

Synthesis of Polycarbonates by Copolymerization of Carbon Dioxide and Cyclohexene Oxide Using Schiff Base Complex as Catalyst

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Abstract A novel Schiff base complex BCED–Zn has been found to be an effective catalyst for copolymerization of CO₂ and cyclohexene oxide to afford alternating copolymer poly(cyclohexenylene carbonate) (PCHC), and the turnover number was up to 421.1 at 110 °C and 4 MPa CO₂ pressure for 24 h. The influence of the reaction conditions such as reaction time, reaction temperature and CO₂ pressure was discussed and optimized. The thermal stability of PCHC was measured by thermogravimetric analysis, indicating that the 5 % weight loss temperature was about 232 °C and the maximum weight loss temperature was around 256 °C.

Keywords Polycarbonate · Carbon dioxide · Cyclohexene oxide · Catalyst · Copolymerization

1 Introduction

Despite its contribution in global warming, CO₂ is an economical C1 resource with the advantages such as abundance, renewability and nontoxicity [1]. CO₂ has already been used

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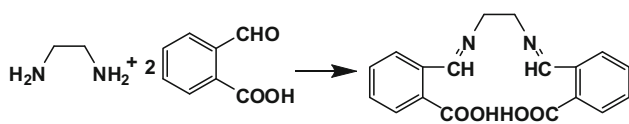
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in some industrial production processings including the productions of salicylic acid, urea and various carbonates [2]. In addition, CO₂ is also considered to be an interesting starting material for the synthesis of polymers and provides a sustainable alternative to the traditional carbon resources based on fossil fuel [3]. Aliphatic polycarbonates as a kind of alternating copolymer can be prepared based on carbon dioxide and epoxides instead of the phosgene route [4]. The carbonates generated from the copolymerization of CO₂ and propylene oxide (PO) or cyclohexene oxide (CHO) have attracted considerable attentions [5]. However, the relatively high thermal stability of CO₂ hinders its application as monomer of the copolymerization. A high efficient and selective catalyst is indispensable for initiation and progression reaction of CO₂ copolymerization. During the past three decades, the great progress in fixation of CO₂ into polycarbonates has been made since the creative work of Inoue et al. [6]. To date, numerous study efforts have focused on the development and optimization of improved catalysts for this reaction.

Most of high active catalysts are metal complexes, which are those of Zn, Cr, Mn, Al, Mg, Co and rare earth coordinated with various ligands including diketoimine [7], salen [8], pyridine [9], porphyrin [10], and phenoxide [11], et al. The bridging Zn–O–Zn existing in the complexes was assumed to contribute to efficient ring opening of epoxide because of coordinative activation between Zn and epoxide. Among them, Schiff base complexes including salen(M)X complexes and BDI–Zn complexes attracted extensively interest due to their high catalytic activity and living polymerization characteristic. The characteristics of Schiff base complexes which are suitable for the CO₂ copolymerization are summarized based on the analysis of the catalytic mechanism. (1) There is C–N bond or C–O bond in the ligand with relatively strong coordination ability and the stable complex can be formed; (2) the steric effect and electronic effect of substituent group



Scheme 1 Synthesis of the ligand

in the complex influence the catalytic property remarkably; and (3) various coordination bonds between ligand and metal can be formed.

Considering the good performances of Schiff base complexes in the CO₂ copolymerization, we report here the preparation of a novel Schiff base Zn complex and its catalytic behavior for the copolymerization of CO₂ and CHO. We attempted to introduce carboxyl into the salen ligand, and a Schiff base complex whose structure was similar to the salen(M)X was prepared. The ligand was prepared by the reaction of 2-carboxybenzaldehyde and ethylenediamine (Scheme 1), and the catalyst was synthesized by the coordination of the ligand and diethyl zinc (ZnEt₂). The structure of such ligand was very simple, and the preparation process was simplified. Moreover, the cocatalyst was not needed when using this catalyst, which played an important role in the traditional salen(M)X catalyst system [12]. So the effect of cocatalyst amount on the catalytic performance could be eliminated. The catalyst showed high activity for CHO and CO₂ copolymerization, and it tended to produce an alternating copolymer with turnover number (TON) as high as 421.1. The best result was obtained from the reaction at 110 °C and 4 MPa CO₂ pressure for 24 h. The obtained copolymer was characterized by IR, NMR and thermogravimetric analysis (TG). The carbonate unit content in polymer was 92.3 %, and the molecular weight M_n was $1.85 \times 10^4 \text{ g mol}^{-1}$.

