Polycarbonate Synthesis

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Selective Formation of Polycarbonate over Cyclic Carbonate: Copolymerization of Epoxides with Carbon Dioxide Catalyzed by a Cobalt(III) Complex with a Piperidinium End-Capping Arm**

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The copolymerization of epoxides with CO_2[1] has been intensively studied in the last decade as one of the most promising processes for CO_2 utilization.[2–11] The concomitant production of cyclic carbonate is an incidental problem in the reaction of terminal epoxides such as propylene oxide (PO). Recently, the [Co(salcy)OAc] complex (salcyH_2 = *trans*-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) was reported to copolymerize PO with CO_2 without the production of cyclic propylene carbonate (PC) in up to approximately 75 % conversion with a turnover frequency (TOF) of 51 [in moles of repeating unit per mol Co per hour ($mol_{ru}\,mol_{Co}^{-1}\,h^{-1}$)].[12] Further enhancement of the catalytic activity was achieved with anionic cobaltate complexes such as $[Co(salcy)Cl(OBzF_5)]^-[PPN]^+$ ($BzF_5 = C(=O)C_6F_5$, $[PPN]^+$ = bis(triphenylphosphoranylidene)ammonium), which release the reactive anionic propagating species more readily than neutral cobalt complexes.[13–15] However, such a high reactivity also leads to the formation of PC at a higher degree of conversion (> 50 %): the polymerization mixture solidifies to retard the intermolecular propagation, thus resulting in relative acceleration of intramolecular degradation, so-called back-biting.[16] Thus, high catalytic activity has been incompatible with the suppression of the formation of cyclic carbonate. Herein, we report the copolymerization of terminal epoxides with CO_2 by using a new cobalt complex that can selectively produce the copolymer, even at high monomer conversion.

To achieve a high epoxide conversion without production of cyclic carbonate, we designed cobaltate complex **1** with two acetate ligands and a salcy-type ligand (Scheme 1). The key of the catalyst design is in the piperidinyl and piperidinium arms.

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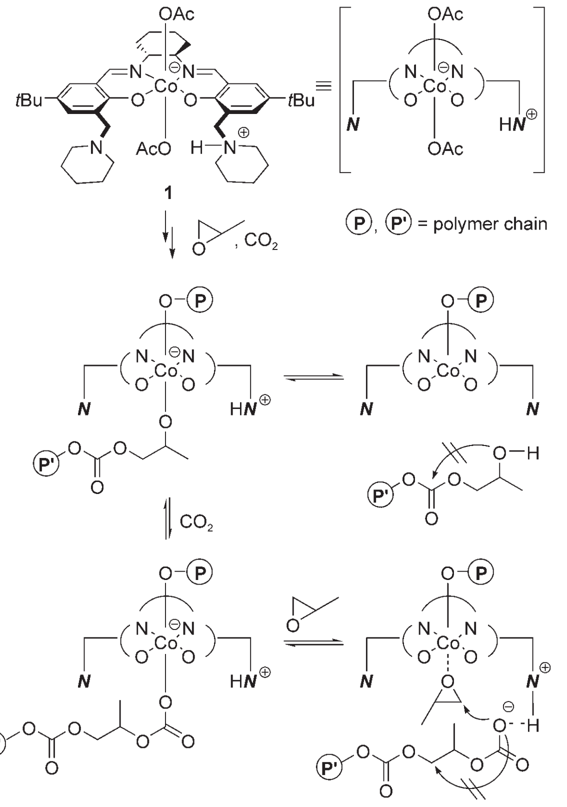


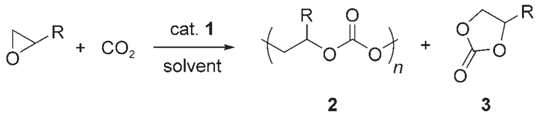
Scheme 1. Catalyst design to suppress the production of cyclic carbonate.

