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Stereospecific CO₂ Copolymers from 3,5-Dioxaepoxides: Crystallization and Functionallization

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Supporting Information

ABSTRACT: Selective transformation of CO_2 into biodegradable polycarbonates (CO_2 -based copolymers) by the alternating copolymerization with epoxides represents a most promising green polymerization process. Despite the tremendous progress this field has made, most of the CO_2 -based polycarbonates are known to be amorphous, and their low thermal resistance makes them difficult to use as structural materials. Herein, we report the selective synthesis of highly isotactic CO_2 copolymers from *meso*-3,5-dioxaepoxides in perfectly alternating nature by the enantiopure dinuclear Co(III)-complex-mediated desymmetrization copolymerization under mild conditions. These isotactic CO_2 -based polycarbonates are typical semicrystalline polymers, possessing



melting points (T_m) of 179–257 °C, dependent on the substitute groups at 4-position of the *meso*-epoxides. As a model monomer of 3,5-dioxa-epoxides, 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO) was studied in detail in the asymmetric copolymerization with CO₂. The isotactic CO₂/CXO copolymer (PCXC) with >99% enantioselectivity possesses a high T_m of 242 °C and a decomposition temperature of 320 °C, while its atactic copolymer has a high T_g of up to 140 °C. Moreover, the acid hydrolysis of highly isotactic PCXC was performed to provide stereoregular poly(1,2-bis(hydroxymethyl)ethylene carbonate)s (PCFC) with two hydroxyl groups in a carbonate unit, which showed a remarkable decrease of ~80 °C in thermal decomposition temperature. This hydroxyl-functionalized CO₂ copolymer accords with an unmet need for a readily degradable biocompatible polycarbonate and was further explored to prepare bush copolymers for biomedical and pharmaceutical applications. This approach was initially demonstrated by the hydroxyl groups appended in polycarbonate backbone of a hydroxyl-functionalized terpolymer serving as macroinitiators for direct graft polymerization via organocatalytic lactide ring-opening polymerization to give fully degradable brush polymers with polycarbonate backbones and polylactide side chains. Furthermore, enantiopure dinuclear Co(III)-complex-mediated asymmetric terpolymerization of CO₂ with CXO and cyclohexene oxide (CHO) at various feed ratios was carried out in toluene solution, affording optically active terpolymers were found to be crystallizable and their crystallization capacity could be tuned by changing the feed ratio of the epoxides.

INTRODUCTION

The catalytic transformation of carbon dioxide into value-added chemicals has received intense attention in recent decades,¹ due to the economic and environmental benefits arising from the utilization of renewable source and the growing concern on the greenhouse effect. One of the most promising reactions is the alternating copolymerization of CO₂ with epoxides (oxiranes) to make degradable polycarbonates,² which was first reported by Inoue and co-workers in 1969.³ In contrast to the alternative route of condensation polymerization involving the use of toxic phosgene, this process represents an environmentally benign approach for the synthesis of polycarbonates. These CO₂-based copolymers have potential applications as ceramic binders, adhesives, coatings, and packaging materials, as well as in the synthesis of engineering thermoplastics and resins.^{4,5} A variety of catalyst systems, typically based on zinc,⁶ aluminum,⁷

chromium,⁸ cobalt,⁹⁻¹¹ and bimetallic complexes,^{12,13} have been developed for this transformation.

Despite the significant progress this field has made, the scope of epoxides used in the production of CO_2 copolymers is very narrow. Most studies have been associated with the formation of polycarbonates from propylene oxide or cyclohexene oxide (Figure 1). Recently, CO_2 copolymers from epoxides with an electron-withdrawing group such as epichlorohydrin or styrene oxide and its derivatives were prepared in perfectly alternating nature using cobalt-based catalyst systems.^{14–16} Also, the co-and terpolymerization of CO_2 with several cyclohexene oxides that had been functionalized at the monomer's 4-position was realized, affording various multiblock copolymers with

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Figure 1. Epoxides employed in the copolymerization with CO₂.

Scheme 1



functionalities.¹⁷ Importantly, Darensbourg and co-worker reported the synthesis of poly(indene carbonate)s with a rigid backbone from the coupling of CO_2 with indene oxide.¹⁸ Notably, the copolymer possesses a glass transition temperature (T_g) of up to 134 °C, the highest reported for CO_2 -based polycarbonates.

