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Completely Recyclable Monomers and Polycarbonate: Approach to Sustainable Polymers

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Abstract: It is of great significance to depolymerize used or waste polymers to recover the starting monomers suitable for repolymerization reactions that reform recycled materials no different from the virgin polymer. Herein, we report a novel recyclable plastic: degradable polycarbonate synthesized by dinuclear chromium-complex-mediated copolymerization of CO₂ with 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine, a mesoepoxide. Notably, the novel polycarbonate with more than 99% carbonate linkages could be recycled back into the epoxide monomer in quantitative yield under mild reaction conditions. Remarkably, the copolymerization/depolymerization processes can be achieved by the ON/OFF reversible temperature switch, and recycled several times without any change in the epoxide monomer and copolymer. These characteristics accord well with the concept of perfectly sustainable polymers.

Recyclable economy is pivotal for establishing sustainable world.^[1] In the polymeric field, it remains of great interest to depolymerize used or waste polymers to convert into the corresponding starting monomers suitable for repolymerization reactions that reform recycled materials no different from the virgin polymer. Usually, depolymerization is performed under harsh conditions such as high temperatures, or/ and high-pressures, and therefore giving the low selectivity for the desired products.^[2] In 2007, Kamimura and Yamamoto reported the efficient depolymerization of polyamides in an ionic liquid at 300 °C to give the corresponding monomeric lactam in good yields (35-86%).^[3] The recovered monomer was collected by direct distillation of the reaction mixture. The most significant study in this area stems from the laboratory of the Eugene Y.-X. Chen research group at Colorado State University, with the use of $La[N(SiMe_3)_2]_3/$ Ph₂CHCH₂OH as an effective catalyst for ring-opening polymerization of γ -butyrolactone at -40 °C to selectively produce degradable poly(y-butyrolactone) with linear and cyclic topologies.^[4] Notably, both of the structures could be recycled back into the monomer in quantitative yield by simple heating the bulk materials at 220 °C (linear polymer) or 300°C (cyclic polymer) for one hour. Recently, the same group reported the synthesis of completely recyclable biopo-

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lymers from the ring-opening polymerization of y-butyrolactone using a novel organic catalyst system consisting of a superbase, tert-Bu-P₄ (1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tri(dimethylamino)-phosphoranylid-enanmino]- $2\lambda^5$, $4\lambda^5$ -catenadi(phosphazene) and Ph₂CHOH or PhCH₂OH at a very low temperature.^[5] Prior to this study, Darensbourg et al. systematically investigated the depolymerization of various polycarbonates made from CO₂ and epoxides.^[6-9] They demonstrated that the depolymerization of aliphatic polycarbonates undergo endwise scission reactions to cleanly generate cyclic carbonates at modest temperatures. The process was discovered to involve the unzipping of the polycarbonate from the chain-end by a backbiting pathway. The same group also performed high-accuracy CBS-QB3(+) calculations for obtaining the free energy barriers for several polycarbonates to undergo alkoxide backbiting to give the corresponding epoxide monomers and CO2.[10] Free energy barriers to epoxide formation $(12.7-17.4 \text{ kcal mol}^{-1})$ were higher than the same starting materials to afford cyclic carbonates (10.7–14.6 kcal mol⁻¹). Surprisingly, only poly(cyclopentene carbonate) differs: epoxide formation has a lower free energy barrier than cyclic carbonate formation. The experimental study on the depolymerization of poly(cyclopentene carbonate) in the presence of the strong base sodium bis(trimethylsilyl)amide in toluene demonstrated the formation of both cyclopentene oxide and cis-cyclopentene carbonate. The latter product should be produced by the backbiting of a carbonate chain end, rather than by an alkoxide chain end. The degradation process was found to be retarded at a 0.7 MPa CO₂ pressure, with the product distribution being enhanced in favor of cis-cyclopentene carbonate, while the reduced pressure is beneficial for cyclopentene oxide formation.^[11]

Although the advances have been significant, apart from poly(γ -butyrolactone), most systems mentioned above suffer from some drawbacks, such as relatively low selectivity or yield for the starting monomers and high depolymerization temperatures. Obviously, the development of efficient and easy methods for depolymerizing polymers into the corresponding monomers in quantitative yield under mild conditions is highly desirable. Herein, we report a completely recyclable polycarbonate made from CO₂ and *N*-heteroepoxide, 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine (BEP), using dinuclear Cr^{III}-salen complex **1** as catalyst. Remarkably, the novel polycarbonate can be recycled back into the epoxide monomer in quantitative yield under mild reaction conditions (Scheme 1).

