 2009, Accepted 17th August 2009***
***First published as an Advance Article on the web 11th September 2009***
**DOI: 10.1039/b916875n**

Downloaded by City College of New York on 22 November 2010
Published on 11 September 2009 on http://pubs.rsc.org | doi:10.1039/B916875N

**A double metal cyanide complex, an efficient catalyst for the copolymerization of $CO_2$ with epoxide, was successfully utilized for the cycloaddition of $CO_2$ to various epoxides in the presence of quaternary ammonium salts without any solvents.**

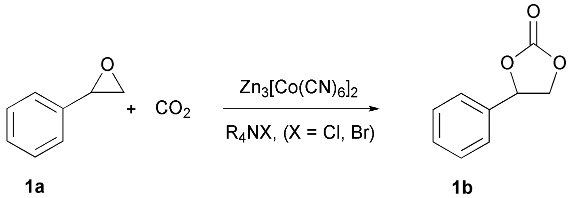
Owing to environmental concerns, fixation of $CO_2$ has received much interest recently. In fact, its utilization as a reactant is currently a widely accepted scheme for its effective sequestration. More specifically, due to the high reactivity of epoxides, $CO_2$ can be effectively added to them for the production of either polycarbonate or cyclic carbonates. Among these, cyclic carbonates have gained much attention due to their broad spectrum of applications, such as aprotic polar solvents, additives and monomers for polymer synthesis. To date there are several catalysts reported for the successful production of cyclic carbonates, comprising simple alkali metal salts, phosphines, main group metal complexes, transition metal complexes and porous metal oxides.[1]

Double metal cyanide complexes are well studied as a catalyst for the ring opening polymerization of epoxides.[2] Very recently, it found a reputable position as catalyst for the copolymerization of epoxides and $CO_2$.[3] In our previous studies, we have synthesized various double metal cyanide complexes and it has been successfully monitored for the production of polycarbonate from $CO_2$ and epoxides.[4] Lately, we have demonstrated the effect of microwave irradiation for the modification of polycarbonate properties using the same double metal cyanide complexes.[5]

Room temperature ionic liquids as environmentally benign media for organic synthesis and catalytic reaction have been widely recognized and accepted.[6] Many reactions have been reported to occur in ionic liquids with good to excellent performance. In the previous studies, the addition of $CO_2$ to epoxides for the preparation of cyclic carbonates was generally conducted at relatively high $CO_2$ pressures and reaction temperatures in the presence of metal halides, metal complexes or ionic liquids as catalysts.[7]

In the present study, the effect of addition of quaternary ammonium salt as a cocatalyst has been studied for the double metal cyanide catalyzed reaction. Until now there are several reactions reported using quaternary ammonium salts as cocatalysts together with organometallic complexes.[8] These routes were disadvantaged by the requirement of high pressure, longer reaction times and high catalyst to reactant ratio. Here in this study, we have utilized a completely heterogenous double metal cyanide complex with quaternary ammonium salts to achieve cycloaddition reactions in a moderate reaction pathway. Moreover the catalyst showed higher activity without the aid of any solvents in the reaction mixture.

During our investigation of the cycloaddition between styrene oxide (**1a**) and $CO_2$ catalyzed by a double metal cyanide complex based on $Zn_3[Co(CN)_6]_2$ in the presence of quaternary ammonium salts (Scheme 1), we found that styrene carbonate (**1b**) could be obtained in 97% yield with almost 99% selectivity. The synthesis and thorough characterization of the double metal cyanide complex is well described in a previous report elsewhere.[5] To the best of our knowledge, this is the first report for the cycloaddition reaction using a double metal cyanide complex as a catalyst. When it is used alone, it undergoes copolymerization reaction to produce the corresponding polycarbonate (Table 1, entry1). On the other hand when $n\mathrm{Bu}_4\mathrm{NCl}$ is used as a catalyst, the reaction activity is found to be poor (Table 1, entry 2). In the previous reports using quaternary salts as catalyst, a high concentration of catalyst or longer reaction time was needed to achieve appreciable conversion.[9] Combining the double metal cyanide complex with quaternary ammonium salts, gave cyclic carbonate selectively with high yields. As shown in Table 1 (entries 3–6), the proposed catalyst system is very sensitive to the reaction temperature. When the reaction temperature is increased from 80 to 140 °C, the yield as well as the selectivity for the cyclic carbonate is increased. 140 °C is found to be the best reaction temperature condition for the complete conversion of styrene oxide to styrene carbonate with 99% selectivity. This could be due to the better activation of catalyst at higher temperature. We also studied the influence of various quaternary ammonium salts such as $n\mathrm{Pr}_4\mathrm{NCl}$, $n\mathrm{Bu}_4\mathrm{NCl}$, $n\mathrm{Hex}_4\mathrm{NCl}$, $n\mathrm{Oct}_4\mathrm{NCl}$, $n\mathrm{Dodec}_4\mathrm{NCl}$ and $n\mathrm{Bu}_4\mathrm{NBr}$ for the cycloaddition reaction. Comparing the entries 5, 7–10 in Table 1, it is clear from the results that the alkyl chain length of the cation has a



