Copolymerization of Carbon Dioxide and Epoxides with a Novel Effective Zn–Ni Double-Metal Cyanide Complex

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ABSTRACT: A novel double-metal cyanide complex based on $Zn[Ni(CN)_4]$ was prepared and used as a catalyst for the copolymerizations of carbon dioxide and propylene oxide (PO) and carbon dioxide and cyclohexene oxide (CHO). The copolymers were characterized by IR and ^{1}H-NMR, and the effects of temperature, pressure, solvent, and preparative methods for the catalysts on catalytic activity and composition of the copolymer were investigated. The results show that this novel catalyst exhibited its highest catalytic efficiency at about 500 g/g of $Zn[Ni(CN)_4]$ for PO and CO_2, whereas the catalytic efficiency for CHO and CO_2 was merely between 5.6 and 22.5 g/g of $Zn[Ni(CN)_4]$. The molar fraction of carbonate linkages for PO–CO_2 and CHO–CO_2 copolymers reached about 0.6 and 0.3, respectively. The results show that a lower temperature and a higher CO_2 pressure were favorable for the incorporation of CO_2 into the copolymer, and the nonpolar solvents were better media for copolymerization. As a complexing agent, glycol ether exhibited better promoting effects on catalytic efficiency among those investigated, but the catalysts prepared by different complexing agents showed no significant differences in the compositions of the copolymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3871–3877, 2008

Key words: catalysts; copolymerization; polycarbonates

INTRODUCTION

With carbon resources derived from petroleum gradually being depleted, an increasing number of studies have been done on the use of natural carbon resources in recent years. As a carbon resource with a huge abundance, carbon dioxide is a suitable potential feed for the chemical industry both for its economy and its security. The production of aliphatic polycarbonate via the direct copolymerization of carbon dioxide with epoxide, which was first discovered by Inoue et al.,[1] provided an alternative route for the use of CO_2 as a chemical feed. This copolymerization has attracted great interest, and intensive study has been done because the process is energy-saving and the product is a kind of useful material. Many catalytic systems, such as $ZnEt_2$ alcohol, zinc carboxylate, metal salen (metal = Cr, Al, or Co), and metal porphyrin, have been employed as catalysts.[2–4] However, most catalytic systems have exhibited relatively low catalytic efficiency (10–80 g of copolymer/g of catalyst). In recent years, zinc bis(2,6-diphenyl phenoxide) derivatives[5–7] and zinc β-diiminate[8–10] have been developed as catalysts, and they exhibited improved catalytic efficiency. However, the former

only behaved well for the copolymerization of cyclohexene oxide (CHO) and carbon dioxide. Moreover, most catalysts are sensitive to moisture and other substances containing active groups, which can make them partially or even entirely lose catalytic activity; thus, strict conditions should be ensured during preparation and usage. Double-metal cyanide complexes (DMCs), which have the common formula $Zn_a[M(CN)_b]_c \cdot xZnCl_2 \cdot yL \cdot zH_2O$ (where M is a transition metal and L is a water-soluble organic solvent, viz., the complexing agent), is a category of catalyst for the ring-opening polymerization (ROP) of epoxide.[11] It is easy to prepare and is not sensitive to moisture. Particularly, a double-metal cyanide complex catalyst based on $Zn_3[Fe(CN)_6]_2$ (Zn–Fe DMC) was used in the copolymerization of carbon dioxide and propylene oxide (PO) and exhibited a catalytic efficiency at about 50 g of copolymer/g of catalyst.[12,13] Recently, we investigated a double-metal cyanide complex catalyst based on $Zn_3[Co(CN)_6]_2$ (Zn–Co DMC), which showed an obvious increase in catalytic efficiency.[14,15] It clearly hinted that the center metal of DMC had a significant impact on its catalytic behavior. Thus, it was worth extensive exploration of DMC with other center metals. With many attempts, we found that another effective DMC catalyst in which nickel was employed as a center metal exhibited a balanced performance, including a much lower content of byproduct, cyclic carbonate, and a remarkably enhanced efficiency
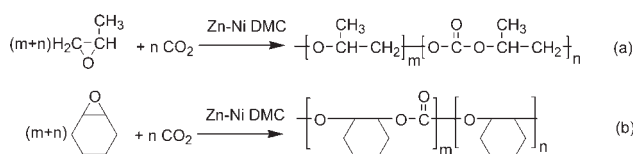
Scheme 1 Copolymerization of (a) PO and (b) CHO with CO_2.

