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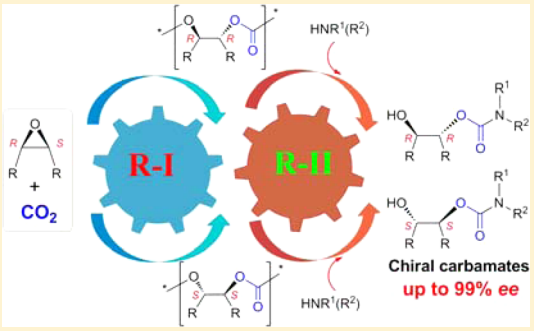
CO_2-Mediated Formation of Chiral Carbamates from *meso*-Epoxides via Polycarbonate Intermediates

Ye Liu,* Wei-Min Ren, Ke-Ke He, Wen-Zhen Zhang, Wen-Bing Li, Meng Wang, and Xiao-Bing Lu*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

Supporting Information

ABSTRACT: Carbon dioxide has attracted broad interest as a renewable C1 feedstock for efficient transformation into value-added organic chemicals; nevertheless, far less attention was paid to its stereochemically controlled catalytic fixation/conversion processes. Here, we report a new strategy for the selective synthesis of chiral carbamates from carbon dioxide via polycarbonate intermediates, which are formed by the desymmetric copolymerization of *meso*-epoxides using enantiopure dinuclear Co(III) catalyst systems with 99% enantioselectivity. Subsequent degradation reaction of the resultant polycarbonates with various primary or secondary amine nucleophiles can afford optically active carbamates, with the complete configuration retention of the two chiral carbon centers. Our accomplishment reported here opens up a new route to prepare a wide range of CO_2-based carbamate scaffolds with excellent yields and 99% enantiomeric excess.



INTRODUCTION

The efficient transformation of carbon dioxide (CO_2) into value-added organic compounds can contribute to a more sustainable chemical industry since CO_2 is an abundant, inexpensive, and nontoxic renewable C1 resource.[1−7] CO_2 is a thermodynamically stable molecule and the end product in any carbon-based combustion process; thus, relatively high-energy reactants are often used to gain thermodynamic driving force for facilitating its transformation. As a consequence, the quantity of CO_2 consumed in these transformation processes is likely always to be a very small fraction of the total CO_2 generated from the emission-based human activity. However, this strategy potentially provides access to the more environmentally benign routes to produce useful chemicals otherwise made from the reagents detrimental to the environment. Indeed, the majority of reactions using CO_2 as a feedstock concern the preparation of relatively simple achiral chemicals, with an emphasis on CO_2 incorporation efficiency, while far less attention was paid to the stereochemically controlled catalytic CO_2 fixation/conversion processes.[8−10]

Carbamate derivative scaffolds, the key structural elements of various naturally occurring compounds, play very important and ubiquitous roles in pharmaceutical, agrochemical, and material terrains.[11,12] However, the conventional methods for the formation of carbamates usually concerned the toxic phosgene or isocyanates. The use of CO_2 as an alternative reagent for the direct synthesis of organic carbamates is highly desirable.[13−18] Recently, Jiang and co-workers reported a base-promoted three-component coupling of CO_2, amines, and *N*-tosylhydrazones to provide organic carbamates, and the reaction was suggested to proceed via carbocation intermediates.[19] Also, the aminolysis reaction of cyclic carbonates using simple alkylamines is well-documented under mild conditions.[20−23] More recently, Kleij et al. succeeded in employing aromatic amines as nucleophiles for the aminolysis in the presence of triazabicyclodecene.[24] Nevertheless, rare examples were reported regarding the synthesis of enantiopure carbamates, and the processes in these limited reports generally suffered from moderate product selectivity or/and very low enantioselectivity.[25,26]

Previously, we have demonstrated that enantiopure biphenol-linked dinuclear Co(III) complex **I** was a rare privileged chiral catalyst for the enantioselective copolymerization of CO_2 with *meso*-epoxides, affording the corresponding polycarbonates with complete alternating structure and ≥98% enantioselectivity (Figure 1).[27−29] Since the main-chain chirality originates from the two contiguous chiral carbon atoms, the degradation of the optically active polycarbonates into small molecule compounds by the nucleophilic attack at the carbonyl carbon atom should not affect the configuration of the two stereogenic centers. With this idea in mind, it was of great interest to us to systematically explore the further transformation of these enantiopure polycarbonates to chiral fine chemicals with high levels of stereoretention. Herein, we present a tandem strategy for selective synthesis of chiral carbamates from CO_2 via polycarbonate intermediates, using various amines nucleophiles (Figure 1). Our accomplishment reported here opens up a new route to prepare a wide range of CO_2-based carbamate scaffolds with excellent yields and 99% enantiomeric excess.

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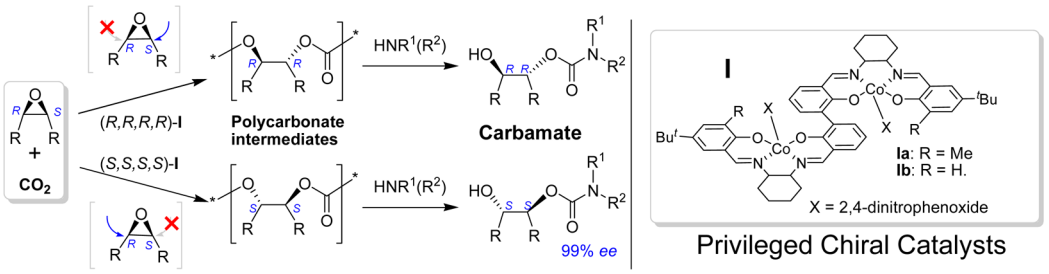


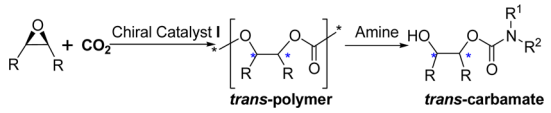
Figure 1. Tandem desymmetric CO_2/*meso*-epoxide copolymerization and nucleophilic depolymerization for preparing chiral carbamates.

