

Copolymerization of CO₂ and Cyclohexene Oxide Using a Novel Polymeric Diimide Catalyst

Min Zhang,^{1, 2} Liban Chen,¹ Gang Qin,¹ Baohua Liu,¹ Zhairong Yan,¹ Zhuomei Li²

¹Guangzhou Institute of Chemistry, Chinese Academy of Sciences, P. O. Box 1122, 510650, Guangzhou, China

²Institute of Polymer Science, Zhongshan University, 510275, Guangzhou, China

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ABSTRACT: A catalyst for the copolymerization of CO₂ and cyclohexene oxide was prepared by using acetylacetone and 4,4'-methylenedianiline. The catalyst was characterized as composed of a novel structure of the polymeric diimide Zn complex. The catalyst tended to produce an alternative copolymer with efficiency as high as 128 g polymer/g of catalyst. The obtained copolymers were characterized by IR and NMR. Effects of reaction conditions such as reaction time and temperature, CO₂ pressure, and catalyst concen-

tration on copolymerization were investigated. Best results were obtained from the reaction at 90°C for 24 h, with catalyst concentration of 0.13 g/mL, and CO₂ pressure of 2–3 MPa. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1123–1128, 2003

Key words: carbon dioxide; cyclohexene oxide; copolymerization; catalyst

INTRODUCTION

In recent years, great progresses have been achieved for the catalytic synthesis and practical applications of CO₂-epoxides copolymers.^{1–9} Chelating diimide Zn complexes reported by Cheng and Coates¹⁰ are one type of the best catalysts. These complexes are especially effective for the copolymerization of CO₂ and cyclohexene oxide (CHO). One gram of the catalyst generated 130 g of poly(cyclohexylene carbonate) (PCC). Compared with poly(propylene carbonate) (PPC), PCC possess much higher glass transition temperature and much higher thermal stability. Obviously PCC is superior as a prospective plastic material.

The structures of the above mentioned diimide Zn complexes are illustrated in Scheme 1. Sterically hindered aromatic groups were involved in the complex, and were thought to be important for the high catalytic efficiency. Therefore it was necessary to employ some rather expensive reagents such as 2, 6-diisopropylaniline or 2, 6-ditertbutylaniline.

This paper describes the synthesis and application of a novel polymeric diimide Zn complex, in which the high steric hindrance was provided by polymeric structure instead of the expensive reagents. The complex was found to have similarly high efficiency for

the copolymerization of CO₂, and CHO and was believed to be a more practical catalyst for the reaction.

EXPERIMENTAL

Reagents and instruments

4,4'-Methylenedianiline (MDA) (Acros, purity over 98%) was obtained commercially. Acetylacetone (AR) was purified before use by distillation under reduced pressure. Cyclohexene oxide (CHO) (Acros, purity over 98%) was treated over calcium hydride to reduce the water content less than 200 ppm by Kart Fisher titration. Other reagents (propylene oxide, methylene chloride, methanol, etc.) were dried with routine methods. CO₂ was commercially obtained without further purification. Nitrogen with 99.99% purity was applied as the system atmosphere.

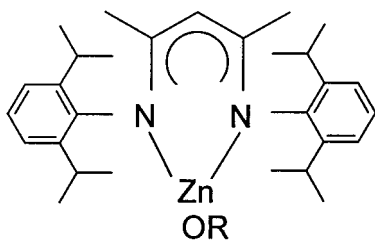
The IR spectrum was obtained using RFX-65A FTIR instrument (Analect). ¹H-NMR and ¹³C-NMR spectra were recorded using DRX-400 (Bruker). Intrinsic viscosity [η] was measured in chloroform at 30°C using an Ubbelohde viscosity meter. Molecular weight of polymers was recorded by gel permeation chromatography in tetrahydrofuran (THF) using polystyrene standards. Analysis of zinc was determined by chemical method.

Ketone–amine condensation

Acetylacetone (1 g, 10 mmol) was added to a solution of MDA (1.98 g, 10 mmol) in ethanol (30 mL). The resulting mixture was heated at reflux for 64 h and then concentrated to a viscous brown residue, which

Correspondence to: Chen Liban (lbchen@mail.gic.ac.cn).

