

Copolymerization of Phenyl Glycidyl Ether with Carbon Dioxide Catalyzed by Ionic Liquids

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Abstract—The copolymerization of phenyl glycidyl ether (PGE) and carbon dioxide was performed without any solvent in the presence of ionic liquid as catalyst. The reaction was carried out in a batch autoclave reactor. The carbonate content of polycarbonate was affected by the structure of imidazolium salt ionic liquid; the one with the cation of bulkier alkyl chain length and with more nucleophilic anion showed better reactivity. However, the yield of carbon dioxide addition decreased when hexyl or octyl containing ionic liquids were used in place of butyl group in 1-alkyl-3-methyl imidazolium salts. The carbonate content and turnover number (TON) of the polycarbonate increased as the reaction temperature increased from 40 to 80 °C. However, the carbonate content decreased with increasing reaction time.

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

INTRODUCTION

A potential application of carbon dioxide as a feedstock is to use it as a comonomer in polymer synthesis. For example, polycarbonates can be synthesized by direct copolymerization of CO₂ with cyclic ethers. Inoue et al. [1969] 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 contributed by Rokicki et al. [1981], Super et al. [1997] and Darensbourg et al. [1996] have described this topic well, where the importance of catalyst was never overestimated.

Among catalysts reported, zinc dicarboxylates (for example, zinc glutarate) are known to afford the most active catalysts for the copolymerization of CO₂ and cyclic ethers to produce high molecular weight polycarbonates [Rokicki, 1990]. However, the conversion in the copolymerization was reported to be far below 100%. In addition to the organozinc catalyzed copolymerization, the discovery of immortal polymerization using aluminum complexes has expanded the utility of CO₂ as a comonomer in the production of polycarbonates [Darensbourg et al., 1996; Aida et al., 1986].

Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extraction has become widely recognized and accepted. Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability, and special characteristics in comparison with conventional organic and inorganic solvents. Many reactions catalyzed with ionic liquids and showing high performance have been reported [Song et al., 2000]. Propylene carbonate has been synthesized from CO₂ and propylene oxide with 1-*n*-butyl-3-methylimidazolium (BMIm) salt ionic liquid [Welton, 1999].

Darensbourg et al. [2003] reported (salen)Cr^{III}Cl complex catalyst for the reaction of CO₂ with propylene oxide or cyclohexene oxide.

They discovered that N-methylimidazole acted as co-catalyst by enhancing the rate of chain propagation.

In our previous works [Yu et al., 2005; Shin et al., 2003], we reported a successful synthesis of 4-(phenoxymethyl)-1,3-dioxolane-2-one [PMEC] from CO₂ and phenyl glycidyl ether (PGE) using soluble and immobilized quaternary ammonium salt catalysts. PMEC is a good example of cyclic carbonate having high polarity and high reactivity for introduction of functional groups. However, to our knowledge, there has been no report on the copolymerization of PGE and CO₂ using ionic liquid as catalyst.

In the present work, we studied the catalytic performance of alkylmethyl imidazolium salt ionic liquid in the synthesis of polycarbonate from the copolymerization of CO₂ with PGE. The influences of copolymerization variables like catalyst structure, operating pressure and temperature on the yield and carbonate content of the polycarbonate have been discussed.

EXPERIMENTAL

1. Materials

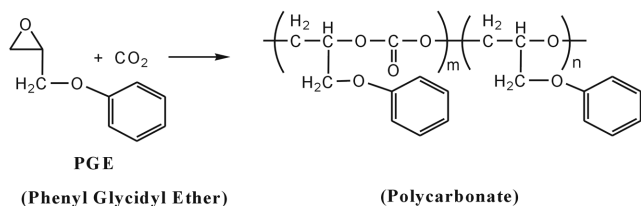
Phenyl glycidyl ether (PGE) of a purity of 99% (Aldrich) was distilled before use. CO₂ of purity higher than 99% (Aldrich) was used as received. Ionic liquids based on 1-*n*-ethyl-3-methylimidazolium (EMIm), 1-*n*-butyl-3-methylimidazolium (BMIm), 1-*n*-hexyl-3-methylimidazolium (HMIm) and 1-*n*-octyl-3-methylimidazolium (OMIm) with different anions such as Cl⁻, BF₄⁻, PF₆⁻ were prepared according to the procedures reported previously. The purities of all the ionic liquids was over 96%, and they were dried and degassed under vacuum at 100 °C for 4 h prior to use.