compared with Zn–Co DMC. Herein, we report its preparation and features toward copolymerization involving PO and CHO (Scheme 1).

EXPERIMENTAL

Materials and measurements

$K_2[Ni(CN)_4]$ was synthesized according to published procedures;[16] the crude product was recrystallized twice before use. PO and CHO (Aldrich, St. Louis, MO) were distilled over calcium hydride. CO_2 (> 99.9%) was used as received. $ZnCl_2$, toluene, xylene, dimethylformamide (DMF), *tert*-butyl alcohol (TBA), 1,2-dimethoxyethane, 2-methoxyethanol, 1-methoxy-2-propanol, 1,2-propandiol, and glycol were analytical grade and were used without further purification.

The molecular weight and the distribution of copolymers were determined by gel permeation chromatography with 2× Polymer Laboratory (Varian Inc.) gel columns at 35°C in THF at 0.8 mL/min; six monodisperse polystyrene standards were used to generate a calibration curve (580 to 3×10^4 Da).

The composition of catalyst was analyzed with a Hitachi 180-50 atomic absorption spectrophotometer (Tokyo, Japan) and a Flash EA1112 elemental analyzer (Waltham, MA). Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 (Ettlingen, Germany), ^{1}H-NMR spectra were recorded on an AVANCE DMX 500 superconducting high-resolution spectrometer (500 MHz) (Billerica, MA) with $CDCl_3$ as the solvent, For the PO–CO_2 reaction, the accurate molar fraction of carbonate linkages in the copolymer (F) and the weight percentage of propylene carbonate (W_{PC}) were as follows:

$$F = \frac{(A_{5.0} + A_{4.2} - 2 \times A_{4.58})}{(A_{5.0} + A_{4.2} - 2 \times A_{4.58}) + A_{3.5}}$$

$$W_{PC} = \frac{102 \times A_{1.50}}{58 \times A_{1.14} + 102 \times (A_{1.33} + A_{1.50})}$$

Note that the peaks of propylene carbonate (PC; $\delta = 4.89$ and 4.04) overlapped with the peaks of the copolymer; thus, these peak areas were subtracted in the calculation of F. Because the peak area at 4.89 or 4.04 ppm was equal to the peak area at 4.58 ppm

according to the standard spectra of PC and the peak area at 4.58 ppm could be integrated distinctly, the peak area at 4.58 ppm replaced the peak area at 4.89 or 4.04 ppm in the calculation of F.

To indicate the relative tendency of CO_2 transformation into the copolymer against product of the coupling reaction, herein, the index R is defined as the ratio between the moles of CO_2 incorporated into copolymer and the moles of CO_2 incorporated into PC, which was calculated from the ^{1}H-NMR spectra as

$$R = \frac{A_{1.50} + (A_{4.2} - A_{4.58})}{A_{1.50}} \text{ or } R = \frac{A_{1.33}}{A_{1.50}}$$

F of the CHO–CO_2 copolymer was calculated with the following equation:

$$F = \frac{A_{4.6}}{A_{4.6} + A_{3.5}}$$

Preparation of the DMC catalyst

Under vigorous stirring, 10 mL of a $K_2[Ni(CN)_4]$ solution (0.2 mol/L) was added dropwise into a $ZnCl_2$ solution consisting of 8 g of $ZnCl_2$, 40 mL of water, and 20 mL of complexing agent (e.g., TBA) at 35°C; the resulting white suspension was filtered to isolate the precipitate of DMC catalyst and resuspended in a solution consisting of the complexing agent and water (1 : 1 v/v) by vigorous stirring. Then, the precipitate was filtered again. It was washed three times with gradually increasing portions of complexing agent against water to exclude potassium ion, which was detrimental to its catalytic efficiency. Finally, the precipitate was resuspended in complexing agent to exclude water, filtered, dried at 50°C for 8 h, and then pulverized for further use.