RESULTS AND DISCUSSION

Chiral Carbamates Synthesis. Since *cis*-2,3-epoxybutane exhibits both high reactivity and enantioselectivity in copolymerizing with CO_2, it was chosen as a model monomer of *meso*-epoxides for testing the aminolysis of the polycarbonate intermediate using various amines. First, the asymmetric copolymerization of CO_2 with *cis*-2,3-epoxybutane mediated by enantiopure dinuclear Co(III) catalyst (*S,S,S,S*)-**Ia** could realize the complete conversion of epoxides, affording the highly enantiopure poly(*trans*-2-butene carbonate) with (*S,S*)-configuration. Without further purification, piperidine was added to the reaction mixtures, and the aminolysis reaction could be carried out smoothly at room temperature within 2 h, affording the corresponding carbamate (*S,S*)-**1a** with 68% yield (Table 1, entry 1). The enantiomeric excess (*ee*) of the resulting carbamate was determined by chiral HPLC using an AD column to be 99% with an *S,S*-configuration, which was in accordance with that of poly(*trans*-2-butene carbonate). This result suggests that the aminolysis process did not affect the stereochemistry of the two contiguous chiral centers. It was found that the presence of trace water was very important for this aminolysis reaction. The yields were increased to 87% at 40 °C and 97% at 60 °C (Table 1, entries 2 and 3). Notably, no change in product selectivity and enantioselectivity was observed when the reaction was carried out at 80 °C (Table 1, entry 4). The carbamate with (*R,R*)-configuration was also isolated with 95% yield from (*R,R,R,R*)-**Ia** mediated *cis*-2,3-epoxybutane/CO_2 copolymerization (Table 1, entry 5). Moreover, dimethylamine, diethylamine, morpholine, ethylamine, *n*-butylamine, and benzyl amine as nucleophiles could also transform the polycarbonate intermediate into the corresponding carbamates in high yields with a prolonged time of 4−8 h at 60 °C (Table 1, entries 6−11). Because the desymmetric ring-opening of *meso*-epoxides was a typical S_N2 reaction, *cis*-carbamate was not detected during this transformation (see Experimental Section and Figures S63−S66 in Supporting Information). Of importance, all resulting carbamates have 99% enantioselectivity, suggesting the complete configuration retention during the aminolysis process. It is worth while noting here parenthetically that no change in yield and enantioselectivity was observed in the aminolysis reaction of the purified poly(*trans*-2-butene carbonate) after complete removal of metal catalyst precursor. This implies that the presence of the catalyst for CO_2/epoxide copolymerization has no influence on the subsequent aminolysis of the resultant polycarbonates.

We were delighted to find that tryptamine (a common alkaloid) could be also employed as a nucleophilic reagent for the aminolysis reaction with chiral poly(*trans*-2-butene carbonate). The yield of the corresponding carbamate (*S,S*)-**1h** was 86%, and the enantioselectivity was up to 99% (Table 1,

Table 1. Synthesis of Enantiopure Carbamate Derivatives from *cis*-2,3-Epoxybutane and CO_2[a]



Entry	Product	Temp. (°C)	Time (h)	Yield (%)[b]	*ee* (%)[c]	Specific rotation (o)[d]
1	(*S,S*)-**1a**	25	2	68	99 (*S,S*)	8 (+)
2		40	2	87	99 (*S,S*)	8 (+)
3		60	2	97	99 (*S,S*)	8 (+)
4		80	2	98 (96)	99 (*S,S*)	8 (+)
5[e]	(*R,R*)-**1a**	60	2	96 (95)	99 (*R,R*)	8 (-)
6[f]	(*S,S*)-**1b**	60	4	89	99 (*S,S*)	5 (+)
7	(*S,S*)-**1c**	60	4	91	99 (*S,S*)	3 (+)
8	(*S,S*)-**1d**	60	8	95	99 (*S,S*)	10 (+)
9[g]	(*S,S*)-**1e**	60	8	90	---[h]	11 (+)
10	(*S,S*)-**1f**	60	8	88	---[h]	9 (+)
11	(*S,S*)-**1g**	60	8	94	99 (*S,S*)	9 (+)
12	(*S,S*)-**1h**	60	12	86	99 (*S,S*)	12 (+)
13[e]	(*R,R,R*)-**1i**	60	8	93	99 (*R,R,R*)	32 (+)
14	(*R,S,S*)-**1i**	60	8	92	99 (*R,S,S*)	50 (+)

[a]For detailed experimental procedures for polymerization and the aminolysis reaction, see Experimental Section; amine/H_2O/epoxide = 1/1/1, molar ratio. [b]^{1}H NMR yield and isolated yield are in brackets. Yield was calculated based on *meso*-epoxides. [c]Determined by chiral HPLC, and *cis*-carbamate was not detected. [d]Specific rotation was determined by polarimeter in chloroform at 20 °C (*c* = 1). [e]Dinuclear Co(III) complex (*R,R,R,R*)-**Ia** was used. [f]Dimethylamine solution (40 wt % in H_2O, amine/epoxide = 10/1, molar ratio) was used. [g]Ethylamine solution (70 wt % in H_2O, amine/epoxide = 10/1, molar ratio) was used. [h]The *ee* value was not determined because of the low ultraviolet response in HPLC analysis.

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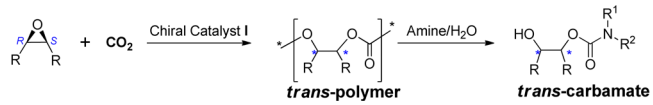
Table 2. Tandem CO_2/*meso*-Epoxide Copolymerization and Aminolysis of Polycarbonates to Prepare Chiral Carbamate[a]



CO_2/*meso*-epoxides copolymerization									Aminolysis reaction					
Entry	Epoxide	Catalyst[b] (Cat./epoxide)	Temp (°C)	Time (h)	Polycarbonate	M_n[c] (Kg/mol)	PDI[c]	*ee*[d] (%)	Amine	Time (h)	Carbamate	Yield[e] (%)	*ee*[f] (%)	Specific rotation[g] (o)
1										48	(*S*,*S*)-**2a**	54	98 (*S*,*S*)	6 (-)
2[h]		(*S*,*S*,*S*,*S*)-**Ib** (1/1000)	0	6		58.2	1.21	98 (*S*,*S*)		48	(*S*,*S*)-**2b**	48	98 (*S*,*S*)	20 (-)
3										48	(*S*,*S*)-**2c**	51	98 (*S*,*S*)	20 (-)
4[h]		(*R*,*R*,*R*,*R*)-**Ib** (1/1000)	0	6		57.2	1.22	98 (*R*,*R*)		48	(*R*,*R*)-**2b**	50	98 (*R*,*R*)	21 (+)
5										48	(*S*,*S*)-**3a**	66	99 (*S*,*S*)	32 (-)
6		(*S*,*S*,*S*,*S*)-**Ia** (1/1000)	25	6		73.4	1.28	99 (*S*,*S*)		72	(*S*,*S*)-**3b**	80	---[i]	28 (-)
7										72	(*S*,*S*)-**3c**	68	99 (*S*,*S*)	29 (-)
8		(*S*,*S*,*S*,*S*)-**Ia** (1/1000)	25	12		50.2	1.22	99 (*S*,*S*)		24	(*S*,*S*)-**4a**	87	99 (*S*,*S*)	3 (+)
9		(*R*,*R*,*R*,*R*)-**Ia** (1/1000)	25	12		49.2	1.21	99 (*R*,*R*)		24	(*R*,*R*)-**4a**	88	99 (*R*,*R*)	3 (-)
10		(*S*,*S*,*S*,*S*)-**Ia** (1/1000)	25	24		26.1	1.27	99 (*S*,*S*)		24	(*S*,*S*)-**4b**	86	99 (*S*,*S*)	4 (+)
11		(*S*,*S*,*S*,*S*)-**Ia** (1/1000)	10	24		---[j]	---[j]	99 (*S*,*S*)		48	(*S*,*S*)-**5a**	80	99 (*S*,*S*)	6 (+)
12[k]		(*S*,*S*,*S*,*S*)-**Ib** (1/500)	25	4		24.5	1.17	99 (*S*,*S*)		48	(*S*,*S*)-**6a**	76	99 (*S*,*S*)	34 (+)
13[k]		(*R*,*R*,*R*,*R*)-**Ib** (1/500)	25	4		24.7	1.18	99 (*R*,*R*)		48	(*R*,*R*)-**6a**	75	99 (*R*,*R*)	34 (-)
14		(*S*,*S*,*S*,*S*)-**Ia** (1/1000)	0	12		29.8	1.16	99 (*S*,*S*)		48	(*S*,*S*)-**7a**	86	99 (*S*,*S*)	56 (+)

