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Aliphatic polycarbonate synthesis by copolymerization of carbon dioxide with epoxides over double metal cyanide catalysts prepared by using ZnX_2 ($X = F$, Cl, Br, I)

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Abstract

As means of the chemical fixation of carbon dioxide and the synthesis polycarbonates, copolymerizations of carbon dioxide with various epoxides, such as cyclohexene oxide, cyclopentene oxide and propylene oxide were investigated in the presence of double metal cyanide (DMC) catalysts. The DMC catalysts were prepared by reacting $K_3Co(CN)_6$ with ZnX_2 ($X = F$, Cl, Br, I) together with tertiary butyl alcohol and poly(tetramethylene ether glycol) as complexing reagents and were characterized by various spectroscopic methods. The DMC catalysts showed high activity for epoxides and CO_2 copolymerization to yield aliphatic polycarbonates of narrow polydispersity and moderate molecular weight.

Keywords: Carbon dioxide; Catalysis; Copolymerizations; Double metal cyanide; Epoxides; Polycarbonates; Ring-opening

1. Introduction

Chemical fixation of CO_2 is a very attractive subject not only from viewpoint of carbon resource utilization, but also from increasing environmental concerns. As a kind of potential approach, one of the most promising areas of CO_2 utilization is its application as a direct material for polymer synthesis. The past three decades witnessed the great progress in fixation of CO_2 into polycarbonates since the creative work of Inoue et al. [1,2]. To date, many excellent reviews in different period contributed by Kuran [3], Super [4,5], Darensbourg [6–10] and Kim [11] have made good description of this topic, where the importance of catalyst was never overestimated.

Double metal cyanide complexes (DMC) are well-known catalysts for the ring-opening polymerization of epoxides. Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [12–15]. The catalysts are highly active and give polyether polyols that have low unsaturation and narrow molecular weight distribution compared with similar polyols synthesized using conventional KOH catalysis, resulting in high performance polyurethane products [16]. While DMC catalysts offer significant advantages for the ring-opening polymerization of epoxides, few reports have been published on the copolymerization of epoxides with CO_2 thereby [17].

In this study we have prepared a series of DMC catalysts by changing metal salt, ZnX_2 ($X = F$, Cl, Br, I), which is the most important component of the DMC catalyst, and investigated the effect of the change of the metal salt on various epoxides/CO_2 copolymerizations. The resultant copolymers are subjected to ^1H NMR spectroscopy, infrared spectroscopy and gel permeation chromatography analyses.

2. Experimental

2.1. Materials

All materials, such as potassium hexacyanocobatate(III) ($K_3Co(CN)_6$), zinc fluoride (ZnF_2), zinc chloride ($ZnCl_2$), zinc bromide ($ZnBr_2$), zinc iodide (ZnI_2) and tertiary butyl alcohol (^tBuOH) were purchased from Aldrich and used without further purification. Cyclohexene oxide (CHO, 98%), cyclopentene

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oxide (CPO, 98%) and propylene oxide (PO, 99.5%) were all purchased from Aldrich and refluxed over calcium hydride (CaH_2), it was then distilled and stored over Linde type 4 Å molecular sieve. Carbon dioxide of 99.99% purity was used without further purification. Polymerization grade of poly(-tetramethylene ether glycol) (PTMEG, molecular weight = 1800) was donated by BASF Korea Ltd.

2.2. Preparation of catalysts

A solution of $ZnCl_2$ (220 mmol) in deionized water (115 mL) and ^{t}BuOH (21 g) is taken in the first beaker (solution 1). A solution of $K_3Co(CN)_6$ (3.15 g, 9.5 mmol) in deionized water (42 mL) is taken in the second beaker (solution 2). The third beaker contains a mixture of deionized water (1 mL), ^{t}BuOH (20 mL) and PTMEG (3.5 g) (solution 3). Solution 2 is added to solution 1 dropwise for a period of over 60 min at 50 °C with continuous stirring using a mechanical stirrer. Solution 3 is then added and the mixture is stirred for an additional 3 min. The mixture is then centrifuged. The resulting catalyst (**DMC-Cl**) cake is dried at 60 °C under vacuum (30 inHg) to a constant weight. The catalysts using ZnF_2 (**DMC-F**), $ZnBr_2$ (**DMC-Br**) and ZnI_2 (**DMC-I**) were prepared by similar procedures.