Copolymerization of CO_2 and the epoxides

The copolymerization of CO_2 and epoxides was performed in a 50-mL autoclave equipped with a magnetic stirrer and a pressure indicator. Before the experiment, the autoclave was heated to 80°C for 1 h, and the desired amount of catalyst and 20 mL of PO (or 6 mL of CHO) were added. Then, the autoclave was heated to the reaction temperature rapidly and charged with CO_2 to the proper pressure. After the desired time, it was cooled, and the pressure was slowly released. The catalyst was removed by centrifugation; in some cases, extra epoxide could be added to facilitate separation by a reduction in the viscosity of mixture. Finally, the excess monomer was evacuated by the heating of the product *in vacuo*; thus, product free of catalyst was obtained.

RESULTS AND DISCUSSION

Preparation and the catalytic mechanism of DMC

In general, a DMC catalyst refers to a complex in which zinc cyanometalate is the main composition. In most cases, zinc chloride and a complexing agent are also present. It was first developed for the production of polyether polyols with high molecular weights and low unsaturations by ROP of PO in 1960s. Zn–Fe DMC had been investigated as a catalyst for the copolymerization of PO and CO$_2$. However, this kind of catalyst received less attention in previous decades because of its relatively low catalytic activity. Recently, we focused on its use as a potential catalyst for the copolymerization of CO$_2$ and epoxide by the modification of the central metal. Our consideration was based on the structure of its main composition, $Zn_u[M(CN)_n]_v$, and on previous study. From the viewpoint of structure, $Zn_u[M(CN)_n]_v$ constructs a three-dimensional network bridged by bonds as Zn—N—C—M, in which both M^{n+} and Zn^{2+} are surrounded by cyanide ions.[17] It is generally acknowledged that in the ROP of epoxide, epoxide first coordinates with zinc, and the ring opening of coordinated epoxide occurs in the subsequent step. In copolymerization, it supposedly includes the coordination of CO$_2$ as well; thus, the coordinative surroundings of zinc will have a significant impact on the catalytic behavior and the composition of the product. Because zinc and the central metal (M^{n+}) are bridged by cyanide ions, the influence of the central metal on the coordination status of zinc can imposed by the changing of the distribution of the electron cloud on the cyanide ion. On the basis of these facts, a variety of transition metals were tested as the central metal. Ni^{2+} was also a good candidate in addition to Fe^{3+} and Co^{3+} and showed differences in the catalytic characteristics for the copolymerization of epoxide and CO$_2$.

A DMC catalyst based on Zn[Ni(CN)$_4$] [zinc tetracyanonickelate (ZTCN)] was prepared by the precipitation reaction of K$_2$Ni(CN)$_4$ and ZnCl$_2$ solution, in which an excess amount of ZnCl$_2$ relative to K$_2$Ni(CN)$_4$ was used to ensure better catalytic efficiency of the final catalyst. In addition, several kinds of water-soluble organic solvents containing oxygen atoms were used as complexing agents, whose lone-pair electrons provided them with the capacity to coordinate with ZnCl$_2$ in solution. This variation of local surroundings for the precipitation reaction resulted in DMC catalysts with different morphologies; most were amorphous. Thus, their catalytic efficiencies could be enhanced to a great extent.