[a]For detailed experimental procedures for polymerization and the aminolysis reaction, see Experimental Section; amine/H_2O/epoxide = 5/5/1, molar ratio. [b]Molar ratio. [c]Determined by using gel permeation chromatography in THF, calibrated with polystyrene. [d]Determined the resultant diol by chiral GC or the dibenzoate using benzoyl chloride by chiral HPLC, and *cis*-diol was not detected. [e]^{1}H NMR yield, and yield was calculated based on meso-epoxides. [f]Determined by chiral HPLC, and *cis*-carbamate was not detected. [g]Specific rotation was determined by a polarimeter in chloroform at 20 °C (*c* = 1). [h]Dimethylamine solution (40 wt % in H_2O, amine/epoxide = 10/1, molar ratio) was used. [i]The ee value was not determined because of the low ultraviolet response in HPLC analysis. [j]The polymer with high molecular weight and isotacticity was not soluble in THF, chloroform, or DMF, even in 1,2,4-$Cl_3C_6H_3$, and the M_n and PDI could not be determined. [k]The reaction was carried out in toluene solution (epoxide/toluene = 1/4, molar ratio).

entry 12). Also, the chiral (*R*)-*α*-phenylethylamine can be employed as the nucleophilic reagent for the aminolysis of (*R*,*R*)- or (*S*,*S*)-poly(*trans*-2-butene carbonate)s to prepare optically active diastereoisomeric (*R*,*R*,*R*) or (*R*,*S*,*S*)-carbamates (Table 1, entries 13 and 14). This tandem approach for the synthesis of carbamates from epoxides and CO_2 via polycarbonate intermediates demonstrated that this methodology was very effective for various alkaloids.

The scope of this tandem approach regarding *meso*-epoxides was demonstrated by the reaction of various polycarbonates with piperidine under the optimized conditions (Table 2). In comparison with *cis*-2,3-epoxybutane, the formation of the corresponding carbamate products from alicyclic *meso*-epox-

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ides/CO_2 copolymers proceeded very slowly, especially for **2a**, **2b**, and **2c** (48−54% yields) from cyclohexene oxide. However, the enantioselectivities of the resultant carbamates were all ≥98% *ee*, the same as that of the corresponding polycarbonates (Table 2, entries 1−4). Various chiral carbamates with 99% *ee* can be produced from CO_2-based polycarbonates from cyclopentene oxide, 3,4-epoxytetrahydrofuran, 3,5-dioxa-epoxides, 1,4-dihydronaphthalene oxide, and 1,2-epoxy-4-cyclohexene (Table 2, entries 5−14) (for NMR and HPLC spectra of various carbamates, see Figures S1−S60 in Supporting Information). Furthermore, a chiral (*S,S*)-carbamate derivative possessing one heavy bromine atom, which was prepared by treatment of (*S,S*)-**2a** with 4-bromobenzoic acid (for the detailed synthesis procedure, see Experimental Section), succeeded in isolating in crystal state (Figure 2). The X-ray

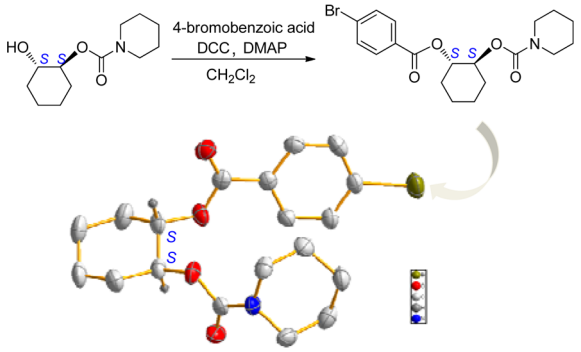

Figure 2. X-ray molecular structures of the (*S,S*)-carbamate derivative. The substrate was prepared by treatment of (*S,S*)-**2a** with 4-bromobenzoic acid (hydrogen atoms and uncoordinated solvent were omitted for clarity). Thermal ellipsoids are at the 30% probability level.

single crystal study revealed that the absolute configuration of the resulting carbamate derivative was the same as that of the corresponding polycarbonate, suggesting the aminolysis reaction only concerns the nucleophilic addition of amine to the carbonyl group of the CO_2-based polycarbonates, rather than the two chiral carbon centers.

Mechanism Understanding. It is worth noting here that the reaction of poly(*trans*-2-butene carbonate) with piperidine was finished only within 2 h, while the aminolysis of the CO_2-based polycarbonates from alicyclic *meso*-epoxides (such as cyclohexene oxide and cyclopentene oxide) proceeded very slowly for the formation of the corresponding carbamate products, giving relatively low yields even at a prolonged time of 24−72 h, together with the formation of 1,2-diol byproducts to a certain extent. The unexpected results prompted us to consider the different aminolysis routes for the two kinds of polycarbonates.