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R = Me, Ac

Scheme 1 Structures of diimide Zn complexes reported by Cheng and Coates.

was the catalyst precursor diimide polymer (AMDA). The molecular weight of AMDA was roughly estimated according to its structure (Scheme 2) by the following equation:

$$MW = 198 + 1048 \cdot I_{12.3}/I_{3.5}$$

in which $I_{12.3}$ and $I_{3.5}$ were the integrated intensities of the $^1\text{H-NMR}$ signals at $\delta(\text{ppm})$ 12.3 and $\delta(\text{ppm})$ 3.5.

Catalyst preparation

To a solution of AMDA (0.327 g, 1 mmol) in toluene (10 mL) was slowly added diethyl zinc (0.61 mL, 5.9 mmol) at 0°C . After stirring overnight at 80°C , acetic acid (0.34 mL, 5.9 mmol) was added to the reaction mixture at room temperature. After stirring for another hour at room temperature (RT), the catalyst (AMDA) ZnOAc was obtained as a clear solution in toluene.

CO_2 -epoxide polymerization

A 130-mL autoclave was evacuated and flushed with nitrogen, and then charged with the catalyst solution (1 mL, 0.1 mmol). The solution was evacuated to remove the toluene and then flushed with nitrogen.

CHO and CO_2 were added to the autoclave. The reaction was carried out at desired temperature for a certain period. The crude product was redissolved in methylene chloride, precipitated from methanol, and dried *in vacuo* at 70°C for 4 h until the weight reached constant.

RESULTS AND DISCUSSION

Preparation and characterization of catalyst

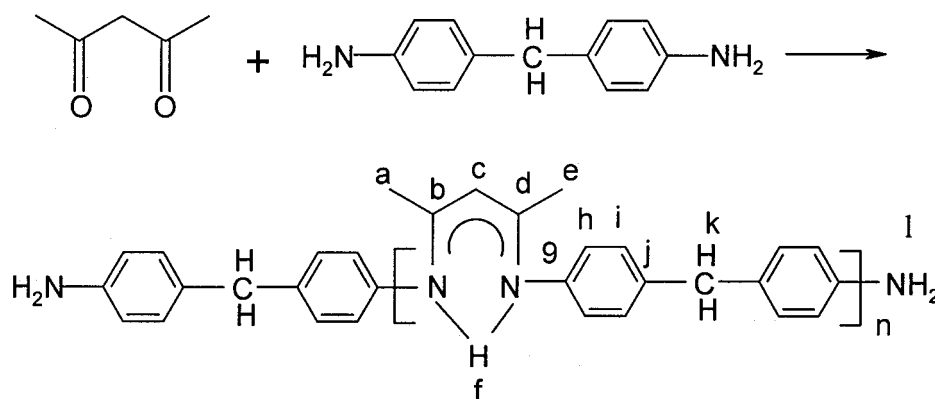
To prepare the catalyst, it is necessary to apply a diimide precursor, which can be obtained from a diketone-amine condensation. To conduct this reaction by using a diamine raw material instead, a diimine AMDA with linear polymeric structure was obtained (Scheme 2). AMDA was characterized spectrometrically to confirm this structure. $^1\text{H-NMR}$ showed signals at δ (ppm) 2.0 (a, e, 6H), 5.1 (c, 1H), 12.3 (f, 1H), 6.6–7.1 (g, h, i, j, 8H), 3.8 (k, 2H), 3.5 (l, weak); $^{13}\text{C-NMR}$ showed at δ (ppm) 160.1 (b, d), 28.7 (a), 97.0 (c), 19.4 (e), 144.0 (g), 130.1 (h), 115.0 (i), 124.0 (j), 40.1 (k). In above parentheses, the symbols a–l correspond to the assignments denoted in Scheme 2. In the IR spectrum, no carbonyl signals were observed and thus all end groups of AMDA were considered to be $-\text{NH}_2$ groups. By evaluation of the $-\text{NH}_2$ and $-\text{NH}-$ intensities in the $^1\text{H-NMR}$ spectrum, the molecular weight of the polymer AMDA was determined roughly to be about 10^3 .

The Zn content in (AMDA) ZnOAc was determined to be 29.1% by elemental analysis. A polymeric structure consists of the zinc diimide complexes as well as the zinc salt as end groups for the catalyst is suggested as illustrated in Scheme 3.