This DMC catalyst was a complex substance of ZTCN, ZnCl$_2$, complexing agent, and H$_2$O; the con-
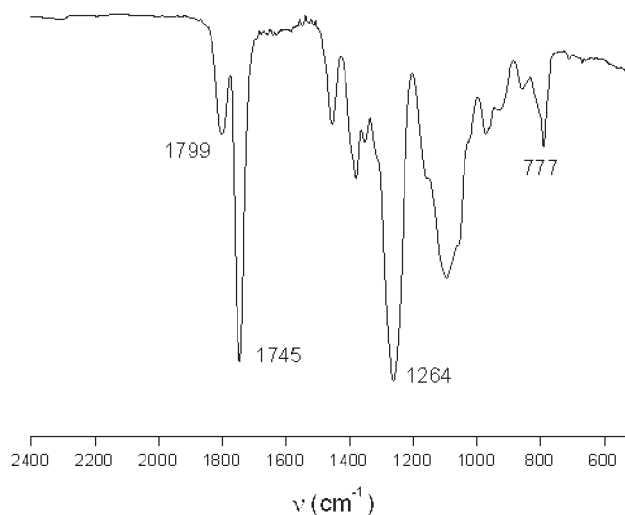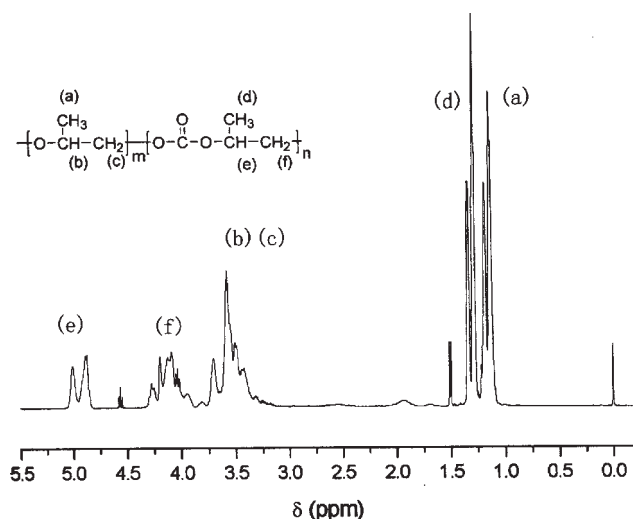

Figure 1 FTIR spectrum of the typical product of PO–CO$_2$ copolymerization.

tent of the later three compositions were variable under different preparative conditions. Thereby, the proper evaluation of catalytic efficiency of the DMC catalyst was based on the amount of included ZTCN in the DMC complex. This also ensured that the comparisons of catalytic efficiency among different kinds of DMC catalyst were reasonable. Elemental analysis indicated that the empirical formula of the catalyst used in these experiments was ZTCN · 0.7ZnCl$_2$ · 1.3TBA · 2.0H$_2$O.

Copolymerization of PO–CO$_2$ with Zn–Ni DMC

Figure 1 shows a typical FTIR spectrum of the product of the PO–CO$_2$ copolymerization. Peaks at 1745 and 1264 cm^{-1} existed in product, which were ascribed to strength vibrations of C=O and C—O, respectively, in oxycarbonyl groups. This indicated the success of the incorporation of CO$_2$ into the copolymer chain. There was also a peak at 1799 cm^{-1}, which was ascribed to the strength vibrations of C=O in PC. The intensities of the peaks varied among the different products; this indicated that the coupling reaction of PO and CO$_2$ presented more or less in a catalytic system, as most investigated catalytic systems do. The ^{1}H-NMR spectrum also confirmed the existence of both polycarbonate and PC, as illustrated in Figure 2. The signals at 5.0 and 4.0–4.3 ppm were ascribed to the hydrogen of CH and CH$_2$ groups, respectively, in the carbonate linkages of the copolymer. In addition, the peaks at 1.33 ppm were ascribed to the hydrogen of CH$_3$ in carbonate linkages. The signals at 3.2–3.8 ppm were ascribed to the hydrogen of both CH and CH$_2$ groups in ether linkages; the signals indicated that copolymer was not an alternative copolymer. At the same time, there were small peaks at 4.89, 4.58, 4.04, and 1.50 ppm;

Figure 2 ^{1}H-NMR spectrum of the typical product of PO–CO$_2$ copolymerization.

the positions of these peaks fully accorded with the standard spectrum of PC and also confirmed the formation of cyclic carbonate.

