

Effect of cocatalyst and carbon dioxide pressure on the synthesis of polycarbonate from phenyl glycidyl ether and carbon dioxide

Ji-Yeon Ahn, Hye-Lim Shim, Kyung-Hoon Kim, Il Kim, Sang-Wook Park, and Dae-Won Park[†]

Division of Chemical Engineering, Pusan National University, Busan 609-735, Korea

(Received 11 October 2007 • accepted 5 January 2008)

Abstract—The copolymerization of phenyl glycidyl ether (PGE) and carbon dioxide was performed in the presence of ionic liquid catalyst. 1-Butyl-3-methyl imidazolium chloride, tetrabutylammonium chloride and 1-*n*-butylpyridinium chloride were used as catalyst for this reaction carried out in a batch reactor. All the ionic liquid catalysts showed good catalytic activity for the synthesis of polycarbonates with very low polydispersity, close to 1. The carbonate content, turnover number (TON), and average molecular weight of the copolymer were affected by the structure of the ionic liquid. High carbon dioxide pressure enhanced TON and carbonate content because of the increase of carbon dioxide absorption in PGE solution. ZnBr₂ and a Zn-Co cyanide complex were also tested as a catalyst and/or cocatalyst for this reaction to compare their catalytic performance with the imidazolium salt ionic liquids.

Key words: Polycarbonate, Phenyl Glycidyl Ether, Carbon Dioxide, Ionic Liquid

INTRODUCTION

The chemistry of carbon dioxide and the carbon dioxide fixation have received much attention from both an economical and an environmental point of view: utilization of the least-expensive carbon source and reduction of global warming gas. The reaction of carbon dioxide with oxiranes to produce cyclic carbonates has been considered a useful method for its fixation by chemical processes [1,2]. Inoue et al. [3] first reported the synthesis of high molecular weight polycarbonates by alternating copolymerization of CO₂ and epoxide using a catalyst derived from diethyl zinc and water. Since then, many excellent reviews in different periods have described this topic well [4-8].

A majority of publications in these reviews involve the reaction of CO₂ with epoxides to generate polycarbonates and/or cyclic carbonate. The cyclic carbonate byproduct (1,3-dioxolane-2-one) is proposed to result from the degradation of the growing copolymer chain, i.e., the back-biting mechanism [9]. The reaction of PGE and CO₂ has been studied to form either five-membered cyclic carbonate or polycarbonate. 4-(Phenoxyethyl)-1,3-dioxolane-2-one [PMEC] is a good example of cyclic carbonate having high polarity and high reactivity for introduction of functional groups. Kihara et al. [10] reported the synthesis of PMEC from PGE-CO₂ reaction under atmospheric pressure using various salt catalysts such as metal halides and quaternary ammonium salts. Nishikubo et al. [11] used polymer-supported catalysts containing pendant quaternary onium salts as catalysts for this reaction. In our previous work [12], we also reported the synthesis of PMEC using immobilized quaternary ammonium salt catalysts. The copolymerization of PGE and CO₂ was also studied using Y(P₂₀₄)₃-Al(*i*-Bu)₃ catalyst [13].

In recent years, for the construction of a clean reaction system without the use of organic solvents, ionic liquids as environmentally benign media for catalytic processes or chemical extraction have

become widely recognized and accepted due to their particular properties, especially with the emergence of the *N,N*-dialkylimidazolium cation derivatives [14]. Both the cationic and the anionic partners can be easily varied, so that these ionic liquid solvents can be designed for particular applications or for particular sets of properties [15]. Many reactions catalyzed with ionic liquids, showing high performance have been reported [16-18].

In our previous works [19,20], we reported the use of imidazolium salt (one of ionic liquids) as a catalyst for the copolymerization of CO₂ with PGE in the batch or semi-batch reactor system. Herein we wish to report a more detailed study on the influences of copolymerization variables like catalyst structure, carbon dioxide pressure, and cocatalyst on the carbonate content, yield, and molecular weight of the copolymer in a batch reactor.