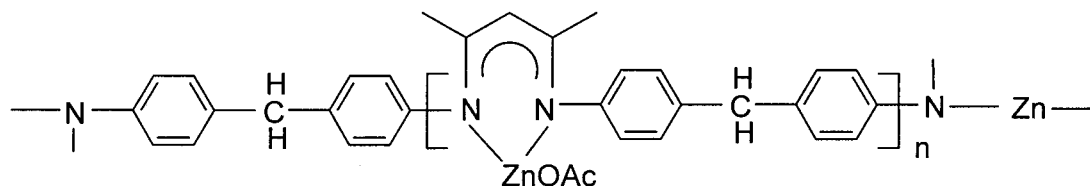
Preparation and characterization of pcc

The reaction of CO_2 and CHO is showed in Scheme 4.

The IR and $^1\text{H-NMR}$ of PCC and poly(cyclohexene oxide) are shown in Figures 1 and 2, in which spectra a and c indicate for poly(cyclohexene oxide), spectra b



Scheme 2 Synthesis of the polymeric diimide catalyst precursor.



Scheme 3 Structure of polymeric diimide zinc complex.

and d indicate PCC. The IR of the copolymer exhibited a strong absorption at 1750 cm^{-1} for C=O vibration in carbonate linkage. No signal around 1800 cm^{-1} was observed, indicating no cyclohexene carbonate by-product contained in the polymer. In the $^1\text{H-NMR}$ of PCC, the cyclohexylene groups adjacent to the carbonate groups were seen at δ 4.60; ether linkage (if any) would be exhibited as a signal at δ 3.45. The relative intensities of these two signals corresponded to the ratio of the epoxide that alternatively copolymerized with CO₂ and those that competitively homopolymerized. The molar fraction of carbonates and cyclohexylene groups can be estimated by intensities of the signals in Figure 2. CO₂ molar fraction for perfectly alternative copolymers is 0.5.

Activity of the catalyst in the epoxide homopolymerization and the epoxide-CO₂ copolymerization

Table I shows experimental results of the epoxide homopolymerization and the copolymerization with CO₂ in the presence of the catalyst. In addition to CHO, propylene oxide (PO) was also evaluated. Little product was obtained from CHO homopolymerization and from any PO reaction. The observation revealed that the catalyst was almost inactive for CHO homopolymerization, although it is very effective for the CO₂-CHO copolymerization. This observation explains why the reaction of CO₂ with CHO tended to form alternative copolymers. It is very likely that the copolymerization of CO₂ with different comonomers (PO or CHO) followed somewhat different mechanisms, which should be further studied.

Influence of temperature on the copolymerization

Figures 3 and 4 showed that both the catalytic efficiency in copolymerization and intrinsic viscosity $[\eta]$

of PCC raised with increasing reaction temperature from 20 to 90°C. This is because higher temperature accelerates the chain initiation and chain propagation. At temperature above 90°C, the polymer yield and intrinsic viscosity went down with further increasing temperature due to serious degradation of the obtained polymer.

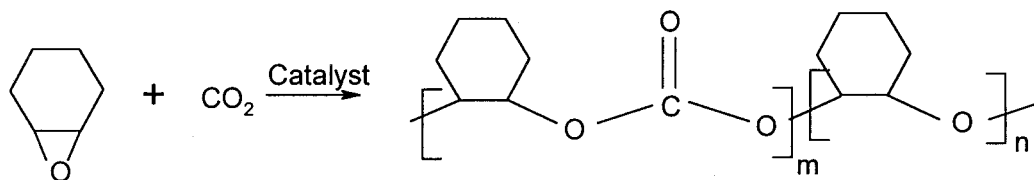
As illustrated in Figure 5, it was also found that the CO₂ molar fraction in the copolymer was increased simply with increasing reaction temperature from 20 to 100°C, and perfect alternative copolymer was obtained around 100°C. It can then be concluded that higher temperature favors the copolymerization reaction.

