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Functionalized Polyesters via Stereoselective Electrochemical Ring-Opening Polymerization of *O*-Carboxyanhydrides

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KEYWORDS: living polymerization, electrochemical polymerization, polyester, *O*-carboxyanhydride

ABSTRACT: Ring-opening polymerization is used to prepare polyesters with precisely controlled molecular weights, molecular weight distributions, and tacticities. Herein, we report a newly developed Co/Zn catalytic system that can be activated by an electrical current to mediate efficient ring-opening polymerization of enantiopure *O*-carboxyanhydrides, allowing for the synthesis of isotactic functionalized polyesters with high molecular weights (>140 kDa) and narrow molecular weight distributions ($M_w/M_n < 1.1$). We also demonstrate that these catalysts can be used for stereoselective ring-opening polymerization of racemic *O*-carboxyanhydrides to synthesize syndiotactic or stereoblock copolymers with different glass transition temperatures compared with their atactic counterparts.

Electrochemical reactions are among the most energy-efficient chemical reactions: the application of an electrical potential to reactants enables the addition or removal of electrons, which is the fundamental driving force in chemistry. In efforts to control cationic¹ and radical polymerizations,² electricity has been used as an external stimulus to temporally regulate system variables such as monomer reactivity.^{1,2e} Compared to electricity, light is a less energy efficient stimulus because photonic flux decreases exponentially with the depth of the reaction medium, as dictated by the Beer-Lambert law.³ However, electrochemical control of other types of polymerizations, such as ring-opening polymerization (ROP), remains a challenge. Although metal-catalyzed ROP is an efficient, industrially applicable method for synthesizing degradable and biocompatible polyesters, and many well-defined metal catalysts have been developed to mediate stereoselective ROP of cyclic lactones,⁴ electricity was only used to activate the metal complex used in ROP.⁵ Additionally, to our knowledge, stereoselective electrochemical polymerization has never been achieved.

To fill the above-mentioned gaps, we have developed a new Co/Zn catalytic system that can be activated by an electrical current to mediate efficient ROP of enantiopure *O*-carboxyanhydrides (OCAs), allowing for the synthesis of isotactic polyesters with high MWs and narrow MW distributions ($M_w/M_n < 1.1$, Scheme 1). The use of OCAs, which are highly active alternatives to lactide and lactone monomers,⁶ enabled the generation of polyesters with various pendant side-chain functional groups. We note that current synthetic methods involving organocatalysts result in uncontrolled polymerization including epimerization for some OCAs (e.g., **2** and **5** in Scheme 1), and unpredictable MWs.^{6d,7} In addition, we show

that by judicious selection of ligands for the Co and Zn complexes, we could use this electrochemical ROP (eROP) for stereoselective polymerization of racemic OCAs to prepare syndiotactic or stereoblock copolymers.

Scheme 1. Electrochemical Ring-Opening Polymerization of *O*-Carboxyanhydrides by Co/Zn Complexes

- High-MW polymers (>140 kDa)
- No epimerization
- Electrochemically stereoselective ring-opening polymerization
- Living polymerization ($\bar{D} < 1.1$)
- Simple setup in mild reaction conditions

The discovery of Co/Zn catalysts for eROP originated from studies to find alternatives to Ni/Ir photocatalysts in our photoredox ROP protocol.^{6d} Specifically, **Co-1** (i.e., (bpy)Co[N(SiMe₃)₂]₂, bpy = 2,2'-bipyridine, Scheme 1) could replace both Ni/Ir photocatalysts and mediated ROP of OCA **L-1** at 0 °C in the presence of **Zn-1** and benzyl alcohol ([**L-1**]/[**Co-1**]/[**Zn-1**]/[BnOH] = 700/1/1/1) and light (300–500 nm) to afford poly(**L-1**) with a M_n of 107.8 kDa (M_n , number-average MW), which is close to the calculated MW ($M_{W,cal}$, 118.5 kDa), and a narrow $\bar{D}$ of 1.04 ($\bar{D}$ =

Table 1. Optimization of Conditions for Electrochemical Ring-Opening Polymerization of *O*-Carboxyanhydrides ^a

Entry	Conditions	FR	Temp (°C)	Time (h)	Conv (%) ^b	<i>M_n</i> (kDa) ^c	<i>MW_{cal}</i> (kDa)	<i>Đ</i> ^c
1	As shown	700	0	2	100	103.5	103.7	1.06
2	As shown	900	0	2	100	135.1	133.3	1.02
3	As shown	900	r.t.	2	100	69.2	133.3	1.04
4	No Co-1	700	0	2	53	52.5	103.7	1.22
5	No Zn-1	700	0	2	33	65.8	103.7	1.74
6	No BnOH	700	0	2	42	34.4	103.7	1.44
7	No current	700	0	4	35	49.6	103.7	1.21
8	Recycled Mg anode ^d	700	0	2	100	105.7	103.7	1.04

^a Abbreviations: OCA, *O*-carboxyanhydride; FR, OCA/Zn catalyst ratio in the feed; Temp, temperature; Conv, monomer conversion; *M_n*, number-average molecular weight; *MW_{cal}*, molecular weight calculated on the basis of the FR ratio (assuming 100% monomer conversion); *Đ*, molecular weight distribution; r.t., room temperature. [**Co-1**]/[**Zn-1**]/[BnOH] = 1/1/1; [L-1] = 130.2 mM in all entries. ^b Determined from the intensity of the peak at 1805 cm⁻¹ in the Fourier transform IR spectrum, which corresponds to the anhydride group of the OCA. ^c Determined by gel permeation chromatography. ^d For details of recycling Mg anode, see Figures S8 and S9.

M_w/*M_n*, where *M_w* is weight-average MW, all determined by gel permeation chromatography [GPC]; Table S1). During our catalyst screening, we noticed that Co^I and Co^{III} and most Co^{II} complexes were much less effective than **Co-1** (Figure S1). By means of a series of control experiments (Table S1), we demonstrated that each of the catalytic components was necessary.