2 Experimental

2.1 Material

CO₂ (>99.99 %) and N₂ (>99.99 %) were used as received. CHO (Aldrich Chemicals Co.) was freshly distilled over calcium hydride under N₂ atmosphere. 2-Carboxybenzaldehyde and ethylene diamine (Alfa Aesar Chemicals Co.) were all analytical grade. All other reagents were purchased commercially and used as received. ZnEt₂ was synthesized by ourselves and kept in a 10 % (V/V) toluene solution.

3 Preparation of Catalysts

3.1 Synthesis of Ligand bis(2-carboxybenzaldehyde)-N-ethylenediamine (BCED)

For the synthesis of BCED, 2-carboxybenzaldehyde 2.25 g (15 mmol) and ethylenediamine 0.50 mL (7.5 mmol) were

dissolved in 30 and 15 mL methanols, respectively. The ethylenediamine solution was dropped in the 2-carboxybenzaldehyde solution slowly, and the white floc precipitation was formed rapidly. And then, the solution was stirred for 30 min followed by the diethyl ether washing (15 mL \times 2) and drying. At last, some white powder was obtained. ¹H NMR (400 MHz, CDCl₃): δ 11.53(s, 2H, -COOH), 7.82(s, 2H, -CH=N), 7.71, 7.54(m, 8H, aromatic H), 5.74(s, 4H, CH₂); m.p. 173.5–175.9 °C, literature: 172.5–174.0 °C; IR ν (cm⁻¹): 3407(OH), 1731 (C=O), 1642 (C=N); Anal. Calc. for C₁₈H₁₆N₂O₄: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.58; H, 5.02; N, 8.93 %.

3.2 Synthesis of Complex BCED–Zn

The toluene solution of ZnEt₂ (10 % (V/V)) (2 mL) was slowly added to the toluene solution of 0.592 g (2 mmol) BCED (10 mL) by syringe in ice bath. After stirring for 30 min, the solvent and excess ZnEt₂ were removed by vacuum distillation.

3.3 Copolymerization of CO₂ and CHO

Copolymerization of CHO and CO₂ was performed in a 100 mL autoclave equipped with pressure indicator and magnetic stirring. After the autoclave was dried in vacuo at 100 °C for 1 h, the catalyst and CHO were loaded via the injection port followed by charging with CO₂ to proper pressure; then, the reaction was carried out for desired time. After cooling and venting, the copolymer was extracted using a dichloromethane solution with methanol as precipitant and dried under vacuum at 100 °C.

