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Efficient Polymerization and Selective Depolymerization of Poly(cyclopentene carbonate) Mediated Solely by Heterometallic Rare-Earth(III)/Zinc(II) Complexes

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Cite This: *Macromolecules* 2024, 57, 10041−10052 Read Online

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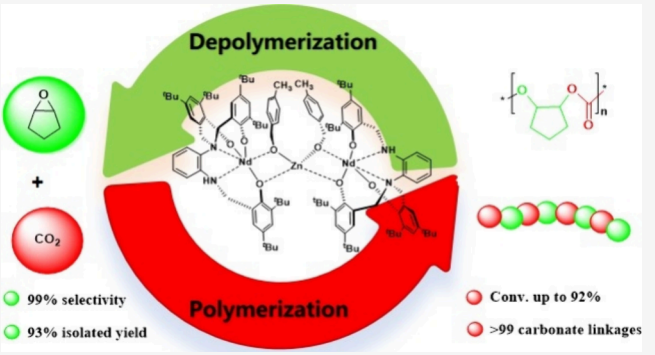
ABSTRACT: Poly(cyclopentenyl carbonate) (PCPC) is a recyclable polymer with great potential applications. However, the selective preparation of PCPC from cyclopentene oxide (CPO) and CO_2 copolymerization and the chemical recycling of PCPC back to the original monomer CPO are of great challenge. In this work, it was found that the heterometallic rare-earth metal(III)/Zn(II) complexes (RE(III)-Zn(II) complexes) supported by phenylenediamine-bridged triphenols could serve as highly active catalysts for the copolymerization of CPO and CO_2 to give pure PCPC. Remarkably, the same complexes alone could also promote the selective depolymerization of PCPC to CPO only by simply raising the reaction temperature up to ca. 160 °C. The copolymerization and depolymerization mechanisms were also proposed.



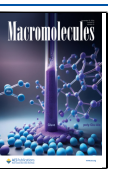
INTRODUCTION

The vast majority of synthetic polymers used in modern life are derived from petrochemicals. Therefore, the raw materials used to produce them have environmental implications.[1] Notably, once synthetic polymers serve their designated purpose, they bring out a serious problem, as most of them are difficult to degrade naturally. As such, end-of-life recycling is driving increasing efforts to develop sustainable polymers based on biomass-derived renewable feedstocks.[2−5] In particular, there is a strong desire to design sustainable polymers with unique recyclability, which can be depolymerized into their virgin monomers or high value-added chemicals by thermal,[6,7] mechanical,[8] or chemical methods.[9−11] In an effort to establish a circular monomer−polymer−monomer economy, although lots of achievements have been made, several concerns such as renewable feedstock, depolymerization catalyst, monomer recovery selectivity, etc. should be addressed.[12−14]

CO_2-based polycarbonates, generated from the alternating copolymerization of CO_2 with epoxides, have received increasing attention for their potential application as an engineering plastic and their excellent biodegradability.[15−17] CO_2 is an abundant, cheap, nontoxic renewable C1 resource, while epoxides can be derived from biomass, which give the opportunity to produce fully renewable polycarbonates.[18−23] Poly(cyclopentene carbonate) (PCPC) is a copolymer from CO_2 and cyclopentene oxide (CPO), and it is a promising recyclable engineering plastic. However, due to the relatively small difference in activation energies between PCPC (14.7 kcal mol^{-1}) and cyclopentene carbonate (cPC) (10−12 kcal mol^{-1}),[24] there is an intense tendency to form cyclic carbonate during the copolymerization, rendering the efficient copolymerization of CPO and CO_2 to produce PCPC a great challenge. This is strikingly in contrast to its six-membered ring counterparts like cyclohexene oxide (CHO), which preferentially produces polycarbonate over cyclic carbonate in the copolymerization. Therefore, despite the first example of CO_2/epoxide copolymerization reported by Inoue et al. in 1969,[25] only limited literature studies have described the successful preparation of PCPC from CPO/CO_2 copolymerization to date.[26−35]

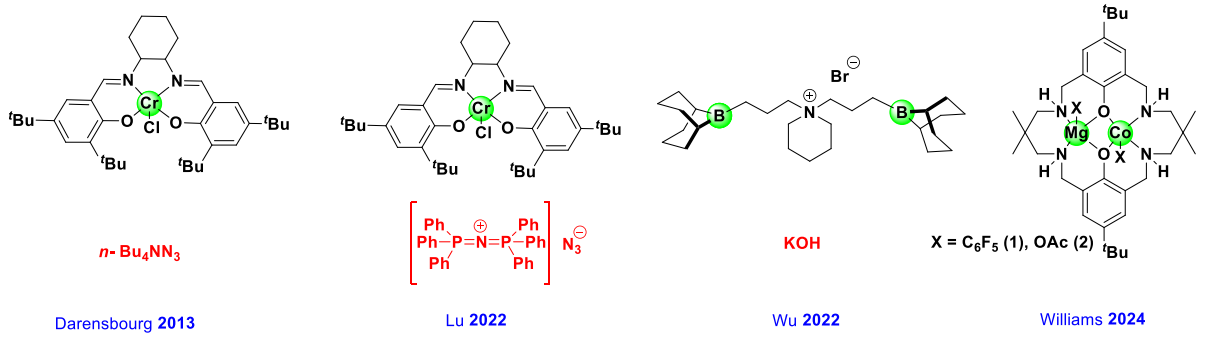
Furthermore, to realize the chemical recycling of PCPC back to its virgin monomer CPO, some great progress has been achieved. In 2013, the Darensbourg group reported the first example of PCPC depolymerization by use of [Cr(III)(salen)-Cl] complex/*n*-Bu_4NN_3 as the catalyst system; in the presence of a strong base like NaHMDS, it could depolymerize PCPC into CPO with a selectivity up to 92%, along with an inevitable byproduct cPC.[36] Later on, Lu and co-workers reported that the dinuclear salen-Cr(III) complexes were effective for the

Received: September 2, 2024
Revised: October 22, 2024
Accepted: October 23, 2024
Published: October 30, 2024

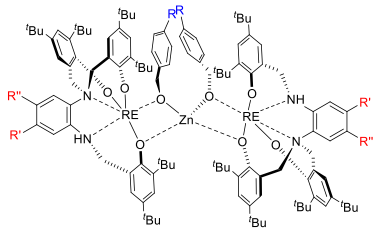


https://doi.org/10.1021/acs.macromol.4c02086
Macromolecules 2024, 57, 10041−10052

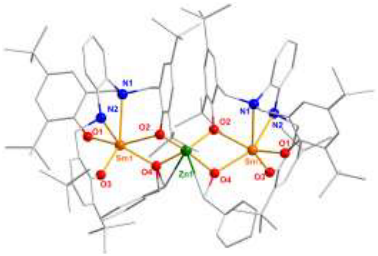
Chart 1. Representative Catalysts for PCPC Depolymerization



Scheme 1. Heterometallic RE(III)-Zn(II) Complexes Employed in This Work and the Molecular Structure of 3



RE = La, R = H, R'' ,R' = H, H (**1**)
RE = Nd, R = H, R'' ,R' = H, H (**2**)
RE = Sm, R = H, R'' ,R' = H, H (**3**)
RE = Y, R = H, R'' ,R' = H, H (**4**)
RE = Nd,R = Me, R'' ,R' = H, H (**5**)
RE = Nd, R = ^{t}Bu , R'' ,R' = H, H (**6**)
RE = Nd, R = CF_3, R'' ,R' = H, H (**7**)
RE = Nd, F_5PhCH_2OH, R'' ,R' = H, H (**8**)
RE = Nd, R = H, R'', R' = H, OMe (**9**)
RE = Nd, R = H, R'', R' = Cl, Cl (**10**)



Solid state structure of complex **3** with thermal ellipsoids drawn at the 30% probability level. Carbon atoms are drawn in the form of wireframe. All hydrogen atoms (except for NH) are omitted for clarity.

Table 1. Copolymerization of CO_2 and CPO Catalyzed by 1−10[a]

entry	cat.	conv.[b] (%)	TOF[c] (h^{-1})	poly(carbonate) selectivity[b] (polymer%)	$M_{n,GPC}$[d] (kg/mol)	$M_{n,est}$[e] (kg/mol)	$Đ$[d]
1	**1**	22	12	>99	3.8	28.2	2.62
2	**2**	78	43	>99	13.0	99.9	1.74
3	**3**	69	38	>99	9.5	88.4	2.12
4	**4**	51	28	>99	6.5	65.3	1.26
5	**5**	77	43	>99	14.2	98.6	1.39
6	**6**	83	46	>99	14.7	106.3	1.36
7	**7**	79	44	>99	11.2	101.2	1.69
8	**8**	49	27	>99	7.8	62.7	1.35
9	**9**	73	41	>99	12.1	93.5	1.55
10	**10**	76	42	>99	11.7	97.3	1.40

[a]Conditions: [CPO]:[catalyst] = 1000:1, V_{CPO}:V_{Tol} = 1:1, 70 °C, 18 h, 30 bar. [b]Determined by ^{1}H NMR spectroscopy, using tris-methoxybenzene (10 mol %) as an internal standard, through comparison of integration at 6.80 ppm (for tris-methoxybenzene) and 5.02 ppm (for polycarbonate).[34] [c]TOF = mole [CPO] consumed per mole catalyst per hour. [d]Determined by GPC versus polystyrene standards. [e]$M_{n,est}$ = [(epoxide conv.)(epoxide equiv)(MW repeat unit)].

copolymerization-depolymerization process in a one-pot mode by simply changing reaction temperature in the presence of PPN-N_3.[37] Very recently, Wu and co-workers disclosed that the dinuclear organoboron catalysts exhibited good performance in the selective depolymerization of PCPC to CPO with the assistance of KOH.[34] Despite these elegant achievements, however, single-component catalysts for PCPC depolymerization remain scarce (Chart 1). To our knowledge, the Mg(II)/Co(II) complexes developed by Williams et al. and Lu et al. could serve as the highly selective depolymerization of polycarbonates to epoxides and CO_2.[35,38−40] Remarkably, recent interest in polycarbonate depolymerization has unveiled that rare-earth metal complexes can efficiently promote such catalytic process,[41,42] then the application of rare-earth-metal-based catalysts in the depolymerization of polycarbonates into epoxides and CO_2 has no precedent.