Scheme 2. Proposed Mechanism of Electrochemical Ring-Opening Polymerization of *O*-carboxyanhydrides

The success of the Co/Zn-mediated photoredox ROP at 0 °C (compared with -15 °C for Ni/Ir/Zn system) without exogenous Ir- or Ru-based polypyridyl photocatalysts inspired us to explore whether this reaction could be modulated electrochemically. Indeed, the cyclic voltammogram (CV) of **Co-1** exhibited a reversible redox wave with an *E*_{1/2}^{red} (Co^{III}/Co^{II}) of 0.769 V versus SCE (saturated calomel electrode); whereas the CV of the L-1/**Co-1**/**Zn-**

1/BnOH reaction mixture (1 equiv of each) also showed a reversible redox wave with an *E*_{1/2}^{red} (Co^{IV}/Co^{III}) of 1.251 V versus SCE (Figure S2). Given the oxidation potential of the amino acid carboxylate (*E*_{1/2}^{red} = 0.832 V versus SCE for *N*-(carbobenzoyloxy)-L-phenylalanine, Figure S2) and literature reports,⁷ we thus hypothesized that the redox status of the Co complex could be readily manipulated via the application of an electric current for decarboxylation. Specifically, anodic oxidation of **Co-1** could lead to the formation of a **Co-1**/OCA intermediate, which could undergo cathodic reduction resulting in decarboxylation, followed by transmetalation with a Zn complex to generate a reactive Zn-alkoxide terminus for polymerization (Scheme 2).⁸

We began our studies of eROP of L-1 under galvanostatic (constant current) conditions in an undivided cell and thoroughly evaluated the electrode materials, electrolyte, current, and temperature, aiming to avoid a cumbersome electrochemical reaction setup from an industrial scale-up standpoint. We found that Mg was optimal for the anode (working electrode) and that Pt was best for the cathode (counter electrode, Figure S3). THF proved to be the ideal solvent (Table S2). The use of tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M in THF) as the electrolyte led to better control of the polymerization than other tetraalkylammonium salts, whereas Li and Mg salts gave unsatisfactory results (Table S3). A current of 4 mA was optimal when the OCA concentration was approximately 0.15 M; lower current led to decreased monomer conversion (Table S4). Better polymerization results (i.e. *M_n* value close to the calculated MW) were obtained at 0 °C than at room temperature (compare entries 2 and 3 in Table 1). We also demonstrated that each of the catalytic components was necessary (entries 4–7; prolonged reaction time would not improve conversions of **1**). Unsurprisingly, polymerization was incomplete in the absence of current (entry 7). Notably, variation of the **Co-1** concentration had little effect on obtained polymers' MWs (Table S5). At a constant

Figure 1. Electrochemically controlled polymerization of L-1 ($[Co-1]/[Zn-1]/[BnOH] = 1/1/1$, $[L-1] = 130.2$ mM in all studies; all reactions are performed at 0 °C using Mg(+)/Pt(-) electrodes and 4mA current). (a) Plots of M_n and MW distribution (M_w/M_n) of poly(L-1) versus $[L-1]/[Zn-1]$ ratio at 0 °C. (b) Logarithmic plots of L-1 conversion versus time at various Zn-1 concentrations. (c) Dependence of the rate of L-1 conversion on the presence or absence of the current (electricity) applied to the reaction. The dashed lines indicate periods during which no current was applied; solid lines indicate the period during which a current of 4 mA was applied.

current of 4 mA, the polymerization proceeded smoothly within 2 h at 0 °C when Mg was used as the anode; under these conditions, the M_n of the poly(L-1) product increased linearly with initial $[L-1]/[Co-1]/[Zn-1]$ ratio up to 1000/1/1 (Figures 1a and S4). Note that the D values of all the obtained polymers were less than 1.1 (Table S6). No epimerization of the α -methine hydrogen was observed in the homodecoupled 1H NMR spectrum of high-MW poly(L-1) ($M_n = 135.1$ kDa, $D = 1.02$), which suggests that the application of a current did not induce epimerization during the eROP (Figure S5). We note that no THF could be polymerized under the optimized eROP conditions in the absence of **1** (Figure S6). The addition of 2,2-diphenyl-1-picrylhydrazyl, a radical scavenger, effectively disrupted chain propagation with a monomer conversion of 27.8% in 2 h. Additionally, first-order reaction kinetics were observed for eROP of L-1 at 0 °C (Figures 1b and S7). The kinetics of the eROP of L-1 can be described by the following equation:

$$-d[L-1]/dt = k_p [Co-1] [Zn-1] [L-1] \quad (1)$$

where k_p is the rate constant for chain propagation (Figure S7).

We noticed that after eROP, the surface of the Mg anode was contaminated by oxidized TBAH, which was confirmed by energy-dispersive X-ray spectroscopy and scanning electron microscopy (Figures S8 and S9). The salt on the anode surface could be cleaned by scraping it with a blade⁹ and washing it with acetone; and the cleaned anode could be reused for eROP (Table 1, entry 8). Energy-dispersive X-ray spectroscopic studies of the Pt cathode after eROP indicated the absence of TBAH salts (Figure S8). Additionally, dialyzing the polymer solution against THF readily removed nearly all metal complexes and TBAH, as indicated by inductively coupled plasma mass spectrometry (Table S7).

We examined whether Co/Zn-mediated eROP allows for the temporal modulation of polymerization rates. At a $[L-1]/[Zn-1]$ ratio of 700, applying current (4 mA) to the reaction solution for 15 min resulted in 27% conversion of L-1. When the current was then turned off, the conversion of L-1 slightly increased to 29% over 30 min. Once the current was resumed, the polymerization revived with a conversion of L-1 to 82% over 60 min (Figure 1c, blue line). Such “electricity on-off” eROP was repeated twice: each time the current was switched off, the ROP almost stopped, and it proceeded again rapidly when the current was resumed (Figure 1c, red line).

Next we evaluated the generality of our eROP protocol by testing it on various OCA monomers (L-2–L-5, Scheme 1). In all cases, polymers were obtained with decent polymerization control of monomer conversions and D values, as was the case for poly(L-1) (Table S8, entries 1–10). None of the monomers epimerized during the eROP (Figures S10–S13). Note that considerable epimerization of L-5, which has an acidic α -methine proton, is often observed in ROP,^{7a, 7c, 10} but this was not so in our system (Figure S13). As anticipated, diblock copolymers such as poly(**1-b-3**) could be readily prepared by sequential addition of the monomers, with remarkable control of the M_n and D values (Figure S14).