**Scheme 1** Cycloaddition of $CO_2$ to styrene oxide (**1a**).

---

*Department of Chemical Engineering, Pusan National University, Busan, 609-735, Korea. E-mail: dwpark@pusan.ac.kr; Fax: +82-51-512-8563; Tel: +82-51-510-2399*

† Electronic supplementary information (ESI) available: Experimental details and product characterizations. See DOI: 10.1039/b916875n

This journal is © The Royal Society of Chemistry 2009

View Online

Downloaded by City College of New York on 22 November 2010
Published on 11 September 2009 on http://pubs.rsc.org | doi:10.1039/B916875N

**Table 1** Effect of reaction parameters on the coupling of $CO_2$ and styrene oxide[a]

| Entry | Catalyst | Quaternary salt | $T/°C$ | Yield[b] (%) | Selectivity (%) | TON[c] |
|---|---|---|---|---|---|---|
| 1 | $Zn_3[Co(CN)_6]_2$ | — | 120 | —[d] | — | — |
| 2 | — | $n$Bu$_4$NCl | 120 | 14 | 99 | 144 |
| 3 | $Zn_3[Co(CN)_6]_2$ | $n$Bu$_4$NCl | 80 | 35 | 99 | 360 |
| 4 | $Zn_3[Co(CN)_6]_2$ | $n$Bu$_4$NCl | 100 | 43 | 99 | 438 |
| 5 | $Zn_3[Co(CN)_6]_2$ | $n$Bu$_4$NCl | 120 | 86 | 95 | 918 |
| 6 | $Zn_3[Co(CN)_6]_2$ | $n$Bu$_4$NCl | 140 | 97 | 99 | 978 |
| 7 | $Zn_3[Co(CN)_6]_2$ | $n$Pr$_4$NCl | 120 | 83 | 93 | 900 |
| 8 | $Zn_3[Co(CN)_6]_2$ | $n$Hex$_4$NCl | 120 | 87 | 95 | 930 |
| 9 | $Zn_3[Co(CN)_6]_2$ | $n$Oct$_4$NCl | 120 | 87 | 95 | 930 |
| 10 | $Zn_3[Co(CN)_6]_2$ | $n$Dodec$_4$NCl | 120 | 94 | 98 | 978 |
| 11 | $Zn_3[Co(CN)_6]_2$ | $n$Bu$_4$NBr | 120 | 97 | 99 | 996 |

[a] Reaction conditions: styrene oxide **1a** (5 ml, 46.1 mmol), catalyst (10 mg, 0.046 mmol Zn), quaternary salt (0.5 mmol), time: 6 h, $CO_2$ pressure: 0.34 MPa. [b] Calculated from GC analysis. [c] moles of styrene oxide converted per mole of Zn. [d] copolymer is obtained, $M_n = 2300$; $MWD = 1.08$, $f_{CO2} = 40\%$.

decisive role in determining the activity of the catalyst system. Among those quaternary salts with varying alkyl substituent on cation, $n$Dodec$_4$NCl showed higher catalytic activity than the rest. The higher activity could be expected to derive from the bulky cation of the quaternary salt. Also, the quaternary salt bearing $Br^-$ anion showed more influence on the catalytic activity than its $Cl^-$ analogue.