Table I shows the catalytic efficiencies and the compositions of the catalytic products at different temperatures. The catalytic efficiencies were in the range 18–582 g of product/g of ZTCN when the temperature was varied from 80 to 150°C, and the catalytic efficiency sharply increased from 119.3 to 482.6 g of product/g of ZTCN when the temperature was increased from 120 to 130°C. This revealed that this DMC catalyst could have only been activated effectively under such high temperatures as 130°C, which was apparently higher than that of Zn–Fe DMC or Zn–Co DMC (ca. 50 and 90°C, respectively). With respect to the catalytic efficiency of the copolymer, it could reach 438.7 g of copolymer/g of ZTCN at 130°C, approximately 10-fold that of Zn–Fe DMC (40–50 g of polymer/g)and 6-fold that of zinc glutarate (60–70 g of polymer/g)[18] but lower than that of Zn–Co DMC. The highest F for the copolymer

reached 0.7 at 80°C, but the corresponding catalytic efficiency was only 17.5 g of copolymer/g of ZTCN. On the contrary, the temperatures above 130°C resulted in an abrupt decrease in F. Thus, a suitable reaction temperature was around 110–130°C, under which moderate catalytic efficiency and moderate F (0.52–0.62) were achieved. However, F of the copolymer was slightly lower than that of the copolymer derived from Zn–Fe DMC (ca. 0.7). With respect to content of PC, it increased slightly with increasing temperature; the content of PC was merely between 6.6 and 9.1% when temperature was in the range 110–130°C. This apparently contrasted with the performance of Zn–Fe and Zn–Co DMC, by which the contents of PC were between 20 and 28 wt % under suitable conditions; for example, for Zn–Co DMC, the content of PC was 28.1% at 110°C and 5.5 MPa. Thus, the R values for Zn–Ni DMC were in the range 4.3–8.1 at 110–130°C, which were generally larger than those for Zn–Co DMC, whose R values were about 1.2–1.5 under optimum temperature (110°C). This means that for Zn–Ni DMC, over 85% of CO$_2$ was transformed into copolymer under optimum conditions; this value presented a contrast with that for Zn–Co DMC (ca. 58%). From the viewpoint of R, this demonstrated an advantage over other kinds of DMC catalysts. The difference in catalytic performance between them probably stemmed from the difference in the coordinative surrounding of zinc, which could be affected by the central metal of the complex.

The number-average molecular weights (M_n's) of the copolymers were below 10,000 and steadily increased with increasing temperature. This was attributed to the increase in the percentage conversion with increasing temperature; thus, Zn–Ni DMC shared the same features as Zn–Co DMC on this point. Because the resulting copolymers obtained at 80–90°C had such low molecular weights that they were beyond the lower limit of the gel permeation chromatography column, their molecular weights are not listed in Table I.

TABLE I
Effect of Temperature on the Catalytic Efficiency and the Compositions of the Products

Temperature (°C)	Total catalytic efficiency (g/g of ZTCN)[a]	W_{PC}	Catalytic efficiency for copolymerization (g/g of ZTCN)[a]	F	R	M_w/M_n/MWD
80	18.2	4.1	17.5	0.70	16.1	
90	32.4	4.5	30.9	0.64	12.5	
110	79.4	6.6	74.3	0.62	8.0	2,360/1,310/1.8
120	119.3	7.2	110.7	0.58	6.6	5,040/1,790/2.8
130	482.6	9.1	438.7	0.52	4.3	21,660/6,770/3.2
150	582.1	10.0	523.9	0.32	2.1	35,390/8,230/4.3

M_w = weight-average molecular weight; MWD = molecular weight distribution. All reactions were carried out at 5.0 MPa for 20 h. The amount of catalyst was equivalent to 30 mg of ZTCN.
[a] All catalytic efficiencies were calculated on the basis of the weight of ZTCN.