As our continuous effort to exploit rare-earth metal catalysts for CO_2 utilization,[43−45] recently, we have successfully developed the heterometallic complexes composed of rare-earth metal (RE)(III) and Zn(II) for the copolymerization of CO_2 and CHO.[46−48] These results illustrate the synergistic mode involving the rare-earth(III) and zinc(II) centers. The highly oxophilic rare-earth(III) ions are responsible for epoxide coordination and activation, while the zinc(II) benzyloxide moiety is responsible for CO_2 insertion. The active polymer chain shuttles between the two metal ions. High activity and selectivity of the copolymerization of epoxides and CO_2 are believed to result from the synergism.

https://doi.org/10.1021/acs.macromol.4c02086
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Table 2. Influences of Different Reaction Conditions on CPO/CO_2 Copolymerization with 6[a]

entry	cat./CPO (mol %)	T/°C	P/bar	t/h	conv.[b] (%)	TOF[c] (h^{-1})	poly(carbonate) selectivity[b] (polymer %)	$M_{n,GPC}$[d] (kg/mol)	$M_{n,est}$[f] (kg/mol)	$Đ$[d]
1	0.1	60	30	18	69	38	>99	9.5	88.4	2.12
2	0.1	70	30	18	83	46	>99	14.7	106.3	1.35
3	0.1	80	30	18	79	44	>99	11.6	101.2	1.48
4	0.1	90	30	18	75	42	>99	10.4	96.0	1.59
5	0.1	100	30	18	73	41	>99	10.8	93.5	1.63
6	0.1	70	10	18	82	46	>99	10.7	105.0	1.38
7	0.1	70	20	18	80	44	>99	11.2	102.4	1.38
8	0.1	70	40	18	88	49	>99	19.7	112.7	1.67
9	0.1	70	40	10	68	68	>99	7.7	87.1	1.23
10	0.1	70	40	24	90	38	>99	22.5	115.2	1.58
11	0.1	70	40	48	91	19	>99	20.8	116.5	1.64
12	0.2	70	40	10	81	41	>99	14.3	51.9	1.47
13	0.05	70	40	10	12	24	>99	1.8	30.7	2.60
14[e]	0.1	70	40	18	92	51	>99	23.0	117.8	1.92

[a]All the polymerizations were carried out in 100 mL autoclaves unless otherwise mentioned. conv., conversion. [b]Determined by ^{1}H NMR spectroscopy, using tris-methoxybenzene (10 mol %) as an internal standard, through comparison of integration at 6.80 ppm (for tris-methoxybenzene) and 5.02 ppm (for polycarbonate).[34] [c]TOF = mole [CPO] consumed per mole catalyst per hour. [d]Determined by GPC versus polystyrene standards. [e]V_{CPO}:V_{Tol} = 2:1. [f]$M_{n,est}$ = [(epoxide conv.)(epoxide equiv)(MW repeat unit)].

Interestingly, an in-depth study revealed that the heterometallic RE(III)-Zn(II) complexes ligated by the phenylenediamine-bridged triphenolate could serve as highly active catalysts for CPO/CO_2 copolymerization. Remarkably, the selective depolymerization process of PCPC to CPO could be realized only by simply raising reaction temperature solely in the presence of the same heterometallic RE(III)-Zn(II) complexes. The copolymerization and depolymerization mechanisms were proposed based on some control experiments. Here, we report these interesting results.

RESULTS AND DISCUSSION

Copolymerization of CPO and CO_2. The phenylenediamine-bridged triphenolate ligated heterometallic RE(III)-Zn(II) complexes employed in this work were prepared according to the synthetic strategy developed previously by our group.[48] The one-pot reaction of $Cp_3RE(THF)$ with the phenylenediamine-bridged triphenol, and subsequently treatment with $ZnEt_2$ and BnOH, after workup, afforded the heterometallic RE(III)-Zn(II) complexes **1**−**10** with different steric and electronic configurations in good isolated yields, as shown in Scheme 1. The molecular structure of **3** is presented in Scheme 1.

To reveal the structure−reactivity relationship, we explored the copolymerization of CPO and CO_2 with these complexes. To understand the effect of metal size on the copolymerization activity, the heterometallic RE(III)-Zn(II) complexes **1**−**4** bearing the same ligand framework and initiation group (−OCH_2Ph), in which RE = La (**1**), Nd (**2**), Sm (**3**), and Y (**4**) for the copolymerization of CPO and CO_2 was tested. The copolymerization was conducted at 70 °C in the presence of 30 bar CO_2, and the results are summarized in Table 1. It was found that **1**−**4** were active for CPO/CO_2 copolymerization, giving the PCPC copolymer with >99% selectivity. Notably, the formation of cPC was negligible. Among them, **4** (Nd−Zn complex) exhibited the best performance, suggesting that the activity was balanced by ionic radius and Lewis acidity of central metal, not solely dependent on metal size (Table 1, entry 2).[49] The effect of the benzyloxy groups as the initiation group on the copolymerization was also compared using **5**−**8** as the catalysts. While *p*-CF_3-substituted benzyloxy complex **5** and *p*-methyl-substituted benzyloxy complex **7** showed a similar activity toward the copolymerization of CPO and CO_2 (Table 1, entries 5 and 7), **8** bearing a pentafluorobenzyloxy group displayed a much lower activity (TOF = 27 h^{-1}) (Table 1, entry 8). It might be ascribed to the low nucleophilicity of the pentafluorobenzyloxy group that hampered the ring-opening of CPO.[48] Moreover, neither the electron-donating group nor the electron-withdrawing group on the backbone of *o*-phenylenediamine ligand sets had a distinct influence on the CO_2/CPO copolymerization, as **9** (with an electron-donating group −OMe in **9**) and **10** (with an electron-withdrawing group − Cl in **10**) shared an identical activity (Table 1, entries 9 and 10). The steric hindrance complex **6** with a *p*-*tert*-butyl benzyloxy group showed the highest activity (TOF = 46 h^{-1}) for CPO/CO_2 copolymerization among **1**−**10**. Although these complexes were highly selective for CPO/CO_2 copolymerization to produce pure PCPC, high activity remained to be improved compared to the most active catalysts such as the bifunctional salen-Co^{III} complex (108 h^{-1})[27] and the dinuclear salen-Co^{III} complex (647 h^{-1}).[28]

Since **6** exhibited a promising activity toward CPO/CO_2 copolymerization, it was employed as the catalyst to explore the copolymerization reactivity under different conditions. As shown in Table 2, when the copolymerization was conducted at 60 °C, a much lower conversion was observed under 30 bar of CO_2 pressure (Table 2, entries 1 and 2). However, increasing the temperature from 70 to 100 °C did not lead to a higher conversion. This experimental phenomenon was consistent with the previously reported example by Lu et al.[37] No significant difference in the activity was observed by changing the pressure of CO_2 from 10 to 40 bar (Table 2, entries 2, 6−8), which was also consistent with the most reported literature.[48] As anticipated, when the catalyst loading was increased from 0.05 to 0.2 mol %, the copolymerization activity showed an increasing trend. Meanwhile, a high conversion of up to 92% was reached when the concentration of CPO was increased (Table 2, entries 14). The experimental molecular weights of PCPC were observed to be much lower than theoretical values (Table 2, entries 1−14). These

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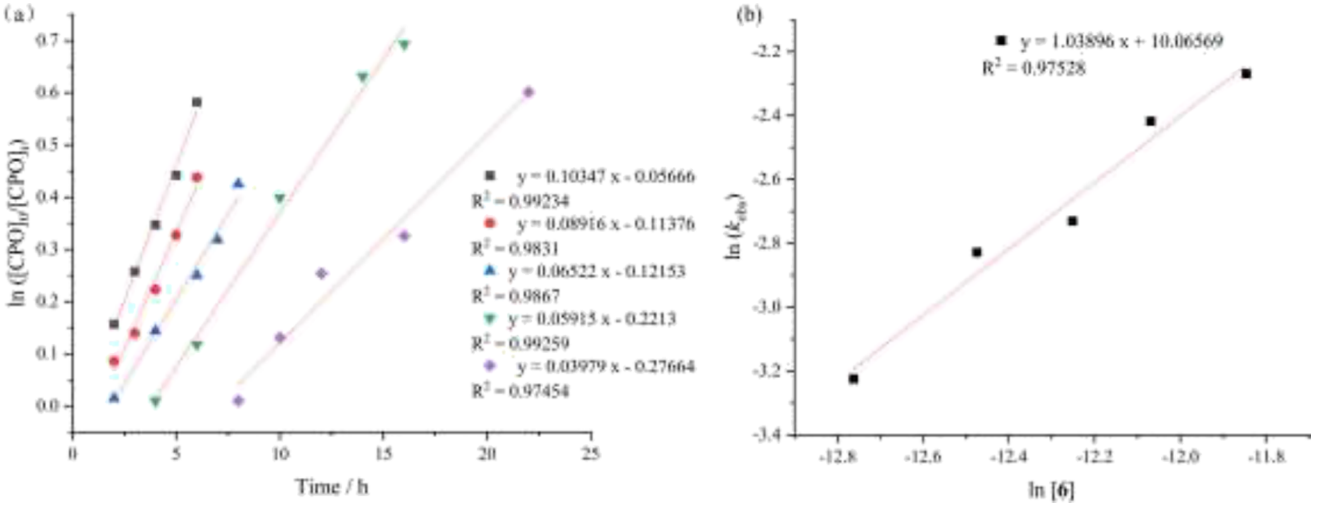

Figure 1. (a) The kinetic graph of $\ln([CPO]_0/[CPO]_t)$ versus time for CO_2/CPO copolymerization with **6** at 70 °C and 40 bar of CO_2 pressure under different catalyst concentrations ($[CPO]_0$:$[\mathbf{6}]_0$ (black diamond) 800:1, (red circle) 1000:1, (blue triangle) 1200:1, (green triangle) 1500:1, (purple diamond) 2000:1). (b) Double logarithmic plot of k_{obs} vs concentration of **6**.