Scheme 3. Co/Zn Complex-Mediated Stereoselective Electrochemical Ring-Opening Polymerization of *rac*-1

Table 2. Stereoselective Electrochemical Ring-Opening Polymerization of Racemic *O*-Carboxyanhydrides Mediated by Co/Zn Complexes^a

Entry	OCA (FR)	Co/Zn	Conv (%) ^b	M_n (kDa) ^c	MW_{cal} (kDa)	D ^c	P_m ^d
1	<i>rac</i> -1 (300)	Co-1/ Zn-2	100	67.6	44.5	1.05	0.95
2	<i>rac</i> -1 (300)	Co-2/ Zn-3	100	46.2	44.5	1.07	0.21 ^e
3	<i>rac</i> -3 (200)	Co-1/ Zn-2	100	34.7	44.1	1.04	0.98
4	<i>rac</i> -4 (300)	Co-1/ Zn-2	100	32.2	21.7	1.08	0.90

5	<i>rac</i> - 4 (300)	Co-2 / Zn-3	100	49.6	21.7	1.07	0.89
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^a Abbreviations: OCA, *O*-carboxyanhydride; FR, OCA/Zn catalyst ratio in the feed; Conv, monomer conversion; M_n , number-average molecular weight; MW_{cal} , molecular weight calculated on the basis of the FR ratio; $\bar{P}$, molecular weight distribution; P_m , maximum probability of meso dyad formation. Polymerization conditions: [L-OCA]/[D-OCA] = 1/1, [Co]/[Zn]/[BnOH] = 1/1/1, 0 °C, 4 mA in 0.1 M tetrabutylammonium hexafluorophosphate/THF solution, Mg(+)/Pt(−) electrodes. ^b Determined by Fourier transform IR spectroscopy. ^c Determined by gel permeation chromatography. ^d Determined by ¹³C NMR spectroscopy. ^e $P_t = 1 - P_m = 0.79$, where P_t is the probability of racemic dyad formation. eROPs that were mediated by other Co/Zn combinations are listed in Table S9.

We also explored whether our method could be adapted for stereoselective eROP of racemic OCAs (Scheme 3). The use of isoselective complex **Zn-2**¹¹ together with **Co-1** under the optimized eROP conditions at 0 °C ([L-1]/[D-1]/[Co-1]/[Zn-2]/[BnOH] = 150/150/1/1/1) afforded stereoblock (*sb*) copolymer poly(*sb*-1) with a M_n of 67.6 kDa, which is close to the MW_{cal} (44.5 kDa), a narrow $\bar{P}$ (1.05; Table 2, entry 1), and a high probability of meso dyad formation (P_m , 0.95; Figure S15a). In contrast, the use of **Co-2**, a Co^{II} complex with a pyridine ligand, and **Zn-3**, a Zn complex with a bulky β -diiminate ligand,^{4a} initiated syndioselec- tive polymerization of *rac*-1 ([L-1]/[D-1]/[Co-2]/[Zn-3]/[BnOH] = 150/150/1/1/1) and afforded syndiotactic (*sd*) poly(*sd*-1) with a M_n of 46.2 kDa, a $\bar{P}$ of 1.07 (entry 2), and a decent P_t (probability of racemic dyad formation) of 0.79 (Figure S15b). Note that when eROPs of *rac*-1 were mediated by **Co-1/Zn-3** or **Co-2/Zn-2**, the above-mentioned stereoregularity were not observed (Table S9, entries 3 and 6; Figure S15); **Zn-1**, either with **Co-1** or **Co-2**, could not efficiently mediate polymerization of *rac*-1 (entries 1 and 4); **Zn-2** or **Zn-3** alone was incapable to initiate polymerization of *rac*-1 (entries 14–15). Kinetics studies showed that the conversion of *rac*-1 was significantly slower than the conversions of L-1 and D-1 in the **Co-1/Zn-2**-mediated eROP; whereas the conversion of *rac*-1 was slightly faster than the conversions of L-1 and D-1 in the **Co-2/Zn-3**-mediated reaction (Figure S16). The difference in microstructure between the two obtained polymers was confirmed by differential scanning calorimetry: poly(*sb*-1) had a glass transition temperature (T_g) of 46 °C, whereas poly(*sd*-1) exhibited a T_g of 58 °C (Figure S17). Note that the atactic poly(*rac*-1) had a T_g of 51 °C.^{11b} Because stereoselectivity is usually mediated solely by the Zn-alkoxide complex in ROP, this finding indicates that the ligands of both the Co complex and the Zn complex markedly affected the stereoselectivity during enchainment of *rac*-1. Surprisingly, this strong effect on the stereoselectivity was not observed in the eROP of *rac*-4: reactions mediated by both **Co-1/Zn-2** and **Co-2/Zn-3** resulted in poly(*sb*-4) with similar T_g values (compare entries 4 and 5 in Table 2, and see Figures S17 and S18). These results indicate that both the pendant functional group of the OCA and the ligands of the metal complexes could affect eROP stereoselectivity.

In summary, we have developed a protocol for eROP that allows for temporal control of chain growth and the preparation of high-MW polyesters with pendant functional groups. Our protocol provides access to various stereoregular polyesters and is a rare example of a method that permits stereoselectivity to be controlled by tuning the ligands of both catalysts. Considering that industrial production of poly(lactic acid) via ROP requires high temperature

(135–160 °C) and that the photoredox reaction has a scalability problem,³ our eROP method is particularly appealing for potential application in terms of its energy efficiency and scalability with recyclable electrodes. We are currently carrying out mechanistic studies and developing additional catalysts to expand the scope of this powerful polymerization chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Website.

Experimental procedures and characterization data for all polymers including ¹H and ¹³C NMR spectra, DSC data and CV curves.

AUTHOR INFORMATION

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Notes

Provisional patents (U.S. Patent Application No: 62/414,016 and VTIP No. 19-112) have been filed pertaining to the results presented in this paper.

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could not initiate any polymerization when using together with Co complex.