TABLE II
Effect of Pressure on the Catalytic Efficiency and the Compositions of the Products

Pressure (MPa)	Temperature (°C)	Total catalytic efficiency (g/g of ZTCN)	PC (wt %)	Catalytic efficiency for copolymerization (g/g of ZTCN)	F	R
6.5	110	86.5	5.2	82.1	0.67	11.8
5.0	110	79.6	6.6	74.3	0.62	8.0
3.0	110	74.6	11.4	66.1	0.57	3.6
1.5	110	68.7	12.1	60.4	0.44	2.7
6.5	130	514.3	6.7	479.8	0.60	7.6
5.0	130	482.6	9.1	438.7	0.52	4.3
3.0	130	463.1	12.7	404.3	0.43	2.5

The amount of catalyst was equivalent to 30 mg of ZTCN; 20 mL of PO was used. The reaction time was 20 h.

Table II shows the effect of pressure on the results of copolymerization. Unexpectedly, unlike other kinds of DMC catalysts (Zn–Co DMC or Zn–Fe DMC), the content of PC decreased with increasing CO_2 pressure at temperatures of 110 or 130°C catalyzed by Zn–Ni DMC. For instance, W_{PC} decreased from 12.7 to 6.7 when CO_2 pressure was increased from 3.0 to 6.5 MPa at 130°C. At the same time, this was accompanied by increased catalytic efficiency (479.8 g/g for copolymer) and a higher F (F = 0.60). This means that a higher concentration of CO_2 in the reaction system was more favorable for the copolymerization than the coupling reaction; thus, it is possible that the content of PC could be suppressed to a lower level and F of CO_2 could be higher under even higher CO_2 pressure above 6.5 MPa. The reasons for the difference between them may relate to the mechanism of catalysis, which is still obscure because of the difficulty of direct characterization of the active site.

For PO–CO_2 copolymers, there were still a considerable number of ether linkages. The reason for this may be attributed to the much high concentration of PO relative to the concentration of CO_2 in the reaction system; therefore, a more rapid homopolymerization of PO occurred and led to a lower F. To confirm this, inert and nonpolar solvents, such as toluene and xylene, or inert and polar solvents, such as DMF, were added to dilute PO, which made the feed concentration of PO as low as even 16% (Table III).

TABLE III
Results of PO—CO_2 Copolymerization in Different Solvents

Solvent	Concentration of PO (wt %)	W_{PC}	F	R
Toluene	35	3.5	0.60	14.5
Xylene	35	3.1	0.62	17.3
Xylene	16	3.9	0.56	13.2
DMF	35	8.6	0.44	3.9
DMF	16	10.3	0.38	2.7

All reactions were carried out at 110°C and 5.0 MPa.

However, F did not increase compared with that of the solvent-free system; it even decreased when DMF was used as the solvent. This was ascribed to the fact that the DMC catalyst was a heterogeneous catalyst and thus made the relative reaction rate of polymerization (homopolymerization of PO vs copolymerization) less sensitive to the concentration of monomer. Interestingly, the contents of PC varied in different manners for different solvents; that is, nonpolar solvents, such as toluene and xylene, led to a slightly decreasing content of PC; strong polar solvents, such as DMF, led to a slightly increasing content of PC.