2.3. Copolymerization of epoxdies and CO_2

Copolymerization of epoxides (CHO, CPO and PO) and CO_2 were carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. The dried catalyst (20 mg) was added into the reactor, followed by adding a desired amount of the purified epoxides (5 mL) using a syringe. Then the reactor was capped by the reactor head and entire assembly was transferred to a pressure cell. The reactor was purged with several times with CO_2. The reactor was then pressurized with CO_2 and then heated at a desired temperature with stirring. After a certain period reaction time, unreacted CO_2 was completely released from the reactor to reduce pressure, terminating the copolymerization. The polymer powder was separated by precipitation using excess methanol followed by filtration. The product solution was concentrated to proper volume using a rotary evaporator. The polymer precipitate was filtered off, followed by drying at room temperature in a vacuum oven. The solvents used were removed from the filtrate by distillation. The polymerization yield was determined by gravimetry.

2.4. Characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained with a RINT2000 wide angle goniometry 185 using Cu Kα radiation at 40 kV and 30 mA. X-ray photoelectorn spectroscopy (XPS) analysis of the catalysts was performed on an ESCALAB 250 induced electron emission spectrometer with Al Kα (1486.6 eV, 12 mA, 20 kV) X-ray sources. IR spectra of the catalysts were obtained in transmission mode using a React IR. ^{1}H NMR spectra of the polymers were performed on a Varian Gemini 2000 and HP5P $CDCl_3$ as a solvent. Molecular weight distributions (MWD) were measured using a Waters 150-C instrument, operated at 35 °C, with a set at 103, 104 and 500 Å columns (dimethylformamide as a solvent).

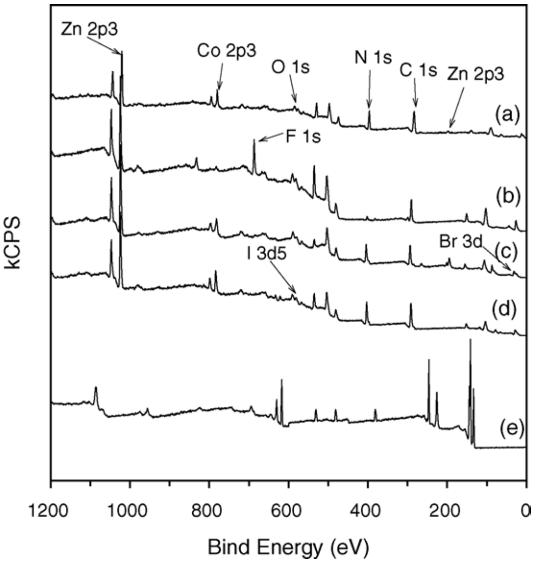


Fig. 1. XPS spectra of various DMC catalysts: (a) **DMC-Cl**, (b) **DMC-F**, (c) **DMC-Br** and (d) **DMC-I**, and XPS spectrum of (e) $K_3[Co(CN)_6]_2$.

3. Results and discussion

3.1. Catalyst characterization

The DMC catalyst prepared by ZnX_2, such as ZnF_2 (**DMC-F**), $ZnCl_2$ (**DMC-Cl**), $ZnBr_2$ (**DMC-Br**) and ZnI_2 (**DMC-I**) and $K_3Co(CN)_6$ in the presence of ^{t}BuOH as a complexing agent (CA) is expected to have a general formula [17]: $Zn_3Co(CN)_6xZnX_2yH_2OzCA$.

The qualitative and quantitative surface formulations of the DMC catalysts were investigated by XPS. The XPS spectra of the DMC catalysts prepared by using various zinc halides, such as ZnF_2 (**DMC-F**), $ZnCl_2$ (**DMC-Cl**), $ZnBr_2$ (**DMC-Br**) and ZnI_2 (**DMC-I**) are shown in Fig. 1. The formation of zinc hexacyanocobaltate(III) led the binding energy (1023.7 eV) of zinc atom in $ZnCl_2$ to shift towards lower values. The reaction of $ZnCl_2$ with $K_3[Co(CN)_6]_2$ ([Zn]/[Co] = 5.0) in the presence of complexing agents led shift of the binding energy of zinc atom to 1021.3 eV. Similar shifts were observed for the DMC catalysts prepared by using $ZnBr_2$ (1023.7–1020.8 eV) and ZnI_2 (1023.7–1021.1 eV) as metal salts. However, no shift was observed for ZnF_2 and a clear F 1 s peak was appeared at 684.8 eV, demonstrating zinc hexacyanocobaltate(III) complex is not formed by using ZnF_2.