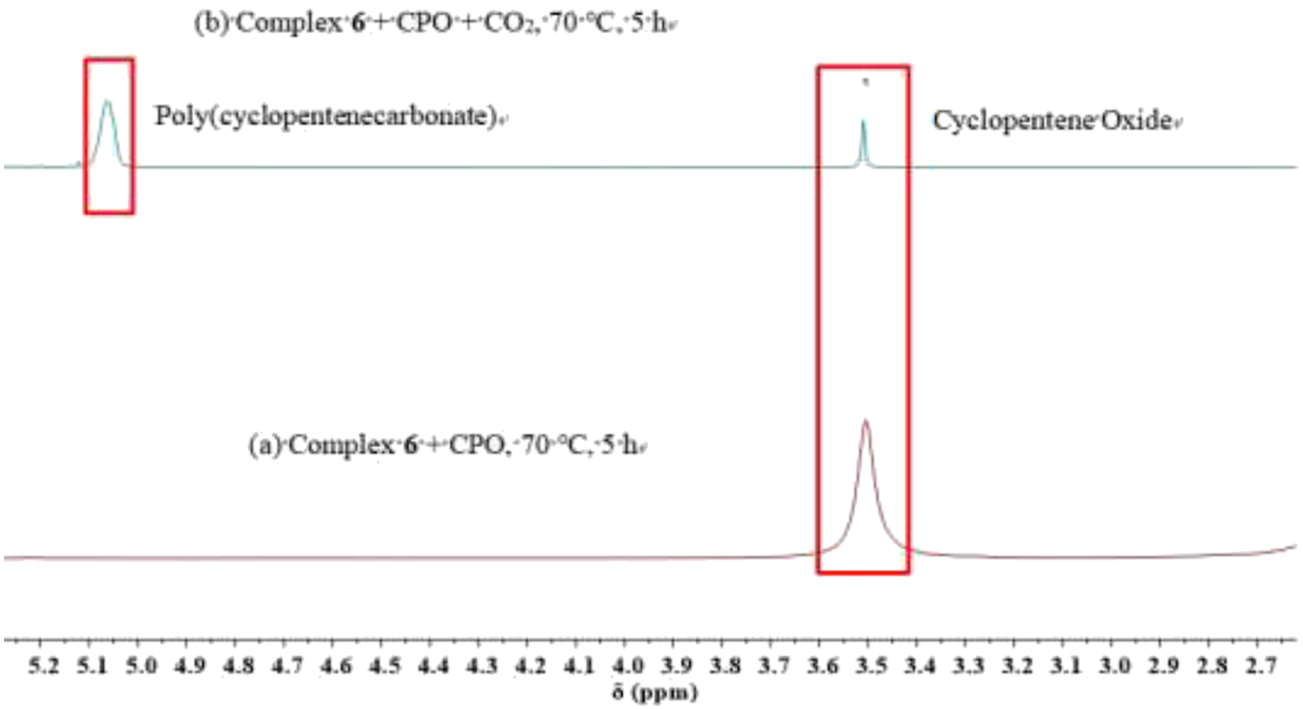

Figure 2. ^{1}H NMR spectra ($CDCl_3$) of the reaction mixtures from (a) reaction of **6** with CPO at 70 °C for 5 h ([**6**]:[CPO] = 1:100); (b) further reaction at 70 °C under 40 bar of CO_2 pressure for 5 h.

differences may be attributed to the trace amount of cyclopentanediol present in cyclopentene oxide that leads to transesterification and hence lower molecular weight and wide dispersity, which can be proven by polymer chains capped by cyclopentanol that are detected by MALDI-TOF mass spectrometry (*vide infra*). Similar observations have been reported.[35,46,48]

The effect of alcohols as additives on the copolymerization reaction was also studied (Table S4, entries 1−4). The copolymerization was inhibited with the addition of alcohol, which may be because alcohol destroys the RE(III)-Zn(II) complexes that are metal alkoxides and thus leads to a decrease in their activity. These results agree with previous reports.[50]

Study on the Kinetics of CPO/CO_2 Copolymerization. To shed light on the copolymerization process, we conducted the kinetic studies under the conditions of 70 °C and 40 bar of CO_2 using **6** as a catalyst. The kinetic profiles were obtained by ^{1}H NMR spectroscopy. The initial concentration of monomer was $[CPO]_0$ = 5.734 mM/L, and the molar ratio of monomer to catalyst was ranged from 800:1 to 2000:1. The plots of $\ln([CPO]_0/[CPO]_t)$ versus time displayed a good linear relationship, suggesting the first-order dependence on the CPO concentration (Figure 1a). The catalyst order of 1.03 was deduced from the slope of the $\ln(r_{obs})$ versus $\ln[\mathbf{6}]$ curve (Figure 1b). In addition, as shown in Table 2, changing the pressure of CO_2 (10−40 bar) produced almost similar conversions, suggesting a zero-order dependence on CO_2

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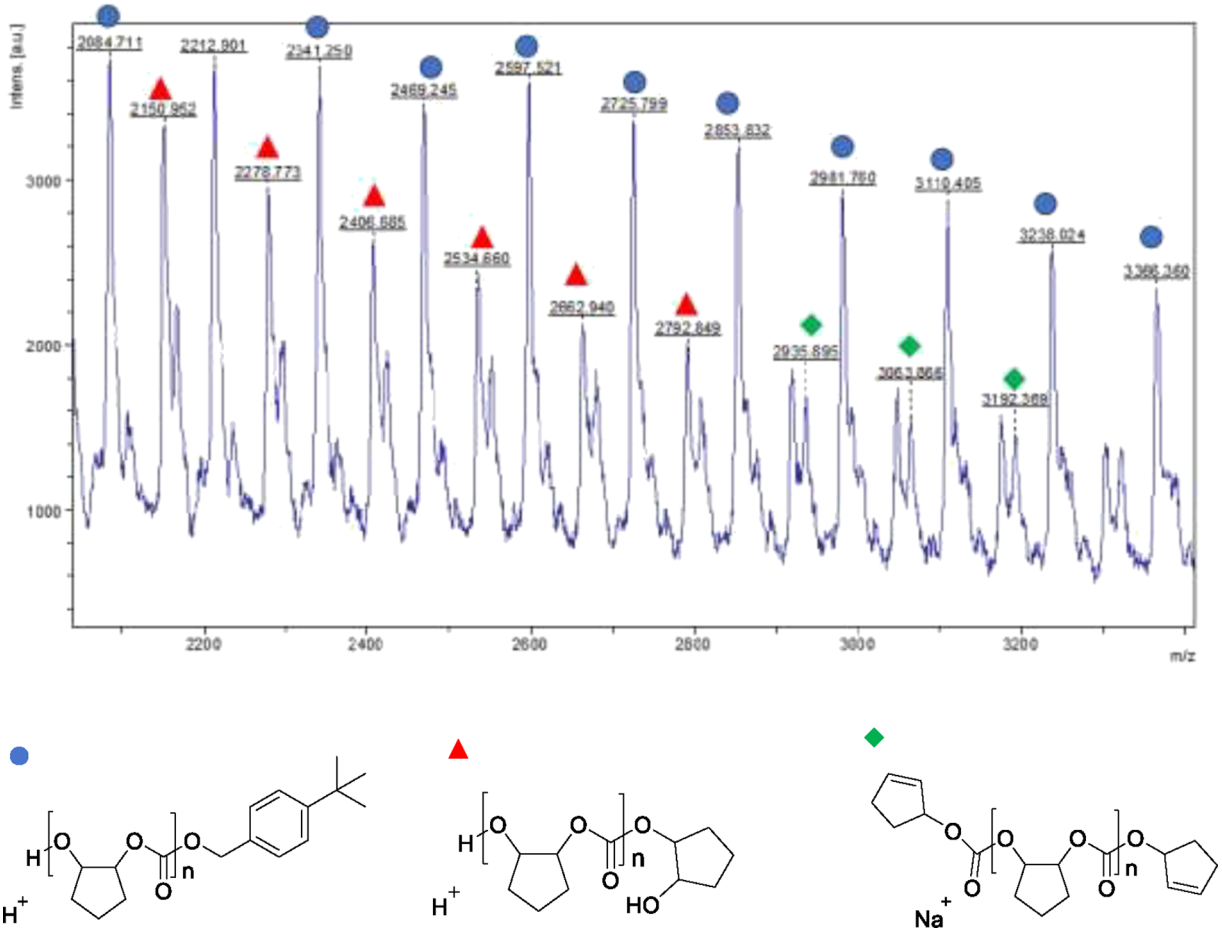