EXPERIMENTAL

1. Materials

PGE of a purity of 99% (Aldrich) was distilled before use. Carbon dioxide of purity higher than 99.9% was used as received. 1-*n*-butyl-3-methylimidazolium chloride (BMImCl) and 1-*n*-butylpyridinium chloride (BPyCl) were prepared according to the procedures reported previously. Tetrabutyl ammonium chloride (TBAC) was purchased from Aldrich and used without further purification. Typical double metal cyanide (DMC, Zn₂[Co(CN)₆]₂·ZnCl₂·yH₂O·zCA) complex catalyst with complexing agent (CA, tertiary butyl alcohol) was prepared according to the literature procedures [21].

2. Copolymerization of CO₂ and PGE

Copolymerization of CO₂ and PGE was carried out in a 50 mL autoclave which was equipped with a magnetic stirrer. For each typical reaction, ionic liquid (2 mmol) and PGE (40 mmol) were charged into the reactor without solvent, and purged several times with CO₂. The reactor was then pressurized with CO₂ to a preset pressure at room temperature. The reactor was heated to a desired temperature, then the reaction was started by stirring. The reactor pressure increased about 34.5-103.4 kPa depending on the reaction

[†]To whom correspondence should be addressed.

E-mail: dwpark@pusan.ac.kr

temperature due to vapor pressure of the reactants.

The polymerization reaction was terminated by adding an excess of ethanol containing dilute hydrochloric acid, and the resulting copolymer of CO₂ and PGE could be precipitated by adding more ethanol to the solution. To purify the precipitated copolymer, it was dissolved in THF first and then was reprecipitated by adding aqueous ethanol solution. After purification, the copolymer collected was dried under vacuum at 50 °C for 40 h prior to analysis.

3. Analysis

¹H-NMR spectra of the copolymers were recorded at room temperature on a Varian Gemini 2000 spectrometer using tetramethylsilane as internal reference. The carbonate or ether unit content in the copolymerization product was calculated from ¹H-NMR spectra according to literature [22]. ¹³C-NMR can also be useful in that each of the carbonates, be it cyclic or polymer, gives a unique signal. IR spectra of the polymers were obtained with a React IR (ASI Model 1000). Molecular weight of the copolymer was measured from MALDI (Matrix Assisted Laser Desorption Ionization) and GPC (gel permeation chromatography) analysis.

RESULTS AND DISCUSSIONS

1. Characterization

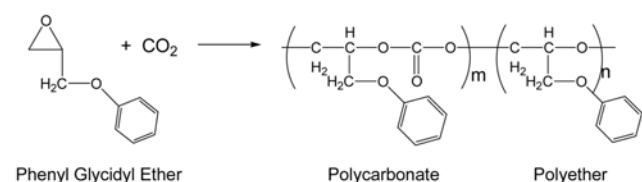
Copolymerization of PGE and CO₂ using ionic liquid catalysts was performed in the temperature range between 40 and 120 °C. The PGE/CO₂ copolymerization produced an alternating copolymer, i.e., polycarbonate unit with pendant phenyl functionality and ether unit, as shown in Scheme 1.

If the addition of CO₂ is perfect, only carbonate group could be generated. However, homopolymerization of PGE results in ether linkage. ¹H-NMR and ¹³C-NMR spectra of the obtained polycarbonate confirmed its expected copolymer structure. The ¹H-NMR spectrum of the polymer reveals only a very weak signal of the ring methine proton of the cyclic carbonate (δ =4.87 ppm), while the ¹³C-NMR spectrum fits well the alternative structure of the polycarbonate.

FT-IR spectra of the copolymer showed strong absorption band at 1,750 and 1,240 cm⁻¹, characteristic of stretching vibration C=O bond and C-O-C bond of the carbonate group, respectively. Percentage of carbonate linkage in the purified polymer was calculated from the relative intensities of the ¹H-NMR signals of the methines next to the carbonate linkage (δ =4.6 ppm) and polyether linkage (δ =3.5 ppm). As indexed for the proton peaks in the NMR spectrum, the polycarbonate was detected as a reaction product as reported previously [19].