A series of epoxide substrates were examined for the synthesis of corresponding cyclic carbonates in the presence of $Zn_3[Co(CN)_6]_2$/$n$Bu$_4$NCl at 0.34 MPa $CO_2$ pressure and 120 °C (Table 2). Cyclic carbonate with alkyl side chain groups **2b–5b** (entries 1–4) were successfully synthesized from each epoxide **2a–5a** in high yield. The disubstituted epoxide, cyclohexene oxide **6a** gave lower activity towards the production of the corresponding cyclic carbonate, which might probably be due to the effect of the high steric hindrance of cyclohexene oxide.[10] All cyclic carbonates were obtained with almost 100% selectively, and were identified by GC/MS.

The catalyst recyclability was examined by separating it from the reaction mixture by filtration. The reusability tests were performed by scaling up the reaction conditions, keeping the same epoxide/catalyst/cocatalyst ratio. The catalyst was found to be reusable for up to 4 cycles, after that the isolation of catalyst became difficult to separate from the reaction mixture due to its high dispersive nature (see section 1.4 of ESI).†

A possible mechanism is deduced from the obtained results. The double metal cyanide complex promotes the ring opening of epoxide. The following addition of $CO_2$ to the ring opened epoxide may be preferred by the presence of quaternary ammonium salt, which stabilizes the polarized intermediate. Thus, selective formation of cyclic carbonate could be expected by the presence of quaternary ammonium salts, which may restrict the extension of the polymer chain. The formation of cyclic carbonates could be expected either through direct formation or depolymerization of the formed polycarbonate. To explain the mechanism of the reaction, the product mixture was analyzed by IR spectroscopy in the $\nu(CO_2)$ region to ascertain the extent of polycarbonate formation (Fig. 1). The intense absorbance at approximately 1800 $cm^{-1}$, which corresponds to the $\nu(CO_2)$ vibration of cyclic carbonate, differentiate its formation from polycarbonate copolymer ($\nu(CO_2) \approx 1750\ cm^{-1}$) (Fig. 2). Generally, formation of polycarbonate predominates at lower reaction temperatures. Hence the reaction mixture was analyzed at different reaction temperatures. Even at lower temperatures, a strong absorption around 1800 $cm^{-1}$ with a high energy shoulder indicates the selective formation of cyclic carbonate over polycarbonate. The absence of polycarbonate

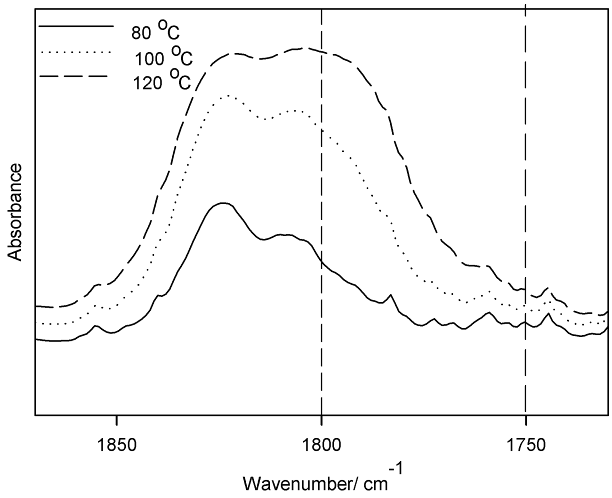


**Fig. 1** Infrared spectrum in the $\nu(CO_2)$ region of the reaction mixture at different temperature.

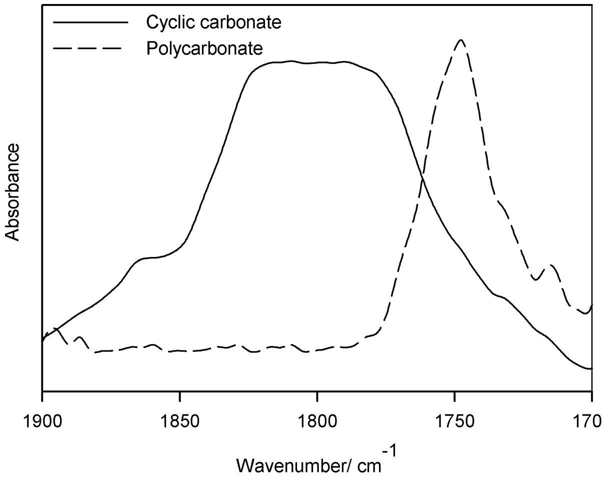
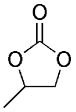
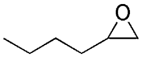
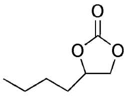
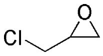
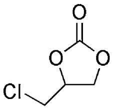
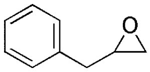
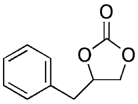
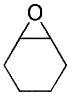
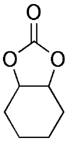