Figure 3. MALDI-TOF mass spectrum of the oligomer (polymerization conditions: 70 °C, 40 bar of CO_2, 18 h, [CPO]:[**6**] = 100:1).

pressure. Therefore, the overall rate law dependence could be determined as the polymerization rate $\nu = k_p[\mathbf{6}]^1[\mathrm{CPO}]^1 p(\mathrm{CO_2})^0$, where k_p was the propagation rate constant. The kinetic studies indicated that CO_2 insertion was not the rate-determining step, while the ring-opening of CPO was the rate-determining step during the copolymerization. The kinetic studies also suggested the presence of the induction period, which may be due to the dissociation of the bridging benzyloxy group to give a coordinative vacancy for epoxide.[51] Another possible reason may be CO_2 dissolving.[52]

Copolymerization Mechanism Study. To further elucidate the process of CPO/CO_2 copolymerization, some control experiments employing **6** as a catalyst were carried out in a J. Young NMR tube. No signal for polycarbonate was observed in the NMR spectrum in the absence of CO_2 after 5 h. However, the formation of polycarbonate was detected with the introduction of CO_2 for another 5 h (Figure 2). This finding showed that the key step of the copolymerization was the reaction of CO_2 with the heterometallic complex. To get further information on the polymerization process, the oligomer prepared with **6** was subjected to MALDI-TOF mass spectroscopy. As shown in Figure 3, there were three sets of signals, and the main peaks could be assigned to be the polymeric chain capped by *p*-$C(CH_3)_3$−$C_6H_5CH_2OCOO$−, which was generated from the *p*-*tert*-butyl benzyloxy group as the initiating group. This finding indicated that the copolymerization was initiated by the preferential insertion of CO_2 into the *p*-*tert*-butyl benzyloxy group *p*-$C(CH_3)_3$−$C_6H_5CH_2O$−. Of the two other sets of signals, one corresponded to the oligomer chain terminated by cyclopentanediol, and the other was assignable to the oligomer chain terminated by cyclopentanediol dehydration; both resulted from the cyclopentanediol-initiated polymerization.

Based on these facts and the previous literature,[32,44] a possible polymerization mechanism was proposed as shown in Scheme 2. The copolymerization starts from the insertion of CO_2 into the Zn−O(Bn) bond of **6**, which generates a carbonate species I, as evidenced by the MALDI-TOF mass spectrum (Figure 3). A similar trinuclear Nd−Zn heterometallic carbonate complex has been isolated and structurally characterized.[44] The carbonate group then intramolecularly attacks a CPO molecule that is bound with the more oxyphilic neodymium center (II) and forms a Nd−Zn alkoxide (III). The alternative insertion of CO_2 and CPO into the metal-propagating chain leads to the propagation of the polymer chain. Finally, the polymerization is terminated by a protonic reagent, and poly(carbonate) is generated.

Depolymerization Study. To investigate the depolymerization behavior of PCPC, a PCPC sample was prepared from CPO/CO_2 copolymerization (M_n = 13.0 kg/mol, $Đ$ = 1.74). The onset decomposition temperature T_d of the PCPC sample (defined by the temperature of 5% weight loss) was 231 °C via thermogravimetric analysis (TGA) (Figure S8 in the Supporting Information). Additionally, a glass transition temperature value (T_g = 73.6 °C) was determined by differential scanning calorimetry (DSC) (Figure S9 in the

https://doi.org/10.1021/acs.macromol.4c02086
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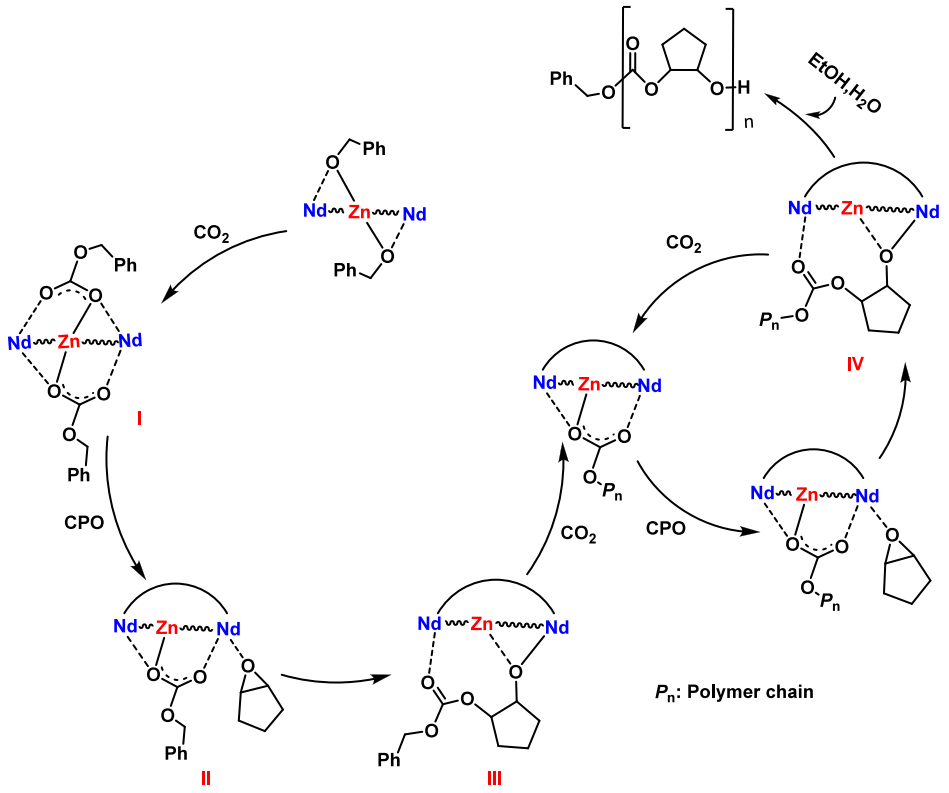
Scheme 2. A Plausible Mechanism for CPO/CO_2 Copolymerization Catalyzed by 6



Supporting Information). PCPC depolymerization was carried out under static vacuum conditions in a Schlenk flask. To our delight, all these heterometallic RE(III)-Zn(II) complexes **1**−**10** alone were able to catalyze the depolymerization, producing CPO in excellent selectivity at a catalyst loading of 0.2 mol % at 160 °C (Table S7, entries 1−10). Among them, **6** showed the highest activity. As shown in Table 3, when the temperature was decreased to 140 °C, complete and selective depolymerization to CPO could also be achieved in 24 h (Table 3, entry 3). Of great importance, depolymerization operation at 200 °C accelerated the reaction and still maintained excellent selectivity (Table 3, entry 5), indicating good high-temperature tolerance of the catalyst. The depolymerization selectivity was higher than that of [Cr(III)-(salen)Cl] complex/PPN-N_3 under the depolymerization temperature of 200 °C.[53] In addition, the depolymerization of PCPC with different molecular weights catalyzed by complex **6** was further investigated (Table S8, entries 1−5). It is observed that the molecular weights have a negligible effect on the PCPC depolymerization.

Table 3. Depolymerization of PCPC with 6[a]

entry	T/°C	t/h	conv.[b] (%)	CPO selectivity[b](%)	*cis*-CPC selectivity[b](%)
1	120	64	81	97	3
2	140	24	>99	>99	
3	160	4	>99	>99	
4	180	3	>99	>99	
5	200	40 min	>99	>99	

[a]Reactions were performed with a PCPC repeating unit/**6** molar ration of 500/1, 0.10 g of PCPC (M_n = 13.0 kg/mol, $Đ$ = 1.74). [b]Determined by ^{1}H NMR spectroscopy.

Depolymerization Process Study. In order to get more insight into the depolymerization mechanism, we conducted kinetic studies by use of thermogravimetric analysis (TGA). The kinetic profiles were obtained by calculating the initial reaction rate coefficient (k_{obs}) at different catalyst concentrations. To determine the order for **6**, depolymerizations were carried out using $[PCPC]_0$:$[6]_0$ from 100:1 to 500:1 (Figure 4a). The catalyst order of 1.04 was deduced from plotting the natural logarithm of the calculated k_{obs} versus the natural logarithm of the catalyst concentration curve, indicating a first order for **6** (Figure 4b). An exponential fit was obtained by plotting the mass loss against reaction time, indicating a first-order dependence on PCPC (Figures S12−S16). Therefore, the PCPC depolymerization rate could be derived as $\nu = k_d[\text{catalyst}]^1[PCPC]^1$. Additionally, the depolymerization activation barrier was calculated using an Arrhenius plot. Plots of $\ln(k_{obs})$ against the inverse temperature (1/T) were in a good linear relationship (Figure 5b). As a result, the activation barrier of PCPC depolymerization was 129.4 ± 1.7 kJ/mol. Furthermore, a polymerization thermodynamic study showed thermodynamic parameters of ΔH_p° = −19.4 kJ/mol and ΔS_p° = 2.6 J/mol/K and a ceiling temperature (T_c) of 209 °C (Table S3, Figure S7), reflecting feasibility for chemical recycling under mild depolymerization conditions.[54]

To reveal the depolymerization mechanism, a representative PCPC sample with M_n of 13.0 kg/mol ($Đ$ = 1.74) was depolymerization with **6**. Conversion, selectivity, and molecular weight changes over time were measured by ^{1}H NMR and GPC tests. ^{1}H NMR spectra showed that there was no CPO generation in the initial 0.3 h, suggestive of a high energy barrier during the induction period (Figure 6a). TGA showed that the induction period could be shortened by raising the depolymerization temperature. By monitoring the molecular