In order to better assess the mechanistic aspects of the aminolysis process, *in situ* FTIR spectroscopy was used to monitor the reaction (for the detailed experimental procedure, see Experimental Section). As is easily observed, the intense absorbance for the asymmetric ν(C═O) vibration of polycarbonates appears at ∼1750 cm^{-1}, while that of carbamate derivatives is usually found at 1698 cm^{-1}. For the aminolysis reaction of poly(*trans*-2-butene carbonate) with piperidine, we clearly observed not only the decrease in absorbance at 1747 cm^{-1} (for polycarbonate) and the continuous increase in peak intensity at 1698 cm^{-1} (for carbamate derivatives) but also a new species at 1813 cm^{-1}, which increased at first and disappeared gradually as a function of time. The absorbance at 1813 cm^{-1} was originated from *trans*-2-butene carbonate, a cyclic carbonate (Figure 3, plots a and b). This result indicates that the aminolysis reaction using piperidine as a nucleophilic reagent underwent the cyclic carbonate intermediate, which was formed from the degradation of poly(*trans*-2-butene carbonate) by a backbiting mechanism, starting from the copolymer chain end (Figure 4, route A). Another degradation route is the random depolymerization caused by the nucleophilic attack of

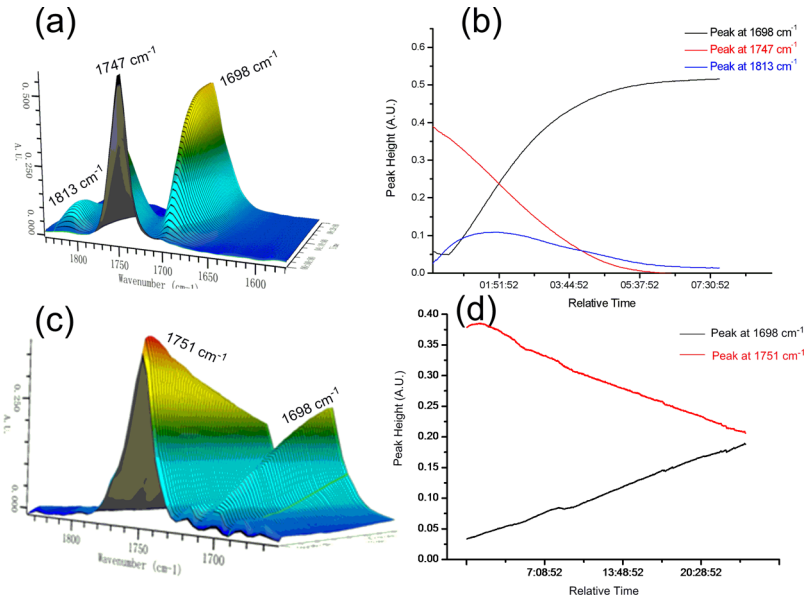

Figure 3. IR spectra of the aminolysis reaction of various CO_2-polymers and piperidine. Plots a and c: Three-dimensional stack plot of the IR spectra collected every 1 min during reaction. Plots b and d: Reaction profiles for the aminolysis reaction as a function of time. Plots a and b are the aminolysis reaction of poly(*trans*-2-butene carbonate), and plots c and d are the aminolysis reaction of poly(cyclopentene carbonate). Peak at 1698 cm^{-1} for carbamates derivatives, peak at ∼1750 cm^{-1} for CO_2-polymers, and peak at 1813 cm^{-1} for *trans*-2-butene carbonate.

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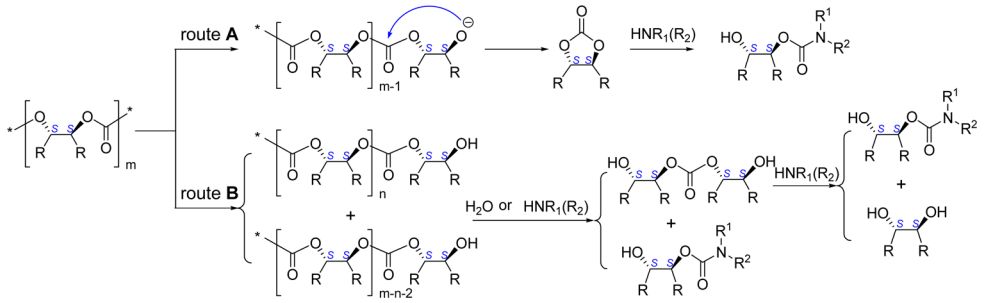

Figure 4. Two routes for the formation of chiral carbamates from the aminolysis reaction of enantiopure CO_2-based polycarbonates using amines as nucleophiles. Route A underwent the cyclic carbonate intermediate for poly(*trans*-2-butene carbonate). Route B was the random depolymerization for poly(cyclopentene carbonate).

amine or water to the carbonyl group of CO_2-based polycarbonates (Figure 4, route B).

Interestingly, for the aminolysis reaction of poly(cyclopentene carbonate) with piperidine, we did not observe the formation of cyclopentene carbonate (the absorbance peak at ~1800 cm^{-1}) and only discovered the consecutive decrease in absorbance at 1751 cm^{-1} (for poly(cyclopentene carbonate)) and the continuous increase in peak intensity at 1698 cm^{-1} (for carbamate derivatives) (Figure 3, plots c and d). This implies that the aminolysis reaction did not concern the cyclic carbonate intermediate, probably due to the ring strain placed on the five-membered carbonate ring in order to accommodate the conformational requirements of the alicyclic cyclopentenyl ring.[30,31] Furthermore, we succeeded in isolating an intermediate, 2,2′-carbonyldioxydicyclohexanol, which should be formed in the random depolymerization (Figure 4, route B).[32]

CONCLUSIONS

In summary, we have developed an effective methodology for the highly enantioselective synthesis of various chiral carbamates from CO_2 via enantiopure polycarbonate intermediates formed by dinuclear Co(III) complex mediated desymmetric copolymerization of CO_2 and *meso*-epoxides at mild conditions. This methodology showed broad substrate scope for both amine nucleophiles and *meso*-epoxides, predominantly affording the corresponding optically active products in high isolated yields and up to 99% enantioselectivity. The mechanistic study showed that two degradation routes are responsible for the formation of chiral carbamates from the aminolysis reaction of amines with enantiopure CO_2-based polycarbonates. This study is expected to open up a new route to prepare a wide range of chiral CO_2-based chemicals with excellent enantioselectivity.

EXPERIMENTAL SECTION

General Information. All manipulations involving air- and/or water-sensitive compounds were carried out in a glovebox or with the standard Schlenk techniques under dry nitrogen. The asymmetric copolymerization of CO_2 with various *meso*-epoxides mediated by enantiopure dinuclear cobalt complexes was according to the literature methods.[27−29,33] Epoxides were distilled over calcium hydride.

Mass Spectrometry. A Micromass Q-Tof mass spectrometer equipped with an orthogonal electrospray source (Z-spray) was used for the cobalt complexes in positive ion mode (capillary = 2000 V; sample cone = 20 V).