Time influence on copolymerization of CO₂ and cyclohexene oxide

As illustrated in Figure 6, the catalytic efficiency is enhanced with increasing time at the beginning. It reached a maximum around 24 h, and then dropped slowly. This was because at the end of the reaction the competing degradation was becoming more important while the propagation was getting slower due to the consumption of the epoxide monomer.

The molecular weight of the copolymer depended on the reaction time of the other coordination polymerization, as shown in Figure 7. At the beginning M_w increased quickly, and then gradually reached equilibrium. It seemed that the competing degradation during the copolymerization (Fig. 6) was mainly unzipping reaction instead of random chain breaking. Therefore M_w did not decrease at the end of the copolymerization but reach equilibrium.

The molar fraction of CO₂ in copolymer chain depended on the reaction time, as illustrated in Figure 8. It is interesting to find that CO₂ fraction as low as 0.17 was observed at the very beginning; afterward the



Scheme 4 The copolymerization of CO₂ and cyclohexene oxide.

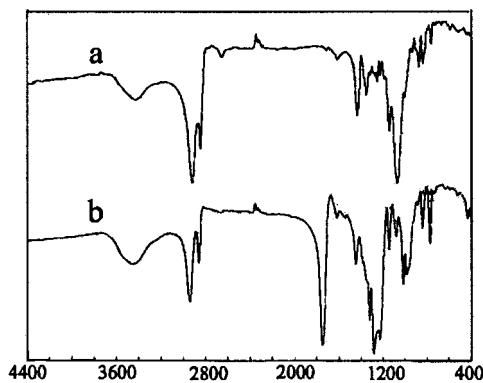


Figure 1 IR of Poly(cyclohexene oxide) (a) and PCC (b).

copolymerization quickly tended to proceed alternatively. This suggests that the epoxide monomer is important for the initiation and/or for the first propagation. Therefore formation of ether linkage was favored at the beginning, and the copolymerization became normal only after this stage. This is consistent with previous kinetic observation,^{11–13} which revealed that the initiation step of the copolymerization involved the reaction between the catalyst and epoxide but CO₂.

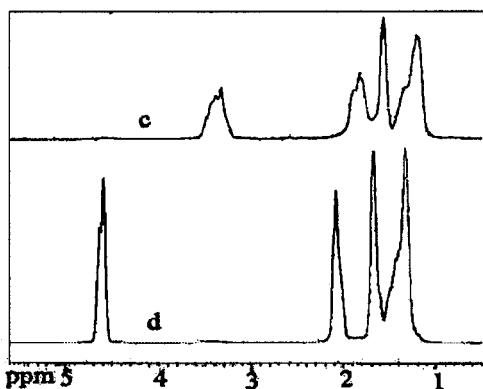


Figure 2 ¹H-NMR of Poly(cyclohexene oxide) (c) and PCC (d).

TABLE I
Catalytic Activities for Epoxide Homopolymerization and CO₂-Epoxide Copolymerization^a

| Run | Epoxide/ Amount (mL) | CO ₂ / Amount (MPa) | Yield (g/g of Catalyst) | M_n | M_w |
|-----|----------------------------|--------------------------------------|-------------------------------|--------|--------|
| 1 | CHO/3 | 2.0 | 84.8 | 19,250 | 37,532 |
| 2 | CHO/3 | — | 2.4 | — | — |
| 3 | PO/10 | 5.9 | Trace | — | — |
| 4 | PO/10 | — | Trace | — | — |

^a Reaction time: 24 h; Reaction temperature: 80°C for CHO and 60°C for PO.

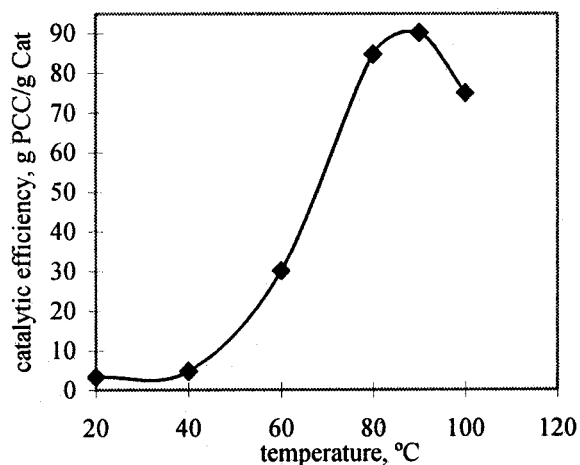


Figure 3 Temperature influence on catalytic efficiency.