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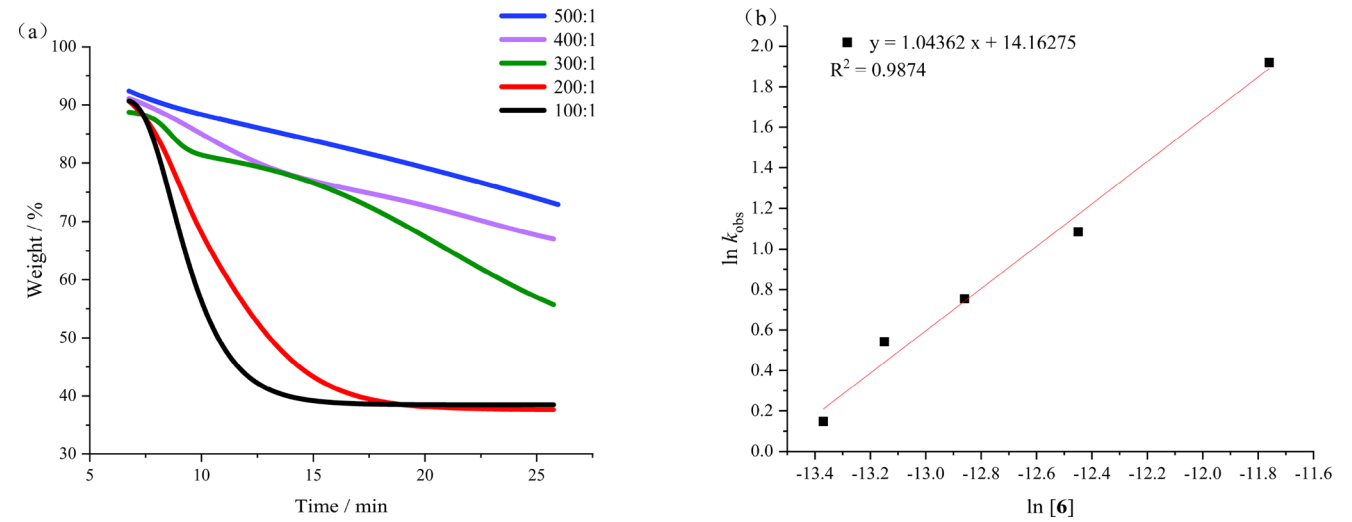

Figure 4. (a) Weight % vs time data for the depolymerization of PCPC under different catalyst concentrations ($[PCPC]_0$:$[\mathbf{6}]_0$ (from 100:1 to 500:1). (b) Double logarithmic plot of k_{obs} vs concentration of **6**.

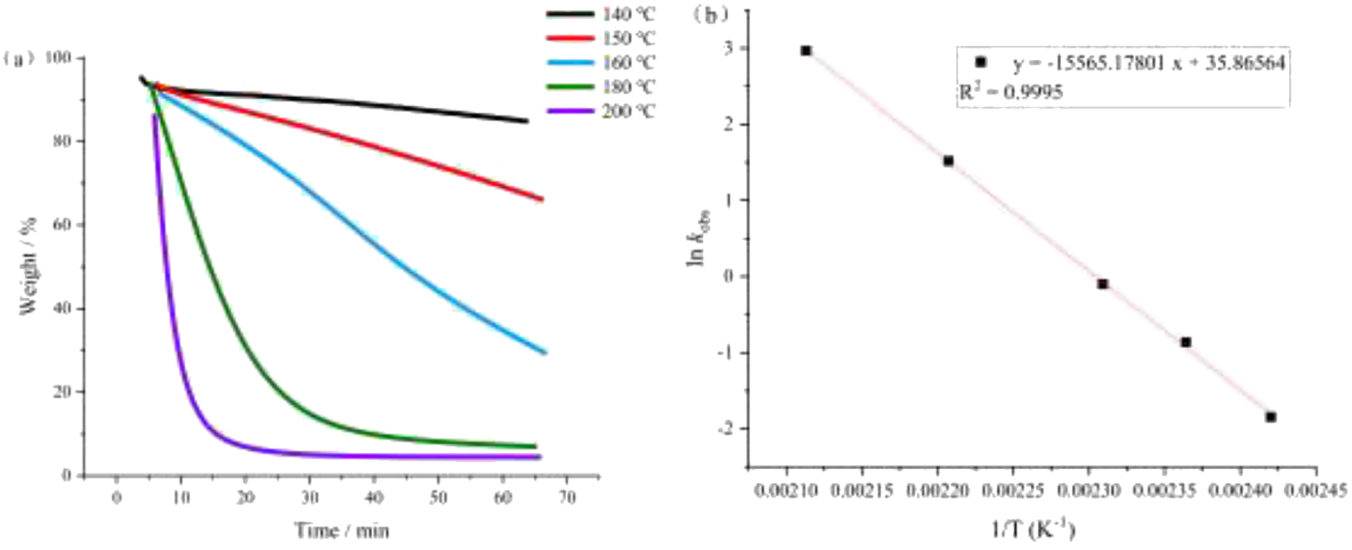

Figure 5. (a) PCPC depolymerizations using **6** (1:500) at the temperature range from 140 to 200 °C. (b) Arrhenius plot for PCPC depolymerization ($\ln(k_{obs})$ vs 1/T) using data collected from 140 to 200 °C.

weights of the polymer during degradation, it is found that the molecular weights of the polymer decreased rapidly (from M_n = 13.0 kg/mol to M_n = 8.1 kg/mol), and the molecular weight distribution became broader (from $Đ$ = 1.74 to $Đ$ = 1.91) (Figure 6b), indicative of a random chain decomposition process.[34] The depolymerized products of a representative PCPC sample (M_n = 13.0 kg/mol, $Đ$ = 1.74) decayed at 140 °C for 4 h were analyzed by MALDI-TOF. As shown in Figure 7, the major series separated by 128 mass units corresponded to the alternating copolymer with dihydroxyl groups, the minor series were generated from further dehydration of hydroxyl chain ends, and the middle series of peaks resulted from the *p-tert*-butyl benzyloxy group. On the basis of these observations, it was deduced that the random chain-breaking process of polymer took place in the presence of the catalyst, and the initial concentration of the reactive hydroxyl end group was too low to promote the backbiting reaction (to generate CPO) because of chain folding and winding.[55] Therefore, the depolymerization process could be divided into two steps: the first stage was chain scission, and the second stage was chain backbiting. This depolymerization process was very similar to that reported by the Wu group.[34]

Understanding the Depolymerization. On the basis of the above experiment results and the previous reports,[34,56] a possible chemical depolymerization process is proposed in Scheme 3. During the initiation period, the long PCPC chains were broken into short chains through chain scissions in two ways in the presence of **6**. One way was the deprotonation of hydroxyl end groups by a benzyloxy group ($-CH_2Ph$) in the state of I to form an alkoxo-ended polymer chain III, in which the polymer alkoxide was coordinated to the electron-deficient Zn^{2+} center of catalyst **6**, and the neighboring electron-rich carbonyl group interacted with Nd^{3+}. The other way was the random chain scission initiated by the nucleophilic attack of the benzyloxy group on the carbonate unit in state II, which also led to the generation of III. Subsequently, the alkoxide backbiting reaction taking place at the adjacent β-methine carbon led to the release of the CPO molecule as shown in IV, along with the formation of a carbonate anion stabilized by the Nd/Zn species V. Decarboxylation of the carbonate chain end

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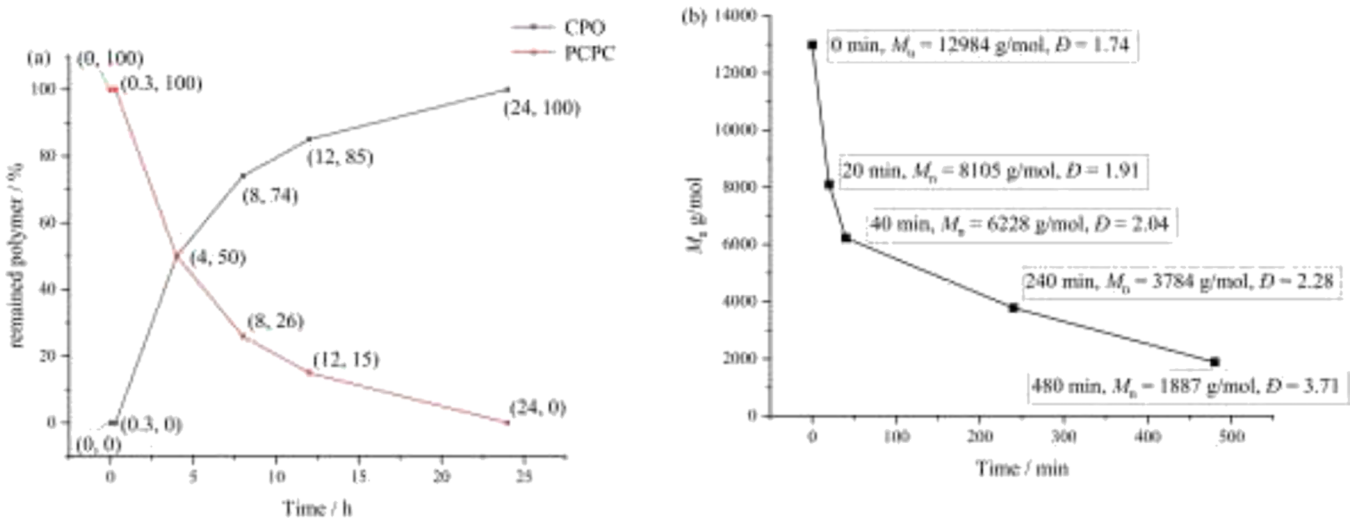

Figure 6. (a) Plots of the percentage of remained polymer and produced monomer as a function of the depolymerization time calculated from ^{1}H NMR data. (b) Molecular weights and molecular weight distributions against depolymerization time.