- ✓ *High-MW polymers (>140 kDa)*
- ✓ *Living polymerization ($\bar{D} < 1.1$)*
- ✓ *No epimerization*
- ✓ *Simple setup in mild reaction conditions*
- ✓ *Electrochemically stereoselective polymerization*

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Functionalized Polyesters via Electrochemical Stereoselective Ring-Opening Polymerization of *O*-Carboxyanhydrides

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Supplementary information

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S1. Materials

S1.1 General

Bis(1,5-cyclooctadiene) nickel(0) (Ni(COD)_2), 2,2'-bipyridine (bpy), bis[2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine] iridium(III) hexafluorophosphate (**Ir-1**), chlorotris(triphenylphosphine) cobalt(I), (1*R*,2*R*)-(-)-1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butylsalicylidene) cobalt(II), cyclopentadienylcobalt dicarbonyl, dichloro[1,1'-bis(diphenylphosphino)ferrocene]cobalt(II), cobalt(II) dibromo(1,2-dimethoxyethane), anhydrous cobalt(II) chloride and *meso*-tetraphenylporphyrin cobalt(II) were purchased from Strem Chemicals (Newburyport, MA). *O*-benzyl-L-serine, *O*-benzyl-D-serine, L-glutamic acid- γ -benzyl ester and D-glutamic acid- γ -benzyl ester were purchased from Chem-Impex (Wood Dale, IL). L-phenylalanine and D-phenylalanine was purchased from Alfa Aesar (Haverhill, MA). Anhydrous tetrahydrofuran (THF) was dried by alumina columns and stored with 4 Å molecular sieve in the dark bottle in the glove box. Anhydrous THF-*d*₈, benzyl alcohol, hexane, benzene, toluene, diethyl ether, diisopropyl ether, pyridine and dichloromethane were dried and stored by 4 Å molecular sieves in the glove box. All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO) unless otherwise noted.

S1.2 OCA monomers

L-PheOCA (**L-1**) and D-PheOCA (**D-1**),¹ L-Ser(Bn)OCA (**L-2**) and D-Ser(Bn)OCA (**D-2**),² L-Glu(Cbz)OCA (**L-3**) and D-Glu(Cbz)OCA (**D-3**),³ L-LacOCA (**L-4**) and D-LacOCA (**D-4**),⁴ and L-ManOCA (**L-5**) and D-ManOCA (**D-5**),⁵ were synthesized and recrystallized according to the literature. All OCA monomers were recrystallized three times and stored in -30 °C freezer in the glove box.

S1.3 Zn complexes

Zn(HMDS)_2 (**Zn-1**) was prepared and distilled according to the literature.⁶ (**NNO-1**) $\text{ZnN(SiMe}_3)_2$ (**Zn-2**) was prepared following the literatures.⁷ β -diiminate Zn complexes (**Zn-3**) were synthesized according to the literature.⁸ All Zn complex were stored in the glove box freezer (-30 °C).

S1.4 Ni complex

The Ni complex solution was prepared freshly prior to the reaction. In a glove box, Ni(COD)_2 (5.5 mg, 0.02 mmol) was mixed with bipyridyl ligand (e.g., bpy, 3.1 mg, 0.02 mmol) or or

tricyclophosphine (11.2 mg, 0.04 mmol) in THF solution (300 μ L) at room temperature and stirred for 1-2 hour to ensure all Ni(COD)₂ dissolved. The Ni complex solution could be stored in the glove box freezer (-30 °C) no longer than seven days.

S1.5 Co(II) complexes

Co(HMDS)₂ was prepared and distilled according to the literature.⁹ The Co(II) complexes were prepared freshly prior to the polymerization. In general, Co(HMDS)₂ (2.9 mg, 7.6 μ mol) was mixed with the ligand (e.g., bpy, 1.2 mg, 7.6 μ mol, or other phosphine ligand at same equivalent) in toluene solution (1 mL) at room temperature and stirred for 2 hours to ensure all Co(HMDS)₂ dissolved. The Co complex solution could be stored in the glove box freezer (-30 °C) no longer than seven days.

S1.5.1 Synthesis of Co-1

In a glove box, Co(HMDS)₂ (2.9 mg, 7.6 μ mol) was mixed with the bpy (1.2 mg, 7.6 μ mol) in toluene solution (1 mL) at room temperature and stirred for 2 hours to ensure all Co(HMDS)₂ dissolved. The **Co-1** complex solution could be stored in the glove box freezer (-30 °C) no longer than seven days.

S1.5.2 Synthesis of Co-2

In a glove box, 5.0 mg (5.1 μ L) anhydrous pyridine was mixed with toluene to prepare 1 mL solution. Co(HMDS)₂ (1.5 mg, 3.9 μ mol) was mixed with 62.5 μ L above pyridine in toluene solution, and was further diluted to 1 mL by adding 937.5 μ L toluene at room temperature. The mixture was stirred for 2 hours to ensure all Co(HMDS)₂ dissolved. The **Co-2** complex solution could be stored in the glove box freezer (-30 °C) no longer than seven days.

S2. Instrument and Characterization

S2.1 NMR

All room temperature NMR and homodecoupling ^1H NMR spectra were recorded on Agilent U4-DD2 (400 MHz) or Bruker Avance II (500 MHz). Low temperature ^1H and ^{13}C NMR spectra were measured on Bruker Avance III (600 MHz) after the inner temperature of the NMR machine reached $-20\text{ }^\circ\text{C}$ for 20 min. The samples were kept at $-20\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ with a dry ice/ethylene glycol bath before the low-temperature NMR acquisition.

S2.2 FTIR

Fourier-transform infrared spectra were recorded on an Agilent Cary 630 FTIR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with Diamond ATR and transmission sampling accessory.

Monomer conversion measurement:

A small aliquot of polymer solution (20 μL) was removed out of the glove box and quenched with 5% acetic acid / THF solution (20 μL). The mixture ($\sim 10\text{ }\mu\text{L}$) was immediately dropped onto the FTIR-ATR diamond sampler and formed a film within 10-20 seconds for the spectra measurement. The peak at 1800 cm^{-1} is assigned as the anhydride bond stretch in OCA; the peak at 1760 cm^{-1} corresponds to the formation of the ester bond in the polymer. The monomer conversion was determined by the intensity ratio between 1760 cm^{-1} and 1800 cm^{-1} :
$$\text{conversion\%} = I_{1760} / (I_{1760} + I_{1800}).^{10}$$

S2.3 Gel permeation chromatography (GPC)

GPC experiments were performed on a system equipped with an isocratic pump with degasser (Agilent 1260 series, Agilent Technologies, Santa Clara, CA, USA), Wyatt DAWN HELEOS multiangle laser light scattering (MALS) detector (GaAs 30 mW laser at $\lambda=690\text{ nm}$), and an Wyatt Optilab rEX differential refractive index (DRI) detector with a 690 nm light source (Wyatt Technology, Santa Barbara, CA, USA). Separations were performed using serially connected size exclusion columns (100 $\text{\AA}$, 500 $\text{\AA}$, $10^3\text{ }\text{\AA}$, and $10^4\text{ }\text{\AA}$ Phenogel columns, 5 μm , $300 \times 4.6\text{ mm}$, Phenomenex, Torrance, CA, USA) at $35\text{ }^\circ\text{C}$ using THF as the mobile phase with a flow rate of 0.35 mL/min. The polymer molecular weight (MW) and molecular weight distribution ($\mathcal{D}$) were determined using Zimm model fit of MALS-DRI data by ASTRA software (Version 6.1, Wyatt Technology).