Indeed, the synthesis of degradable CO₂-based polycarbonates with T_{gs} similar to that of bisphenol A polycarbonates is highly desired. Except for the high T_g of 150 °C, the crystallizability associated with bisphenol A polycarbonates made them suitable for structural materials with wide applications, though arguments and disputes regarding the safety of this material for foodstuff containers have never stopped since it realized industrialization as early as 1960s.¹⁹ Unfortunately, the previously reported CO₂ copolymers with atactic structure were proved to be difficultly crystallizable. In a recent study, we found that highly isotactic poly(cyclohexene carbonate)s were crystallizable and possessed a high melting point (T_m) of 215–230 °C and one decomposition temperature of \sim 310 °C.²⁰ Further research confirmed that isotactic CO2 copolymers from epichlorohydrin and phenyl glycidyl ether were also crystallizable, but their $T_{\rm m}$ s are only 108 and 75 °C, respectively.^{21,22} More recently, Nozaki and co-workers reported iron-corrole-complex-catalyzed phenyl glycidyl ether/CO₂ copolymerization to provide a crystalline material owing to the isotactic polyether moiety.²³ Pursuant to our own efforts toward the development of highly efficient stereoregular catalysts for CO₂/epoxide coupling,^{10,21,22,24} we became interested in designing crystalline and functional CO_2 copolymers from meso-epoxides. In the present contribution, we report the selective synthesis of highly isotactic CO₂ copolymers from 3,5-dioxaepoxides (functional meso-epoxides,) via a stereospecific copolymerization utilizing chiral dinuclear Co(III)-based catalyst systems (Scheme 1). The investigation

provided herein also involves a study on crystallization and functionallization of these novel CO₂ copolymers.

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RESULTS AND DISCUSSION

The desymmetrization of meso-epoxides in the alternating copolymerization with CO₂ using chiral catalysts is regard as a valuable strategy for the synthesis of optically active polycarbonates with main-chain chirality. Pioneer studies by Nozaki and Coates using enantiopure zinc complexes provided moderate enantioselectivity for CO₂/cyclohexene oxide coupling.^{25,26} Similar result was also observed in the copolymerization of CO₂ with meso-epoxides using ternary catalyst systems consisted of optically active dinuclear aluminum complexes of β -ketoiminate or aminoalkoxide, in conjunction with a bulky Lewis base as catalyst activator.²⁷ Recently, we achieved the highly efficient synthesis of isotactic CO₂ copolymers from both cyclohexene oxide and the less reactive cyclopentene oxide using chiral dinuclear Co(III)-based catalyst systems.²⁸ The resultant copolymers possess an unprecedented enantioselectivity of 99% ee for poly(cyclopentene carbonate)s and 98% ee for poly(cyclohexene carbonate)s. However, these CO₂ copolymers from cyclohexene oxide and cyclopentene oxide have no possibility for further functionallization.

3,5-Dioxaepoxides (Figure 1), consisted of one 3-membered epoxy-ring and one 7-membered ring with two oxygen atoms, has a relatively high reactivity with CO_2 by its epoxy-ring in the presence of a metal catalyst, while its 7-membered ring easily forms two hydroxyl groups by deprotection, affording the opportunity for further functional modification for biomedical and pharmaceutical applications. These *meso*-epoxides were easily prepared from epoxidation of 2-substituents-1,3-dioxep-5-enes, an intermediate, formed through the nucleophilic addition of *cis*-2-butene-1,4-diol to aldehyde or ketone catalyzed by *p*-toluenesulfonic acid.²⁹

Table 1. Enantiopure Co(III)-Complex-Mediated Asymmetric Copolymerization CO₂ with CXO^a