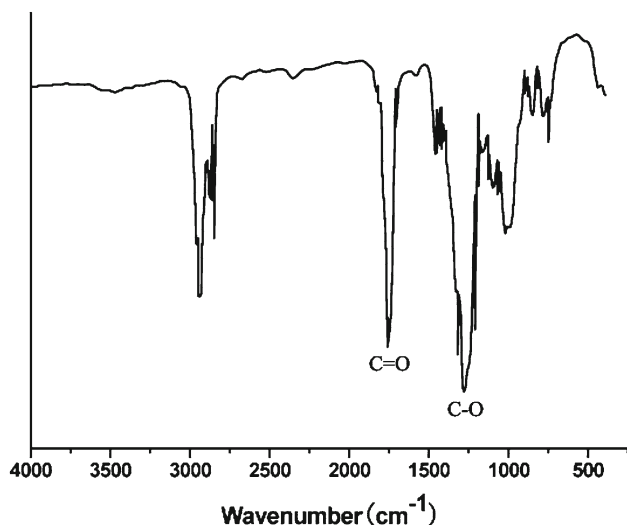
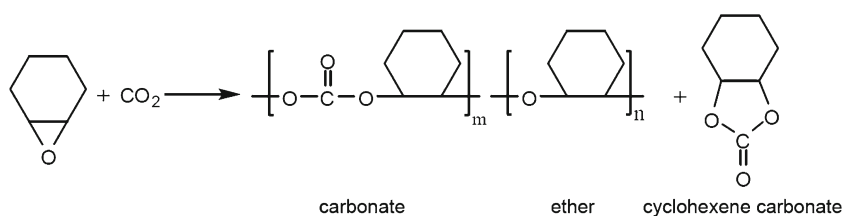
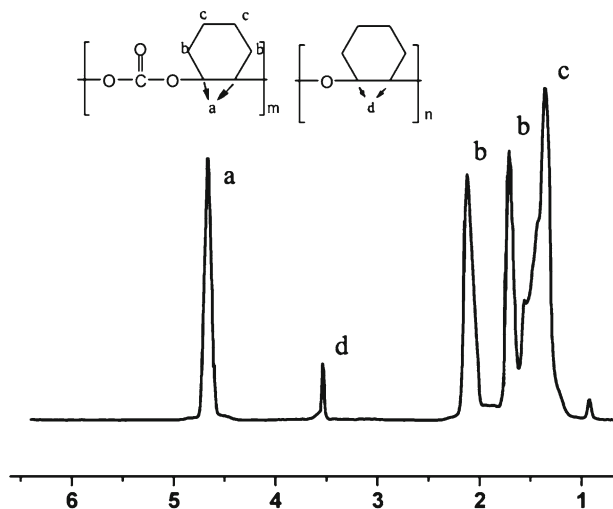
3.4 Measurements

¹H NMR measurements were performed using CDCl₃ on a Bruker type DPX-400 spectrometer, where the chemical shifts were determined with TMS as internal standard. IR spectra were recorded with a Nicolet Protégé 460 infrared spectrophotometer. Molecular weight was investigated by gel permeation chromatograph (GPC) on a PL-GPC50 instrument using THF as eluent. Measurement of thermal stability was carried out by a NETZSCH TA-2920 thermogravimetric analyzer under N₂ atmosphere with heating rate of 10 °C/min.

4 Results and Discussion

4.1 Characterization of Poly(Cyclohexene Carbonate) (PCHC)

PCHC is synthesized by the copolymerization of CO₂ and CHO, and the general reaction scheme is presented in

Scheme 2 Copolymerization of CO₂ and CHO**Fig. 1** FTIR of PCHC catalyzed by BCED-Zn**Fig. 2** ¹H NMR spectrum of PCHC catalyzed by BCED-Zn

Scheme 2. There is usually not pure carbonate linkage in the result polymer after copolymerization, in which ether linkage generated from the homopolymerization of CHO always exists and so does the cyclohexene carbonate resulted from the cyclization. The IR spectrum of the polymer was measured to distinguish the existence of carbonate linkage in the result polymer as shown in Fig. 1. It showed a strong absorption around 1750 cm⁻¹ for intense asymmetric ν(C=O) stretching vibration in carbonate linkage. No signal at 1800 cm⁻¹ was observed in the spectrum indicating no cyclohexene carbonate formed in the polymer. Relative amount of carbonate linkage could be calculated by ¹H NMR spectroscopy. Figure 2 shows a ¹H NMR spectrum of the result polymer prepared by BCED-Zn catalyst at 110 °C and 4 MPa CO₂ pressure for 24 h. The cyclohexylene groups adjacent to the carbonate groups were corresponded to δ 4.63, and the ether linkage was assigned to the chemical shift of δ 3.46. The percentage of carbonate linkage in the copolymer could be estimated from the relative intensities of these two chemical shifts.