2. Copolymerization

Copolymerization of CO₂ and PGE shown in Scheme 1 was carried out in a 50 mL autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (2 mmol) and phenyl glycidyl ether (40 mmol) were charged into the reactor without solvent, and CO₂ was introduced at room temperature to a preset pressure. The reaction was started by stirring when the desired temperature and

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Scheme 1. Synthesis of polycarbonate from PGE and CO₂.

pressure were attained.

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 [Chen et al., 1991]. ¹³C-NMR can also be useful in that each of the carbonate, be it cyclic or polymer, gives a unique signal. IR spectra of the polymers were obtained by using 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 DISCUSSION

Copolymerization of PGE and CO₂ using ionic liquid catalysts has carried out between 40 and 120 °C. The PGE/CO₂ copolymeriza-

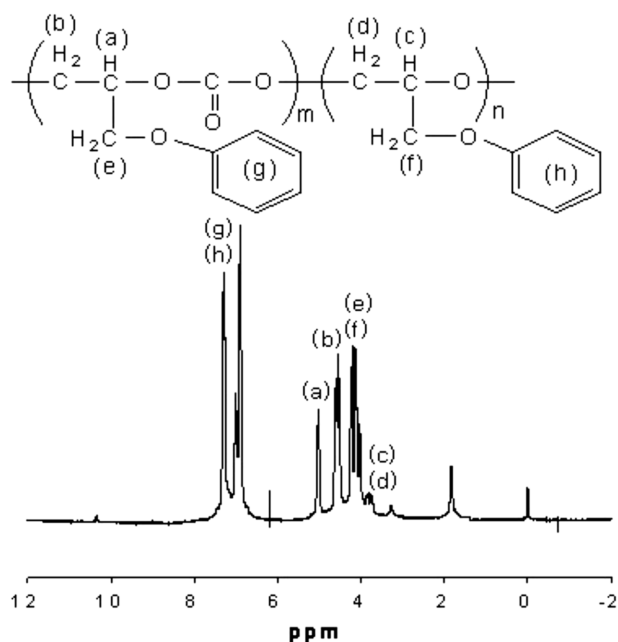


Fig. 1. ¹H-NMR spectrum of polycarbonate obtained from the copolymerization of CO₂ and PGE.

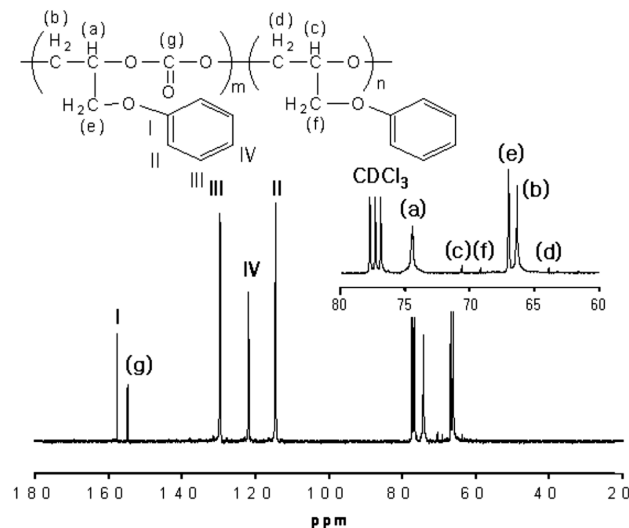


Fig. 2. ¹³C-NMR spectrum of polycarbonate obtained from the copolymerization of CO₂ and PGE.

tion 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 a carbonate group could be generated. However, homopolymerization of PGE results in ether linkage. ¹H-NMR (Fig. 1) and ¹³C-NMR (Fig. 2) spectra of the obtained polycarbonate confirmed its expected structure. The ¹H-NMR spectrum of the polymer reveals only a very weak signal of the ring methine portion of the cyclic carbonate (δ =4.87 ppm), while the ¹³C-NMR spectrum fits well the alternative structure of the polycarbonate.