entry	catalyst	CXO/catalyst/PPNY ^b	CO ₂ pressure (MPa)	temp (°C)	time (h)	$\begin{array}{c} { m TOF}^c \ ({ m h}^{-1}) \end{array}$	$M_{\rm n}^{\ d}$ (kg/mol)	PDI ^d	ee ^e (%)	specific rotation ^f (deg)
1	(<i>S,S,S,S</i>)-1a	1000/1/-	2	25	6	52	11.3	1.10	62 (<i>S</i> , <i>S</i>)	63 (+)
2	(<i>S,S,S,S</i>)-1b	1000/1/-	2	25	6	59	16.6	1.14	73 (<i>S</i> , <i>S</i>)	75 (+)
3	(<i>S,S,S,S</i>)-1a	1000/1/2	2	25	2	150	12.2	1.09	90 (<i>S</i> , <i>S</i>)	92 (+)
4	(<i>S,S,S,S</i>)-1b	1000/1/2	2	25	2	180	17.5	1.18	>99 (S,S)	102 (+)
5	(<i>S,S,S,S</i>)-1c	1000/1/2	2	25	2	191	18.4	1.12	>99 (S,S)	102 (+)
6	(R,R,R,R)- 1b	1000/1/2	2	25	2	185	18.1	1.15	>99 (R,R)	102 (-)
7	(<i>S,S,S,S</i>)-1b	1000/1/2	2	0	8	35	16.2	1.13	>99 (S,S)	103 (+)
8	(<i>S,S,S,S</i>)-1b	1000/1/2	2	50	0.5	876	20.3	1.21	98 (S,S)	101 (+)
9	(<i>S,S,S,S</i>)-1b	1000/1/2	0.1	25	6	22	6.7	1.16	>99 (S,S)	103 (+)
10	(<i>S,S,S,S</i>)-1b	1000/1/2	0.6	25	2	98	11.5	1.12	>99 (S,S)	102 (+)
11	(<i>S,S,S,S</i>)-1b	1000/1/2	4	25	2	198	19.7	1.17	>99 (S,S)	102 (+)
12	(<i>S,S,S,S</i>)-1b	2000/1/2	2	25	4	137	18.4	1.20	>99 (S,S)	102 (+)
13	(<i>S,S,S,S</i>)-1b	5000/1/2	2	25	10	68	10.3	1.19	>99 (S,S)	102 (+)
14^g	(<i>S,S,S,S</i>)-1b	1000/1/2	2	25	12	83	50.2	1.22	>99 (S,S)	102 (+)
15	2a	1000/1/2	2	25	12	20	12.1	1.15	0	0

^{*a*}The reaction was performed in neat 4,4-dimethyl-3,5,8-trioxa-bicyclo[5.1.0] octane (CXO) (2.6 mL, 30 mmol) in a 20 mL autoclave. The selectivity for polycarbonates over cyclic carbonate and carbonate linkages of all resultant polymers are >99% based on ¹H NMR spectroscopy. ^{*b*}Molar ratio, PPN = bis(triphenylphosphine)iminium, Y = 2,4-dinitrophenoxide. ^{*c*}Turnover frequency (TOF) = mol of product (polycarbonates)/mol of cat per hour. ^{*d*}Determined by gel permeation chromatography in THF, calibrated with polystyrene. ^{*e*}Measured by hydrolyzing the copolymer and analyzing the resulting diol by chiral GC. ^{*f*}Specific rotation of the copolymers was determined by polarimeter in chloroform at 20 °C (*c* = 1). ^{*g*}The reaction was carried out in dichloromethane solution with [CXO]/[dichloromethane] = 1/2 (volume ratio).



Figure 2. ¹H NMR spectrum of a representative sample of CO₂ copolymers from 4,4-dimethyl-3,5,8-trioxa-bicyclo[5.1.0]octane in CDCl₃.

Since 4,4-dimethyl-3,5,8-trioxa-bicyclo[5.1.0]octane (CXO) is easily obtained in a great quantity, it was chosen as model *meso*-epoxide for copolymerizing with CO₂ using dinuclear Co(III)-based catalyst systems. We discovered that dinuclear complexes (*S*,*S*,*S*,*S*)-1a and 1b alone could operate at high efficiency in catalyzing CO₂/CXO copolymerization, with turnover frequencies (TOF) of about 70 h⁻¹ at ambient

temperature; however, the enantioselectivity was moderate (Table 1, entries 1 and 2). We delightedly discovered that in the presence of PPNY (PPN = bis(triphenylphosphine)iminium, Y = 2,4-dinitrophenoxide) as cocatalyst, enantiopure dinuclear Co(III) complexes (*S*,*S*,*S*,*S*)-1a could effectively catalyze this coupling reaction to selectively produce the corresponding polycarbonate with a TOF of 150 h⁻¹ at ambient





Figure 3. DSC thermograms (left) in second heating and WAXD profiles (right) of (A) atactic copolymer (ee = 0%, Table 1, entry 15), and (B) highly isotactic CO₂ copolymer (ee > 99%, entry 4) from *meso*-CXO.