The refractive index increment dn/dc value was determined by the Wyatt Optilab rEX refractive index detector using ASTRA software dn/dc template (Version 6.1, Wyatt Technology). Five polymer / THF solutions with different concentrations were sequentially injected into the refractive index detector and the refractive index values were plotted versus concentration in ASTRA software. The slope of the linear fitting data is the dn/dc value.

The dn/dc values: poly(L-1), 0.1670; poly(L-2), 0.1377; poly(L-3), 0.1057; poly(L-4), 0.042; poly(L-5), 0.084.

S2.4 DSC

Differential scanning calorimetry (DSC) measurements were performed on TA Instruments DSC Q2000 instrument equipped with photocalorimeter accessory and RCS90 cooling system. Polymer samples in crimped aluminum pans were analyzed under nitrogen at a heating rate of 10 °C/min from 0 to 220 °C. Glass transition temperature (T_g) and melting temperature (T_m) were obtained and reported from the second heating run.

S2.5 Cyclic voltammetry

Cyclic voltammetries (CVs) were performed in a three-electrode measurement setup in a glove box with a Gamry Interface 1010 potentiostat/galvanostat at a potential sweep rate of 50 mV/s. The measurements were carried out in a 20 mL Gamry Dr. Bob's electrochemical cell with approximately 1 mM concentration of Co complex in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) in anhydrous THF, fitted with a glassy carbon working electrode (3 mm in diameter, Gamry), a Ag/AgNO₃ reference electrode (a silver wire in 0.01 M AgNO₃ and 0.1 M TBAH in anhydrous acetonitrile), and a platinum wire (Gamry) counter electrode. Ferrocene (Fc) was measured as an internal standard,¹¹ and all potentials versus Fc/Fc⁺ were subsequently referenced to SCE (adding 380 mV) based on the reported method.¹²

S3. Polymerization Procedures

S3.1 The photoredox polymerization of L-1 initiated by Co-1 / Zn-1 / BnOH

In a glove box, prior to the polymerization, all reagents were cooled in the cold trap equipped with a thermometer at 0 °C, which was cooled by the liquid nitrogen and ethanol in a dewar. The monomer **1** (15 mg, 150 μ L of 100 mg/mL in THF, 0.078 mmol, 700 equiv.) was mixed with **Co-1** (9.9 μ L of 3.7 mg/mL in toluene, 0.112 μ mol, 1 equiv.), **Zn-1** (9.0 μ L of 4.2 mg/mL in THF, 0.112 μ mol, 1 equiv.), and BnOH (2.8 μ L of 3.7 mg/mL in THF, 0.112 μ mol, 1 equiv.) in a 7-mL glass vial equipped with a magnetic stir bar. The solution was stirred and irradiated with a 34 W blue LED lamp (Kessil KSH150B LED Grow Light 150) at -15 ± 5 °C (with a cooling fan to keep the reaction temperature) over 1-2 hours. The OCA monomer conversion was monitored by FTIR. The resulted polymer's MW and $\bar{D}$ were directly measured by GPC after the polymerization.

S3.2 The electrochemical polymerization of L-1 initiated by Co-1 / Zn-1 / BnOH in IKA ElectraSyn 2.0.

In a glove box, prior to the polymerization, all reagents were cooled in the cold trap equipped with a thermometer at -5 to 0 °C, which was cooled by ice water and NaCl in a dewar. Tetra-*n*-

butylammonium hexafluorophosphate (TBAH, 75.7 mg) was dissolved in THF (2 mL) to make 0.1 M TBAH/THF solution. The monomer **L-1** (50 mg, 0.260 mmol, 700 equiv) was dissolved in 800 μ L TBAH/THF solution and was subsequently mixed with **Co-1** (38.4 μ L of 3.9 mg/mL in toluene, 0.372 μ mol, 1 equiv.), **Zn-1** (45.1 μ L of 3.4 mg/mL in THF, 0.372 μ mol, 1 equiv.) and BnOH (16.4 μ L of 2.6 mg/mL in THF, 0.372 μ mol, 1 equiv.) in an ElectraSyn electrochemical cell (IKA, 5 mL) equipped with a magnetic stir bar at -5-0 $^{\circ}$ C. The solution was diluted by 0.1 M TBAH/THF solution to a final volume of 2 mL. The ElectraSyn cell cap was loaded with a Mg anode and a Pt cathode plates (both from IKA, left panel), assembled with the cell, and plugged into ElectraSyn 2.0 via an IKA ElectraSyn GOGO extension module (right panel). The detailed ElectraSyn electrochemical cell assembly and program setup was also reported in the literature.¹³ The reaction was performed at 0 $^{\circ}$ C under a constant current of 4 mA over 1-2 hour. The OCA monomer conversion was monitored by FTIR. The obtained polymer solution was completely dried under vacuum and washed by cold methanol (5 mL) for three times to remove TBAH salt. MW and *D* were measured by GPC after the purification. Note for NMR studies, the polymer was only washed by methanol once to avoid excessive salt peaks in spectra while maintaining the structure information. Isolated yield: 79.9 % after purification.