Influence of pressure of CO₂ on copolymerization of CO₂ and cyclohexene oxide

Table II shows that increasing CO₂ pressure, while was less than 2 MPa, enhanced catalytic efficiency.

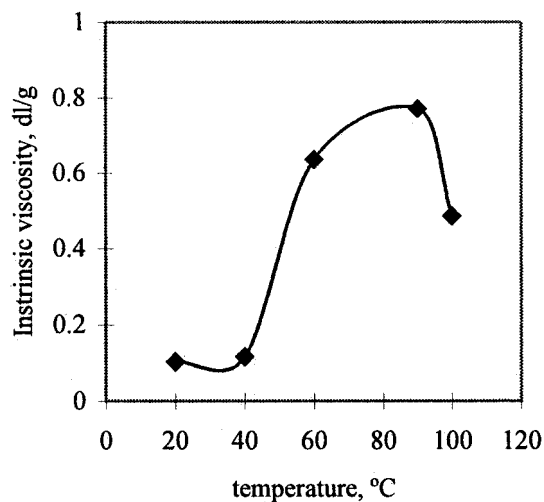


Figure 4 Temperature influence on intrinsic viscosity.

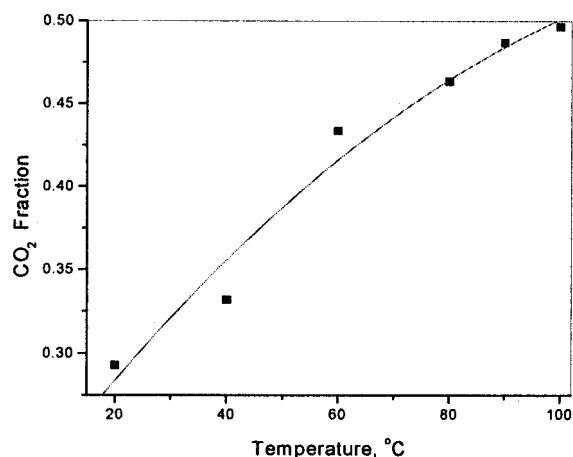


Figure 5 Temperature influence on molar fraction of CO₂.

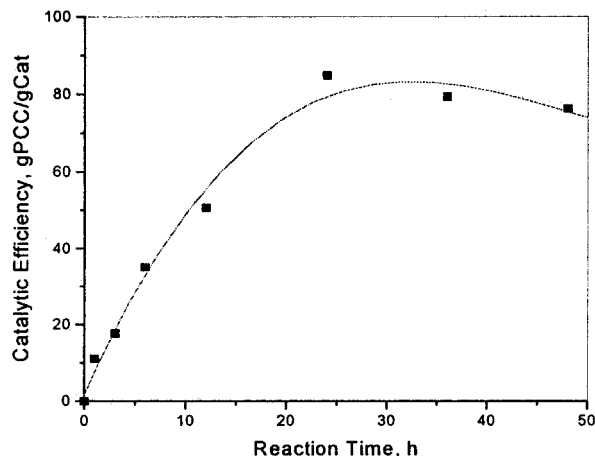


Figure 6 Time influence on catalytic efficiency.

However, it has been revealed that in the copolymerization with epoxides, CO₂ may behave not only as a monomer but also as an active chain stopper. Therefore too much CO₂ was harmful to copolymerization. CO₂ pressure influenced $[\eta]$ of the copolymer in a similar way but giving a maximum $[\eta]$ value at the pressure of 2.7 MPa. CO₂ molar fraction in the copolymer did not show much dependence on the pressure

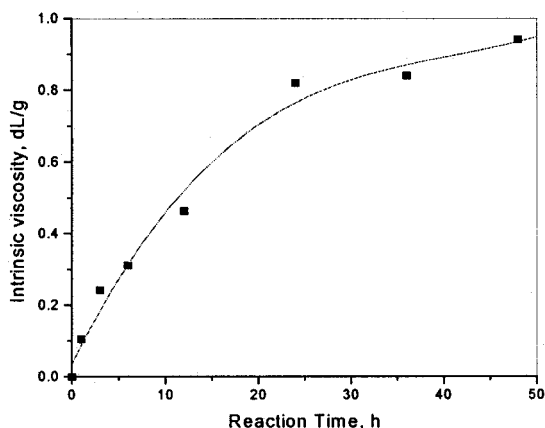


Figure 7 Time influence on intrinsic viscosity.