Infrared spectra of $K_3Co(CN)_6$ and DMC catalysts (Fig. 2) show a shift of the ν(CN) band from 2133.4 cm^{-1} for $K_3Co(CN)_6$ to 2195.9 cm^{-1} for DMC catalysts. The ν(CN) of free CN^- is 2080 cm^{-1} [17–19]. The ν(CN) shifts to higher frequencies demonstrate that the CN^- ion acts as not only a σ-donor by donating electrons to the cobalt but also an electron donor by coordination to zinc metal. In addition, the band of

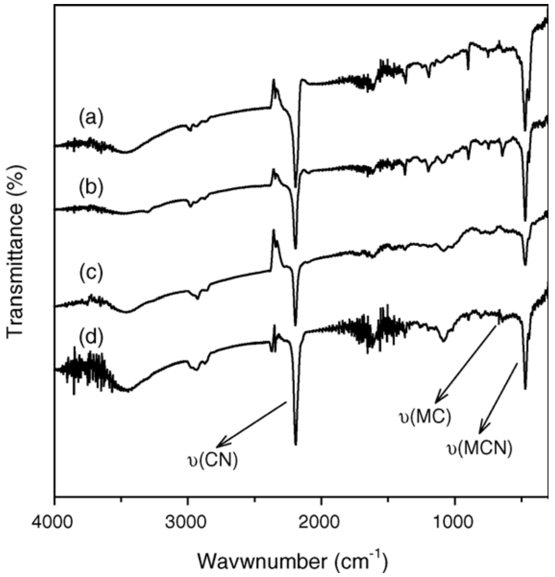


Fig. 2. Infrared spectra of (a) **DMC-Cl**, (b) **DMC-F**, (c) **DMC-Br** and (d) **DMC-I**.

585.1 cm^{-1} assigned to ν(Co–CN) bond for $K_3Co(CN)_6$ shifts to lower frequency of 472.6 cm^{-1} for DMC catalysts. These shifts of ν(CN) and ν(Co–CN) bands demonstrate that the main composition of the DMC catalyst, $Zn_3Co(CN)_6$, was successfully formed by using different zinc halide salts except ZnF_2.

Alteration of the crystal structure was investigated by X-ray diffraction patterns (Fig. 3). The X-ray patterns for DMC catalysts prepared in the absence of the organic complexing agent resembled that for highly crystalline zinc hexacyanocobaltate hydrate and it was not active for the homo- and copolymerizations of epoxides. The X-ray patterns for DMC catalysts, which were synthesized in the presence of ^{t}BuOH and PTMEG, exhibit broad signals at *d*-spacing of 5.75, 5.07, 3.59, 2.54 and 2.28 Å, ascribing to a cubic lattice structure of $Zn_3Co(CN)_6$ [12,17,20]. This means that the crystallinity of the DMC catalysts is substantially low, even though they are not completely amorphous. The crystallinity of the heterogeneous DMC catalyst may strongly influence the catalytic activity. Especially, **DMC-I** showed most high activity but **DMC-F** showed lowest activity (vide infra). Again, the X-ray diffraction pattern of DMC-F catalyst, which resembles that of crystalline $K_3Co(CN)_6$, demonstrates that the DMC catalyst is hardly prepared by using ZnF_2.