Representative Procedure for Copolymerization/Aminolysis Reaction. In a predried 20 mL autoclave equipped with a magnetic stirrer, dinuclear Co(III) complex (*S*,*S*,*S*,*S*)-**Ia** (0.01 mmol, 0.001 equiv), PPN-DNP (PPN = bis(triphenylphosphine)iminium, DNP = 2,4-dinitrophenoxide, 0.02 mmol, 0.002 equiv) as cocatalyst, and *meso*-epoxide (10 mmol, 1 equiv) were dissolved in toluene (*meso*-epoxide/toluene =1/2 (volume ratio)) in an argon atmosphere. After CO_2 was introduced, the reaction mixture was stirred at a desired temperature for an appropriate time. Then CO_2 was released, and a small amount of the resultant mixture was removed from the autoclave for ^{1}H NMR analysis to quantitatively give the conversion of *meso*-epoxide, the selectivity of polycarbonate to cyclic carbonate, as well as carbonate linkages. Then, GPC analysis was performed to give the polymer molecular weight (M_n) and molecular weight distribution (PDI). Then, piperidine (10 mmol, 1 equiv) and water (10 mmol, 1 equiv) in 10 mL THF were added the polymerization mixture. The resultant mixture was stirred for a desired time at a designated temperature. Then, water (10 mL) was added, and the organic layer was extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with petrol ether/ethyl acetate to give the corresponding carbamate derivatives.

Representative Procedure for the Aminolysis Reaction Monitored by *in Situ* FTIR Spectroscopy. In a typical experiment, a 100 mL stainless steel autoclave reactor, modified with a ZnSeW AR window to allow for the use of an ASI ReactIR 45 system equipped with a MCT detector and 30 bounce DiCOMP *in situ* probe, is heated to the desired temperature. In this manner, a single 256-scan background spectrum was collected. The poly(*trans*-2-butene carbonate) (1.0 g, 8.6 mmol) and piperidine (8.6 mmol, 1 equiv to per carbonate unit) were dissolved in THF (20 mL), and then the mixture solution was injected into the reactor via the injection port at 60 °C, and the FTIR probe began collecting scans. The infrared spectrometer was set up to collect one spectrum every 1 min over a certain period.

Determination of Carbamate Derivatives. 1: (2*S*,3*S*)-3-hydroxybutan-2-yl piperidine-1-carboxylate ((*S*,*S*)-**1a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 96% yield as a light yellow oil (1.93 g, 9.60 mmol) (Table 1, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69−4.63 (m, 1H), 3.76−3.71 (m, 1H), 3.42 (s, 4H), 2.48 (br, 1H), 1.60−1.52 (m, 6H), 1.22 (d, J = 6.6 Hz, 3H), 1.18 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 75.8, 70.4, 44.8, 25.6, 25.5, 24.3, 19.0, 16.5. HRMS (m/z): Calcd for $[C_{10}H_{20}NO_3]^+$ ([**M**+H]$^+$), 202.1443; found, 202.1445.

2: (2*S*,3*S*)-3-hydroxybutan-2-yl dimethylcarbamate ((*S*,*S*)-**1b**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 86% yield as a light yellow oil (1.38 g, 8.57 mmol) (Table 1, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70−4.64 (m, 1H), 3.77−3.71 (m, 1H), 2.94 (s, 6H), 1.25 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 75.8, 70.1, 36.3, 35.7, 18.7, 16.3. HRMS (m/z): Calcd for $[C_7H_{16}NO_3]^+$ ([**M**+H]$^+$), 162.1130; found, 162.1135.

3: (2*S*,3*S*)-3-hydroxybutan-2-yl diethylcarbamate ((*S*,*S*)-**1c**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 87% yield as a light yellow oil (1.64 g, 8.68 mmol) (Table 1, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.72−4.65 (m, 1H), 3.78−3.72 (m, 1H), 3.29 (s, 4H), 1.24 (d, J =

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6.8 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H), 1.13 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 75.5, 70.4, 41.8, 41.2, 18.9, 16.3, 14.0, 13.4. HRMS (m/z): Calcd for $[C_9H_{20}NO_3]^+$ ([**M**+H]$^+$), 190.1443; found, 190.1442.

4: (2*S*,3*S*)-3-hydroxybutan-2-yl morpholine-4-carboxylate ((*S*,*S*)-**1d**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 90% yield as a light yellow oil (1.83 g, 9.01 mmol) (Table 1, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74−4.68 (m, 1H), 3.79−3.73 (m, 1H), 3.67 (s, 4H), 3.49−3.48 (m, 4H), 1.25 (d, J = 6.4 Hz, 3H), 1.19 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 75.6, 69.5, 66.2, 43.9, 43.7, 18.5, 15.9. HRMS (m/z): Calcd for $[C_9H_{18}NO_4]^+$ ([**M**+H]$^+$), 204.1236; found, 204.1234.

5: (2*S*,3*S*)-3-hydroxybutan-2-yl ethylcarbamate ((*S*,*S*)-**1e**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2) in 85% yield as a light yellow oil (1.37 g, 8.51 mmol) (Table 1, entry 9). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70−4.62 (m, 2H), 3.75−3.68 (m, 1H), 3.27−3.20 (m, 2H), 1.22 (d, J = 6.4 Hz, 3H), 1.19 (d, J = 6.4 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 75.0, 70.1, 35.7, 18.9, 16.4, 15.0. HRMS (m/z): Calcd for $[C_7H_{16}NO_3]^+$ ([**M**+H]$^+$), 162.1130; found, 162.1138.

6: (2*S*,3*S*)-3-hydroxybutan-2-yl butylcarbamate ((*S*,*S*)-**1f**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 84% yield as a colorless oil (1.59 g, 8.41 mmol) (Table 1, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79 (br, 1H), 4.68−4.62 (m, 1H), 3.75−3.68 (m, 1H), 3.21−3.16 (m, 2H), 1.53−1.45 (m, 2H), 1.40−1.31 (m, 2H), 1.22 (d, J = 6.4 Hz, 3H), 1.19 (d, J = 6.4 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 74.9, 69.9, 40.5, 31.8, 19.7, 18.8, 16.3, 13.5. HRMS (m/z): Calcd for $[C_9H_{20}NO_3]^+$ ([**M**+H]$^+$), 190.1443; found, 190.1449.

7: (2*S*,3*S*)-3-hydroxybutan-2-yl benzylcarbamate ((*S*,*S*)-**1g**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) in 90% yield as a light yellow oil (2.01 g, 9.01 mmol) (Table 1, entry 11). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.27 (m, 5H), 5.08 (br, 1H), 4.73−4.67 (m, 1H), 4.38 (d, J = 5.6 Hz, 2H), 3.76−3.69 (m, 1H), 1.24 (d, J = 6.4 Hz, 3H), 1.19 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 138.4, 128.3, 127.1, 127.0, 75.0, 69.6, 44.6, 18.6, 16.2. HRMS (m/z): Calcd for $[C_{12}H_{18}NO_3]^+$ ([**M**+H]$^+$), 224.1287; found, 224.1290.