2. Comparison of Catalysts

Table 1 summarizes the performance of different types of catalysts in the polycarbonate synthesis from PGE and CO₂. BMImCl,



Scheme 1. Copolymerization of PGE and CO₂.

Table 1. Performance of different catalysts for the copolymerization of PGE and CO₂ at 80 °C

Cat.	f _{CO2} (%) ^a	TON ^b	TOF ^c	Mn ^d	Mw/Mn ^d
BMImCl	95.3	11.97	1.20	1586	1.02
TBAC	76.5	5.20	0.87	1259	1.01
BPyCl	74.6	1.60	0.27	934	1.23
ZnCo	12.7	39.02	6.50	7800	3.20
ZnBr ₂	5.67	9.44	1.57	476	1.12

Polymerization conditions: PGE=40 mmol, Catalyst=2 mmol, Time=6 h, Temp.=80 °C, PCO₂ (25 °C)=1.07 MPa.

^a{[carbonate]/([carbonate]+[ether])} × 100 determined by ¹H-NMR spectra.

^bTurnover number: moles of PGE reacted/moles of catalyst.

^cTurnover frequency: (moles of PGE reacted/moles of catalyst)/h.

^dData from GPC.

BPyCl, TBAC, Zn-Co double metal cyanide (ZnCo DMC) and zinc bromide (ZnBr₂) were used. The reaction was carried out in a batch reactor system with CO₂ pressure (25 °C) of 1.07 MPa for 6 h at 80 °C. The polymer yield TON is presented as [moles of PGE reacted]/[moles of catalyst], and TOF is calculated by dividing TON by reaction time in h. BMImCl showed higher carbonate content and TON than TBAC, BPyCl and ZnBr₂. ZnBr₂ showed the lowest carbonate content, TON, TOF and Mn. BPyCl also showed lower catalytic activity than BMImCl. Pyridinium salts are another type of ionic liquid having lower catalytic activity than imidazolium salts [17]. ZnCo DMC showed lower carbonate content but very high TON. ZnCo DMC is considered to be a very effective catalyst for the synthesis of polyether units. ZnCo DMC is a catalyst generally used in the ring-opening polymerization of heterocyclic monomers.

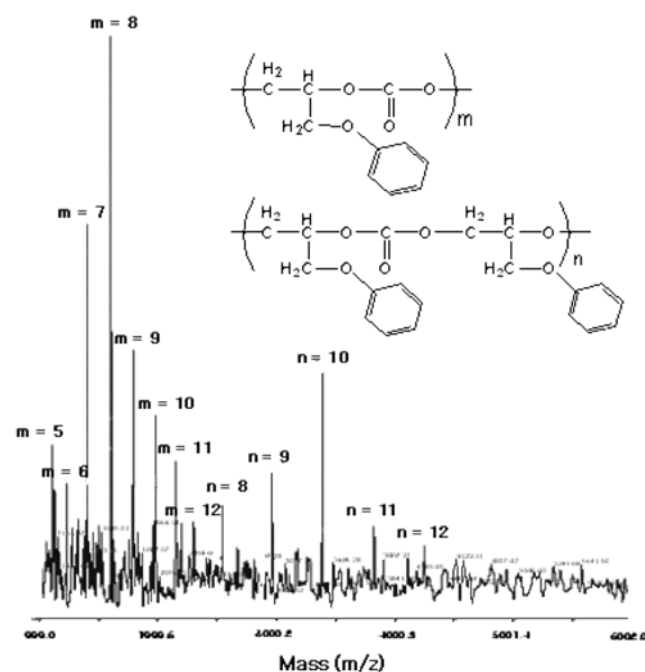


Fig. 1. MALDI-TOF mass spectra of polycarbonate obtained with BMImCl at 80 °C.