Table 2. Enantiopure Dinuclear Co(III) Complex 1b-Mediated Asymmetric Copolymerization CO_2 with Other 3,5-Dioxaepoxides^a

	0. R1	\sim \sim \sim \sim \sim \sim \sim \sim \sim \sim	+ CO ₂ —	(S,S,S,S)-1b →	* 0, F	$R_1 \sim C_1 \sim C_2$	×	
Entry	epoxide	Time	Con ^[b]	TOF ^[c]	<i>M</i> n ^[d]	PDI ^[d]	ee ^[e]	Specific	<i>T</i> g∕ <i>T</i> m ^[9]
		(h)	(%)		(Kg/mol)		(%)	$Rotation^{[f]}(^{\circ})$	(°C)
1		8	80	50	7.4	1.21	92(<i>S</i> , <i>S</i>)	75(+)	118/ ^[h]
2	\sim	4	91	114	12.6	1.26	>99(<i>S,S</i>)	109(+)	^[h] /179
3	o √ _o O Ph	24	<1	<1	[1]	[1]	[1]	[i]	[1]
4	O O Ph	8	>99	63	8.9	1.28	[0]	78(+)	123/257

^{*a*}The reaction was performed in toluene (4 mL) in 20 mL autoclave at 25 °C. [(S,S,S,S)-1b]/[PPNY]/[epoxide] = 1/2/500 (molar ratio), [epoxide]/[toluene] = 1/2 (molar ratio), Y = 2,4-dinitrophenoxide. The selectivity for polycarbonates over cyclic carbonates and carbonate linkages of all the resulted polymer are >99% based on ¹H NMR spectroscopy. ^{*b*}The conversion was determined by ¹H NMR spectroscopy. ^{*c*}Turnover frequency (TOF) = mole of product (polycarbonates)/mol of cat per hour. ^{*d*}Determined by gel permeation chromatography in THF, calibrated with polystyrene. ^{*c*}Measured by hydrolyzing the polymer or derivatizing the resultant diol and analyzing by chiral GC or HPLC (for detailed procedures, see Supporting Information). ^{*f*}Specific rotation of the polymers was determined by polarimeter in chloroform at 20 °C (*c* = 1). ^{*g*}The polycarbonates in entries 1 and 4 undergo the end-capping reaction using acetic anhydride in CH₂Cl₂ (for detailed synthesis procedures, see Supporting Information), as determined by DSC. ^{*h*}Not detected. ^{*i*}Not applicable. ^{*j*}The polycarbonates were decomposed easily under the hydrolysis conditions.

temperature (Figure S6 in the Supporting Information). The resultant copolymers possess perfectly alternating nature with >99% carbonate unit content (Figure 2) and show a specific rotation value of $+92^{\circ}$ (c = 1, in CHCl₃) at 20 °C (entry 3). After hydrolysis of the resulting polycarbonate with aqueous NaOH, the enantiomeric excess (*ee*) of the resulting diol was determined by chiral GC to be 90% with an *S*,*S*-configuration. It was found that the decrease in the steric hindrance of the phenolate ortho substituents significantly improved product enantioselectivity and also increased the reaction rate to a certain extent (entries 4 and 5). Substituted for (*S*,*S*,*S*,*S*)-1a with complex (*S*,*S*,*S*,*S*)-1b or (*S*,*S*,*S*,*S*)-1c resulted in an enantioselectivity from 90% increasing to >99% for *S*,*S*-

configuration, corresponding to a specific rotation value of $+102^{\circ}$ (c = 1, in CHCl₃). Similar activity and enantioselectivity were observed in the (R,R,R,R)-1b mediated CO₂/CXO copolymerization, and the obtained copolymer has a specific rotation value of -102° (c = 1, in CHCl₃) (entry 6). Notably, the (S,S,S,S)-1b-based catalyst system could be performed at an elevated temperature of 50 °C with a TOF of 876 h⁻¹, affording the copolymer with 98% enantioselectivity (entry 8). Additionally, changes in CO₂ pressure or/and catalyst loading had no effect on product enantioselectivity and the selectivity for copolymer, but caused a significant influence on reaction rate (entries 9–13). With the use of dichloromethane as an organic solvent, we achieved the complete conversion in the

copolymerization performed at 25 °C within prolonged time, affording the polycarbonates with a high molecular weight of 50200 without any loss in enantioselectivity (entry 14, Figure S8 in the Supporting Information). It is worthwhile noting here parenthetically that binary catalyst system consisted of enantiopure mononuclear salenCo(III) complex and PPNY exhibited significantly lower activity (TOF < 2 h⁻¹) and enantioselectivity (*ee* = 12%) for CXO/CO₂ copolymerization at 25 °C and 2.0 MPa CO₂ pressure.