8: (2*S*,3*S*)-3-hydroxybutan-2-yl (2-(1H-indol-3-yl)ethyl)carbamate ((*S*,*S*)-**1h**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:2) in 80% yield as a brown oil (2.21 g, 8.00 mmol) (Table 1, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.02 (s, 1H), 4.81 (br, 1H), 4.68−4.62 (m, 1H), 3.69−3.66 (m, 1H), 3.54−3.50 (m, 2H), 2.99−2.96 (m, 2H), 2.23 (br, 1H), 1.20 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 136.4, 127.2, 122.2, 122.0, 119.3, 118.6, 112.5, 111.3, 75.3, 70.2, 41.2, 25.5, 18.9, 16.6. HRMS (m/z): Calcd for $[C_{15}H_{21}N_2O_3]^+$ ([**M**+H]$^+$), 277.1552; found, 277.1554.

9: (2*R*,3*R*)-3-hydroxybutan-2-yl ((*R*)-1-phenylethyl)carbamate ((*R*,*R*,*R*)-**1i**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) in 88% yield as a white solid (2.09 g, 8.82 mmol) (Table 1, entry 13). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.31 (m, 5H), 5.02 (s, 1H), 4.90 (s, 1H), 4.67 (s, 1H), 3.74 (s, 1H), 2.16 (s, 1H), 1.53 (m, 3H), 1.24 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 143.4, 128.7, 127.5, 126.0, 75.6, 70.6, 50.8, 22.5, 19.3, 16.8. HRMS (m/z): Calcd for $[C_{13}H_{20}NO_3]^+$ ([**M**+H]$^+$), 238.1443; found, 238.1449.

10: (2*S*,3*S*)-3-hydroxybutan-2-yl ((*R*)-1-phenylethyl)carbamate ((*R*,*S*,*S*)-**1i**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) in 85% yield as a light yellow oil (2.02 g, 8.52 mmol) (Table 1, entry 14). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.24 (m, 5H), 5.04 (s, 1H), 4.83 (s, 1H), 4.65−4.62 (m, 1H), 3.70−3.67 (m, 1H), 2.19 (s, 1H), 1.48 (d, J = 6.8 Hz, 3H), 1.22 (s, 3H), 1.15 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 143.5, 128.7, 127.3, 125.9, 75.4, 70.3, 50.7, 22.5, 19.1, 16.6. HRMS (m/z): Calcd for $[C_{13}H_{20}NO_3]^+$ ([**M**+H]$^+$), 238.1443; found, 238.1447.

11: (1*S*,2*S*)-2-hydroxycyclohexyl piperidine-1-carboxylate ((*S*,*S*)-**2a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 50% yield as a light yellow powder solid (1.14 g, 5.02 mmol) (Table 2, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.50−4.44 (m, 1H), 3.55−3.49 (m, 1H), 3.43 (s, 4H), 3.28 (br, 1H), 2.08−2.00 (m, 2H), 1.72−1.69 (m, 2H), 1.62−1.54 (m, 6H), 1.39−1.22 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 79.2, 73.7, 44.9, 33.4, 30.5, 25.7, 25.6, 24.3, 24.0, 23.7. HRMS (m/z): Calcd for $[C_{12}H_{22}NO_3]^+$ ([**M**+H]$^+$), 228.1600; found, 228.1605.

12: (1*S*,2*S*)-2-hydroxycyclohexyl dimethylcarbamate ((*S*,*S*)-**2b**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 41% yield as a white powder solid (0.77 g, 4.12 mmol) (Table 2, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.50−4.44 (m, 1H), 3.56−3.50 (m, 1H), 3.20 (br, 1H), 2.93 (s, 6H), 2.08−2.00 (m, 2H), 1.72−1.70 (m, 2H), 1.39−1.23 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 79.3, 73.6, 36.5, 36.0, 33.4, 30.6, 24.0, 23.7. HRMS (m/z): Calcd for $[C_9H_{18}NO_3]^+$ ([**M**+H]$^+$), 188.1287; found, 188.1285.

13: (1*S*,2*S*)-2-hydroxycyclohexyl diethylcarbamate ((*S*,*S*)-**2c**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 46% yield as a light yellow oil (0.99 g, 4.60 mmol) (Table 2, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.52−4.45 (m, 1H), 3.56−3.49 (m, 1H), 3.30 (m, 5H), 2.08−2.00 (m, 2H), 1.72−1.70 (m, 2H), 1.40−1.25 (m, 4H), 1.13 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 79.0, 73.7, 42.0, 41.5, 33.5, 30.6, 24.0, 23.7, 14.1, 13.5. HRMS (m/z): Calcd for $[C_{11}H_{22}NO_3]^+$ ([**M**+H]$^+$), 216.1600; found, 216.1602.

14: (1*S*,2*S*)-2-hydroxycyclopentyl piperidine-1-carboxylate ((*S*,*S*)-**3a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 62% yield as a light yellow solid (1.33 g, 6.24 mmol) (Table 2, entry 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69−4.65 (m, 1H), 4.08−4.03 (m, 1H), 3.78 (br, 1H), 3.40 (s, 4H), 2.10−2.00 (m, 2H), 1.76−1.53 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 84.6, 78.4, 45.0, 44.8, 32.4, 30.0, 25.6, 24.3, 21.3. HRMS (m/z): Calcd for $[C_{11}H_{20}NO_3]^+$ ([**M**+H]$^+$), 214.1443; found, 214.1445.

15: (1*S*,2*S*)-2-hydroxycyclopentyl butylcarbamate ((*S*,*S*)-**3b**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 77% yield as a light yellow oil (1.55 g, 7.71 mmol) (Table 2, entry 6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73−4.67 (m, 2H), 4.09−4.08 (m, 1H), 3.49 (br, 1H), 3.20−3.15 (m, 2H), 2.07−2.03 (m, 2H), 1.72−1.65 (m, 4H), 1.51−1.46 (m, 2H), 1.39−1.31 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 84.2, 78.3, 40.7, 32.3, 31.9, 30.0, 21.2, 19.9, 13.7. HRMS (m/z): Calcd for $[C_{10}H_{20}NO_3]^+$ ([**M**+H]$^+$), 202.1443; found, 202.1441.

16: (1*S*,2*S*)-2-hydroxycyclopentyl benzylcarbamate ((*S*,*S*)-**3c**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) in 66% yield as a light yellow solid (1.54 g, 6.55 mmol) (Table 2, entry 7).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.29 (m, 5H), 5.06 (s, 1H), 4.73 (s, 1H), 4.38 (d, J = 5.6 Hz, 2H), 4.11 (s, 1H), 3.43 (s, 1H), 2.11−2.05 (m, 2H), 1.74−1.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 138.2, 128.7, 127.6, 127.5, 84.5, 78.3, 45.1, 32.3, 30.1, 21.3. HRMS (m/z): Calcd for $[C_{13}H_{18}NO_3]^+$ ([**M**+H]$^+$), 236.1287; found, 236.1281.

