

Recent progress in the synthesis of polymers based on carbon dioxide*

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Abstract: The alternating copolymerization of carbon dioxide and epoxide to give polycarbonate has attracted the attention of many chemists, because it is one of the most promising methodologies for the utilization of carbon dioxide as a safe, clean, and abundant raw material in the synthetic chemistry. Recent developments of the catalysts for the alternating copolymerization are based on the rational design of metal complexes, especially complexes of transition metal with well-defined structures.

Keywords: carbon dioxide polymers; polycarbonate; alternating copolymerization; rational design; carbon dioxide–epoxide copolymerization.

INTRODUCTION

Carbon dioxide is the most fundamental carbon resource indispensable for the existence of all living organisms on Earth including mankind, via photosynthesis by green plants. On the other hand, chemical utilization of carbon dioxide has been rather limited. Productions of urea, salicylic acid, and some carbonates are the industrialized examples. Many other possibilities are yet to be developed. Recently, the increase in the atmospheric concentration of carbon dioxide is regarded as a possible cause to bring about global warming, and its mitigation is a subject of environmental concern. However, this is obviously the result of excessive use of fossil fuels, and the first choice should be to decrease the generation of carbon dioxide, rather than to trap and discard carbon dioxide somewhere once exhausted. It must be emphasized that chemical utilization of carbon dioxide is an important subject independent of such an environmental issue.

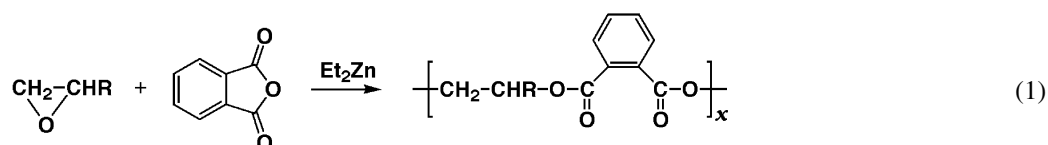
The reaction of carbon dioxide can be classified into two types; reductive and nonreductive reactions. Reductive reactions involve the loss of oxygen atom(s) from CO₂ and/or addition of hydrogen to afford formic acid, methanol, methane, or carbon monoxide. On the other hand, in nonreductive reactions, oxygen atoms of CO₂ are retained, and carbon dioxide is fixed to form carbon–carbon, carbon–nitrogen, or carbon–oxygen bonds; carboxylic acid and the derivatives, carbamate or urea, and carbonate are the products. With respect to atom economy, nonreductive reactions retaining oxygen atoms are considered more advantageous for chemical utilization of carbon dioxide. A representative example is the copolymerization of carbon dioxide and epoxide to form an alternating copolymer, an aliphatic polycarbonate, which is the subject of the present article.

*Paper based on a presentation at the 15th International Symposium on Fine Chemistry and Functional Polymers (FCFP-XV) and the 1st International Symposium on Novel Materials and their Synthesis (NMS-I), 17–20 October 2005, Shanghai, China. Other presentations are published in this issue, pp. 1803–1896.

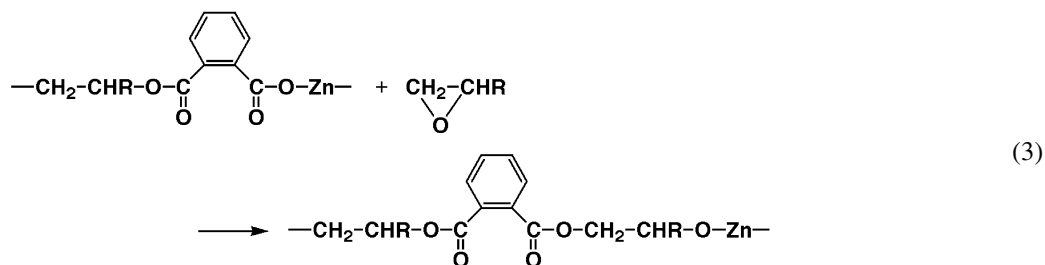
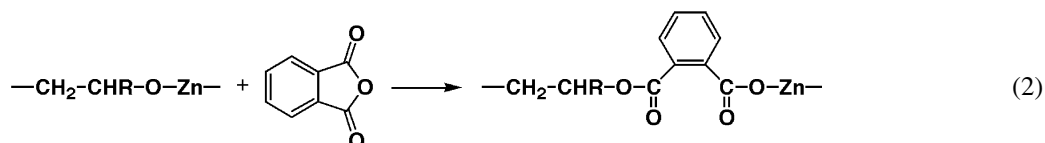
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BACKGROUND OF DISCOVERY OF CARBON DIOXIDE–EPOXIDE COPOLYMERIZATION