Recently, the selective transformation of CO_2 into biodegradable polycarbonates has attracted much attention. Various highly active catalyst systems were developed for

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Scheme 1. Completely recyclable polycarbonate made from CO_2 and 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine (BEP).

selective synthesis of CO₂-based polycarbonates in recent decades.^[12-23] In previous papers, we have shown that the cobalt complex based on the same ligand of dinuclear chromium complex 1 was highly active and enantioselective in catalyzing the unsymmetric copolymerization of CO₂ and various meso-epoxides.^[24,25] Unfortunately, this cobalt complex was found to be not efficient for CO2/BEP copolymerization, perhaps due to the competitive coordination effect of the nitrogen atom in the five-membered ring of the epoxide monomer relative to the oxygen atom in the three-membered epoxy-ring, which significantly inhibited its reactivity. However, we delightedly discovered that in the presence of nucleophilic cocatalyst PPN-F (PPN = bis(triphenylphosphine)iminium), the dinuclear chromium complex 1 was highly efficient for this coupling reaction, selectively affording the copolymer with a turnover frequency (TOF) up to 100 h^{-1} at 60°C (Table 1, entry 1). Notably, the resultant polymers have more than 99% carbonate linkage and narrow molecularweight distributions (see Figures S6-S9 in the Supporting Information). A prolonged reaction time resulted in the complete conversion (entry 2). No activity was observed in the system with complex 1 alone as catalyst (entry 3). For comparative purpose, we also investigated the performance of mononuclear salenCr^{III}Cl 2 in conjunction with PPN-F at a high catalyst loading (1 mol %) at 60 °C (entry 4). Overall, the CO₂/BEP copolymerization by this catalyst system was less active and selective for copolymer formation, in comparison with the corresponding dinuclear chromium complex 1. Decreasing the catalyst loading to 0.1 mol% or performing at room temperature resulted in obvious decrease in polymerization rate, but had no any change in copolymer selectivity (entries 5 and 6). The replacement of the axial F group with NO₃ or N₃, as well as altering the Y anion of the PPN-Y cocatalyst had no obvious effect on the catalytic activity and copolymer selectivity (entries 7-10). Surprisingly, an increase in reaction temperature from 60°C to 80°C led to the significant decrease in catalytic activity (entry 11). Further increase to 100 °C resulted in complete loss in polymerization rate for various catalyst systems (entries 12-14). Interestingly, after the complete conversion of BEP monomer into polycarbonate, the system was raised to 100°C, and fast depolymerization of the resulting polycarbonate to BEP rather than cyclic carbonate was observed. Notably, the complete and selective depolymerization into BEP monomer was finished within only 10 minutes.

In order to monitor the depolymerization of the BEP/CO₂ copolymer, we first performed an insitu FTIR study of the polymer solution at 60 °C, with a probe fitted to a modified

Table 1: Cr^{III}-complex-mediated CO₂/BEP copolymerization.^[a]

$ \begin{array}{c} & & \\ & & $	penjinenzane			
	N + CO ₂	Cr(III)-catalyst	* $\left[\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	Cyclic carbonate

Entry	Cat./Co-cat. (Cat/PPN-Y/BEP) ^[b]	T [°C]	<i>t</i> [h]	TOF $[h^{-1}]^{[c]}$	Polymer selectivity ^[d]	$M_n [\mathrm{kg} \mathrm{mol}^{-1}]^{[\mathrm{e}]}$	PDI ^[e]
1	1 a/PPN-F (1/1/500)	60	4	100	> 99	5.4	1.33
2	1a/PPN-F (1/1/500)	60	6	83	>99	6.0	1.35
3	1 a / - [f] (1 / 0 / 500)	60	24	<1	_[g]	_[g]	_[g]
4	2/PPN-F (1/1/100)	60	24	3	66	_[g]	_[g]
5	1 a/PPN-F (1/1/1000)	60	18	51	>99	10.2	1.35
6	1 a/PPN-F (1/1/500)	25	24	12	>99	2.7	1.30
7	1a/PPN-Cl (1/1/500)	60	6	75	98	5.5	1.29
8 ^[h]	1 a/PPN-F (1/0.5/500)	60	12	42	>99	6.7	1.33
9 ^[h]	1b /PPN-NO ₃ (1/0.5/500)	60	12	42	>99	7.0	1.30
10 ^[h]	1 c/PPN-N ₃ (1/0.5/500)	60	12	42	>99	7.1	1.29
11 ^[h]	1 a/PPN-F (1/0.5/500)	80	12	13	>99	2.8	1.35
12 ^[h]	1 a/PPN-F (1/0.5/500)	100	12	<1	< 1[1]	_[g]	_[g]
13 ^[h]	1b /PPN-NO ₃ (1/0.5/500)	100	12	<1	< 1[1]	_[g]	_[g]
14 ^[h]	1 c/PPN-N ₃ (1/0.5/500)	100	12	<1	< 1 ^[i]	_[g]	_[g]