17: (5*S*,6*S*)-6-hydroxy-2,2-dimethyl-1,3-dioxepan-5-yl piperidine-1-carboxylate ((*S*,*S*)-**4a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 81% yield as a white powder solid (2.21 g, 8.10 mmol) (Table 2, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64−4.60 (m, 1H), 3.82 (d, J = 12.0 Hz, 1H), 3.77−3.76 (m, 2H), 3.69−3.60 (m, 2H), 3.44−3.41 (m, 5H), 1.61−1.54 (m, 6H), 1.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 101.5, 76.0, 71.4, 61.2, 59.4, 44.9, 25.7, 25.5, 24.7, 24.3, 24.2. HRMS (m/z): Calcd for $[C_{13}H_{23}NNaO_5]^+$ ([**M**+Na]$^+$), 296.1474; found, 296.1471.

18: (9*S*,10*S*)-10-hydroxy-7,12-dioxaspiro[5.6]dodecan-9-yl piperidine-1-carboxylate ((*S*,*S*)-**4b**) was obtained after purification by

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column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 80% yield as a white solid (2.51 g, 8.02 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.60−4.57 (m, 1H), 3.79 (dd, J = 12.0, 2.0 Hz, 1H), 3.74−3.73 (m, 2H), 3.67−3.58 (m, 2H), 3.45−3.38 (m, 5H), 1.60−1.48 (m, 14H), 1.40−1.35 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 101.6, 76.2, 71.5, 60.5, 58.6, 45.0, 33.6, 33.3, 25.7, 25.5, 24.3, 22.9. HRMS (m/z): Calcd for $[C_{16}H_{27}NNaO_5]^+$ ([**M**+Na]$^+$), 336.1787; found, 336.1789.

19: (3*S*,4*S*)-4-hydroxytetrahydrofuran-3-yl piperidine-1-carboxylate ((*S*,*S*)-**5a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 77% yield as a light yellow solid (1.65 g, 7.67 mmol) (Table 2, entry 11). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.90−4.83 (m, 1H), 4.31 (m, 1H), 4.16−4.05 (m, 2H), 3.86−3.83 (m, 1H), 3.73−3.69 (m, 1H), 3.40 (m, 4H), 3.09 (s, 1H), 1.61−1.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 81.8, 76.5, 73.3, 71.1, 45.0, 44.8, 25.7, 25.4, 24.2. HRMS (m/z): Calcd for $[C_{10}H_{18}NO_4]^+$ ([**M**+H]$^+$), 216.1236; found, 216.1233.

20: (2*S*,3*S*)-3-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl piperidine-1-carboxylate ((*S*,*S*)-**6a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 75% yield as a white powder solid (2.05 g, 7.45 mmol) (Table 2, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18−7.09 (m, 4H), 4.98−4.92 (m, 1H), 4.09−4.03 (m, 1H), 3.45 (s, 4H), 3.31−3.20 (m, 3H), 2.95−2.86 (m, 2H), 1.67−1.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 133.8, 133.4, 128.7, 128.4, 126.33, 126.26, 75.8, 70.4, 44.9, 36.6, 33.9, 25.6, 24.3. HRMS (m/z): Calcd for $[C_{16}H_{22}NO_3]^+$ ([**M**+H]$^+$), 276.1600; found, 276.1602.

21: (1*S*,6*S*)-6-hydroxycyclohex-3-en-1-yl piperidine-1-carboxylate ((*S*,*S*)-**7a**) was obtained after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) in 81% yield as a light yellow solid (1.83 g, 8.13 mmol) (Table 2, entry 14). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60−5.51 (m, 2H), 4.83−4.77 (m, 1H), 3.90−3.83 (m, 1H), 3.45−3.43 (m, 4H), 2.98−2.97 (br, 1H), 2.60−2.51 (m, 2H), 2.20−2.11 (m, 2H), 1.61−1.54 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 124.4, 123.8, 75.2, 69.8, 44.9, 33.6, 30.8, 25.6, 24.3. HRMS (m/z): Calcd for $[C_{12}H_{20}NO_3]^+$ ([**M**+H]$^+$), 226.1443; found, 226.1445.

Mechanistic Understanding of the Ammonolysis Reaction. *1. Synthesis of cis-Carbamates and Carbamates.* In order to confirm that the diastereoisomer, *cis*-carbamate, was not produced in the aminolysis process, the *cis*-carbamates with (*R*,*S*)- or (*S*,*R*)-configuration were synthesized (Scheme S1 in Supporting Information).

Representative procedures for the synthesis of *cis*-cyclopentene carbonate: In a predried 20 mL autoclave equipped with a magnetic stirrer, Cr(III)-Salen catalyst (0.02 mmol, 1 equiv), PPN-Cl (0.40 mmol, 20 equiv), and cyclopentene oxide (20 mmol, 1000 equiv) were dissolved in toluene (epoxide/toluene = 1/1, volume ratio) in an argon atmosphere. After CO_2 was introduced, the reaction mixture was stirred at 100 °C for 24 h. After the reaction mixture was cooled to room temperature, then CO_2 was released, a small amount of the resultant mixture was removed from the autoclave for ^{1}H NMR analysis, and the results showed that cyclopentene oxide were all converted to *cis*-cyclopentene carbonate as the sole product. The crude product was purified by vacuum distillation as a white solid (2.51 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12−5.11 (m, 2H), 2.20−2.14 (m, 2H), 1.83−1.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 81.8, 33.0, 21.4 (Figures S61 and S62 in Supporting Information). HRMS (m/z): Calcd for $[C_6H_8NaO_3]^+$ ([**M**+Na]$^+$), 151.0371; found, 151.0377.

Representative Procedures for the Synthesis of cis-Carbamate (Scheme S2 in Supporting Information). The *cis*-cyclopentene carbonate (512 mg, 4.0 mmol) was transferred into a flask, and 10 mL of THF was added. After the carbonate was dissolved completely, piperidine (4.0 mmol, 1 equiv to per carbonate unit) and water (4.0 mmol, 1 equiv to per carbonate unit) were added. The resultant mixture was stirred for 2 h at 60 °C. After cooling to room temperature, hydrochloric acid (1 M, 10 mL) was added to the reaction mixture. The organic layer was extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with water, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with petrol ether/ethyl acetate (2/1) to give the *cis*-carbamates as a light yellow oil (790 mg, yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.95−4.91 (m, 1H), 4.20−4.15 (m, 1H), 3.44−3.42 (m, 4H), 2.37 (br, 1H), 1.99−1.52 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 76.6, 72.4, 46.1, 43.9, 29.7, 27.4, 24.6, 23.4, 18.4 (Figures S63 and S64 in Supporting Information). HRMS (m/z): Calcd for $[C_{11}H_{20}NO_3]^+$ ([**M**+H]$^+$), 214.1443; found, 214.1445.