Fig. 3 shows FT-IR spectra of various copolymer compositions. All the IR spectra 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 car-

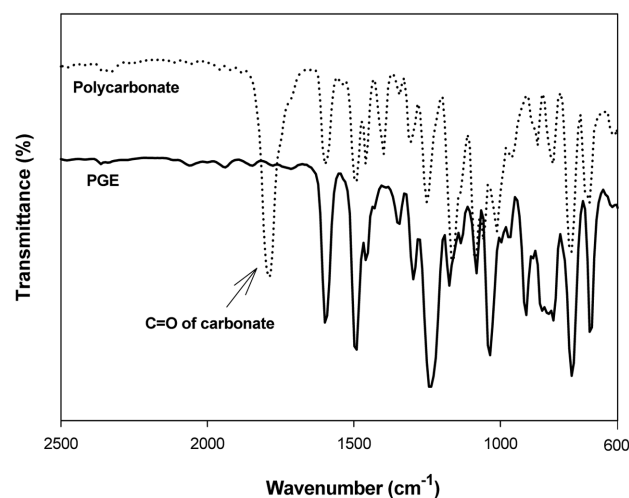


Fig. 3. FT-IR spectrum of polycarbonate obtained from the copolymerization of CO₂ and PGE.

bonate linkage ($\delta=4.8$ ppm) and ether linkage ($\delta=3.6$ ppm). As indexed for the proton peaks in the NMR spectrum, the polycarbonate was detected as a reaction product: $^1\text{H-NMR}$ (δ , CDCl_3), 4.9–5.2 ppm [(a), CH], 4.4–4.7 ppm [(b), CH_2], 3.6–4.0 ppm [(c), (d), CH, CH_2], 4.0–4.4 ppm [(e), (f), CH_2], 6.8–7.4 ppm [(g), (h), C_6H_5]. The $^{13}\text{C-NMR}$ spectra of polycarbonate fractions were found to consist mainly of four aromatic (C_6H_5 : I, II, III, IV) signals and four groups of aliphatic ((a), (b), (c), (d), (e), (f), (g)) signals: $^{13}\text{C-NMR}$ (δ , CDCl_3), 74.6 ppm [(a), CH], 66 ppm [(b), CH_2], 71 ppm [(c), CH], 64 ppm [(d), CH_2], 67 ppm [(e), CH_2], 69 ppm [(f), CH_2], 151 ppm [(g), C=O], 158 ppm [I, C_6H_5], 114 ppm [II, C_6H_5], 130 ppm [III, C_6H_5], 122 ppm [IV, C_6H_5].

Tables 1 and 2 show the results of copolymerization. The reaction was carried out in a batch reactor with an initial carbon dioxide pressure of 140 psig adjusted at 25 °C. When the temperature increased up to a reaction temperature, the reactor pressure increased

Table 1. Effects of the structure of imidazolium salt ionic liquid on the yield and carbonate content of the polycarbonate from PGE and CO_2 at 120 °C after 6 h of reaction

Catalyst	Carbonate cont. (%) ^a	TON ^b	TOF ^c
EMImCl	67.8	9.09	1.52
BMImCl	100	14.18	2.36
HMImCl	75.6	8.85	1.48
OMImCl	68.9	8.02	1.34
EMImBF ₄	35.2	6.10	1.02
EMImPF ₆	0	0	0

Polymerization condition: PGE=40 mmol, catalyst=2 mmol, PCO_2 (25 °C)=140 psig.