For a comparison purpose, dinuclear Co(III) complex 2a with nonchiral ethylenediamine backbone was synthesized and used as catalyst for preparing atactic CO₂ copolymer from CXO (Table 1, entry 15). Although the accurate assignation of the microstructure of this polycarbonate proved to be very difficult, ¹³C NMR study could clearly reveal significant differences in both the carbonyl and methine region between the atactic and highly isotactic copolymers (Figure S9 in the Supporting Information). It is deserved to be emphasized that the atactic CO_2 copolymer possesses a high T_g of up to 140 °C. Regarding the highly isotactic copolymer with >99% ee, one should first notice from the DSC (differential scanning calorimetry) trace that the T_{g} peak has disappeared, while a quite sharp and high crystallization endothermic peak is now found at 242 °C with $\Delta H_{\rm m}$ = 29.89 J/g (Figure 3, left plot), indicating a very high degree of crystallinity. Figure 3 (right plots) shows the wideangle X-ray diffraction (WAXD) profiles of atactic and highly isotactic (S,S)-copolymers with >99% ee. No diffraction was observed for the corresponding atactic copolymer, confirming its amorphous feature. On the contrary, for highly isotactic copolymers, sharp diffraction peaks were observed at 2θ values of 11.8°, 14.3°, 16.9°, and 20.4°, demonstrating that the isotactic copolymer is a typical semicrystalline polymer.

Furthermore, a variety of 3,5-dioxa-epoxides derivatives were investigated in the asymmetric copolymerization with CO₂ using enantiopure dinuclear Co(III) complex (S,S,S,S)-1b/ PPNY catalyst system (for synthetic procedures of epoxides, see Supporting Information) (Table 2). In consideration with the solid or slimy state of these employed epoxides at ambient temperature, the copolymerization was carried out in toluene. High TOFs and excellent enantioselectivities were observed in the systems regarding 3,5-dioxaepoxides with H or cyclohexyl substituent at 4-positions (Table 2, entries 1 and 2). As expected, the asymmetric copolymerization provided the complete alternating copolymers with an S,S-configuration. After hydrolysis of the resulting polycarbonates with aqueous NaOH, we succeeded in isolating the corresponding diols in crystal state (Figure 4). X-ray single crystal analysis revealed its S,S-configuration. Interestingly, there was a huge difference in activity between the exo- and endo-4-phenyl-3,5,8-trioxa-



Figure 4. Molecular structure of (S,S)-diol produced from the hydrolysis of isotactic CO₂ copolymers from 3,5,8-trioxaspiro-[bicyclo[5.1.0]octane-4,1'-cyclohexane] (hydrogen atoms and uncoordinated solvent omitted for clarity). Thermal ellipsoids are at the 30% probability level.

bicyclo [5.1.0] octane. The exo-isomer showed a neglected reactivity, but the endo-isomer could be copolymerized with CO₂ smoothly to produce the corresponding polycarbonate (Table 2, entries 3 and 4). It might be attributable to the steric hindrance of the phenyl, significantly retarding the nucleophilic attack of the propagating chain at the coordinated epoxide from its back. The crystallization behaviors of these isotactic copolymers were investigated by DSC method. It was found that CO₂ copolymers from 3,5,8-trioxaspiro[bicyclo[5.1.0]octane-4,1'-cyclohexane] and endo-4-phenyl-3,5,8-trioxabicyclo[5.1.0] octane were crystallizable and their crystallization endothermic peaks appeared in 179 and 257 °C, respectively. Perhaps owning to relatively low enantioselectivity (92% ee) of CO₂ copolymer from simple 3,5,8-trioxa-bicyclo[5.1.0]octane or overlapping of the melting point and decomposition temperature, only a $T_{\rm g}$ of ~118 $^\circ {\rm C}$ was found in the DSC trace (Figure S18 in the Supporting Information).