Copolymerization of CHO–CO_2 with Zn–Ni DMC

For the copolymerization of CHO and CO_2, this catalyst exhibited an unexpectedly low catalytic efficiency, although the copolymer could be obtained. Typical FTIR and ^{1}H-NMR spectra of the product are shown in Figures 3 and 4. The absorption peak
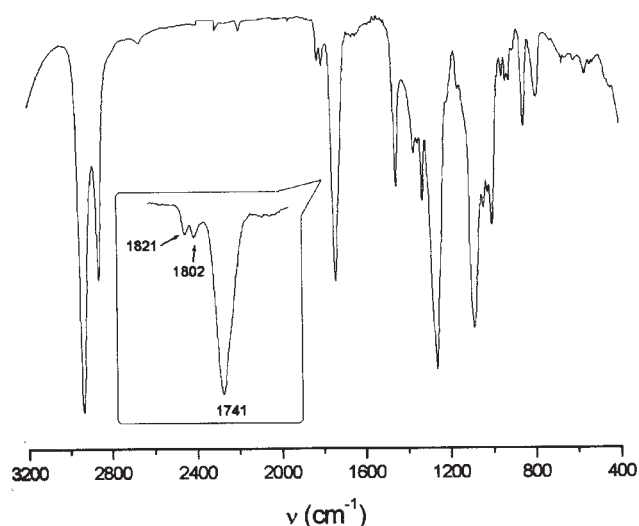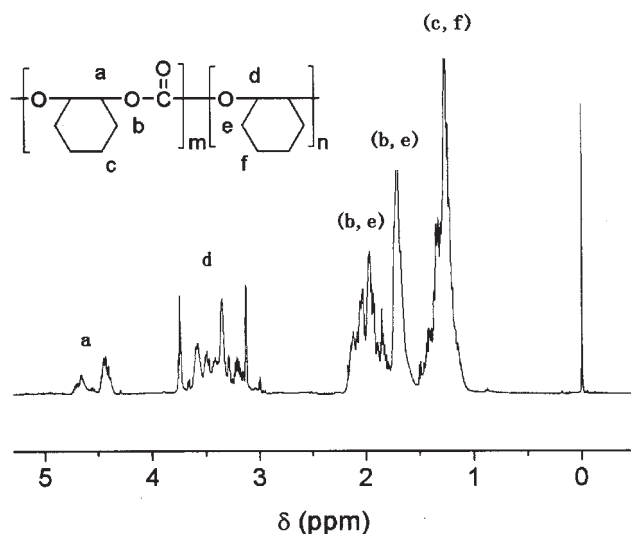

Figure 3 FTIR spectrum of the typical product of CHO–CO_2 copolymerization.

Figure 4 ^{1}H-NMR spectrum of the typical product of CHO–CO$_2$ copolymerization.

at 1741 cm^{-1} clearly indicated the presence of carbonyl groups in the final product (Fig. 3). Moreover, the signals at 4.4–4.8 ppm (Fig. 4), which were ascribed to hydrogens adjacent to oxycarbonyl groups, also confirmed the incorporation of CO$_2$ into the copolymer. In addition, there were small peaks at 1802 and 1821 cm^{-1} in the FTIR spectrum, which were characteristic absorptions of *cis*-cyclohexane carbonate and *trans*-cyclohexene carbonate, respectively. This indicated that cyclohexene carbonate, the product of coupling reaction, also presented in relatively small amounts. The percentage of its content could not be figured out precisely in terms of its corresponding ^{1}H-NMR because its tiny signals were superimposed with signals of the copolymer. In comparison, the coupling reaction did not occur with Zn–Fe DMC and Zn–Co DMC. With respect to its catalytic efficiency, it demonstrated merely 5.6–23.2 g of product/g of ZTCN (Table IV). Below 140°C, its extraordinary low catalytic efficiency made

the conversions of copolymerization so low that the molecular weights of the copolymers were beyond the lower limit of the determining column. Only the products at 140°C had M_n values of 1260–1730. In addition, the F values of the copolymers were in the range 0.28–0.45; the obtained copolymers were sticky liquids instead of solid copolymers. In this sense, this catalyst behaved in a manner obviously inferior to Zn–Fe DMC and Zn–Co DMC for the copolymerization of CHO and CO$_2$. The differences between the PO–CO$_2$ and CHO–CO$_2$ copolymerizations catalyzed by Zn–Ni DMC were attributed to two reasons. One was diversity in steric hindrance between PO and CHO; the greater steric hindrance of CHO may have prevented it from coordinating well with zinc. The other reason was a chemical factor; that is, the electron cloud density of oxygen in CHO was not suitable for its coordination with zinc. However, it was not easy to distinguish their contributions in individual steps because no further study was done on the model reaction for Zn–Ni DMC. Because of its low catalytic efficiency in the CHO/CO$_2$ copolymerization, the following experiments were done with PO and CO$_2$ as monomers.