S3.3 The electrochemical block copolymerization of **L-1** and **L-3** initiated by **Co-1** / **Zn-1** / **BnOH**

In a glove box, prior to the polymerization, all reagents were cooled in the cold trap equipped with a thermometer at -5 to 0 $^{\circ}$ C, which was cooled by ice water and NaCl in a dewar. Similar to

the procedures in **S3.2** using Mg(+)/Pt(-) electrodes, **L-1** (50 mg, 800 μ L TBAH/THF solution, 0.260 mmol, 200 equiv) was mixed with **Co-1** (115 μ L of 4.3 mg/mL in toluene, 1.30 μ mol, 1 equiv.), **Zn-1** (316.7 μ L of 1.6 mg/mL in THF, 1.30 μ mol, 1 equiv.) and BnOH (46.9 μ L of 3.0 mg/mL in THF, 1.30 μ mol, 1 equiv.) in an ElectraSyn electrochemical cell equipped with a magnetic stir bar at -5-0 $^{\circ}$ C. The solution was diluted by 0.1 M TBAH/THF solution to a final volume of 2 mL. The solution was stirred at 0 $^{\circ}$ C under a constant current of 4 mA until complete consumption of **L-1** within 30 min, monitored by FTIR. An aliquot of poly(**L-1**) solution (500 μ L) was taken out of the glove box for GPC characterization. The monomer **L-3** (25.8 mg, 500 μ L TBAH/THF solution, 97.7 μ mol, 100 equiv.) was added into the remaining mixture and stirred at 0 $^{\circ}$ C with constant 4 mA current for 3 hours until complete consumption of the OCA monomers as monitored by FTIR. The resulted polymer solution was dialyzed against THF over 2 days. Both MW and $\bar{D}$ were directly measured by GPC after the dialysis.

S3.4 The electrochemical polymerization of racemic L-1 and D-1 initiated by Co-1 / Zn-2

In a glove box, prior to the polymerization, all reagents were cooled in the cold trap equipped with a thermometer at -5 to 0 $^{\circ}$ C, which was cooled by ice water and NaCl in a dewar. Similar to the procedures in **S3.4** using Mg(+)/Pt(-) electrodes, **L-1** (25 mg, 250 μ L of 100 mg/mL in TBAH/THF solution, 0.130 mmol, 200 equiv.) and **D-1** (25 mg, 250 μ L of 100 mg/mL in TBAH/THF solution, 0.130 mmol, 200 equiv.) were mixed with **Co-1** (88.7 μ L of 2.9 mg/mL in toluene, 0.651 μ mol, 1 equiv.), **Zn-2** (207 μ L of 7.4 mg/mL in THF, 0.651 μ mol, 1 equiv.) and BnOH (134.8 μ L of 2.25 mg/mL in THF, 0.651 μ mol, 1 equiv.) in an ElectraSyn electrochemical cell equipped with a magnetic stir bar at -5-0 $^{\circ}$ C. The solution was diluted by 0.1 M TBAH/THF solution to a final volume of 2 mL. The solution was stirred at 0 $^{\circ}$ C under a constant current of 4 mA until complete consumption of OCA monomers as monitored by FTIR over 2 hours. The obtained polymer solution was completely dried under vacuum and washed by cold methanol to remove TBAH salt. Both MW and $\bar{D}$ were directly measured by GPC after the purification. The P_m of poly(*rac*-**1**) was determined by ^{13}C NMR spectra.

S3.5 Other ring-opening polymerization techniques

The ring-opening polymerizations of OCAs initiated by (bpy)Ni(COD) / Zn(HMDS)₂ / BnOH / **Ir-1** was reported in our previous work.^{10, 14}

S3.6 Kinetic study of the electrochemical polymerization of OCA

In a glove box, prior to the polymerization, all reagents were cooled in the cold trap equipped with a thermometer at -5 to 0 °C, which was cooled by ice water and NaCl in a dewar. Similar to the procedures in **S3.4** using Mg(+)/Pt(-) electrodes, **L-1** (50 mg, in 800 µL 0.1 M TBAH/THF solution, 0.260 mmol, 600 equiv.) was mixed with **Co-1** (38.3 µL of 4.3 mg/mL in toluene, 0.434 µmol, 1 equiv.), **Zn-1** (52.8 µL of 3.2 mg/mL in THF, 0.434 µmol, 1 equiv.) and BnOH (15.6 µL of 3.0 mg/mL in THF, 0.434 µmol, 1 equiv.) in an electrochemical cell (5mL) equipped with a magnetic stir bar at -5-0 °C. The solution was diluted by 0.1 M TBAH/THF solution to a final volume of 2 mL. The mixture was stirred at 0 °C with constant 4 mA current. At the predetermined time point, 10 µL of the polymer solution was taken out and immediately analyzed by FTIR.

All the catalysts' concentrations were varied, and the semi-logarithmic plots were drawn to calculate the kinetic constants and reaction orders according to the kinetic laws:

$$-d[\mathbf{1}]/dt = k_{app} [\mathbf{1}] \quad (\text{eq. 1})$$

where k_{app} is the apparent first-order rate constant. For eq.1 it equals to

$$\ln[\mathbf{1}]_0/\ln[\mathbf{1}]_t = k_{app} t + C \quad (\text{eq. 2})$$

thus $\ln[\mathbf{1}]_0/\ln[\mathbf{1}]_t$ versus t was plotted.

Table S1. The discovery of Co-1/Zn-1 for the photoredox ring-opening polymerization of L-1^a

Entry	Conditions	FR	Time (h)	Conv. (%) ^b	M_n (kDa) ^c	MW _{cal} (kDa)	$\bar{D}$ ^c
1	As shown	700	1	100	107.8	103.7	1.04
2	At 20 °C	700	2	100	84.3	103.7	1.04
3	No Co-1	700	1	33	81.7	103.7	1.09
4	No Zn-1	700	1	19	16.9	103.7	1.41
5	Only Co-1	700	1	11	23.6	103.7	1.35
6	Only Zn-1	700	1	39	84.3	103.7	1.08
7	Co-1 + $h\nu$	700	1	13	14.5	103.7	3.50
8	No BnOH	700	1	67	108.7	103.7	1.05
9	No light	700	1	69	96.9	103.7	1.06
10	Adding 0.1 eq. Ir-1	700	1	67	90.0	103.7	1.08
11	Zn-2 + BnOH (no Co-1)	700	2	41	80.1	103.7	1.05
12	Zn-3 + BnOH (no Co-1)	700	2	21	19.9	103.7	1.57

^a Abbreviations: FR, the feeding ratio of [L-1]/[Zn-1]; Conv., monomer conversion; M_n , number-average molecular weight; MW_{cal}, molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; $\bar{D}$, molecular weight distribution. Polymerization conditions: [Co-1] = [Zn-1] = [BnOH] at 0 °C in a glove box.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

Table S2. Effects of solvent on the electrochemical ring-opening polymerization of L-1 mediated by Co-1/Zn-1/BnOH^a