4.2 Copolymerization of CHO and CO₂

To optimize the catalytic performance of this catalyst system further, the effects of the reaction time, CO₂ pressure and reaction temperature were investigated as given in Table 1.

With the reaction time increasing to 24 h, the TON increased until reaching a maximum 421.1, and then, it decreased. This decrease was caused by the reduced propagation due to the less CHO in the late stage; meanwhile, the rival degradation reaction became more remarkable. The degradation also resulted in a slight decrease in the polymer molecular weight. The carbonate unit content increased quickly with the reaction time. When the reaction time was 12 h, the carbonate unit content was only 65.7%, which suggested that formation of ether linkage was favored at the beginning. The copolymerization became dominant after this stage, and the carbonate unit content improved to 94.5% after 30 h.

The copolymerization was also performed at different temperatures with the fixed reaction time and fixed CO₂ pressure, as shown in Table 1. The TON and *M_n* increased with temperature increasing to about 110 °C and then decreased as the temperature further increased, which was presumably because of the thermal degradation of the polymer during the polymerization. The carbonate unit content increased continuously with reaction temperature increased from 80 to 150 °C, which showed that higher temperature was beneficial to the copolymerization.

The results in Table 1 indicated that the TON and *M_n* reached maximum values at around 4 MPa CO₂ pressure and decreased below or above this pressure. It has been

Table 1 Copolymerization of CO₂ and CHO catalyzed by BCED–Zn

Time (h)	T (°C)	CO ₂ Pressure (Mpa)	TON	Carbonate unit content (%)	$M_n (\times 10^4 \text{ g mol}^{-1})$
12	110	4	265.2	65.7	1.34
24	110	4	421.1	92.3	1.85
30	110	4	415.7	94.5	1.76
36	110	4	413.2	96.1	1.75
24	80	4	303.5	76.4	0.81
24	130	4	405.4	93.3	1.82
24	150	4	397.2	96.8	1.79
24	110	2	207.5	61.3	0.96
24	110	3	336.8	77.5	1.34
24	110	5	352.1	98.7	1.66

Reaction conditions: catalyst dosage, 0.1 g; monomer dosage, 15 mL

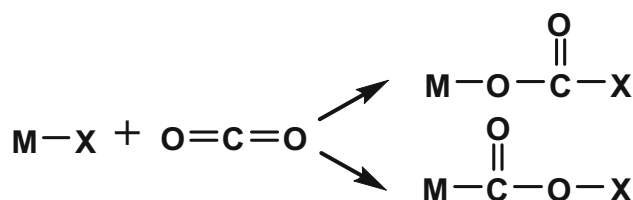
proved that CO₂ might behave not only as a monomer but also as a chain stopper in the copolymerization reaction with CHO, so too much CO₂ was unfavorable to copolymerization. However, higher pressure was in favor of the formation of alternative copolymer as expected.

4.3 Mechanism of Copolymerization of CO₂ and CHO Catalyzed by BCED–Zn

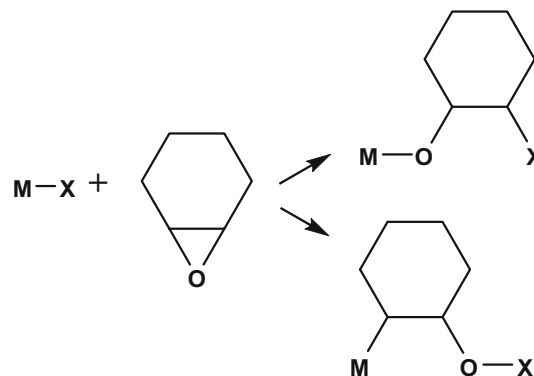
The mechanism of alternating copolymerization of CO₂ and CHO was investigated over BCED–Zn catalyst. Some literatures [13,14] have studied the mechanisms of the copolymerization of CO₂ and epoxides catalyzed by the complex generating from ligand and Zn compound. It was proved that the copolymerization was benefited from the coordination of the complex catalysts.