[a] The reaction was performed in BEP (1.0 g) in toluene solution (epoxide/toluene = 1/1, mass ratio) in 20 mL autoclave and 2.0 MPa CO_2 pressure. The carbonate linkage of all the resultant polymer was >99% based on ¹H NMR spectroscopy. [b] Molar ratio. [c] Turnover frequency (TOF) = mol of product (polycarbonates and cyclic carbonates)/mol of catalyst per hour. [d] Selectivity for polycarbonates over cyclic carbonate, determined by using ¹H NMR spectroscopy. [e] Determined by using gel permeation chromatography in THF, calibrated with polystyrene. [f] Reaction was performed in absence of co-catalyst. [g] Not applicable. [h] Reaction was performed under a CO_2 pressure of 1.0 MPa. [i] All epoxides were reserved and cyclic carbonates and diols did not form.

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stainless steel Parr reactor. The dinuclear Cr^{III}-salen 1b/PPN-NO₃ catalyzed BEP/CO₂ copolymerization (1b/PPN-NO₃/ BEP = 1/0.5/250, molar ratio) was carried out in presence of toluene (epoxide/toluene = 3/4, mass ratio) under 1.0 MPa CO_2 pressure. As is easily observed, the intense absorbance for the asymmetric $v_{C=0}$ vibration of polycarbonates appears at 1755 and 1707 cm⁻¹, while the absorption around 1813 and 1706 cm⁻¹ corresponds to cyclic carbonates and that around 1703 cm⁻¹ corresponds to the BEP monomer (Figure S11). During the whole depolymerization process, we did not observe the appearance in the 1813 cm⁻¹ region of the solution, revealing no formation of cyclic carbonate. Comparatively, the absorption at 1755 cm⁻¹ corresponding to polycarbonates gradually decreases with time. This observation suggests that the depolymerization of the BEP/CO2 copolymer predominantly converts into the starting epoxide monomer. Notably, in the presence of catalyst, the recycled BEP could be further copolymerized with CO₂ at 60°C, affording completely alternating polycarbonate, which is the same as the fresh copolymer. The copolymerization/depolymerization could be recycled several times, without any change in epoxide monomer and polymer (Figure 1).



Figure 1. Reaction profiles for the BEP/CO₂ polymerization/depolymerization as a function of time monitored by in situ FTIR ($\nu_{C=O}$ peak for polycarbonate at 1755 cm⁻¹ vs. reaction time). See the Supporting Information for the detailed experimental procedure.

Moreover, because of the significant differences in ¹H NMR spectra among the BEP monomer, cyclic carbonate, and the corresponding polycarbonate (Figure S6), the ¹H NMR method was also used to study the depolymerization process (Figure 2). When the polymerization was performed at 60 °C for 6 hours, the ¹H NMR spectrum of the reaction mixture showed that all epoxides were transformed into the polymer without the formation of cyclic products (Figure 2A). Heating the reaction mixture to 100 °C led to fast depolymerization to epoxides solely, without the formation of cyclic carbonates or 1,2-diols (Figure 2B). Especially, this polymerization/depolymerization processes can be cycled another time with the retention of the selectivities (>99%) for both polymer and monomer.

The solid CO₂/BEP copolymer after the removal of catalyst is stable at enhanced temperatures up to 200 °C for 10 hours, while the pure polycarbonate could be degraded into epoxide monomer solely without any byproduct at 260 °C for just one hour under a nitrogen atmosphere, which is significantly different from poly(cyclopentene carbonate)^[8]



Figure 2. ¹H NMR spectra of BEP/CO₂ polymerization/depolymerization cycle. A) First cycle-P1 for polymer formation. B) First cycle-D1 for depolymerizaiton of polymer to monomer formation. C) Second cycle-P2 for polymer formation. D) Second cycle-D2 for depolymerizaiton of polymer to monomer formation.

(Figure S12 B). However, the end-capping polycarbonates with acetic anhydride not only retard the depolymerization, but also make the degradation products very complicated (Figure S12 C). This result supported that the depolymerization of polycarbonates undergo endwise scission reactions for the formation of monomers. Additionally, it was found that the presence of Cr^{III} -salen catalyst **1a** and PPNCI is beneficial for the depolymerization of CO_2/BEP copolymer. For example, depolymerization could occur at relative low temperature of 150 °C in polycarbonate solution or in bulk with the addition of Cr^{III} complex **1a**/PPNCI, indicating the catalyst system also is efficient for polycarbonate depolymerization (Figure S13). No matter what depolymerization conditions were employed (with or without catalyst, in bulk or solution), the monomer epoxide was the sole product.