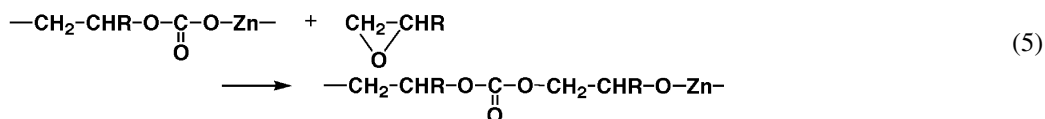
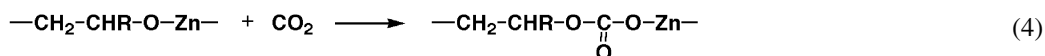
The background of the discovery of carbon dioxide–epoxide copolymerization by Inoue et al. [1] dates back to the early 1960s, when the first successful enantioselective polymerization was accomplished in the polymerization of racemic propylene oxide by diethylzinc–optically active alcohol system [2]. In the course of related studies, the alternating copolymerization of epoxide and cyclic acid anhydride such as phthalic anhydride to form polyester was also examined. This reaction had been already known, but diethylzinc was found as a new catalyst (eq. 1) [3].



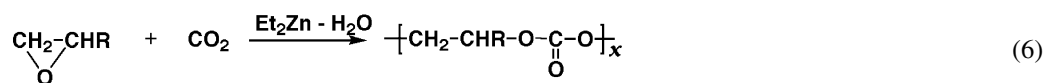
Detailed studies indicate that copolymerization proceeds by the repetition of the following two reactions, that is, the reaction of a zinc alkoxide with acid anhydride to form a zinc carboxylate (eq. 2), and its reaction with epoxide to regenerate a zinc alkoxide (eq. 3).



Then the idea came to mind that, since carbon dioxide is regarded as an acid anhydride of carbonic acid, carbon dioxide would be able to copolymerize with epoxide (eqs. 4 and 5).



The reaction was first attempted in 1968 by using the equimolar reaction mixture of diethylzinc and water as the catalyst. In an autoclave were supplied a solvent such as dioxane, propylene oxide, and the catalyst, and the mixture was stirred under a pressure of carbon dioxide (50 atm) at room temperature for one day. Then the reaction mixture was added by a small amount of acid and poured into methanol. Homopolymer of propylene oxide is soluble in methanol, a methanol insoluble part was found, which showed a strong carbonyl (carbonate) absorption in infrared (IR) spectrum. Analysis showed almost equimolar incorporation of carbon dioxide and the epoxide to the product. The molecular weight was high enough (50 000–150 000). Thus, the first example of the use of carbon dioxide as a monomer in polymerization reaction was accomplished (eq. 6).



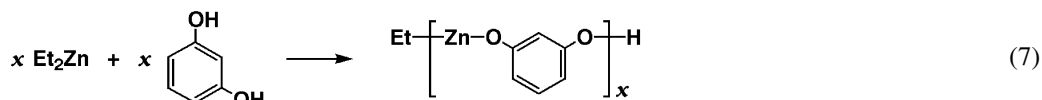
Since this discovery, copolymerizations of carbon dioxide were examined with other cyclic monomers such as oxetane, thiirane, and aziridine. Attempts were also made to copolymerize with unsaturated monomers such as vinyl ether, diene, and diyne. Polycondensation reactions of carbon dioxide with diamine and diol were also examined. However, to date, only carbon dioxide–epoxide copolymers are considered qualified for possible practical production and application. As for the carbon dioxide–epoxide copolymerization, much work has been carried out up to now, mainly to develop the catalyst systems with high activity. Representative catalysts are summarized in Table 1. The progress will be discussed in detail in the latter part of this article.

Table 1 Representative catalysts for alternating copolymerization of carbon dioxide and epoxide.

ZnEt ₂ -H ₂ O	AlEt ₃ -PPh ₃
ZnEt ₂ -RNH ₂	AlEt ₃ -2,2'-bipyridyl
ZnEt ₂ -C ₆ H ₄ (OH) ₂ (<i>o</i> -, <i>m</i> -, <i>p</i> -)	Al(porphyrin)Cl (4a)-EtPh ₃ PBr
ZnEt ₂ -C ₆ H ₃ (OH) ₃ (1,2,3-, 1,3,5-)	Al(Schiff base)Me (5a)-Et ₄ NOAc
ZnEt ₂ -C ₆ H ₄ (NH ₂)(OH) (<i>o</i> -, <i>m</i> -, <i>p</i> -)	Cr(Schiff base)Cl (5b)-Ph ₂ PNPPh ₂ Cl (6)
ZnEt ₂ -C ₆ H ₄ (COOH) ₂ (<i>o</i> -, <i>m</i> -, <i>p</i> -)	Cr(Schiff base)Cl (5c)-DMAP
ZnEt ₂ -C ₆ H ₄ (COOH)(OH) (<i>o</i> -, <i>m</i> -, <i>p</i> -)	Co(porphyrin)Cl (4d)-DMAP
ZnEt ₂ -C ₆ H ₄ (NH) ₂ (<i>o</i> -)	Co(Schiff base)OAc (5d)
ZnEt ₂ -C ₆ H ₄ (SH) ₂ (<i>m</i> -)	Nd(CCl ₃ COO) ₃ -ZnEt ₂ -glycerol
Zn(phenoxide) ₂ (1)	Y(CCl ₃ COO) ₃ -ZnEt ₂ -glycerol
Zn(β-diiminate) ₂ (2)	Y(benzoate) ₃ -ZnEt ₂ -glycerol
ZnO-dicarboxylic acid	Y[(RO) ₂ POO] ₃ (7)-Al ^t Bu ₃ -glycerol
Zn(OH) ₂ -dicarboxylic acid	Mn(porphyrin)OAc (4e)