Table 2. Effect of carbon dioxide pressure on the carbonate content and catalytic activity for the copolymerization of PGE and CO₂

Temp. (°C)	P _{CO₂} (MPa)	f _{CO₂} (%) ^a	TON ^b	TOF ^c	Mn ^d	Mw/Mn ^d
80	0.58	72.2	11.79	1.97	1329	1.01
80	1.07	95.3	12.20	2.03	1586	1.02
80	2.17	100	13.10	2.18	2476	1.05
80	3.55	100	15.43	2.57	2829	1.03
80	5.61	98.8	16.26	2.71	2943	1.03
80	atmosphere ^e	77.7	3.34	0.56	1907	1.02
80	0.58 ^e	98.3	11.22	1.87	1942	1.02
80	1.07 ^e	99.7	12.35	2.06	1963	1.02
40	1.07	45.6	1.91	0.32	1818	1.03
40	1.07 ^e	86.1	2.88	0.48	1851	1.03

Polymerization conditions: PGE=40 mmol, Catalyst=BMIImCl (2 mmol), Time=6 h.

^a{[carbonate]/([carbonate]+[ether])} × 100 determined by ¹H-NMR spectra.

^bTurnover number: moles of PGE reacted/moles of catalyst.

^cTurnover frequency: (moles of PGE reacted/moles of catalyst)/h.

^dData from GPC.

^eSemi-batch reaction.

Therefore, the imidazolium salt ionic liquid can be considered to be the most efficient catalyst for the addition of CO₂ to the epoxide ring of PGE. Fig. 1 shows MALDI result for the copolymer obtained with BMIImCl. From GPC and MALDI results, it was estimated that the main product of the polycarbonate for this experiment was octamer.

3. Effects of CO₂ Pressure

Table 2 shows the effect of carbon dioxide pressure and the type of reaction system on the synthesis of polycarbonate from PGE with CO₂. The carbonate content and TON increased as the CO₂ pressure increased from 0.58 MPa to 5.61 MPa for BMIImCl catalyst in bath operations. High CO₂ pressure could enhance the absorption of CO₂ in PGE. Tan et al. [23] also reported the increase of the copolymer yield in propylene oxide-CO₂ reaction with increasing CO₂ pressure. However, after 4.1 MPa they observed a decrease of copolymer yield with increasing pressure. They explained this as due to the decrease of the solubility of the copolymer at high pressure.

The increase of carbonate content and TON with increasing CO₂ pressure was also observed in semi-batch operations. Semi-batch operations exhibited higher carbonate content and TON than those in batch operations. In order to maintain constant reactor pressure, carbon dioxide was supplied during the reaction in semi-batch operations. Therefore, higher concentration of CO₂ in the PGE solution could be maintained compared to batch operations. The increase of carbonate content and TON in semi-batch operation was more highly indicated at low temperature (40 °C) using the same BMIImCl catalyst. It is also noteworthy that the copolymerization of PGE and CO₂ proceeded under atmospheric pressure of CO₂ at 80 °C in the semi-batch operation.

4. Effects of Cocatalyst

Table 3 shows the effect of cocatalyst on the copolymerization

Table 3. Effect of cocatalyst on the carbonate content and catalytic activity for the copolymerization of PGE and CO₂

Cat.	f _{CO₂} (%) ^a	TON ^b	TOF ^c	Mn ^d	Mw/Mn ^d
BMIImCl ^e	73.9	7.58	1.26	1211	1.02
BMIImCl+ZnBr ₂	56.3	11.69	1.95	1885	1.30
EMIImCl+ZnBr ₂	38.1	8.13	1.36	1626	1.21
BMIImCl+ZnCo	85.7	16.62	2.77	3986	1.06
EMIImCl+ZnCo	50.6	5.75	0.46	2655	1.12

Polymerization conditions: PGE=40 mmol, Catalyst=2 mmol (IL : zinc = 1 : 1), Time=6 h, Temp.=80 °C, PCO₂ (25 °C)=1.07 MPa.

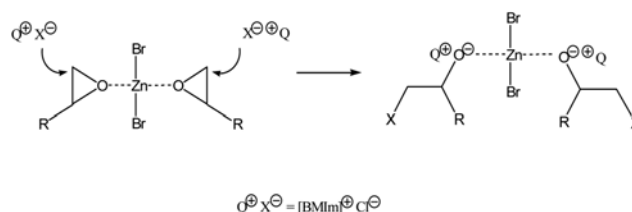
^a{[carbonate]/([carbonate]+[ether])} × 100 determined by ¹H-NMR spectra.