Entry	Solvent	FR	Temp. ($^{\circ}\text{C}$)	Time (h)	Conv. (%) ^b	M_n (kDa) ^c	MW_{cal} (kDa)	$\bar{D}$ ^c
1	THF	700	0	1	100	103.5	103.7	1.06
2	DMF	700	0	2	100	141.6	103.7	1.22
3	ACN	700	0	2	100	26.9	103.7	1.17

^a Abbreviations: FR, the feeding ratio of **[1]**/**[Zn-1]**; Conv., monomer conversion; Temp., temperature; M_n , number-average molecular weight; MW_{cal} , molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; $\bar{D}$, molecular weight distribution. For all polymerization reactions, **[Co-1]** = **[Zn-1]** = **[BnOH]**.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm^{-1} , which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

Table S3. Effects of electrolytes on the electrochemical ring-opening polymerization of L-1 mediated by Co-1/Zn-1/BnOH^a

Entry	Salt (0.1M)	FR	Temp. (°C)	Time (h)	Conv. (%) ^b	<i>M</i> _n (kDa) ^c	MW _{cal} (kDa)	<i>Đ</i> ^c
1	<i>n</i> Bu ₄ NPF ₆	500	0	1	100	86.3	74.1	1.07
2	<i>n</i> Bu ₄ NPF ₆	700	0	1	100	103.5	103.7	1.06
3	<i>n</i> Bu ₄ NBF ₄	700	0	1	39	68.4	103.7	1.06
4	<i>n</i> Bu ₄ NBPh ₄	700	0	1	0	N.D.	103.7	N.D.
5	Et ₄ NBF ₄	700	0	1	0	N.D.	103.7	N.D.
6	Et ₄ NPF ₆	700	0	1	48	52.3	103.7	1.81
7	LiClO ₄	700	0	1	22	23.2	103.7	1.09
8	LiPF ₆	700	0	1	80.5	71.7	103.7	1.13
9	LiBF ₄	700	0	1	0	N.D.	103.7	N.D.
10	LiBr	700	0	1	0	N.D.	103.7	N.D.
11	MgClO ₄	700	0	1	0	N.D.	103.7	N.D.

^a Abbreviations: FR, the feeding ratio of [1]/[Zn-1]; Conv., monomer conversion; Temp., temperature; *M*_n, number-average molecular weight; MW_{cal}, molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; *Đ*, molecular weight distribution; N.D., not determined. For all polymerization reactions, [Co-1] = [Zn-1] = [BnOH] in THF.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

Table S4. Effects of current on the electrochemical ring-opening polymerization of L-1 mediated by Co-1/Zn-1/BnOH^a

Entry	Current (mA)	FR	Temp. (°C)	Time (h)	Conv. (%) ^b	<i>M</i> _n (kDa) ^c	MW _{cal} (kDa)	<i>Đ</i> ^c
1	2	700	0	2	82	94.0	103.7	1.04
2	4	700	0	1	100	103.5	103.7	1.06
3	6	700	0	0.75	100	94.8	103.7	1.03

^a Abbreviations: FR, the feeding ratio of [1]/[Zn-1]; Conv., monomer conversion; Temp., temperature; *M*_n, number-average molecular weight; MW_{cal}, molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; *Đ*, molecular weight distribution. For all polymerization reactions, [Co-1] = [Zn-1] = [BnOH] in THF.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

Table S5. Effects of Co-1 concentration on the electrochemical ring-opening polymerization of L-1 mediated by Co-1/Zn-1/BnOH ^a

Entry	[Co-1]/[Zn-1]	FR	Temp. (°C)	Time (h)	Conv. (%) ^b	<i>M</i> _n (kDa) ^c	MW _{cal} (kDa)	<i>Đ</i> ^c
1	0.5	700	0	2.5	100	99.7	103.7	1.03
2	1	700	0	1	100	105.2	103.7	1.03
3	2	700	0	1	100	96.8	103.7	1.03

^a Abbreviations: FR, the feeding ratio of [1]/[Zn-1]; Conv., monomer conversion; Temp., temperature; *M*_n, number-average molecular weight; MW_{cal}, molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; *Đ*, molecular weight distribution. For all polymerization reactions, [Zn-1] = [BnOH] in THF.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

Table S6. Electrochemical ring-opening polymerization of L-1 mediated by Co-1/Zn-1/BnOH at various feeding ratios ^a

Entry	[Bu ₄ NPF ₆] (M)	FR	Temp. (°C)	Time (h)	Conv. (%) ^b	<i>M</i> _n (kDa) ^c	MW _{cal} (kDa)	<i>Đ</i> ^c
1	0.1	400	0	0.5	100	51.1	59.3	1.02
2	0.1	500	0	0.5	100	77.1	74.1	1.08
3	0.1	600	0	0.5	100	94.4	88.9	1.08
4	0.1	700	0	1	100	103.5	103.7	1.06
5	0.1	800	0	2	100	116.1	118.5	1.07
6	0.1	900	0	2	100	135.1	133.3	1.02
7	0.05	1000	0	3.5	88	146.8	148.1	1.09
8	0.1 ^d	700	0	8	39.7	N.D.	103.7	N.D.

^a Abbreviations: FR, the feeding ratio of [1]/[Zn-1]; Conv., monomer conversion; Temp., temperature; *M*_n, number-average molecular weight; MW_{cal}, molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; *Đ*, molecular weight distribution; N.D. not determined. For all polymerization reactions, [Co-1] = [Zn-1] = [BnOH] in THF.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

^d No current applied to the reaction. The entry is compared to Table 1 entry 7, which confirming that the polymerization stopped when no current is applied. The results indicated that the electricity is necessary for chain propagation, though Co-1/Zn-1 (or Zn-1 itself) may be reactive for ring-opening reaction to convert certain monomers and to form short polymer chains.

Table S7. Measurement of residue metal concentrations in purified polymers by inductively coupled plasma mass spectrometry (ICP-MS) ^a

	[Co] (ppb)	[Zn] (ppb)	[Mg] (ppb)	[Pt] (ppb)
HNO ₃	0	18.6	18.8	0
Electrochemical ROP	22.8	53.2	1786.6	0.3

^a Abbreviations: ROP, ring-opening polymerizations; ppb: parts per billion, that equals to µg/L. The electrochemical polymerization reaction was performed at an [L-1]/[Zn-1]/[Co-1]/[BnOH] ratio of 700/1/1/1 at 0 °C using Mg(+)/Pt(-) electrodes, and the obtained polymer was washed by methanol. For ICP-MS studies, the polymer was dissolved in 10% HNO₃ at 70-80 °C at a concentration of 1 mg/mL for three days in order to completely degrade the polymer. The obtained polymer solution was then analyzed by ICP-MS.