More importantly, the ketal-protecting group of the primary hydroxyl in the CO₂ polymers from 3,5-dioxaepoxides can be easily removed through dilute acid treatment, affording two hydroxyl groups in a carbonate unit, which benefits for further functional modification. In a recent communication, Grinstaff and co-worker reported the synthesis of atactic and isotactic linear poly(benzyl 1,2-glycerol carbonate)s via the Co(III)complex-mediated ring-opening copolymerization of *rac-/(R)*benzyl glycidyl ether with CO₂. Deprotection of the resultant polymers afforded a functionalizable primary hydroxyl group appended polycarbonates, poly(1,2-glycerol carbonate)s, which showed a remarkable increase in degradation rate compared to poly(1,3-glycerol carbonate)s.³⁰

For the functional modification of CO₂ copolymers from 3,5dioxa-epoxides, in a typical procedure, the polymer (e.g., $M_{\rm p}$ = 17.5 kg/mol; PDI = 1.18; Table 1, entry 4) was dissolved in DMF, and then hydrogen chloride/methanol solution was added at 0 °C. The deprotection is rapid and complete. No methyl signal located at 1.35 ppm was observed in the NMR spectrum of the resultant polymers (Figures 5 and S16 in the Supporting Information). Removal of the ketal-protecting group resulted in a reduced molecular weight ($M_{\rm n} = 13.0$ kg/ mol; PDI = 1.11). Owning to a great amount of hydroxyl groups in the resultant polymers, poly(1,2-bis(hydroxymethyl)ethylene carbonate)s are not soluble in a non-polar or low polar organic solvent such as dichloromethane but are easily dissolved in DMF or DMSO. Similar to poly(1,2-glycerol carbonate)s, poly(1,2-bis(hydroxymethyl)ethylene carbonate)s were also found to be sensitive to moisture and easily decomposed at mild temperatures. The thermolysis curve indicates a broad range 210-270 °C of 10%-90% thermal decomposition (Figure 6), compared to a narrow range, 315-330 °C, before deprotection.

Moreover, the asymmetric terpolymerization of CO_2 with *meso*-epoxide mixtures of CXO and cyclohexene oxide (CHO) at various feed ratios were performed in toluene solution with use of (*S*,*S*,*S*,*S*)-**1b**-based/PPNY catalyst system (for detailed procedures, see Supporting Information). The resulting terpolymers {designated as poly(CHC-*co*-CXC)} with different carbonate units from CXO monomer (CXC carbonates) have been synthesized by changing the feed ratios of CHO and CXO (Figures S25–S30 in the Supporting Information). The acid hydrolysis of CXC carbonate in the resultant terpolymers provided the crystalline and hydroxyl-functionalized terpolymers, poly(cyclohexene carbonate-*co*-1,2-bis(hydroxymethyl)-ethylene carbonate)s {designated as poly(CHC-*co*-CFC)}. It



Figure 5. ¹H NMR spectra of PCXC and poly(1,2-bis(hydroxymethyl)ethylene carbonate)s in DMSO-d₆.



Figure 6. Thermolysis curves of (A) isotactic PCXC ($M_n = 17.5 \text{ kg/mol}$; PDI = 1.18; Table 1, entry 4), and (B) its deprotection product, isotactic poly(1,2-bis(hydroxymethyl)ethylene carbonate)s ($M_n = 13.0 \text{ kg/mol}$; PDI = 1.11).

was found that the content of 1,2-bis(hydroxymethyl)ethylene carbonate (CFC) units significantly affected the crystallization capacity (Figure 7)). The presence of hydroxyl groups allows for further graft modification to afford degradable brush polymers (Scheme 2).

To demonstrate the feasibility of the pathways proposed in Scheme 2, a poly(CHC-*co*-CFC) terpolymer with ~10 hydroxyl groups each polycarbonate chain in a unimodal distribution of molecular weights with a M_n value of 13000 g mol⁻¹ and PDI of 1.21 was prepared. These hydroxyl groups appended in polycarbonate backbone could serve as macroinitiators that allow direct graft polymerization via organocatalytic lactide ring-opening polymerization to obtain fully degradable brush polymers with polycarbonate backbones and



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Figure 7. DSC thermograms of various poly(CHC*-co*-CFC) in second heating: (A) CHC/CFC = 3/2; (B) CHC/CFC = 4/1; (C) CHC/CFC = 20/1.

polylactide side chains. In the subsequent experiment, certain quantities of lactide and DBU (1,8-diazabicyclo[5.4.0]undec-7ene) were added *in situ* into the reaction solution to prepare predesigned poly(CHC-*co*-CFC)-*g*-PLA brush copolymers (for detailed procedures, see Supporting Information). The GPC trace of the resultant brush copolymers is shown in Figure 8, where it was apparent that the side polylactide chains leads to an increase in the polymer molecular weight. More importantly, the copolymer displays a monomodal weight distribution with a narrow PDI value of 1.18, demonstrating the successful chain extension from the hydroxyl groups of poly(CHC-*co*-CFC) to afford the predesigned poly(CHC-*co*-CFC)-*g*-PLA brush copolymers. The structure of the brush copolymer was also