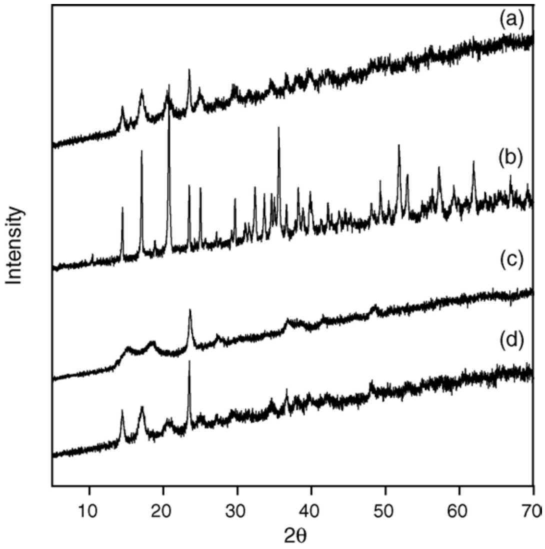
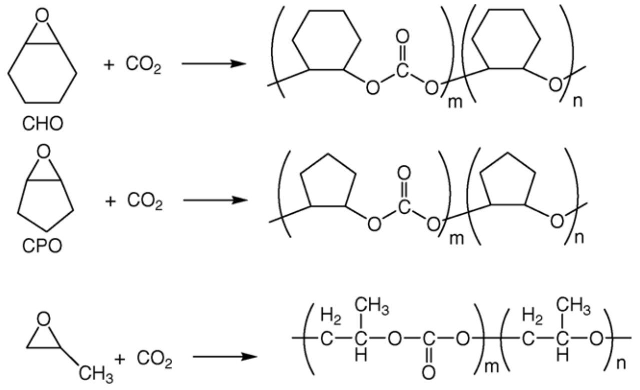


Fig. 3. XRD curves of (a) **DMC-Cl**, (b) **DMC-F**, (c) **DMC-Br** and (d) **DMC-I**.



Scheme 1. Copolymerizations of epoxides and CO_2 and the expected structure of the resulting copolymers.

3.2. Copolymerizations of epoxides and CO_2

The copolymerizations of epoxides and CO_2 using DMC catalyst have been carried out at 50 and 80 °C with CO_2 at 9.6 bar. The generalized scheme of the copolymerization and the proposed structure of the resulting copolymers were summarized in Scheme 1.

If the alternating copolymerization is perfect, only carbonate groups (–OC(O)O–) should be generated. However, kinetically controlled homopolymerization of CHO results in ether linkage (–COC–). The polymers were characterized by FT-IR and ^{1}H NMR spectroscopies utilizing the previously established methodology for similar copolymers produced from other zinc catalyst systems [4,18].

The isolated polycarbonates produced by using CHO, CPO and PO as a comonomer were analyzed by ^{1}H NMR in $CDCl_3$, where the relative amount of ether linkages was determined by integrating the peaks corresponding to methane protons of the polyether units containing no CO_2 chain in its backbone and polycarbonate unit formed by the addition of CO_2 in its backbone (Table 1).

The IR spectra of the copolymers resulting from the copolymerization of CO_2 with epoxides are shown in Fig. 4. The existence of peaks around 1750 cm^{-1} corresponding to carbonyl group ν(C=O) and around 1250 cm^{-1} assigned to ether group ν(C–O) provide an evidence for the presence of carbonate unit in the resultant copolymers.

Copolymerizations of CHO, CPO and PO with carbon dioxide were carried out in the presence of various DMC catalysts prepared by using different ZnX_2, and the results are summarized in Table 2. In CHO/CO_2 copolymerizations, **DMC-I** shows the highest activity (535.09 g-polymer/g-

Table 1
^1H NMR characterization of polycarbonates produced by the copolymerization of CO_2 with various epoxide compounds

Monomer	^1H NMR (ppm, $CDCl_3$)		Carbonate content (f_{CO_2})
	Polycarbonate	Polyether	
CHO	4.2–4.6	3.2–3.6	$A_{4.2–4.6}/(A_{4.2–4.6} + A_{3.2–3.6})$
CPO	4.8–5.2	3.6–4.0	$A_{4.8–5.2}/(A_{4.8–5.2} + A_{3.6–4.0})$
PO	4.9–5.1, 4.0–4.4	3.4–3.6	$(A_{4.9–5.1} + A_{4.0–4.4})/(A_{4.9–5.1} + A_{4.0–4.4} + A_{3.4–3.6})$

Table 2
Results of epoxides/CO_2 copolymerizations obtained by using DMC catalysts