The catalyst reaction of Schiff base Zn catalysts was considered anion coordination mechanism, and the monomers were inserted into the Zn–O bond continuously. CO₂ is a relatively strong ligand and is easy to form complex with metal with possible reversibility; therefore, CO₂ could be activated and involved in the reaction. By this way, CO₂ can insert into the chemical bonds among metal, carbon, silicon, oxygen, nitrogen, hydrogen, phosphorous, halogen, et al. There are two methods for the insertion of CO₂: Mostly, the carbon atom of CO₂ connects to the end with dense electron cloud and the carboxylic ester with structure similar to M–O–C=O can be formed; in addition, sometimes the bonding with electron deficient end is also possible and a complex containing carboxyl and M–C bond is produced (Scheme 3).

There are also two ring opening methods for CHO (Scheme 4), so the structure of copolymer is complicated with some possible linkages existing. The effect of linkage mode was not considered during the following mechanism discussion.



Scheme 3 The insertion modes of CO₂ into M-X



Scheme 4 The insertion modes of CHO into M-X

A proposed mechanism illustrated that the monomer was inserted into the Zn–O bond of the propagating end, as shown in Scheme 5. The coordinated bond to the metal center transferred to the propagating metal–polymer chain, thereby stabilizing the Zn–O bond and facilitating the insertion of CO₂. The CO₂ might be first favorably inserted into the Zn–O bond of the Schiff base complex, followed by the insertion of the CHO. Subsequently, the alternating copolymerization of CHO and CO₂ afforded the repeating unit structure to yield the polycarbonate. The side reaction to produce the cyclic carbonate could occur through the degradation of the growing catalyst–polymer complex, which might result in the lower polymer yield.

Scheme 5 Proposed mechanism of the alternating copolymerization of CO₂/CHO by BCED–Zn

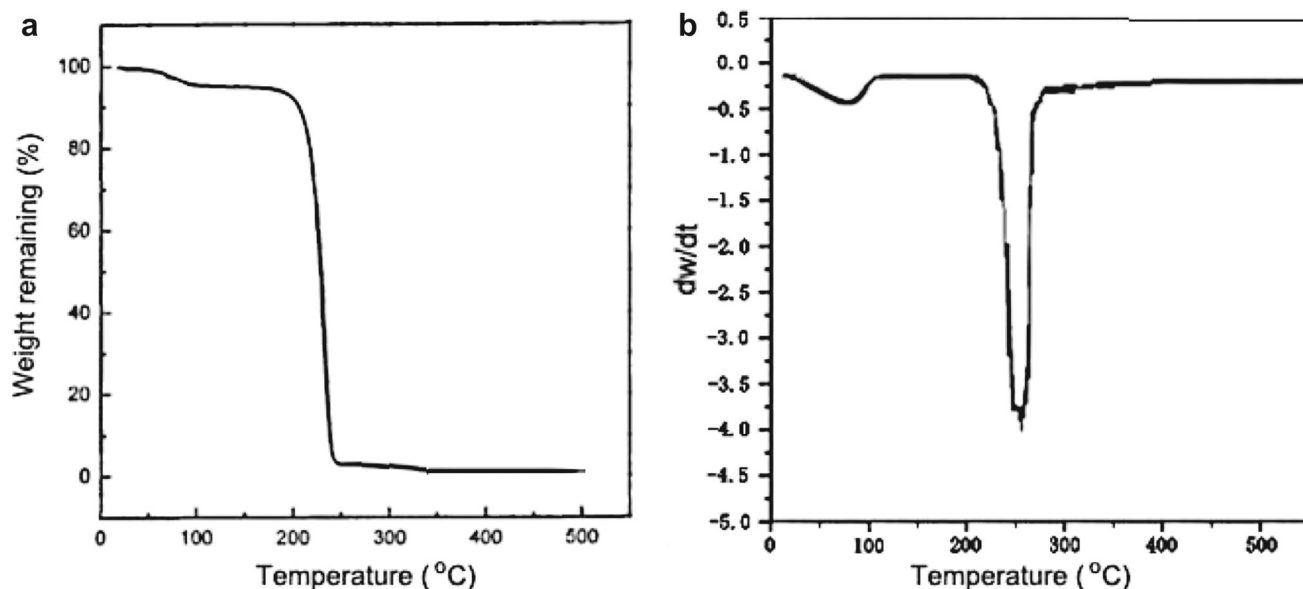
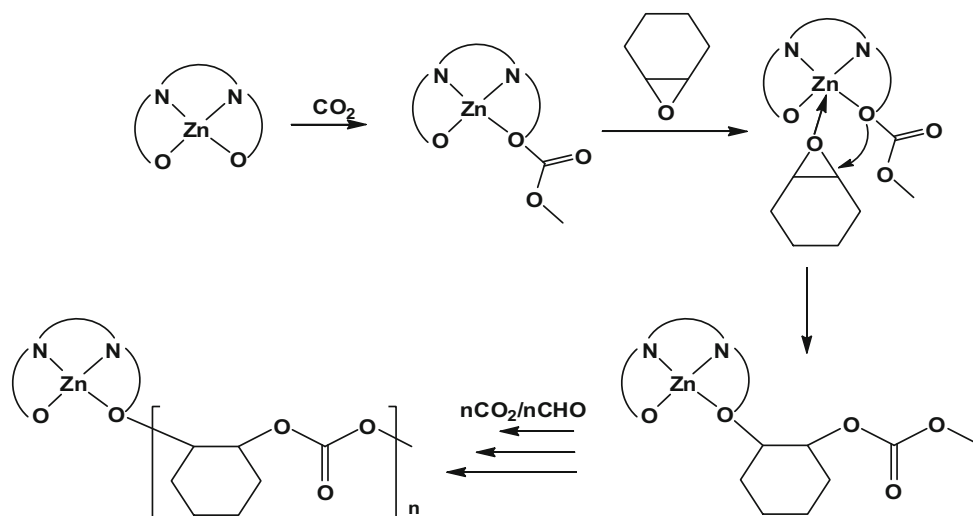