^bTurnover number: moles of PGE reacted/moles of catalyst.

^cTurnover frequency: (moles of PGE reacted/moles of catalyst)/h.

^dData from GPC.

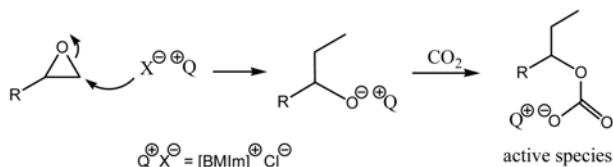
^eBMIImCl=1 mmol.

**Scheme 2. Coordination of PGE with ZnBr₂.**

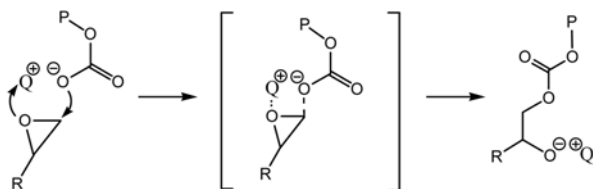
of PGE and CO₂. The TON and molecular weight increased when BMIImCl ionic liquid was used together with the ZnBr₂ cocatalyst. However, the carbonate content decreased in the presence of ZnBr₂ probably due to its high reactivity for the polyether production. The increased activity of BMIImCl with ZnBr₂ may originate from the cooperative action of both the acidic site (Zn) for epoxide activation and basic site (Cl⁻ in BMIImCl and/or Br⁻ in ZnBr₂) for CO₂ activation, as reported previously by Sun et al. [24] for the synthesis of styrene carbonate from styrene oxide and carbon dioxide. The role of ZnBr₂ cocatalyst on the copolymerization of PGE and CO₂ can be explained as follows. At initiation stage, PGE is coordinated with the Lewis acid site Zn to form the adduct of the metal-epoxide complex (shown in Scheme 2). Then the Cl⁻ anion of the ionic liquid makes a nucleophilic attack on the less hindered carbon atom of the coordinated epoxide followed by ring opening. Next, CO₂ is coordinated to the complex through interactions with Br⁻ and O⁻. Fuwei et al. [25] also reported an increase of the yield of propylene carbonate from propylene oxide and CO₂ with the use of ZnBr₂ cocatalyst.

The mixed catalyst of BMIImCl and ZnCo DMC also showed increases in TON and molecular weight for the copolymerization of PGE and CO₂. The mixture of EMIImCl and cocatalyst (ZnCo DMC or ZnBr₂) showed lower TON and molecular weight than the mixture of BMIImCl and cocatalyst did. For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length is reported to increase the hydrophobicity and the viscosity of ionic liquid [17]. Scheme 3 shows the proposed mechanism for the copolymerization of epoxide and CO₂. At the initiation step, the epoxide ring is acti-

Initiation



Chain Propagation



Scheme 3. Reaction mechanism for the copolymerization of epoxide and CO₂.

vated by the imidazolium salt ionic liquid and followed by CO₂ insertion. Repetition of this step results in the formation of long chains consisting of carbonate groups as monomer units. Then, in the chain propagation step, epoxide is inserted into the carbonate position. Therefore, ionic liquid with bulkier alkyl group is expected to activate its attack to the epoxide ring of PGE to form the reaction intermediate of the polycarbonate.

CONCLUSION

Carbon dioxide can be effectively added to the epoxide ring of PGE to produce copolymers of polycarbonate units and polyether units in the presence of ionic liquid catalysts. 1-Butyl-3-methyl imidazolium chloride showed higher carbonate content and TON than TBAC and BPyCl. ZnCo DMC produced mainly polyethers with higher molecular weight. High carbon dioxide pressure enhanced TON and carbonate content because of the increase of carbon dioxide absorption in PGE solution. ZnCo double metal cyanide and ZnBr₂ can be used as good cocatalyst when they are mixed with the ionic liquid catalyst.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-10183-0), and Brain Korea 21 program. S. W. Park is also thankful to the Applied Rheology Center.

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