HISTORY

Most catalysts that are efficient for the alternating copolymerization are the reaction mixture of diethylzinc and a compound having two or more active hydrogens in a molecule, such as water, primary amines [4], dihydric phenols [5–11], trihydric phenols [7,8,10,11], aminophenols [7], aromatic dicarboxylic acids [7], aromatic hydroxycarboxylic acids [12], diamonobenzene [13], and thioresorcinol [13]. These catalysts have been reported by Inoue's group followed by Kuran's group. The structures of these catalysts are not so simple. For example, the equimolar reaction of diethylzinc and resorcinol (1,3-dihydroxybenzene) is considered to give a mixture of oligomeric zinc resorcinolate with various chain lengths (eq. 7) [5]. These oligomers are generally insoluble in common organic solvents, because they are easy to make intermolecular aggregation. As for the diethylzinc–pyrogallol (1,2,3-trihydroxybenzene) system, Kuran et al. characterized in detail the products in various molar ratios by IR, ¹H NMR spectra, and cryoscopy [14,15].



In many cases, the copolymerization of carbon dioxide and epoxide generates as by-product a five-membered cyclic carbonate, a one-to-one cyclic adduct of carbon dioxide and epoxide. Therefore, the alternating copolymerization may proceed via the ring-opening polymerization of the cyclic carbonate. However, under the conditions of the alternating copolymerization, the ring-opening polymer-

ization of the cyclic carbonate does not occur. Thus, the alternating copolymerization of carbon dioxide and epoxide is considered to proceed not via the ring-opening polymerization of the cyclic carbonate, but via the alternating repetition of additions of carbon dioxide and epoxide to the active terminal of the growing polymer. On the other hand, when the reactions of epoxide take place repeatedly, ether bonds are formed in addition to carbonate linkages in the polymer main chain. As the result, the obtained copolymer contains both carbonate and ether linkages.

To summarize, the alternating copolymerization of carbon dioxide and epoxide by organozinc catalyst is illustrated in Fig. 1.

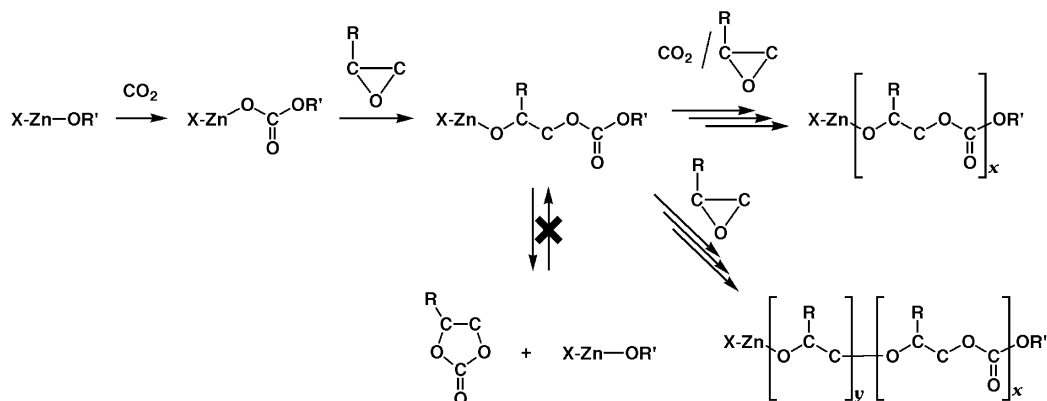


Fig. 1 Alternating copolymerization of carbon dioxide and epoxide and related side reactions.

COPOLYMERIZATION BY ZINC CATALYSTS

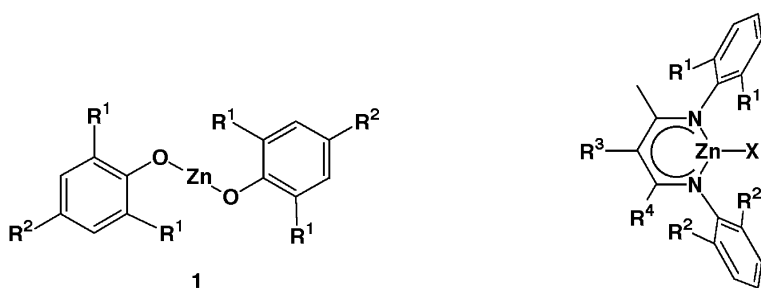
In recent years, zinc complexes with well-defined structures have been reported to exhibit high catalytic activity for the copolymerization of carbon dioxide and epoxide. Some of them can control the molecular weight of the produced polycarbonate.