The retention time of *cis*-carbamate was completely different from that of *trans*-isomer, which confirmed that the *cis*-isomer was not produced during the aminolysis reaction (Figures S65 and S66 in Supporting Information).

2. Determination of the Cyclic Carbonate Intermediates for the Aminolysis Reaction of Poly(trans-2-butene carbonate). Synthesis Procedure for trans-2-Butene Carbonate (Scheme S3 in Supporting Information). The (*S*,*S*)-CO_2 copolymer from *cis*-2,3-epoxybutane (100 mg, 0.86 mmol) and DBU (1.3 mg, 0.0086 mmol) were transferred into a flask, and 5 mL of THF was added. After the polymer was dissolved completely, the resultant mixture was stirred for 12 h at 60 °C. The conversion of the polymer was >99% based on ^{1}H NMR analysis. After cooling to room temperature, hydrochloric acid (1 M, 10 mL) was added to the reaction mixture. The organic layer was extracted with ethyl acetate (10 mL × 3). The combined organic phase was washed with water and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with petrol ether/ethyl acetate (1/1) to give *trans*-(*S*,*S*)-carbonate as a light yellow oil (95 mg, yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39−4.28 (m, 2H), 1.45 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 80.0, 18.4. HRMS (m/z): Calcd for $[C_5H_8NaO_3]^+$ ([**M**+Na]$^+$), 139.0371; found, 139.0372.

From plot A in Figure S67 in Supporting Information, we discovered that *trans*-2-butene carbonate was detected during the aminolysis reaction of poly(*trans*-2-butene carbonate) in the absence of water. This phenomenon was in accordance with the *in situ* FTIR experiments (Figure 3, plots a and b). However, when the reaction was performed in the presence of water (plot B, Figure S67 in Supporting Information), the *trans*-2-butene carbonate was not detected because the reaction proceeded very quickly. The addition of water can accelerate the reaction, and this phenomenon has been frequently observed in ring-opening of epoxides using amine nunucleophiles.[34−37] Moreover, we also isolated the *trans*-2-butene carbonate by a different method; it can react with piperidine, and the product was same as the aminolysis reaction of poly(*trans*-2-butene carbonate) directly (Figure S68 in Supporting Information). This result also indicated that the aminolysis reaction of poly(*trans*-2-butene carbonate) underwent the cyclic carbonate intermediate, which was formed from the degradation of poly(*trans*-2-butene carbonate) by a backbiting mechanism, starting from the copolymer chain end (Figure 4, route A). So the aminolysis reaction of poly(*trans*-2-butene carbonate) shows excellent selectivities (>99%) and yields (>90%), without 1,2-diol byproducts.

3. Determination of the Intermediates for the Aminolysis Reaction of Poly(cyclopentene carbonate). From the aminolysis reaction of poly(cyclopentene carbonate), except for the 1,2-diols, carbamates and polymers, we also discovered a new series of peaks, and then we isolated this new intermediate (Figure S69 in Supporting Information). After cooling the reaction mixture to room temperature, hydrochloric acid (1 M, 10 mL) was added. The organic layer was extracted with ethyl acetate (20 mL × 3). The combined organic phase was washed with water and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with petrol ether/ethyl acetate (2/1). Except for the carbamates, a new intermediate was also separated. On the basis of NMR and HRMS analyses, it was 2,2′-carbonyldioxydicyclohexanol (Figures S70 and S71 in Supporting Information). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79−4.74 (m, 2H), 4.21−4.18 (m, 2H), 2.93 (s, 2H), 2.18−2.01 (m, 4H), 1.79−1.63 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 87.0, 78.1, 32.6, 30.1,

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21.7. HRMS (m/z): Calcd for $[C_{11}H_{18}NaO_5]^+$, 253.1052; found, 253.1056.

The aminolysis reaction of 2,2′-carbonyldioxydicyclohexanol with piperidine was described in Figure S72 in Supporting Information. Formation of 2,2′-carbonyldioxydicyclohexanol not only accelerates the reaction but also results in the formation of 1,2-diol byproducts. Furthermore, water has a positive effect on the reaction rate, and the addition of water can accelerate the reaction; however, it can also result in the formation of 1,2-diols byproducts at the same time (plot A, Figure S72 in Supporting Information). However, for the reaction of 2,2′-carbonyldioxydicyclohexanol with piperidine in the absence of water, the carbamate was not discovered (plot B, Figure S72 in Supporting Information). Because the aminolysis of poly(cyclopentene carbonate) occurred in a random fashion (Figure 4, route B), rather than with a cyclic carbonate intermediate, this reaction suffered from relatively low product selectivities and yields compared with those of poly(*trans*-2-butene carbonate).

Synthesis Procedure for the (S,S)-Carbamate Derivative for X-ray Analysis (Scheme S4 in Supporting Information). A round-bottomed flask containing a magnetic stirring bar was charged with 4-bromobenzoic acid (200 mg, 1.0 mmol), (*S,S*)-**2a** (227 mg, 1 mmol), 4-(dimethylamino)pyridine (DMAP, 134 mg, 1.1 mmol), and dichloromethane (4 mL). *N,N*′-Dicyclohexylcarbodiimide (206 mg, 1.0 mmol) in dichloromethane (1 mL) was added, and the mixture was stirred at room temperature for 12 h. The resulting suspension was filtrated and concentrated under reduced pressure. After removal of the solvent, the residue was purified by column chromatography on silica gel eluted with petrol ether/ethyl acetate (10/1) to give (*S,S*)-carbamate derivative as a white solid (377 mg, yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 5.08−5.02 (m, 1H), 4.90−4.84 (m, 1H), 3.25 (s, 4H), 2.17−2.12 (m, 2H), 1.78−1.76 (m, 2H), 1.24−1.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 153.8, 130.6, 130.2, 128.3, 127.0, 74.3, 73.5, 43.7, 29.7, 29.3, 24.5, 23.3, 22.64, 22.60 (Figures S73 and S74 in Supporting Information). HRMS (m/z): Calcd for $[C_{19}H_{25}BrNO_4]^+$, 410.0967; found, 410.0968.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01616.

NMR and HPLC spectra of various carbamates derivatives (PDF)

X-ray data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*(Y.L.) E-mail: liuye@dlut.edu.cn.

*(X.-B.L.) E-mail: xblu@dlut.edu.cn.

Notes

The authors declare no competing financial interest.

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