When the two acetate ligands initiate the copolymerization, a piperidinium arm should control the nucleophilicity of the propagating species by protonating the anionic propagating species that is released from the cobaltate center. The protonated propagating species is not nucleophilic enough to form cyclic carbonate through back-biting, but it can react with carbon dioxide[16b,c] or activated epoxide[16a] once it is deprotonated by one of the two piperidinyl groups.

Complex **1** was synthesized by the reaction of $Co(OAc)_2$ with the corresponding disalicylidenediamine[17] and subsequent oxidation in the presence of an excess amount of AcOH and air, and the product was sufficiently dried under reduced pressure. The formation of **1** was spectroscopically confirmed as follows.[18] The ^{1}H NMR spectrum of **1** and the ^{1}H and ^{2}H NMR spectra of partially deuterated **1**, which was obtained by using an excess mount of CD_3COOD, clearly show that complex **1** contains two acetate ligands. Accordingly, one of the two piperidinyl groups should be protonated. Moreover, the simple pattern of the ^{1}H NMR spectrum of **1** reflects the symmetrical structure of **1** in solution, thus indicating that a proton is exchanged rapidly between the two piperidinyl groups. Thus, the two piperidinyl groups should contribute equally to the copolymerization.

By using complex **1**, high catalytic activity and high epoxide conversion were accomplished. The copolymerization of PO with CO_2 (1.4 MPa), catalyzed by complex **1** (PO/**1** = 2000), gave the completely alternating copolymer, poly(propylene carbonate) (PPC) in 38% yield (TOF(PPC) = 254 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$, $M_n = 12\,600\ \text{g mol}^{-1}$, $M_w/M_n = 1.13$) without a significant production of PC (PPC/PC = 99:1; Table 1, entry 1).[19] Interestingly, high conversion of epoxide did not result in the formation of PC. The copolymer with a higher M_n value ($23\,900\ \text{g mol}^{-1}$) and narrow polydispersity index (PDI) of 1.14 was selectively produced in 76% yield (TOF(PPC) = 127 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$; Table 1, entry 2). Copolymerization at a higher PO/**1** ratio of 6500 also gave the alternating copolymer with a much higher M_n value ($83\,700\ \text{g mol}^{-1}$) with high selectivity (PPC/PC = 96:4; Table 1, entry 3). The efficient suppression of the back-biting process allowed high-temperature copolymerization (60 °C), thereby giving PPC selectively with higher activity (PPC/PC = 90:10, TOF(PPC) = 602 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$; Table 1, entry 4). It is essential that the piperidinium group is tethered to the salcy-type ligand framework. In fact, the copolymerization of PO with CO_2 by using the reported $[Co(salcy)Cl(OBzF_5)]^-$-$[PPN]^+$ system[14] in the presence of *N*-methylpiperidinium acetate resulted in low selectivity for the copolymer (PO/Co = 6000, 34% yield of PPC, 37% yield of PC, PPC/PC = 42:58).[20] Thus, the highest level of activity together with suppression of PC formation and high conversion of PPC have been accomplished using complex **1**.[21]

Table 1: Copolymerization of epoxides with CO_2 catalyzed by cobalt complex **1**.[a]