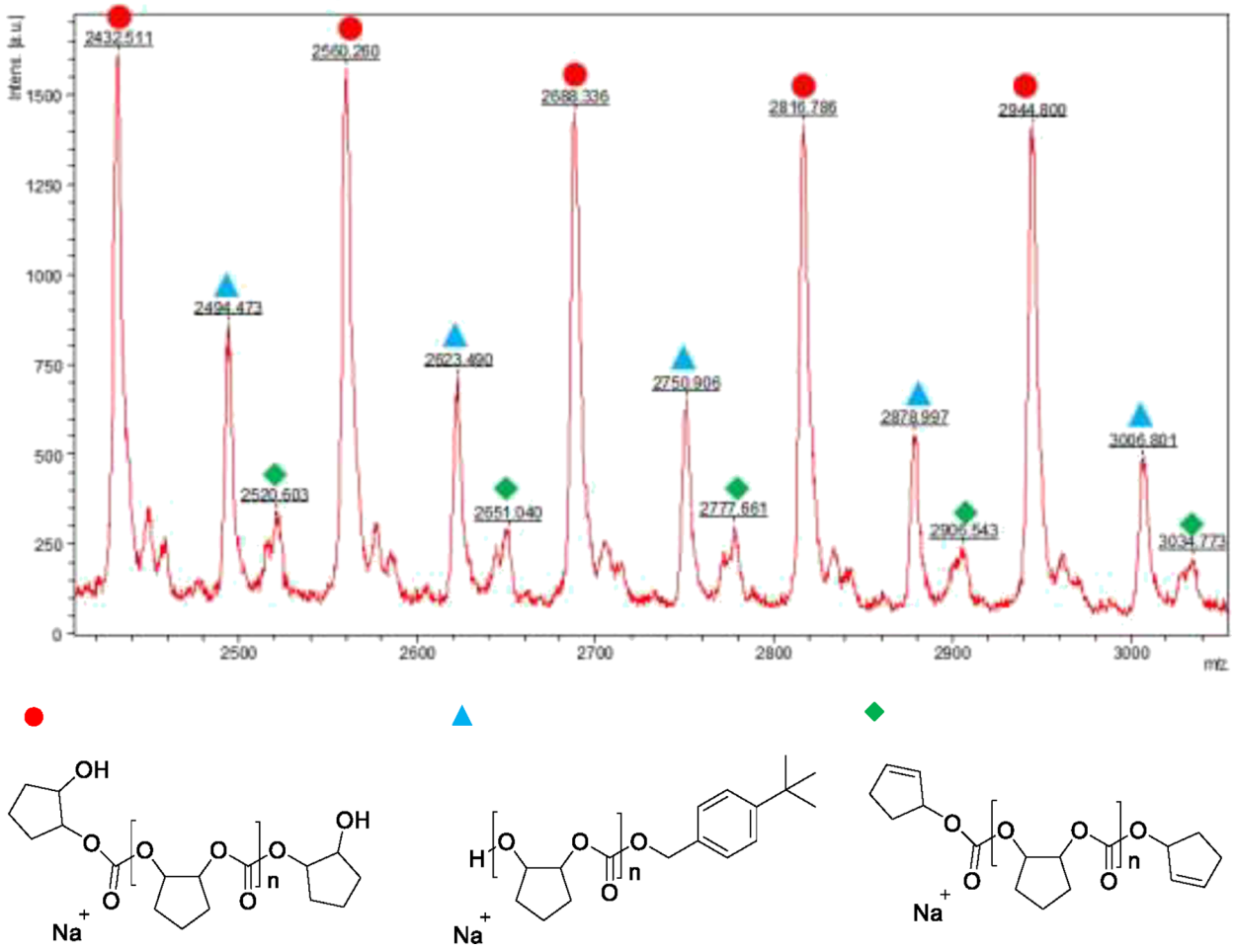

Figure 7. MALDI-TOF mass spectra of depolymerization products. Depolymerization conditions: 140 °C, 4 h, [CPO]:[**6**] = 500:1.

rather than the nucleophilic attack at methine carbon in V generated CO_2. Thus, the alternating backbiting of the alkoxide chain end and the decarboxylation of the carbonate chain end proceeded smoothly to establish a depolymerization cycle.

Chemical Recycling of PCPC. To demonstrate the practical application of this depolymerization method, a scale-up depolymerization of PCPC was carried out. The PCPC sample (2.0 g, 13.0 kg/mol) was doped with 0.2 mol % of **6** at 160 °C. It was found that CPO was recovered in 99% NMR yield and ca. 93% isolated yield (Figure S10 in the Supporting Information). The recovered CPO could be used directly as the starting material to copolymerize with CO_2 to

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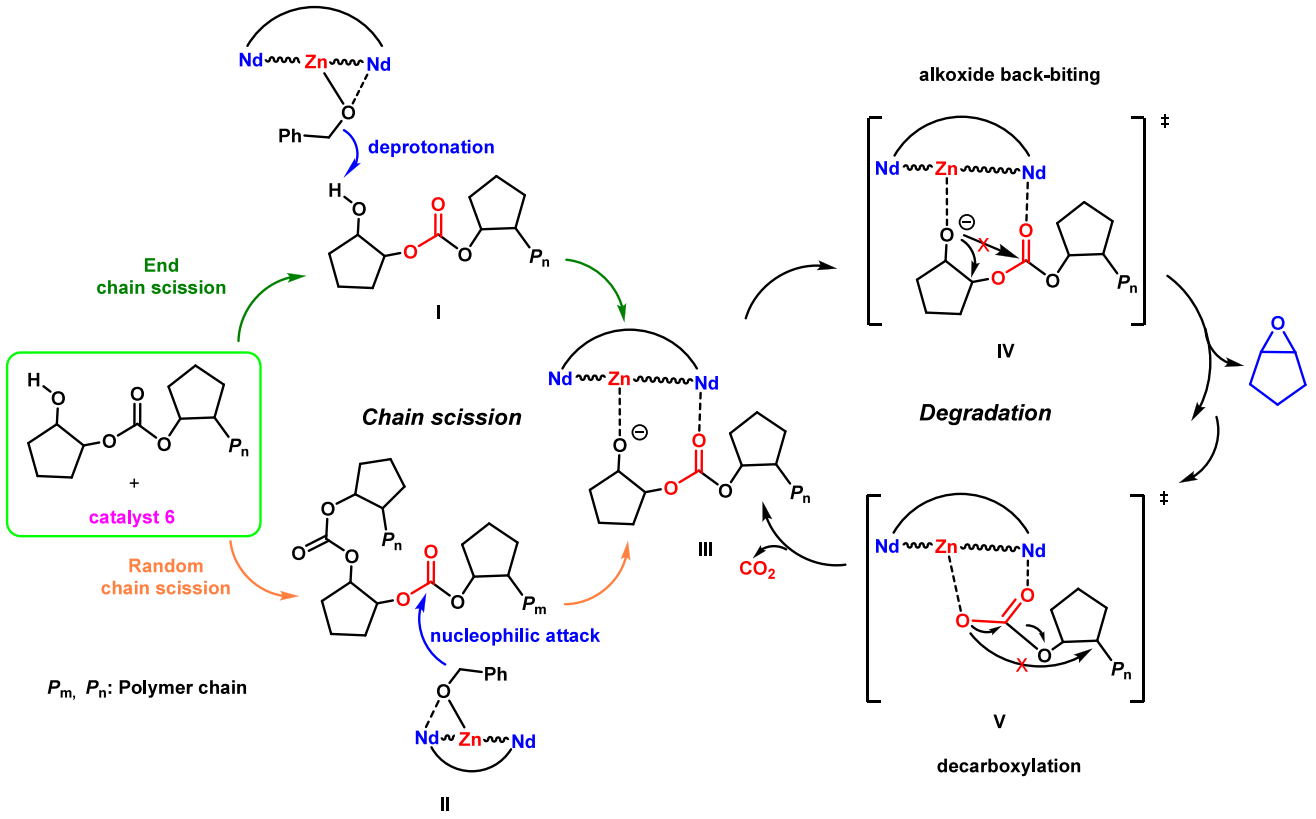
Scheme 3. A Plausible Mechanism for the Depolymerization of PCPC to CPO Catalyzed by 6



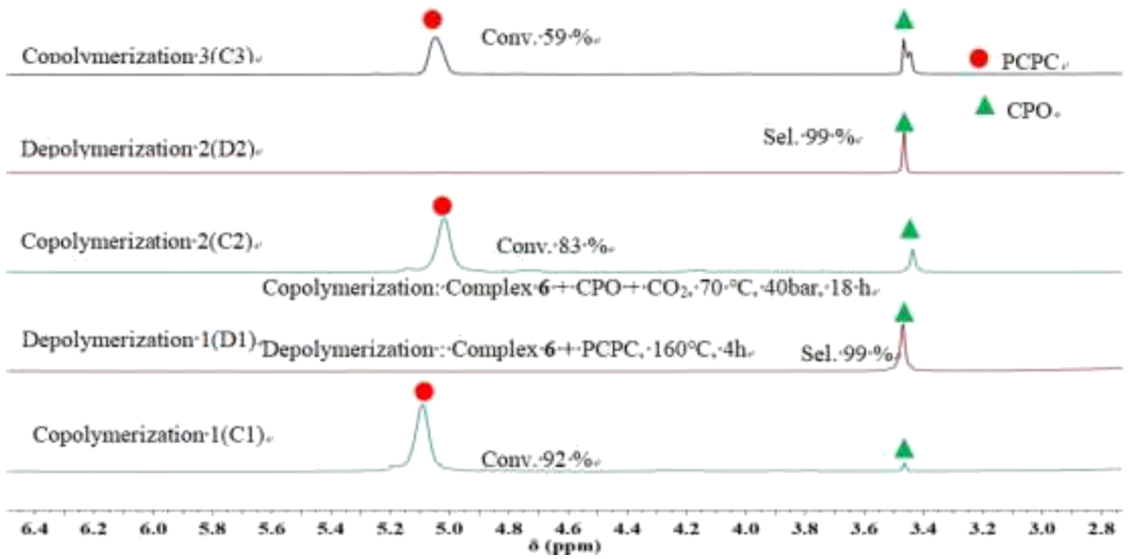


Figure 8. Reusability of the heterometallic Nd(III)/Zn(II) complex in the polymerization-depolymerization process of PCPC.