Mononuclear zinc bis(phenoxides) (**1**) carrying two bulky *ortho*-substituents are reported by Darensbourg et al. to be efficient for the alternating copolymerization of carbon dioxide and 1,2-epoxy-cyclohexane (cyclohexene oxide) [16,17]. The reaction using **1a** proceeded in homogeneous solution to form 602 g of copolymer per 1 g of zinc in 69 h at 80 °C under carbon dioxide at 51 atm (turnover frequency (TOF) [18] = 2.5 h⁻¹). The content of the carbonate linkage in the main chain was above 90 %. The average molecular weight of the copolymer lay in the range of $M_n = 18\,000\text{--}38\,000$, and had a narrower distribution ($M_w/M_n = 2.5\text{--}4.5$) than those of the copolymers obtained by the conventional zinc catalysts.

1b was much more active than **1a** to give 1441 g of copolymer per 1 g of zinc under the identical conditions. On the other hand, when **1c** was used as the catalyst for the copolymerization of carbon dioxide and cyclohexene oxide, the product was a copolymer rich in ether linkages (carbonate linkage:ether linkage = 53:47 %). However, **1c** in the presence of equimolar amount of tricyclohexylphosphine produced a copolymer with a much higher carbonate content (98 %) [19–21].

In order to obtain the alternating copolymer efficiently, the bulky structure of the phenoxide ligands was very important. The copolymerization by using zinc phenoxide with no substituents on phenyl rings afforded the cyclic carbonate, not the alternating copolymer.

Coates and his coworkers have reported that zinc bis(β -diiminates) (**2**) [22–25] are more active than Darensbourg's zinc bis(phenoxides) (**1**) for the alternating copolymerization of carbon dioxide and cyclohexene oxide. The zinc bis(β -diiminates) (**2**) were dimeric in solid state as shown by the X-ray crystallographic analysis [22], while the ¹H NMR data showed that **2** was monomeric in solution. For



1

- a : $R^1 = \text{Ph}$, $R^2 = \text{H}$
 b : $R^1 = R^2 = \text{Me}$
 c : $R^1 = \text{tert Bu}$, $R^2 = \text{H}$

2 ($X = \text{OMe}$, OAc , $\text{N}(\text{SiMe}_3)_2$)

- a : $R^1 = \text{isoPr}$, $R^2 = \text{isoPr}$, $R^3 = \text{H}$, $R^4 = \text{Me}$
 b : $R^1 = \text{isoPr}$, $R^2 = \text{Et}$, $R^3 = \text{CN}$, $R^4 = \text{Me}$
 c : $R^1 = \text{isoPr}$, $R^2 = \text{Et}$, $R^3 = \text{H}$, $R^4 = \text{CF}_3$
 d : $R^1 = \text{Et}$, $R^2 = \text{isoPr}$, $R^3 = \text{H}$, $R^4 = \text{CF}_3$

example, when using **2a** as the catalyst, the alternating copolymerization of carbon dioxide and cyclohexene oxide proceeded rapidly even under very mild conditions at 20 °C at 6.8 atm of carbon dioxide pressure to give the alternating copolymer (TOF = 135) in 2 h. Compared with zinc phenoxide (**1a**) (TOF = 2.5) [15], the polymerization by **2a** proceeded 100 times faster (TOF = 135 at 20 °C to 247 at 50 °C). The content of carbonate linkage in the produced copolymer was 95 % or higher, and the molecular weight had a narrow distribution ($M_w/M_n = 1.07\text{--}1.17$).

As mentioned above, zinc complexes with well-characterized structures are very effective for the alternating copolymerization of carbon dioxide and cyclohexene oxide. However, when cyclohexene oxide is replaced by an acyclic aliphatic epoxide such as propylene oxide, most of the complexes cannot generate the polycarbonate selectively. In such cases, the main products are cyclic carbonate and/or a copolymer rich in ether linkages. For example, zinc phenoxides (**1**) gave propylene carbonate exclusively, under the identical conditions where the polycarbonate was obtained in the reaction of carbon dioxide and cyclohexene oxide.

Very recently, Coates reported that zinc bis(β -diiminato) complexes (**2b–2d**), which carry electron-withdrawing groups in the ligands, accomplished the alternating copolymerization of carbon dioxide and propylene oxide at 10 °C at 20 atm to produce a copolymer (by **2d**: $M_n = 10\,000$, $M_w/M_n = 1.16$; TOF = 37) [26].

Since diethylzinc, which is a starting material of many of the catalysts described above, is expensive and hard to handle, other less expensive zinc-based systems including zinc oxide [27–29] or hydroxide [30] as a component have been explored. The catalysts from inorganic zinc compounds, such as zinc oxide, zinc hydroxide, and zinc nitrate, in combination with glutaric acid were investigated for the alternating copolymerization of carbon dioxide and propylene oxide [31]. Among them, the catalyst obtained from zinc oxide and glutaric acid was highly active to afford the alternating copolymer (64.0 g-copolymer/g-catalyst) in 30-times higher yield than the diethylzinc–glutaric acid system under the identical conditions (2.5 g-copolymer/g-catalyst). The molecular weight of the copolymer was very high ($M_w = 343\,000$, $M_w/M_n = 2.4$). As shown in this example, the catalyst system obtained from zinc oxide and dicarboxylic acid is ranked as one of the most active catalysts for the copolymerization of carbon dioxide and epoxide.