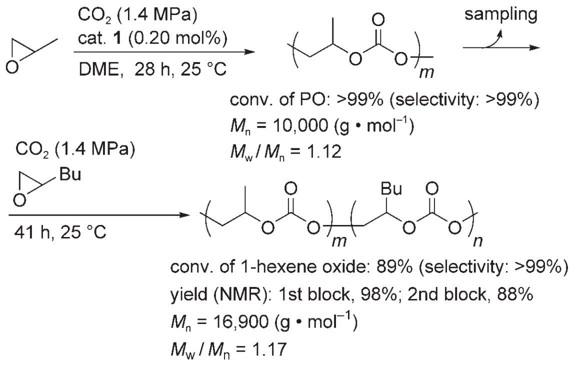


Entry	R	Solvent	t [h]	Yield of **2** + **3** [%][b]	**2**/**3**[b]	M_n [g mol^{-1}][c]	M_w/M_n[c]
1	Me	–	3	38	99:1	12600	1.13
2	Me	–	12	77	99:1	23900	1.14
3	Me	–	116	79	96:4	83700	1.28
4	Me	–	1	34	90:10	7100	1.22
5	Me	DME	6	53	99:1	13200	1.10
6	Me	DME	48	>99	97:3	26500	1.10
7[d]	Me	DME	20	95	95:5	5100	1.06
8	Et	DME	48	89	97:3	31000	1.12
9	Bu	DME	48	89	98:2	34300	1.14

[a] Reaction conditions: epoxide (14.3 mmol in entries 1, 2, and 4–9; 47.2 mmol in entry 3), **1** (epoxide/**1** = 2000 in entries 1, 2, and 4; 6500 in entry 3; 1000 in entries 5–9), CO_2 (initial pressure: 1.4 MPa), DME (1.0 mL in entries 5–9), at 25 °C (entries 1–3 and 5–9) or 60 °C (entry 4). [b] Determined on the basis of ^{1}H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] Determined by size-exclusion chromatography analysis using a polystyrene standard. [d] Methanol (20 equivalents based on **1**) was added.

The complete consumption of epoxide was attained by adding solvents. Since the polymerization mixture becomes viscous with increase of conversion, the addition of solvent is necessary for effective diffusion of the reactant. Copolymerizations of PO with CO_2 (PO/**1** = 1000) in the presence of an organic solvent such as 1,2-dimethoxyethane (DME), toluene, or dichloromethane gave the copolymer. Particularly, employment of DME resulted in the quantitative conversion with high copolymer selectivity (PPC/PC = 97:3, >99% conversion; Table 1, entries 5 and 6). Very recently, a similar solvent effect was reported for the copolymerization with [Co(salcy)Cl(OBzF$_5$)]$^-$[PPN]$^+$, where the use of DME as a solvent achieved the high PPC yield of 75% without a contaminating amount of PC (PPC/PC = 98:2).[22] Under the same reaction conditions, terminal epoxides with a longer alkyl chain were also copolymerized with CO$_2$ by using complex **1** (Table 1, entries 8 and 9). Although the longer alkyl substituents slightly decreased the catalytic activities,[13] completely alternating copolymers were obtained in high yields without formation of a significant amount of cyclic carbonate.

The successful complete consumption of an epoxide without production of cyclic carbonate allowed the synthesis of block polymer. Thus, the block terpolymer was produced by stepwise addition of the two different epoxides, PO and 1-hexene oxide, without significant production of cyclic carbonates (Scheme 2). Such a selective synthesis of a block terpolymer is characteristic of the present catalyst system. Since the previously reported catalysts hardly achieve the complete consumption of an epoxide, the polymerization for a block terpolymer should result in the production of a tapered one.



Scheme 2. Synthesis of a block terpolymer.

Immortal polymerization is indicated in the present PO/CO$_2$ copolymerization system.[23] In all experiments, gel permeation chromatography (GPC) analyses of the obtained copolymers gave bimodal traces. The M_n values of both higher- and lower-molecular-weight copolymers increased linearly in proportion to conversion in the range of 0–99%, and the PDIs remained narrow (1.10–1.11). Moreover, for each conversion, the M_n value of the higher-molecular-weight copolymer was twice as large as that of the lower-molecular-weight one. This difference can be attributed to the chain transfer by contaminant water, which works as a bifunctional initiating group to give a telechelic polymer, as previously demonstrated by Sugimoto et al.[24] MALDI-TOF mass spectrometry of the copolymer revealed the formation of the telechelic copolymer in addition to the copolymer initiated by the acetate group. These results clearly demonstrate the reversible and rapid chain transfer of the propagating species, which is characteristic of successful “immortal” polymerization.[25] To confirm such an immortal nature of the present system, copolymerization of PO with CO$_2$ was carried out in the presence of methanol as a chain-transfer reagent (Table 1, entry 7). When a large excess of methanol (20 equivalents based on **1**) was added, an alternating copolymer with a methoxy initiating group was obtained as a main component. The M_n value of the obtained copolymer was estimated to be 5100 g mol^{-1}, which agrees with the theoretical M_n value of 4300 g mol^{-1} that was calculated from the copolymer yield and the monomer/(methanol+acetate) ratio. Furthermore, the PDI remained narrow (1.06).