Epoxides	Catalysts[a]	T_p	Time (h)	TON[b]	TOF[b]	M_w[c]	M_w/M_n[c]	f_{CO_2}[d]
CHO	**DMC-Cl**	80	4	526.15	131.55	8900	1.7	0.53
	DMC-Br	80	4	527.12	131.78	5100	1.2	0.51
	DMC-I	80	4	535.09	133.77	4000	1.2	0.23
CPO	**DMC-Cl**	80	12	492.27	41.18	2300	1.6	0.36
	DMC-Br	80	12	501.33	41.78	2900	1.0	0.37
	DMC-I	80	12	521.67	43.47	2800	1.4	0.33
PO	**DMC-Cl**	50	24	506.80	21.11	4400	3.9	0.22
	DMC-Br	50	24	515.21	21.47	2800	1.0	0.36
	DMC-I	50	24	520.60	21.69	3300	1.7	0.32

Polymerization conditions: catalyst = 0.02 g, epoxide = 5 mL, P_{CO_2} (25 °C) = 9.6 bar.

[a] **DMC-F** showed negligible activity.

[b] TON in g-polymer/g-Zn and TOF in g-polymer/g-Zn h.

[c] Data from GPC.

[d] [Carbonate]/([carbonate] + [ether]) ratio determined by ^1H NMR spectra (see also Table 1).

catalyst) but the lowest CO_2 contents ($f_{CO_2} = 0.23$). **DMC-F** shows no activity for copolymerization of CO_2 and epoxides as expected. It is interesting to note that the carbonate contents are highest ($f_{CO_2} = 0.53$ at 80 °C) when CHO is used as a comonomer; however, PO comonomer shows the lowest carbonate content ($f_{CO_2} = 0.22$ at 50 °C) using **DMC-Cl** catalsyts. These results indicate that sterically less bulky epoxide monomers (say PO) prefer kinetically controlled homopolymerization to thermodynamically controlled copolymerization. All polymers showed narrow polydispersities with moderate molecular weight ranging from 2300 to 8900.

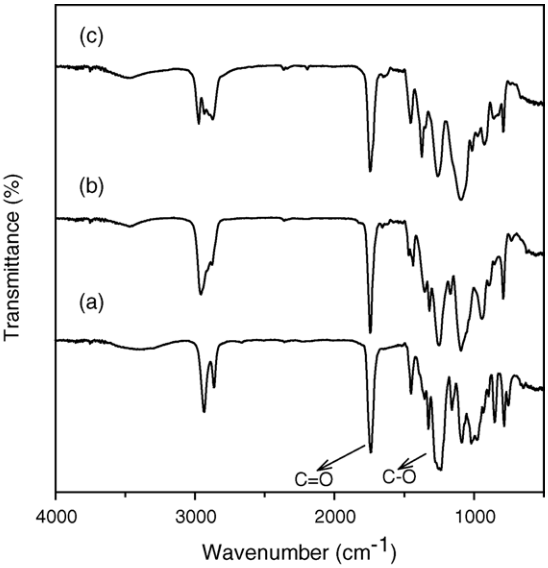


Fig. 4. The IR spectra of aliphatic polycarbonates synthesized by copolymerizations of carbon dioxide and (a) CHO, (b) CPO and (c) PO.

Further mechanistic studies on epoxides/CO_2 copolymerizations by using DMC catalysts are ongoing in order to clarify the effect of zinc salts and metal cyanide salts by changing the catalyst formulations in various ways.

4. Conclusions

DMC catalysts prepared by reacting ZnX_2 (X = F, Cl, Br, I) with $K_3Co(CN)_6$ in the presence of ^tBuOH and PTMEG as complexing reagents were efficient for the copolymerization of various types of epoxide monomers with CO_2. The efficiency of CO_2 fixation was changed according to not only the type of DMC catalysts but also especially the type of epoxide monomers. **DMC-I** shows the highest activity but the lowest CO_2 reactivity. The DMC catalysts showed high activity (TON > 520 g-polymer/g-Zn) and carbonate content ($f_{CO_2} > 0.23$) in the copolymerizations of CHO and CO_2 at 80 °C and $P_{CO_2} = 9.6$ bar. In the case of PO/CO_2 copolymerizations, polymer yield was high but carbonate content was relatively low due to kinetically controlled homopolymerization.

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