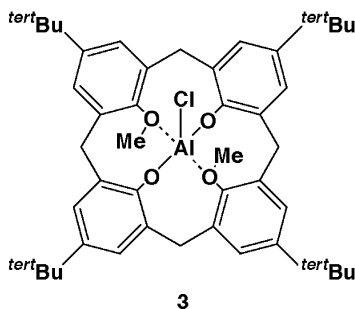
COPOLYMERIZATION BY ALUMINUM CATALYSTS

Trialkylaluminums have attracted interest, since organoaluminum systems are known as the effective catalyst for the homopolymerization of epoxide. Although the copolymerization of carbon dioxide and

epoxide has been examined by using organoaluminum compounds as the catalysts, most of the employed organoaluminum-based systems gave only the product with a low carbon dioxide content even under highly pressurized carbon dioxide atmosphere.

The early investigation utilized the triethylaluminum–water system [32] for comparison with the diethylzinc–water system. For example, when the copolymerization of carbon dioxide and propylene oxide was carried out under 50-atm carbon dioxide in various solvents, the triethylaluminum–water (1:1) system produced a copolymer with carbon dioxide content of only ca. 10 %. On the other hand, the addition of a Lewis base, such as triphenylphosphine or 2,2'-bipyridyl, to the copolymerization system catalyzed by triethylaluminum increased the carbon dioxide content in the produced copolymer to 17 and 22 %, respectively, while *N*-methylimidazole and hexamethylphosphoric triamide retarded the reaction. The copolymerization of carbon dioxide (5 atm) and cyclohexene oxide by the triethylaluminum–triphenylphosphine (1:1) system produced a polycarbonate with a high content of carbonate linkages (80 %).

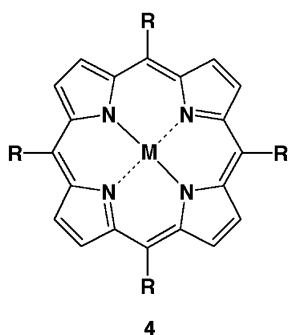
In connection with active zinc bis(substituted phenoxide) complexes, an aluminum complex having a calixarene derivative as the ligand (**3**) was used for the copolymerization of carbon dioxide and epoxide [33]. Propylene oxide or cyclohexene oxide was copolymerized with carbon dioxide (yield with respect to epoxide: 38 % in 168 h and 26 % in 264 h, respectively) at 35 °C at 60 atm of carbon dioxide pressure. The average molecular weights of the obtained polycarbonates were not so high ($M_n = 5620$ and 1930, respectively), and the carbon dioxide contents of the copolymers were fairly low (13 and 18 %, respectively). In these copolymerizations, cyclic carbonates were also generated (14 and 4 % yield). When the copolymerization was conducted at a higher temperature, such as 70 °C, average molecular weights of the copolymer were lowered.



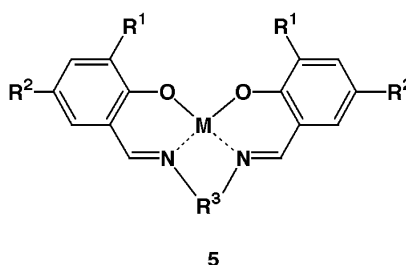
The only successful alternating copolymerization of carbon dioxide and epoxide (ethylene oxide, propylene oxide, and cyclohexene oxide) with aluminum catalyst was achieved by the use of aluminum porphyrin in combination with quaternary phosphonium or ammonium salts as the catalyst system (Aida and Inoue) [34]. The copolymerization of carbon dioxide and cyclohexene oxide at room temperature at 50 atm of carbon dioxide pressure by the aluminum porphyrin (**4a**)–ethyltriphenylphosphonium bromide system produced the polycarbonate having the perfect alternating structure ($M_n = 6800$). The copolymerization proceeded with living nature to give the alternating copolymer with a very narrow molecular weight distribution ($M_w/M_n = 1.06$).

In this copolymerization, all the epoxide molecules were consumed by the copolymerization with carbon dioxide, and the average molecular weight had a linear relationship with the amount of the consumed monomer. Therefore, the molar ratio of the fed epoxide to **4a** determines the molecular weight of the polycarbonate produced at 100 % of epoxide consumption.