**Fig. 2** FT-IR spectra of polycarbonate and cyclic carbonate.

Downloaded by City College of New York on 22 November 2010
Published on 11 September 2009 on http://pubs.rsc.org | doi:10.1039/B916875N

**Table 2** Cycloaddition of $CO_2$ and various epoxides catalyzed by the $Zn_3[Co(CN)_6]_2$ complex in the presence of $n$$Bu_4NCl$[a]

| Entry | Epoxide | Cyclic carbonate | Time/h | Yield[b] (%) | TON[c] |
|---|---|---|---|---|---|
| 1 |  |  | 2 | 95 | 958 |
| 2 |  |  | 4 | 99 | 996 |
| 3 |  |  | 3 | 95 | 963 |
| 4 |  |  | 4 | 96 | 972 |
| 5 |  |  | 6 | 75 | 756 |

[a] Reaction conditions: epoxide (5 ml, 46.1 mmol), catalyst (10 mg, 0.046 mmol Zn), quaternary salt (0.5 mmol), temperature: 120 °C, time: 6 h, $CO_2$ pressure: 0.34 MPa. [b] Calculated from GC analysis. [c] Moles of epoxide converted per mole of Zn.

formation (absence of peak at 1750 $cm^{-1}$) even at lower reaction temperature ruled out the depolymerization mechanism. The presence of ionized species of quaternary ammonium salts in the reaction mixture may hinder the growth of the polymer chain, thereby promoting a ring closure pathway towards the selective production of cyclic carbonate. Thus, the presence of quaternary salt may not only accelerate the diffusion of $CO_2$ in to the reaction mixture but also it favors the back biting mechanism to produce the cyclic carbonate exclusively.

Conclusively, the double metal cyanide based on $Zn_3[Co(CN)_6]_2$ with quaternary ammonium salt is a highly efficient catalyst system towards the production of cyclic carbonate under mild reaction conditions. The double metal cyanide complex is easily synthesizable and stable under general reaction conditions. Besides, the catalyst is found to be reusable up to 4 runs without much loss in its catalytic activity towards the cyclic carbonate formation. The catalyst system is compatible for the production of cyclic carbonates from various epoxides with the use of low $CO_2$ pressure. Hence the cooperative effect between the double metal cyanide complex and quaternary ammonium salt leads to the production of cyclic carbonate by its efficient catalysis under solvent free conditions. The tunability of the double metal cyanide catalyst could be a potential criteria to make it more viable towards its possible industrial applications.

## Experimental

Representative procedure for the reaction of epoxide with carbon dioxide: all reactions were carried out in a 50 ml stainless steel autoclave type reactor equipped with a magnetic stirrer and a pressure gauge. For each reaction, $Zn_3[Co(CN)_6]_2$ (0.01 g), $n$$Bu_4NCl$ (0.5 mmol; 0.138 g) and styrene oxide **1a** (5 ml, 46.1 mmol) were charged into the reactor, successively. The reactor is allowed to equilibrate with carbon dioxide at the desired pressure and then heated to the desired temperature under a constant supply of carbon dioxide. After the required time of reaction, the reactor is cooled to room temperature, and the unreacted carbon dioxide is vented off. The crude product was analyzed by GC (Agilent6890, HP-5 column; 30 m, 0.320 mm, 0.25 μm, 60 to 325/350 °C) and the conversion, selectivity and yield were determined by GC using internal standard method. All cyclic carbonates were isolated by column chromatography and analyzed through FT-IR (IR spectra were recorded on a Shimadzu Fourier Transform Infrared spectrometer IRPrestige-21), GC/MS (Agilent 5975C) and $^1H$-NMR spectroscopy (Varian Gemini 2000, 300 MHz using $CDCl_3$ as solvent).

## Acknowledgements

The authors are grateful to Korea Science and Engineering Foundation (R01-2007-000-10183-0) and BK-21 for the financial support and KBSI, Busan for the analyses.