afford PCPC. This interesting result manifested that this catalyst could mediate a circular monomer−polymer−monomer life cycle of PCPC. Furthermore, the polymerization−depolymerization−polymerization experiments showed that an efficient one-pot cycling process could be established by simply varying the reaction temperature. The copolymerization at 70 °C formed 92% PCPC after 18 h of reaction under 40 bar of CO_2 pressure (C1, Figure 8). Simply elevating the temperature to 160 °C led to complete depolymerization of PCPC after 4 h (D1, Figure 8). Subsequently, in the same reaction system, introducing CO_2 and setting the temperature at 70 °C produced 83% PCPC under the same copolymerization conditions (C2, Figure 8). Interestingly, changing the temperature and introducing CO_2 resulted in repeating depolymerization and copolymerization for at least 3 cycles (D2 and C3, Figure 8). Remarkably, no more catalyst was added after each cycle, indicative of good catalyst reusability.

CONCLUSIONS

In summary, a kind of heterometallic RE(III)-Zn(II) complexes supported by the phenylenediamine-bridged triphenols were explored in the copolymerization of CPO

https://doi.org/10.1021/acs.macromol.4c02086
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and CO_2 as well as in the depolymerization of PCPC back to CPO. These heterometallic RE(III)-Zn(II) complexes were active for CPO/CO_2 copolymerization under mild polymerization conditions, affording pure PCPC with >99% poly(carbonate) selectivity. More importantly, only in the presence of such heterometallic RE(III)-Zn(II) catalysts alone, PCPC could be chemically depolymerized to the original monomer CPO with an excellent isolated yield (up to 93% isolated yield) by simply raising the reaction temperature around 160 °C. This catalyst system represents a promising protocol for producing recyclable polycarbonate PCPO and closing the monomer−polymer−monomer cycle. Further studies on the application of such a kind of heterometallic complexes in catalysis are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02086.

Experimental details and NMR spectra of the heterometallic complexes and polymer samples (PDF)

Accession Codes

CCDC 2373410 for complex **3** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from National Key R&D Program of China (2022YFF0709802), National Natural Science Foundation of China (22271205), and PAPD is gratefully acknowledged.

■ REFERENCES

(1) Van der Ploeg, F. Natural Resources: Curse or Blessing? *J. Econ. Lit.* **2011**, *49*, 366−420.

(2) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. Plastic Waste Inputs from Land into the Ocean. *Science* **2015**, *347*, 768−771.

(3) Gandini, A.; Lacerda, T. M.; Carvalho, A. J.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116*, 1637−1669.

(4) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540*, 354−362.

(5) ODea, R. M.; Willie, J. A.; Epps, T. H. 100th Anniversary of Macromolecular Science Viewpoint: Polymers from Lignocellulosic Biomass. Current Challenges and Future Opportunities. *ACS Macro Lett.* **2020**, *9*, 476−493.

(6) Tang, X.; Hong, M.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. The Quest for Converting Biorenewable Bifunctional α-Methylene-γ-Butyrolactone into Degradable and Recyclable Polyester: Controlling Vinyl-Addition/Ring-Opening/Cross-Linking Pathways. *J. Am. Chem. Soc.* **2016**, *138*, 14326−14337.

(7) Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y.-X. A Synthetic Polymer System with Repeatable Chemical Recyclability. *Science* **2018**, *360*, 398−403.

(8) Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; Kaitz, J. A.; Mar, B. D.; May, P. A.; White, S. R.; Martínez, T. J.; Boydston, A. J.; Moore, J. S. Mechanically Triggered Heterolytic Unzipping of a Low-Ceiling-Temperature Polymer. *Nat. Chem.* **2014**, *6*, 623−628.

(9) MacDonald, J. P.; Shaver, M. P. An Aromatic/Aliphatic Polyester Prepared Via Ring-Opening Polymerisation and Its Remarkably Selective and Cyclable Depolymerisation to Monomer. *Polym. Chem.* **2016**, *7*, 553−559.

(10) Schneiderman, D. K.; Vanderlaan, M. E.; Mannion, A. M.; Panthani, T. R.; Batiste, D. C.; Wang, J. Z.; Bates, F. S.; Macosko, C. W.; Hillmyer, M. A. Chemically Recyclable Biobased Polyurethanes. *ACS Macro Lett.* **2016**, *5*, 515−518.

(11) Yuan, J.; Xiong, W.; Zhou, X.; Zhang, Y.; Shi, D.; Li, Z.; Lu, H. 4-Hydroxyproline-Derived Sustainable Polythioesters: Controlled Ring-Opening Polymerization, Complete Recyclability, and Facile Functionalization. *J. Am. Chem. Soc.* **2019**, *141*, 4928−4935.

(12) Lu, X.-B.; Liu, Y.; Zhou, H. Learning Nature: Recyclable Monomers and Polymers. *Chem.—Eur. J.* **2018**, *24*, 11255−11266.

(13) Hong, M.; Chen, E. Y.-X. Future Directions for Sustainable Polymers. *Trends Chem.* **2019**, *1*, 148−151.

(14) Tang, X.; Chen, E. Y.-X. Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters. *Chem.* **2019**, *5*, 284−312.

(15) Poland, S. J.; Darensbourg, D. J. A Quest for Polycarbonates Provided Via Sustainable Epoxide/CO_2 Copolymerization Processes. *Green Chem.* **2017**, *19*, 4990−5011.

(16) Scharfenberg, M.; Hilf, J.; Frey, H. Functional Polycarbonates from Carbon Dioxide and Tailored Epoxide Monomers: Degradable Materials and Their Application Potential. *Adv. Funct. Mater.* **2018**, *28*, No. 1704302.

(17) Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C. Advances in the Use of CO_2 as A Renewable Feedstock for the Synthesis of Polymers. *Chem. Soc. Rev.* **2019**, *48*, 4466−4514.

(18) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004**, *126*, 11404−11405.

(19) Auriemma, F.; De Rosa, C.; Di Caprio, M. R.; Di Girolamo, R.; Ellis, W. C.; Coates, G. W. Stereocomplexed Poly(Limonene Carbonate): A Unique Example of the Cocrystallization of