Effect of complexing agents on catalytic performance

It is known that DMC catalyst can exhibit different catalytic efficiency toward the ROP of PO when a subtle change of preparative conditions occurs. The most important factor is the kind of complexing agent used, which influences the catalytic characteristics of the DMC catalyst via a change in the condensed state stemming from a variation in the precipitating surroundings. Herein, TBA, an optimum complexing agent for Zn–Co DMC, was used in the preparation of Zn–Ni DMC. However, previous research revealed that the optimum complexing agent may be different for different kinds of DMC catalysts. Several other water-soluble organic solvents

TABLE IV
Results of CHO—CO$_2$ Copolymerization Under Various Conditions

Pressure (MPa)	Temperature (°C)	Total catalytic efficiency (g/g of ZTCN)	F	M_n/M_w/MWD
5.0	90			
5.0	110	5.6	0.45	
5.0	120	8.3	0.41	
5.0	140	23.2	0.34	1350/3510/2.6
3.0	140	22.5	0.33	1260/3530/2.8
2.0	140	18.6	0.28	1760/5460/3.1

M_w = weight-average molecular weight; MWD = molecular weight distribution. The amount of catalyst was equivalent to 30 mg of ZTCN; 6 mL of CHO was used. The reaction time was 20 h.

TABLE V
Effect of Complexing Agent on the Results of PO—CO$_2$ Copolymerization

Catalyst	Complexing agent	Total catalytic efficiency (g/g of ZTCN)	PC (wt %)	Catalytic efficiency for copolymerization (g/g of ZTCN)	F	R
1	1,2-Dimethoxyethane	528.3	6.7	492.9	0.62	8.1
2	2-Methoxyethanol	537.1	7.3	497.9	0.58	6.8
3	1-Methoxy-2-propanol	505.7	7.5	467.6	0.62	7.4
4	Glycol	338.3	6.9	314.9	0.56	6.9
5	1,2-Propandiol	376.5	7.5	348.2	0.60	6.8
6	None	186.3	10.1	166.2	0.54	4.1

All reactions were carried out at 130°C and 6.5 MPa for 20 h.

were examined as complexing agents (Table V); both catalytic efficiency and the composition of the copolymer were investigated. Catalysts with glycol ether as the complexing agent exhibited nearly the same or slightly higher catalytic efficiencies. Catalysts without any complexing agent (catalyst 6) exhibited only one-third of the highest catalyst efficiency. Except for catalysts without any complexing agent, F of the copolymer and the content of PC changed in a very narrow range, which indicated that the different complexing agents had no influence on the composition of the copolymer. For reasons of its advantages, it would be worth investigating more kinds of complexing agent in further research and then seeking more effective complexing agents.

CONCLUSIONS

A DMC catalyst based on ZTCN was prepared by the reaction between K$_2$[Ni(CN)$_4$] and ZnCl$_2$ in the presence of a complexing agent, and its highest catalytic efficiency was approximately 500 g of copolymer/g of Zn[Ni(CN)$_4$], which was several times higher than that of Zn–Fe DMC, zinc carboxylate, and so forth. Moreover, an advantage of this novel DMC catalyst was that a significantly lower content of PC was produced compared with other DMC catalysts; the weight of PC only occupied about 4–6% of the overall weight of the product under optimum conditions. This contrasted with Zn–Co DMC, by which over 20% of the weight of the final product was PC. The molar fraction of CO$_2$ in the copolymer reached about 0.6, which was close to that derived from other DMC catalysts. However, this catalyst

was not suitable for the copolymerization of CHO and CO$_2$. With the features of this novel catalyst for the copolymerization of PO and CO$_2$ in mind, it could be regarded as an effective catalyst.

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