Sugimoto and Inoue have revealed that the aluminum Schiff base complex (**5a**)–quaternary ammonium salt system was an efficient catalyst for the alternating copolymerization of carbon dioxide and cyclohexene oxide [35]. Reaction at 80 °C under carbon dioxide at 50 atm by using aluminum Schiff base complex (**5a**) in the presence of the equimolar amount of tetraethylammonium acetate proceeded



- a : R = Ph, M = Al-Cl
 b : R = Ph, M = Al-(OCH(CH₃)CH₂)₂-Cl
 c : R = Ph, M = Cr-Cl
 d : R = Ph, M = Co-Cl
 e : R = Ph, M = Mn-OAc
 f : R = C₆F₅, M = Cr-Cl



- a : R¹ = R² = H, R³ = *o*-phenylene, M = Al-Me
 b : R¹ = R² = *tert*Bu, R³ = 1,2-cyclohexene, M = Cr-Cl
 c : R¹ = R² = *tert*Bu, R³ = *o*-phenylene, M = Cr-Cl
 d : R¹ = *tert*Bu, R² = Br, R³ = 1,2-cyclohexene, M = Co-OAc
 e : R¹ = R² = *tert*Bu, R³ = 1,2-cyclohexene, M = Co-OAc

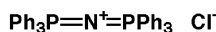
readily to afford a copolymer with the alternating sequence (content of carbonate linkages = 94 %) with M_n and M_w/M_n of 10 000 and 1.5, respectively.

COPOLYMERIZATION BY TRANSITION-METAL COMPLEXES

Copolymerization by chromium complexes

Chromium porphyrin is also active for the copolymerization of carbon dioxide and cyclohexene oxide as reported by Kruper et al. [36]. The alternating co-oligomer was obtained by the reaction by using the 4*c*-dimethylaminopyridine (DMAP) system at 95 °C under carbon dioxide at 50 atm for 18 h.

Darensbourg's group employed a chromium bis(salicylidene)diamine complex (**5b**) as catalyst [37–39]. **5b** catalyzed the alternating copolymerization of carbon dioxide and cyclohexene oxide at 80 °C at 58 atm (TOF = 10.4) to afford a copolymer with M_n of 8900 (M_w/M_n = 1.20). The incorporation of carbon dioxide into the copolymer was almost quantitative, but the formation of cyclic carbonate was not avoidable. When *N*-methylimidazole (5 equiv) was used together with **5b**, the copolymerization was highly accelerated (TOF = 32.2). Bis(triphenylphosphoranylide)ammonium chloride (**6**) was a more efficient additive (cocatalyst) (TOF = 251) [40].



6

5b was not an effective catalyst for the alternating copolymerization of carbon dioxide and propylene oxide. **5b** alone at 75–80 °C at 58 atm [37] or the **5b**–DMAP (1:1) system at 75 °C at 6.8 atm [41] produced propylene carbonate predominantly. On the other hand, **5c** in the presence of DMAP (1 equiv with respect to **5c**) system was highly active (TOF = 160) for the alternating copolymerization of carbon dioxide and propylene oxide at 75 °C at 35 atm to afford in 4 h a copolymer with M_n of 16 700 (M_w/M_n = 1.38) and the content of carbonate linkages of 98 % [42].

Copolymerization by cobalt complexes

Recently, Coates reported that cobalt Schiff base complexes (**5d**) were very efficient for the alternating copolymerization of carbon dioxide and propylene oxide at high carbon dioxide pressures [43]. Under

the optimized conditions (22 °C, 54 atm, 2 h), **5d** gives a copolymer with 96 % of carbonate linkage (TOF = 75).

On lowering the carbon dioxide pressure to 41 atm, **5d** exhibits lower activity, where the rate of the copolymerization was one-fourth of that at 54 atm. Activity of **5d** was very sensitive to the reaction temperature. At a higher or lower temperature than 25 °C, catalyst activity decreases. At 40 °C, the produced copolymer by using **5d** increased its ether linkage. **5e** afforded the almost perfectly alternating copolymer (content of carbonate linkage = 99 %; TOF = 59).

Sugimoto reported that cobalt porphyrin (**4d**) in combination with DMAP is also a good catalyst for the alternating polymerization of carbon dioxide and epoxide [44]. In the presence of DMAP (0.5 equiv with respect to **4d**), **4d** produced an alternating copolymer quantitatively from carbon dioxide (50 atm) and cyclohexene oxide without any by-products at 80 °C, 24 h. Polycarbonate had nearly 100 % carbonate linkages, M_n of 14 500 and M_w/M_n of 1.1. The number of equivalents of DMAP was very important to obtain copolymers with high carbonate contents. In the presence of 0.5–1 equiv of DMAP, polycarbonate was the only product. With 10 equiv of DMAP under otherwise identical conditions, polycarbonate and cyclic by-products were produced. Without DMAP under otherwise identical conditions, poly(cyclohexene oxide) was the only product.

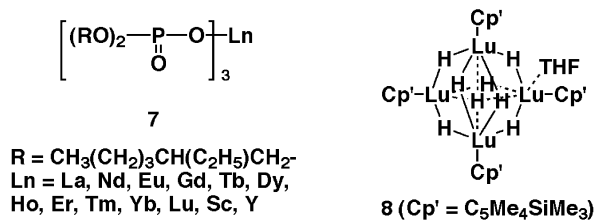
In sharp contrast, Nguyen demonstrated that the **4d**–DMAP system produced propylene carbonate in almost quantitative yield at 120 °C at 20 atm in 1 h [45]. Poly(propylene carbonate) was obtained by the copolymerization of carbon dioxide and propylene oxide with **4d**–DMAP system at lower reaction temperature, such as 25–80 °C [45].