Amorphous Enantiomeric Polymers. *Angew. Chem., Int. Ed.* **2015**, *54*, 1215−1218.
(20) Hauenstein, O.; Agarwal, S.; Greiner, A. Bio-Based Polycarbonate as Synthetic Toolbox. *Nat. Commun.* **2016**, *7*, 11862.
(21) Li, C. L.; Sablong, R. J.; Koning, C. E. Chemoselective Alternating Copolymerization of Limonene Dioxide and Carbon Dioxide: A New Highly Functional Aliphatic Epoxy Polycarbonate. *Angew. Chem., Int. Ed.* **2016**, *55*, 11572−11576.
(22) Tsai, F.-T.; Wang, Y.; Darensbourg, D. J. Environmentally Benign CO_2-Based Copolymers: Degradable Polycarbonates Derived from Dihydroxybutyric Acid and Their Platinum-Polymer Conjugates. *J. Am. Chem. Soc.* **2016**, *138*, 4626−4633.
(23) Kindermann, N.; Cristòfol, A.; Kleij, A. W. Access to Biorenewable Polycarbonates with Unusual Glass Transition Temperature (T_g) Modulation. *ACS Catal.* **2017**, *7*, 3860−3863.
(24) Darensbourg, D. J.; Yeung, A. D. Kinetics of the (Salen)Cr(III)-and (Salen)Co(III)-Catalyzed Copolymerization of Epoxides with CO_2, and of the Accompanying Degradation Reactions. *Polym. Chem.* **2015**, *6*, 1103−1117.
(25) Inoue, S.; Koinuma, H.; Tsuruta, T. Copolymerization of Carbon Dioxide and Epoxide. *J. Polym. Sci. Part B* **1969**, *7*, 287−292.
(26) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. Enantiomerically-Enriched Organic Reagents Via Polymer Synthesis: Enantioselective Copolymerization of Cycloalkene Oxides and CO_2 Using Homogeneous, Zinc-Based Catalysts. *Chem. Commun.* **2000**, 2007−2008.
(27) Darensbourg, D. J.; Chung, W.-C.; Wilson, S. J. Catalytic Coupling of Cyclopentene Oxide and CO_2 Utilizing Bifunctional (Salen)Co(III) and (Salen)Cr(III) Catalysts: Comparative Processes Involving Binary (Salen)Cr(III) Analogs. *ACS Catal.* **2013**, *3*, 3050−3057.
(28) Liu, Y.; Ren, W.-M.; Liu, J.; Lu, X.-B. Asymmetric Copolymerization of CO_2 with *meso*-Epoxides Mediated by Dinuclear Cobalt(III) Complexes: Unprecedented Enantioselectivity and Activity. *Angew. Chem., Int. Ed.* **2013**, *52*, 11594−11598.
(29) Ellis, W. C.; Jung, Y.; Mulzer, M.; Di Girolamo, R.; Lobkovsky, E. B.; Coates, G. W. Copolymerization of CO_2 and *meso* Epoxides Using Enantioselective β-Diiminate Catalysts: A Route to Highly Isotactic Polycarbonates. *Chem. Sci.* **2014**, *5*, 4004−4011.
(30) Hua, Y.-Z.; Yang, X.-C.; Liu, M.-M.; Song, X.; Wang, M.-C.; Chang, J.-B. Asymmetric Copolymerization of Cyclopentene Oxide and CO_2 Using a Dinuclear Zinc-AzePhenol Catalyst: Enlightened by DFT Calculations. *Macromolecules* **2015**, *48*, 1651−1657.
(31) Huang, L.-S.; Tsai, C.-Y.; Chuang, H.-J.; Ko, B.-T. Copolymerization of Carbon Dioxide with Epoxides Catalyzed by Structurally Well-Characterized Dinickel Bis(Benzotriazole Iminophenolate) Complexes: Influence of Carboxylate Ligands on the Catalytic Performance. *Inorg. Chem.* **2017**, *56*, 6141−6151.
(32) Deacy, A. C.; Kilpatrick, A. F. R.; Regoutz, A.; Williams, C. K. Understanding Metal Synergy in Heterodinuclear Catalysts for the Copolymerization of CO_2 and Epoxides. *Nat. Chem.* **2020**, *12*, 372−380.
(33) Deacy, A. C.; Moreby, E.; Phanopoulos, A.; Williams, C. K. Co(III)/Alkali-Metal(I) Heterodinuclear Catalysts for the Ring-Opening Copolymerization of CO_2 and Propylene Oxide. *J. Am. Chem. Soc.* **2020**, *142*, 19150−19160.
(34) Yang, G.-W.; Wang, Y.; Qi, H.; Zhang, Y.-Y.; Zhu, X.-F.; Lu, C.; Yang, L.; Wu, G.-P. Highly Selective Preparation and Depolymerization of Chemically Recyclable Poly(Cyclopentene Carbonate) Enabled by Organoboron Catalysts. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202210243.
(35) Rosetto, G.; Vidal, F.; McGuire, T. M.; Kerr, R. W. F.; Williams, C. K. High Molar Mass Polycarbonates as Closed-Loop Recyclable Thermoplastics. *J. Am. Chem. Soc.* **2024**, *146*, 8381−8393.
(36) Darensbourg, D. J.; Wei, S.-H.; Yeung, A. D.; Ellis, W. C. An Efficient Method of Depolymerization of Poly(Cyclopentene Carbonate) to Its Comonomers: Cyclopentene Oxide and Carbon Dioxide. *Macromolecules* **2013**, *46*, 5850−5855.
(37) Liu, Y.; Zhou, H.; Guo, J.-Z.; Ren, W.-M.; Lu, X.-B. Completely Recyclable Monomers and Polycarbonate: Approach to Sustainable Polymers. *Angew. Chem., Int. Ed.* **2017**, *56*, 4862−4866.
(38) McGuire, T. M.; Deacy, A. C.; Buchard, A.; Williams, C. K. Solid-State Chemical Recycling of Polycarbonates to Epoxides and Carbon Dioxide Using a Heterodinuclear Mg(II)Co(II) Catalyst. *J. Am. Chem. Soc.* **2022**, *144*, 18444−18449.
(39) Singer, F. N.; Deacy, A. C.; McGuire, T. M.; Williams, C. K.; Buchard, A. Chemical Recycling of Poly(Cyclohexene Carbonate) Using a Di-Mg (II) Catalyst. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202201785.
(40) Yu, Y.; Ren, B.-H.; Liu, Y.; Lu, X.-B. Chemical Recycling of Poly(Cyclohexene Carbonate)s via Synergistic Catalysis. *ACS Macro Lett.* **2024**, *13*, 1099−1104.
(41) Kobylarski, M.; Berthet, J.-C.; Cantat, T. Reductive Depolymerization of Polyesters and Polycarbonates with Hydroboranes by Using a Lanthanum(III) Tris(Amide) Catalyst. *Chem. Commun.* **2022**, *58*, 2830−2833.
(42) Ma, Y.; Zhao, Z.; Chen, J.; Chen, Y.; Wang, B.; Luo, Y. Hydroborative Depolymerization of Polyesters and Polycarbonates to Diols Catalyzed by Heterogeneous Lanthanum Materials La-$(CH_2C_6H_4NMe_2\text{-}o)_3$@SBA-15. *Inorg. Chem.* **2024**, *63*, 17574−17583.
(43) Hua, L.; Li, B.; Han, C.; Gao, P.; Wang, Y.; Yuan, D.; Yao, Y. Synthesis of Homo- and Heteronuclear Rare-Earth Metal Complexes Stabilized by Ethanolamine-Bridged Bis(Phenolato) Ligands and Their Application in Catalyzing Reactions of CO_2 and Epoxides. *Inorg. Chem.* **2019**, *58*, 8775−8786.
(44) Feng, C.; Mu, D.; Zhu, X.; Wang, Y.; Yuan, D.; Yao, Y. Synthesis of Benzoxazine Functionalized Amine-Bridged Bis(Phenolato) Rare Earth Complexes and Their Application in Ring-Opening Polymerization of *rac*-Lactide. *Chin. J. Chem.* **2022**, *40*, 2516−2524.
(45) Song, Y.; Yin, K.; Chen, Y.; Zhao, B.; Zhang, Y.; Zhu, X.; Yuan, D.; Yao, Y. Synthesis of Heterometallic Rare Earth(III)-Cobalt(II) Complexes and Their Application in Alternating Copolymerization of Cyclohexene Oxide and Carbon Dioxide. *Chin. J. Chem.* **2023**, *41*, 805−813.
(46) Qin, J.; Xu, B.; Zhang, Y.; Yuan, D.; Yao, Y. Cooperative Rare Earth Metal-Zinc Based Heterometallic Catalysts for Copolymerization of CO_2 and Cyclohexene Oxide. *Green Chem.* **2016**, *18*, 4270−4275.
(47) Xu, R.; Hua, L.; Li, X.; Yao, Y.; Leng, X.; Chen, Y. Rare-Earth/Zinc Heterometallic Complexes Containing Both Alkoxy-Amino-Bis(Phenolato) and Chiral Salen Ligands: Synthesis and Catalytic Application for Copolymerization of CO_2 with Cyclohexene Oxide. *Dalton Trans.* **2019**, *48*, 10565−10573.
(48) Yao, Q.; Wang, Y.; Zhao, B.; Zhu, X.; Luo, Y.; Yuan, D.; Yao, Y. Syntheses of Heterometallic Neodymium−Zinc Complexes and Their Performance in the Copolymerization of CO_2 and Cyclohexene Oxide. *Inorg. Chem.* **2022**, *61*, 10373−10382.
(49) Yao, Q.; Chen, Y.; Wang, Y.; Yuan, D.; You, H.; Yao, Y. Alternating Copolymerization of CO_2 and Cyclohexene Oxide Initiated by Rare-Earth Metal Complexes Stabilized by *o*-Phenylenediamine-Bridged Tris(Phenolate) Ligand. *J. Rare Earths* **2022**, *40*, 1471−1479.
(50) Nakano, K.; Nozaki, K.; Hiyama, T. Asymmetric Alternating Copolymerization of Cyclohexene Oxide and CO_2 with Dimeric Zinc Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 5501−5510.
(51) Trott, G.; Garden, J. A.; Williams, C. K. Heterodinuclear Zinc and Magnesium Catalysts for Epoxide/CO_2 Ring Opening Copolymerizations. *Chem. Sci.* **2019**, *10*, 4618−4627.
(52) Romain, C.; Garden, J. A.; Trott, G.; Buchard, A.; White, A. J. P.; Williams, C. K. Di-Zinc-Aryl Complexes: CO_2 Insertions and Applications in Polymerisation Catalysis. *Chem.—Eur. J.* **2017**, *23*, 7367−7376.
(53) Yu, Y.; Gao, B.; Liu, Y.; Lu, X.-B. Efficient and Selective Chemical Recycling of CO_2-Based Alicyclic Polycarbonates Via Catalytic Pyrolysis. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202204492.

https://doi.org/10.1021/acs.macromol.4c02086
Macromolecules 2024, 57, 10041−10052

(54) Cao, Q.; Tu, Y.-M.; Fan, H.-Z.; Shan, S.-Y.; Cai, Z.; Zhu, J.-B. Torsional Strain Enabled Ring-Opening Polymerization towards Axially Chiral Semiaromatic Polyesters with Chemical Recyclability. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202400196.
(55) Yu, Y.; Fang, L.-M.; Liu, Y.; Lu, X.-B. Chemical Synthesis of CO_2-Based Polymers with Enhanced Thermal Stability and Unexpected Recyclability from Biosourced Monomers. *ACS Catal.* **2021**, *11*, 8349−8357.
(56) Smith, M. L.; McGuire, T. M.; Buchard, A.; Williams, C. K. Evaluating Heterodinuclear Mg(II)M(II) (M = Mn, Fe, Ni, Cu, and Zn) Catalysts for the Chemical Recycling of Poly(Cyclohexene Carbonate). *ACS Catal.* **2023**, *13*, 15770−15778.

NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on October 30, 2024. Figure 4 was replaced and the corrected version was reposted on October 31, 2024.

https://doi.org/10.1021/acs.macromol.4c02086
Macromolecules 2024, 57, 10041−10052