Indeed, the design of BEP epoxide monomer was enlightened from two fundamental understandings: the increased strain in forming cyclic carbonate imposed by the conformation of five-membered ring regarding the alicyclic epoxides, and the enhanced depolymerization tendency of CO₂-based polycarbonates promoted by the large steric hindrance in carbonate units originating from the used epoxide monomer. In order to better understand the depolymerization process of CO₂/BEP copolymers, a computational study was performed to determine the free energy barriers for possible depolymerization products, trans-cyclic carbonate, cis-cyclic carbonate, and the starting epoxide monomer. As a matter of fact, the degradation of CO₂based polycarbonates will lead to the loss of one carbonate repeat unit through a metal bond, as well as metal-free carbonate and alkoxide backbiting reactions. The backbiting reaction of alkoxide intermediate to attack at the carbonyl carbon atom affords trans-carbonate, while the attack of carbonate intermediate at methine position leads to the formation of cis-carbonate. The backbiting reaction of alkoxide intermediate to attack at methine carbon atom

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produces the epoxide (Scheme S6). In comparison with the metal bond, the metal-free carbonate and alkoxide backbiting reactions have lower free energy barriers.^[6] In order to simplify the calculations, three types of backbiting process for model compounds regarding the metal-free carbonate and alkoxide were examined by density functional theory (DFT; Scheme 2). First, the structures of cyclic carbonates with *cis*-



Scheme 2. Model backbiting reactions of various intermediates.

and trans-structures were optimized (Figure S14), cis-isomer is lower in enthalpy than the *trans*-isomer by 20.4 kcalmol⁻¹ due to the extreme angle strain found at its tetrahedral bridgehead carbon (O-CH-CH₂ trans-: 127.2°, cis-: 111.5°). For detailed DFT calculation parameters see the Supporting Information. The ring strain placed on the five-membered carbonate ring in order to accommodate the conformational requirements of the alicyclic cyclopentenyl ring makes cisisomer more stable. The relative stabilities of the trans- and cis-isomers are very important because they directly influence the enthalpy of carbonate formation using the backbiting process. The formation of cis-carbonates is exothermic [Eq. (2) in Scheme 2], while *trans*-carbonates formation is endothermic [Eq. (1) in Scheme 2]. Moreover, the free energy barriers of the aforementioned processes were computed. The backbiting of alkoxide to form a tetrahedral intermediate with four oxygen substituents is barrierless, however, the elimination of a methanolate to yield transcarbonate has a free energy barrier of 26.6 kcalmol⁻¹ (Figure S15 in the Supporting Information). Notably, the free energy of activation for the formation of cis-carbonate and methyl carbonate concerning the backbiting of the carbonate intermediate to the methine carbon atom is 14.5 kcalmol⁻¹ (Figure S16). This result indicates that the trans-fused carbonate is less stable than the cis-fused isomer due to the strained geometries. Besides, the free energy of meso-epoxide formation obtained by a backbiting reaction of the alkoxide intermediate to the methine carbon atom is 12.3 kcalmol⁻¹ [Scheme 2, Eq. (3) and Figure S17]. This suggests that the depolymerization into the starting epoxide monomer is the more competitive route. The calculation results, in combination with the fact that the enhanced reaction temperatures

beyond 100 °C resulted in complete loss in catalytic activity, provide a great possibility for complete transformation of the BEP/CO₂ copolymer into the starting epoxide monomer.

In summary, we have designed a novel *N*-hetero-epoxide, 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine, which easily copolymerizes with CO_2 mediated by dinuclear chromiumcomplex-based catalyst systems at 60 °C to produce the corresponding polycarbonate with more than 99 % carbonate linkage and narrow polydispersity. Upon heating the resultant polycarbonate at 100 °C the polymer rapidly depolymerizes into the starting epoxide monomer in quantitative yield. Notably, the copolymerization/depolymerization processes was achieved by altering the temperature, and the polymer was recycled several times, without any change in the epoxide monomer and copolymer. The characteristic of the completely recyclable polycarbonate is in accordance with that of truly sustainable polymers, which easily convert into their corresponding monomers under mild conditions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide · depolymerization · polycarbonates · recyclable polymers · temperature switch

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Completely Recyclable Monomers and Polycarbonate: Approach to Sustainable Polymers



A sustainable plastic was synthesized by dinuclear chromium-complex-mediated copolymerization of CO_2 with an epoxide that could be recycled back into the monomer in quantitative yield under mild conditions. Temperature was used as a reversible switch in the recycle process. These characteristics are in accordance with the concept of perfectly sustainable polymers.

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