Copolymerization by lanthanoid-metal complexes

Rare-earth, or lanthanoid, metal complexes, which have been widely utilized for organic syntheses since 1990s, have been developed as the catalysts for the alternating copolymerization of carbon dioxide and epoxide. As shown by Chinese groups, lanthanoid trihaloacetates were utilized as the catalysts along with the diethylzinc–glycerol system. When the ternary catalysts, such as the $Y(CF_3COO)_3$ [46,47], or $Nd(CCl_3COO)_3$ [48,49] diethylzinc–glycerol systems, were used, carbon dioxide under 30 atm and propylene oxide were rapidly copolymerized in dioxane to afford the alternating copolymer of which average molecular weight reaches into the tens of thousands. Both catalyst systems were more active than the diethylzinc–glycerol system. In China, by using Wang's catalyst, production of poly(propylene carbonate) was industrialized a few years ago.

A series of the yttrium-substituted benzoates–diethylzinc–glycerol ternary systems was also shown by Wang et al. to possess a high catalytic activity [50]. The catalytic activity, the molecular weight, and its distribution of the resultant copolymer depended on the substituents and their positions on the benzoate ligand.

Inorganic rare-earth metal salts were also used in combination with the organoaluminum-based systems. Shen and his coworkers reported that the rare-earth phosphonate (**7**)–triisobutylaluminum–glycerol system was reported to be effective for the copolymerization of carbon dioxide and propylene oxide [51]. Among the examined rare-earth phosphonates, yttrium phosphonate showed the best result. The yield and molecular weight of the product obtained by copolymerization at 60 °C at 30–40 atm were very high. However, the product was not the alternating copolymer. It had a low carbonate unit content of 30–40 %.



Recently, Hou reported the first lanthanoid catalyst with high catalyst activity for the alternating copolymerization of carbon dioxide and cyclohexene oxide based on a lutetium complex with well-defined molecular structure (**8**) [52]. At 90 °C, under carbon dioxide at 12 atm, **8** gave a copolymer ($M_n = 39\,800$, $M_w/M_n = 4.49$) with 99 % of carbonate linkage in 24 h (TOF = 1121).

Copolymerization by manganese complexes

Sugimoto and Inoue have reported that a manganese porphyrin (**4e**), which was reported to act as good catalyst for the polymerizations of epoxides [53], readily brought about the alternating copolymerization of carbon dioxide and cyclohexene oxide to afford polycarbonate without the formation of any by-products, such as a cyclic carbonate and a polyether [54]. When the copolymerization of carbon dioxide and cyclohexene oxide was conducted at 80 °C under carbon dioxide at 50 atm, the alternating copolymer with M_n of 6700 ($M_w/M_n = 1.3$; carbonate linkage = 99 %) was obtained in 24 h.

RECENT TOPICS

Utilization of supercritical fluid carbon dioxide

In recent years, for the purpose of enhancing the efficiency of the alternating copolymerization of carbon dioxide and epoxide, and for the construction of a clean reaction system without use of organic solvents, carbon dioxide in supercritical or subcritical state is used both as comonomer and as solvent.

As previously mentioned, the zinc catalyst prepared from zinc oxide and glutaric acid is effective for the alternating copolymerization of carbon dioxide and propylene oxide. Because this catalyst was poorly soluble in the copolymerization medium, the copolymerization of carbon dioxide and epoxide proceeded heterogeneously in liquid or supercritical fluid carbon dioxide. Darenbourg et al. reported that by varying the carbon dioxide pressure from 52 to 82 atm at 60 °C without cosolvent, the copolymerization of carbon dioxide and propylene oxide gave the alternating copolymer (9.6–24 g of polymer/g of Zn) with carbonate linkage of 95 % or higher ($M_w = 65\,000$ – $153\,000$) [55]. On the contrary, when the reaction was carried out at lower carbon dioxide pressures such as 20–34 atm, the ether linkage in the copolymer was increased. When the polymerization temperature was raised up to 85 °C, the polymer yield increased, but the molecular weight of the copolymer lowered.

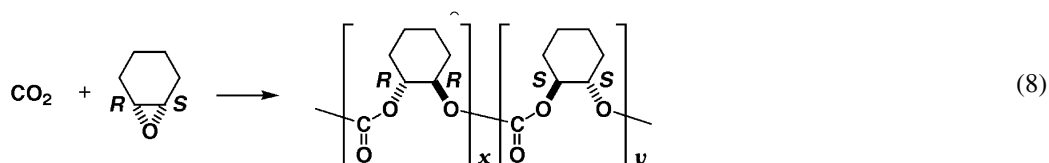
There are examples of catalysts that are soluble in supercritical carbon dioxide. The zinc catalyst obtained from the reaction between zinc oxide, maleic anhydride, and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanol reported by Beckman et al. [56], which is soluble in supercritical carbon dioxide, realized the homogeneous reaction. This catalyst system at 100–120 °C produced the alternating copolymer from supercritical fluid carbon dioxide (136 atm) and cyclohexene oxide (>400 g of polymer/g of Zn). The average molecular weight of the copolymer was in the range of 43 400–299 000.