Fig. 3 TG (a) and DTG (b) curve of PCHC catalyzed by BCED–Zn

4.4 Thermal Stability of the Copolymer

The resultant polymer catalyzed by BCED–Zn was investigated by TG to determine the thermal stability as illustrated in Fig. 3. According to the TG curve (Fig. 3a), the value of the 5% weight loss temperature ($T_{-5\%}$) was above 230 °C and higher than the T_g temperature about 100 °C [15], implying PCHC had good thermal stability. This property indicated that the produced PCHC could be conventionally hot processed without thermal decomposition. The TG curve was steep, indicating that the temperature range of thermal weight loss was very narrow. The maximum weight loss temperature (T_m) of 256 °C was revealed by differential thermogravimetry (DTG) curve (Fig. 3b). The one-step decomposition containing only one T_m was proved by the DTG. In general, there are two kinds of thermal

decomposition method of PCHC, of which one is random decomposition and the other is unzipping depolymerization. In this case, the main method should be the latter, which resulted from the relatively low M_n compared with the literature [15].

5 Conclusion

An alternating polycarbonate was prepared from the copolymerization of CO₂ and CHO in the presence of a novel Schiff base complex catalyst BCED–Zn, which was simply synthesized by using 2-carboxybenzaldehyde and ethylenediamine for ligand and ZnEt₂ for complex. The utilization of BCED–Zn was easier than the traditional salen(M)X catalyst because of the cancellation of the cocatalyst. The copolymerization

could be efficiently catalyzed by BCED–Zn with the TON of 421.1 and M_n of $1.85 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$. The influence of reaction conditions such as reaction time, reaction temperature and CO_2 pressure was investigated, and the optimized condition was at 110°C and 4MPa CO_2 pressure for 24 h. PCHC had good thermal stability with $T_{-5\%}$ of 232°C and T_m of 256°C .

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