In conclusion, the cobaltate complex with a piperidinium arm was found to copolymerize terminal epoxides with CO$_2$ with high activity and without a significant amount of associated cyclic carbonate. In particular, complete consumption of the epoxide was accomplished with high copolymer selectivity. This feature is the key to the successful synthesis of the block terpolymer.

Experimental Section

Representative procedure for the copolymerization of propylene oxide with CO$_2$ (Table 1, entry 1). A 50-mL autoclave was charged with propylene oxide (1.0 mL, 14.3 mmol) and **1** (5.8 mg, 7.2×10^{-3} mmol) under argon. After CO$_2$ (1.4 MPa) was introduced, the reaction mixture was stirred at 25 °C for 3 h. The CO$_2$ pressure was released, and the polymerization mixture was quenched with methanol, diluted with CH$_2$Cl$_2$, and transferred into a round-bottom flask. Phenanthrene (34 mg, 0.19 mmol) was added as an internal standard to the resulting solution. A small aliquot of the mixture was taken out and concentrated under reduced pressure by rotary evaporation. Analyses by ^{1}H NMR spectroscopy and GPC gave the yields of copolymer (38%) and propylene carbonate (< 0.1%), the ratio of them (99:1), as well as the molecular weight (12600 g mol^{-1}) and molecular-weight distribution (1.13) of the copolymer.

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[18] See the Supporting Information.

[19] The M_n value is not close to the estimated value. This difference could be a result of the chain transfer by concomitant water.

[20] The copolymerization using [Co(salcy)Cl(OBzF$_5$)]$^-$[PPN]$^+$ in the absence of *N*-methylpiperidinium acetate (PO/Co = 6000, 1.4 MPa of CO$_2$, 3 h) was also carried out, and resulted in a high catalytic activity (yield of **2** + **3** = 25 %, TOF(PPC) = $492\ \text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$, $M_n = 36000\ \text{g}\,\text{mol}^{-1}$, $M_w/M_n = 1.12$) and high selectivity (PPC/PC = 99:1) as reported in reference [14]. The prolonged copolymerization (68 h), however, led to the partial degradation to PC (yield of **2** + **3** = 84 %, PPC/PC = 72:28) and a broader molecular-weight distribution (M_w/M_n = 1.71).

[21] High catalytic activity (500–1000 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$) was reported by using cobaltate complexes.[13,14] However, such a system was found to produce PC in greater than 50 % conversion. Other systems using chromium complexes or zinc complexes also show high activity of 100–200 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$ and are classified into a highly active catalyst system, although a contaminant amount of PC is produced even at low conversion.[4,8] As mentioned above, the use of a [Co(salcy)OAc] complex has been the successful example which achieves both the high catalytic activity (51 $\text{mol}_{\text{ru}}\,\text{mol}_{\text{Co}}^{-1}\,\text{h}^{-1}$) and suppression of PC formation even at high monomer conversion.[12]

[22] Although the employment of DME improved the yield of PPC, the prolonged reaction did not result in a yield higher than 75 %; see: C. T. Cohen, G. W. Coates, *J. Polym. Sci. Part A* **2006**, *44*, 5182 – 5191.

[23] Immortal polymerization is a living polymerization that involves rapid, reversible chain transfer; that is, the chain transfer does not lead to simple chain termination, and the dormant chain end can repropagate when activated on a catalyst center. Because the chain-transfer reaction proceeds much faster than the propagation reaction, polymers are obtained with low PDI values. See reference [25].

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