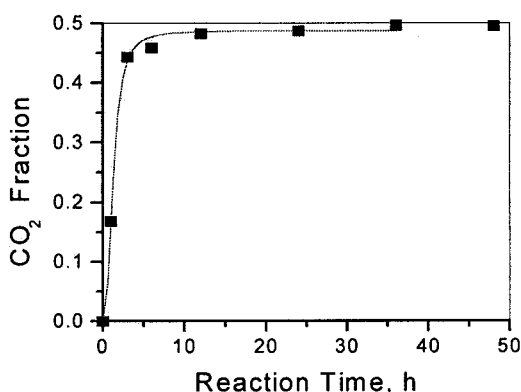


Figure 8 Time influence on molar fraction of CO₂.

TABLE II
Influence of Pressure of CO₂ on Copolymerization of CO₂ and Cyclohexene Oxide^a

| Run | Pressure of CO ₂ (MPa) | Catalytic efficiency (g/g) | Molar fraction of CO ₂ in copolymer | $[\eta]$ (dL/g) |
|-----|-----------------------------------|----------------------------|--|-----------------|
| 1 | 1.0 | 22.1 | 0.479 | 0.44 |
| 2 | 1.5 | 53.8 | 0.443 | 0.66 |
| 3 | 2.0 | 84.8 | 0.487 | 0.82 |
| 4 | 2.7 | 61.9 | 0.495 | 1.00 |
| 5 | 3.2 | 22.9 | 0.474 | 0.62 |
| 6 | 4.2 | 19.2 | 0.5 | 0.64 |

^a Reaction temperature: 80°C; reaction time: 24 h; catalyst concentration: 0.13 g/mL.

of CO₂. Higher pressure favored the formation of alternative copolymer as expected, but rather high CO₂ fraction values were still obtained while the pressure took other values.

Influence of catalyst concentration on copolymerization

Data in Table III shows that low catalyst concentration led to polymers with higher molecular weights. For example, catalyst of 0.01 mol/L gave $[\eta]$ of 1.17 dL/g, but a catalyst of 0.05 mol/L gave $[\eta]$ of 0.52 dL/g. However, unlimitedly high molecular weight copolymers cannot be produced by unlimitedly decreasing the catalyst concentration. An experiment with 0.001 mol/L of catalyst concentration failed to produce any copolymer. Maximum catalytic efficiency was observed in the presence of catalyst around 0.08 mol/L. The catalyst concentration seemed not to influence the CO₂ molar fraction in the copolymer significantly. Highly alternative copolymers were obtained in all cases.

CONCLUSION

As described, a novel catalyst for the copolymerization of CO₂ and cyclohexene oxide (CHO) has been

TABLE III
Influence of Concentration of Catalyst on Copolymerization^a

| Run | Concentration of catalyst (g/mL) | Catalytic efficiency (g/g) | Molar fraction of CO ₂ in copolymer | $[\eta]$ (dL/g) |
|-----|----------------------------------|----------------------------|--|-----------------|
| 1 | 0.04 | 116.4 | 0.500 | 1.17 |
| 2 | 0.08 | 127.7 | 0.474 | 1.03 |
| 3 | 0.13 | 84.8 | 0.487 | 0.82 |
| 4 | 0.20 | 69.0 | 0.494 | 0.52 |

^a CO₂ pressure: 2.0 MPa; reaction time: 24 h; reaction temperature: 80°C.

successfully prepared. The catalyst was characterized to be a zinc diimide complex with a polymeric structure, which has never been reported. The polymeric structure offered necessary steric hindrance, which was conventionally obtained by using some inexpensive reagents. The catalyst favored the copolymerization in an alternative way and showed activity as high as 128 grams of copolymer per gram of the catalyst. The copolymers from CO₂ and epoxides now have found many applications. The new progress in catalysis will certainly accelerate the development of such copolymers as practical materials.

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