In supercritical carbon dioxide, chromium porphyrin-bearing peripheral perfluorophenyl groups (**4f**) were utilized by Holmes and his coworkers [57]. Fluoro-substitution on the peripheral phenyl rings of the porphyrin ligand makes the chromium complex more soluble in supercritical carbon dioxide. The combined use of **4f** with DMAP in supercritical fluid carbon dioxide at 95–110 °C under 232 atm enabled the alternating copolymerization of carbon dioxide and cyclohexene oxide to afford the alternat-

ing copolymer in 35–56 % yield. The average molecular weight of the copolymer was not so high ($M_n = 2960$ – 9370), but had a narrow distribution ($M_w/M_n = 1.1$).

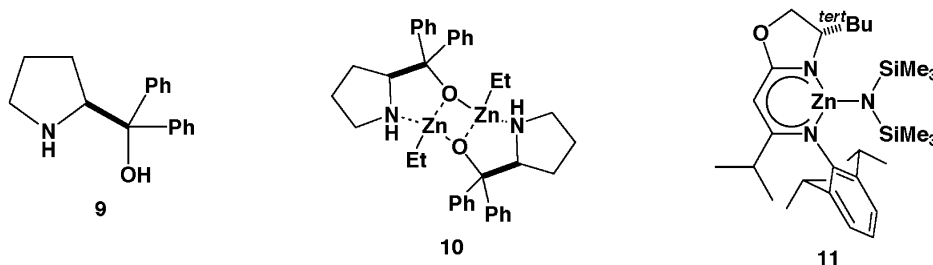
Asymmetric copolymerization

As seen in the examples outlined above, the alternating copolymer is more easily obtained by the alternating copolymerization of carbon dioxide with cyclohexene oxide than with other epoxides, such as ethylene oxide and propylene oxide. When cyclohexene oxide is incorporated into the copolymer, two adjacent chiral carbons in the cyclohexane diol unit give *R,R* or *S,S* sequences (eq. 8). If the copolymerization by chiral catalyst proceeds with preference for the formation of one isomeric unit over the other, the alternating copolymer with high stereoregularity will be obtained.



Nozaki and her coworkers have succeeded in the *meso*-desymmetrization in the alternating copolymerization of carbon dioxide and cyclohexene oxide by using the complex obtained by the equimolar reaction between diethylzinc and an optically active (*S*)-diphenyl(pyrrolidin-2-yl)methanol (**9**) [58,59]. At 60 °C under 30 atm in 24 h, the alternating copolymer was obtained in high yield ($M_n = 13\,000$; $M_w/M_n = 3.6$). Alkali-catalyzed hydrolysis of the copolymer gave (*R,R*)-1,2-cyclohexanediol in 51 % ee, indicating that the copolymerization proceeded with asymmetric induction. Dimeric structure of the complex (**10**) obtained from diethylzinc and **9** was revealed by X-ray crystallographic analysis. Addition of ethanol to **10** improved the catalytic activity [60].

Coates et al. have reported the stereoselective alternating copolymerization of carbon dioxide and cyclohexene oxide by using a chiral zinc β -diiminate carrying optically active oxazoline unit (**11**), where the optical purity of (*R,R*)-1,2-cyclohexanediol obtained by the hydrolysis of the copolymer was as high as 76 % ee [61].



Copolymerization under 1-atm carbon dioxide

In general, a high carbon dioxide pressure (usually 10–50 atm) is needed to realize the activity of the catalyst and/or the high carbon dioxide content of the obtained copolymer. Very recently, the first example of the alternating copolymerization under 1 atm pressure of carbon dioxide was achieved by Sugimoto and Inoue by employing a manganese porphyrin (**4e**) as the catalyst [54]. When the copolymerization of carbon dioxide and cyclohexene oxide was carried out at 80 °C at 1 atm, the alternating copolymer with M_n of 3000 ($M_w/M_n = 1.6$; carbonate linkage = 95 %) was obtained in 90 h.

Cobalt porphyrin (**4d**) was more effective for the alternating copolymerization under milder conditions. At 1 atm of CO₂, the **4d**-DMAP system produced poly(cyclohexene carbonate) (carbonate linkages 97 %, M_n of 1700, M_w/M_n of 1.2) [44].

Poly(propylene carbonate) was also produced by the copolymerization under carbon dioxide at 1 atm by a zinc catalyst [62].

SUMMARY AND OUTLOOK

The study of the alternating copolymerization of carbon dioxide and epoxide has a history of more than 35 years, but still remains a fascinating subject. This is largely due to the interest in polymer synthesis using carbon dioxide as a monomer as well as the possible utility of the product, polycarbonate. Especially in the latest decade, catalyst design based on transition-metal complexes of well-defined structure has brought about remarkable results. However, although many catalysts developed in recent years are very effective for the alternating copolymerization of carbon dioxide and cyclohexene oxide, they do not function well in the alternating copolymerization of carbon dioxide and other, more common epoxides such as propylene oxide. Therefore, the next research tasks are not only the development of more active catalysts under milder conditions, but the exploration of catalysts that produce the copolymer from a wide variety of epoxides.

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