## References

1 (*a*) D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155–174; (*b*) A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH Publishers, New York, 1988; (*c*) M. Aresta, *Carbon Dioxide Recovery and Utilization*, Kluwer Academic Publishers,

This journal is © The Royal Society of Chemistry 2009

Downloaded by City College of New York on 22 November 2010
Published on 11 September 2009 on http://pubs.rsc.org | doi:10.1039/B916875N

Netherlands, 2003; (*d*) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27–59; (*e*) D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063–2095; (*f*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387; (*g*) T. Sakakura and K. Kohnoa, *Chem. Commun.*, 2009, 1312–1330.

2 (*a*) Y. J. Huang, G. R. Qi and L. S. Chen, *Appl. Catal., A*, 2003, **240**, 263–271; (*b*) X.-H. Zhang, Z.-J. Hua, S. Chen, F. Liu, X.-K. Sun and G.-R. Qi, *Appl. Catal., A*, 2007, **325**, 91–98; (*c*) S. Lee, S. T. Baek, K. Anas, C.-S. Ha, D.-W. Park, J. W. Lee and I. Kim, *Polymer*, 2007, **48**, 4361–4367.

3 (*a*) D. J. Darensbourg, M. J. Adams, J. C. Yarbrough and A. L. Phelps, *Inorg. Chem.*, 2003, **42**, 7809–7818; (*b*) S. Chen, Z. Hua, Z. Fang and G. Qi, *Polymer*, 2004, **45**, 6519–6524; (*c*) X.-K. Sun, X.-H. Zhang, F. Liu, S. Chen, B.-Y. Du, Q. Wang, Z.-Q. Fan and G.-R. Qi, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 3128–3139.

4 I. Kim, M. J. Yi, K. J. Lee, D.-W. Park, B. U. Kim and C.-S. Ha, *Catal. Today*, 2006, **111**, 292–296.

5 M. M. Dharman, J.-Y. Ahn, M.-K. Lee, H.-L. Shim, K.-H. Kim, I. Kim and D.-W. Park, *Green Chem.*, 2008, **10**, 678–684.

6 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083; (*b*) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459–2477; (*c*) R. Sheldon, *Chem. Commun.*, 2001, 2399–2407; (*d*) *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, 2nd edn, Wiley-VCH Verlags GmbH & Co. KGaA, Wainheim, 2008.

7 (*a*) J. Peng and Y. Deng, *New J. Chem.*, 2001, **25**, 639–641; (*b*) K. Kossev, N. Koseva and K. Troev, *J. Mol. Catal. A: Chem.*, 2003, **194**, 29–37; (*c*) H. S. Kim, J. J. Kim, H. Kim and H. G. Jang, *J. Catal.*, 2003, **220**, 44–46; (*d*) J. Sun, S. Fujita, F. Zhao and M. Arai, *Green Chem.*, 2004, **6**, 613–616; (*e*) H. Kawanami, A. Sasaki, K. Matsuia and Y. Ikushima, *Chem. Commun.*, 2003, 896–897; (*f*) X.-B. Lu, X.-J. Feng and R. He, *Appl. Catal., A*, 2002, **234**, 25–33.

8 (*a*) X.-B. Lu, J.-H. Xiu, R. He, K. Jin, L.-M. Luo and X.-J. Feng, *Appl. Catal., A*, 2004, **275**, 73–78; (*b*) X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li and H. Wang, *J. Mol. Catal. A: Chem.*, 2004, **210**, 31–34; (*c*) J. Meléndez, M. North and R. Pasquale, *Eur. J. Inorg. Chem.*, 2007, 3323–3326; (*d*) X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 3732–3733; (*e*) X.-B. Lu, R. He and C.-X. Bai, *J. Mol. Catal. A: Chem.*, 2002, **186**, 1–11; (*f*) X.-B. Lu, H. Wang and R. He, *J. Mol. Catal. A: Chem.*, 2002, **186**, 33–42; (*g*) A. Berkessel and M. Brandenburg, *Org. Lett.*, 2006, **8**, 4401–4404; (*h*) S.-W. Chen, R. B. Kawthekar and G.-J. Kim, *Tetrahedron Lett.*, 2007, **48**, 297–300; (*i*) M. North and R. Pasquale, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946–2948.

9 V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561–2563.

10 F. Li, C. Xia, L. Xu, W. Sun and G. Chen, *Chem. Commun.*, 2003, 2042–2043.