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Scheme 2



Figure 8. GPC traces of (A) poly(CHC-co-CFC) and (B) poly(CHC-co-CFC)-g-PLA.

revealed by ¹H NMR spectroscopy. That is, as illustrated in Figure S31 in the Supporting Information, the resonance at 4.7 ppm from the polycarbonate backbone and resonance at 5.2 and 1.5 ppm from polylactide side chains were clearly seen.

It is worthwhile noting here parenthetically that the excellent chiral induction for desymmetric ring-opening of both CXO and CHO was also observed in the (S,S,S,S)-1b-mediated terpolymerization with CO₂, though the random distribution of CXC and CHC units in the terpolymers resulted in a decrease in crystallization capacity. Importantly, the acid hydrolysis of CXC units in the resultant terpolymers and further graft modification via organocatalytic lactide ring-opening polymerization did not have any influence on the main-chain chirality.

CONCLUDING REMARKS

In summary, we have realized the highly selective synthesis of isotactic CO_2 copolymers from *meso*-3,5-dioxa-epoxides in perfect alternating nature through stereospecific polymerization using enantiopure dinuclear Co(III)-complex catalyst systems. In the presence of a nuclephilic cocatalyst PPNY (Y = 2,4-dinitrophenoxide), (*S*,*S*,*S*,*S*)-1b could efficiently catalyze the asymmetric copolymerization of CO_2 with 4,4-dimethyl-3,5,8-trioxa-bicyclo[5.1.0]octane (CXO) at ambient temperature, affording the corresponding polycarbonates with more than 99% enantioselectivity for *S*,*S*-configuration. Moreover, the catalyst system proved to be very effective at an elevated temperature of 50 °C to provide highly isotactic copolymers

with 98% *ee* in an enhanced TOF of 876 h⁻¹. In addition, the isotactic CO₂/CXO copolymer (PCXC) is a typical semicrystalline thermoplastic, and possesses a high $T_{\rm m}$ of 242 °C, while its atactic copolymer has a high $T_{\rm g}$ of up to 140 °C, the highest record for the reported CO₂ copolymers from epoxides. Moreover, the isotactic CO₂ copolymers from 3,5,8-trioxaspiro-[bicyclo[5.1.0]octane-4,1'-cyclohexane] and *endo*-4-phenyl-3,5,8-trioxa-bicyclo[5.1.0]octane were found to be crystallizable and their crystallization endothermic peaks appear in 179 and 257 °C, respectively.

Importantly, the acid hydrolysis of these isotactic CO₂ copolymers from meso 3,5,8-trioxa-epoxides further provided stereoregular poly(1,2-bis(hydroxymethyl)ethylene carbonate)s with two hydroxyl groups in a carbonate unit, which showed a remarkable decrease of ~80 °C in thermal decomposition temperature. This hydroxyl-functionalized CO₂ copolymer accords with an unmet need for a readily degradable biocompatible polycarbonate and also affords chances of graft modification to prepare bush copolymers for biomedical and pharmaceutical applications. This approach was initially demonstrated by organocatalytic ring-opening polymerization of lactide onto a hydroxyl-functionalized terpolymer, in which the hydroxyl groups appended in polycarbonate backbone serve as macroinitiators and DBU (1,8-diazabicyclo[5.4.0]undec-7ene) as catalyst, affording fully degradable brush polymers with polycarbonate backbones and polylactide side chains.

Furthermore, enantiopure dinuclear Co(III)-complex-based catalyst systems were demonstrated to be efficient in catalyzing asymmetric terpolymerization of CO₂ with CXO and cyclohexene oxide at various feed ratios, with excellent chiral induction for desymmetric ring-opening of *meso*-epoxides incorporated into the polycarbonates. The crystallization capacity of the resultant terpolymers could be tuned by altering the feed ratio of the both epoxides. This result provides us possibility for designing various crystalline CO₂ copolymers with desired properties, which will become our next goal. In addition, further studies on detailed crystallization behavior and kinetics are currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

General experimental procedures and characterizations of catalyst, organic bases, and copolymers and a .cif crystallographic file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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