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

^bTurnover number: g of polymer/g of catalyst

^cTurnover frequency: g of polymer/g of catalyst/h

Table 2. Effects of temperature and reaction time on the yield and carbonate content of the polycarbonate from PGE and CO_2

Catalyst	Temp. (°C)	Time (h)	Carbonate cont. (%) ^a	TON ^b	TOF ^c
HMImCl	40	6	62.2	8.35	1.39
HMImCl	60	6	85.4	9.24	1.54
HMImCl	80	6	100	13.14	2.19
HMImCl	100	6	89.4	10.86	1.81
HMImCl	120	6	75.6	8.85	1.48
BMImCl	80	6	100	14.43	2.41
BMImCl	80	24	78.5	9.47	0.39
BMImCl	80	48	60.8	11.28	0.24
BMImCl	80	72	28.0	12.34	0.17

Polymerization condition: PGE=40 mmol, catalyst=2 mmol, PCO_2 (25 °C)=140 psig.

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

^bTurnover number: g of polymer/g of catalyst

^cTurnover frequency: g of polymer/g of catalyst/h

a little due to the increase of the vapor pressure of PGE. At 120 °C the initial reactor pressure increased to 165 psig. The reactor pressure was recorded during the reaction. It decreased to 0 psig after 6 h reaction with BMImCl catalyst. The polymer yield TON is presented as [g of polymer]/[g of catalyst], and TOF is calculated by dividing TON by reaction time in h.

Table 1 shows carbonate content and yield of polycarbonates when 1,3-dialkylimidazolium salts of different alkyl groups (EMIm⁺, BMIm⁺, HMIm⁺, OMIm⁺) and anions (Cl^- , BF_4^- , PF_6^-) were used as catalyst. BMImCl showed the highest yield (TON=14.18) and 100% carbonate content. However, they decreased when bulkier ionic liquids such as HMImCl or OMImCl were used. This may be due to the steric hindrance of bulky ionic liquid. For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length was also reported to increase the hydrophobicity and the viscosity of ionic liquid [Olivier-Bourbigou et al., 2002]. The order of catalytic activity for the different anions in EMIm salt ionic liquids decreased as $\text{Cl}^- > \text{BF}_4^- > \text{PF}_6^-$. EMImPF₆ could not catalyze the polymerization of PGE with carbon dioxide because of their low solubility. Olivier-Bourbigou et al. [2002] reported that the solubility of 1-hexane decreased in the order of $\text{Cl}^- > \text{PF}_6^- > \text{BF}_4^-$. From GPC results, it was estimated that the main products of the polycarbonates for these experimental runs in Table 1 were pentamers or hexamers.

Table 2 shows the effects of temperature and reaction time on the synthesis of the polycarbonates from PGE and CO_2 . The carbonate content and TON increased as the temperature increased from 40 °C to 80 °C for HMImCl catalyst. However, they decreased at temperatures over 100 °C, probably due to the increase of cyclic carbonate monomer production at high temperatures. Darensbourg et al. [2003] also reported the increase of propylene carbonate monomer production at higher temperature in the copolymerization of CO_2 and propylene oxide using chromium salene complex catalyst. When the reaction time increased from 6 h to 72 h, the content of carbonate and TOF greatly decreased. A slight increase of propylene carbonate with the increase of reaction time was also reported [Darensbourg et al., 2003].

CONCLUSION

Carbon dioxide can be effectively added to the epoxide ring of phenyl glycidyl ether to produce polycarbonate. Imidazolium ionic liquids showed good catalytic performance for the copolymerization of PGE and CO_2 . BMImCl ionic liquid showed the highest yield (TON=14.18) and 100% carbonate content at 120 °C for 6 h. The catalytic activity of different anions in EMIm ionic liquid decreased as $\text{Cl}^- > \text{BF}_4^- > \text{PF}_6^-$. The TON and carbonate content increased as the temperature increased from 40 °C to 80 °C, but they decreased over 100 °C. A more detailed kinetic study will be necessary for better understanding of the reaction mechanism of this reaction.

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