Table S8. Electrochemical polymerization and block copolymerization of various *O*-carboxyanhydrides ^a

Entry	Monomer	FR	Time (h)	Conv. (%) ^b	M_n (M_n - b1) (kDa) ^c	MW_{cal} (MW_{cal} - b1) (kDa)	$\bar{D}$ ($\bar{D}$ -b1) ^c
1	2	200	1	100	37.0	35.7	1.06
2	2	300	1.5	100	57.3	53.4	1.07
3	2	400	2	100	71.8	71.3	1.03
4	3	200	0.75	100	47.0	44.1	1.07
5	3	300	1	100	64.3	66.1	1.04
6	3	400	1.5	100	83.3	88.1	1.03
7	4	300	1	100	55.8	21.7	1.06
8	4	600	1	100	62.7	43.3	1.08
9	5	50	1	100	15.3	6.8	1.14
10	5	100	2	100	46.2	13.6	1.13
11	1/3	400/100	1/2	100	94.6 (78.1)	81.3 (59.3)	1.02 (1.08)

^a Abbreviations: FR, the feeding ratio of $[\text{OCA}]/[\text{Zn}]$; Conv., monomer conversion; Temp., temperature; M_n , number-average molecular weight; MW_{cal} , molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; $\bar{D}$, molecular weight distribution. M_n -b1 and $\bar{D}$ -b1 refer to the molecular weight and molecular weight distribution of the first block polymer.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm^{-1} , which corresponds to the anhydride group of the OCA.

^c For homopolymers, M_n and $\bar{D}$ were determined by gel-permeation chromatography. For copolymers, M_n -b1, $\bar{D}$, and $\bar{D}$ -b1 were determined by GPC; M_n of the block copolymer was calculated on the basis of the ¹H NMR integration ratio of the α -methine peaks of the different blocks.

Table S9. Electrochemical polymerization of racemic *O*-carboxyanhydrides ^a

Entry	OCA (FR)	Co / Zn	Time (h)	Conv. (%) ^b	<i>M</i> _n (kDa) ^c	MW _{cal} (kDa)	<i>D</i> ^c	<i>P</i> _m ^d	<i>T</i> _g ^e
1	<i>rac</i> - 1 (400)	Co-1 / Zn-1	2	17	N.D.	59.3	N.D.	N.D.	N.D.
2	<i>rac</i> - 1 (300)	Co-1 / Zn-2	1	100	67.2	44.5	1.05	0.95	46
3	<i>rac</i> - 1 (300)	Co-1 / Zn-3	1	100	46.2	44.5	1.13	0.62	N.D.
4	<i>rac</i> - 1 (200)	Co-2 / Zn-1	1	24	N.D.	29.7	N.D.	N.D.	N.D.
5	<i>rac</i> - 1 (300)	Co-2 / Zn-3	1	100	46.2	44.5	1.07	0.21 ^f	58
6	<i>rac</i> - 1 (200)	Co-2 / Zn-2	2	100	58.5	29.7	1.06	0.58	N.D.
7	<i>rac</i> - 3 (200)	Co-1 / Zn-2	1	100	34.7	44.1	1.04	0.98	4
8	<i>rac</i> - 4 (300)	Co-1 / Zn-2	1	100	32.2	21.7	1.08	0.90	50
9	<i>rac</i> - 4 (300)	Co-2 / Zn-3	1	100	49.6	21.7	1.07	0.89	50
10	<i>rac</i> - 1 (300)	Co-1 / Zn-2 no current	2	21.1	N.D.	44.5	N.D.	N.D.	N.D.
11	<i>rac</i> - 1 (300)	Co-1 / Zn-2 no current	4	25.5	N.D.	44.5	N.D.	N.D.	N.D.
12	<i>rac</i> - 1 (300)	Co-2 / Zn-3 no current	2	14.8	N.D.	44.5	N.D.	N.D.	N.D.
13	<i>rac</i> - 1 (300)	Co-2 / Zn-3 no current	4	16.9	N.D.	44.5	N.D.	N.D.	N.D.
14	<i>rac</i> - 1 (300)	Zn-2 (no Co complex)	2	<5%	N.D.	44.5	N.D.	N.D.	N.D.
15	<i>rac</i> - 1 (300)	Zn-3 (no Co complex)	2	<5%	N.D.	44.5	N.D.	N.D.	N.D.

^a Abbreviations: FR, the feeding ratio of [**1**]/[**Zn-1**]; Conv., monomer conversion; Temp., temperature; M_n , number-average molecular weight; MW_{cal} , molecular weight calculated from the ratio of the amount of monomer to the amount of catalyst; $\bar{D}$, molecular weight distribution; P_m , maximum probability of meso dyad formation. Polymerization conditions: [L-OCA]/[D-OCA] = 1/1, [Co]/[Zn]/[BnOH] = 1/1/1, 0 °C, 4 mA in 0.1 M tetrabutylammonium hexafluorophosphate/THF solution, Mg(+)/Pt(-) electrodes.

^b Determined from the intensity of the Fourier transform infrared peak at 1805 cm⁻¹, which corresponds to the anhydride group of the *O*-carboxyanhydride.

^c Determined by gel-permeation chromatography.

^d Determined by ¹³C NMR spectroscopy. See NMR spectra in Figure S15 and S18.

^e Determined by differential scanning calorimetry. See Figure S17 and its discussion of results.

^f $P_r = 1 - P_m = 0.79$

Discussion:

For entries 10-15, we note that the prolonged reaction time would not improve the monomer conversions. The prolonged reaction time would not improve the monomer conversion (chain end likely dead). We also note that it is very difficult to separate and purify oligomers in those entries for detailed microstructure analysis, as dialysis and washing significantly could further decrease the yield of such oligomers.

Co^I complex

Conversion: 27%

Conversion: 53%

Co^{III} complex

Conversion: 57%

Conversion: 57%

Co^{II} complex

Conversion: 62%

Conversion: 58%

Conversion: 23%

Conversion: 44%

M_n : 72.1 kDa; $\bar{D}$: 1.08

Ligand for Co(HMDS)₂

M_n : 66.0 kDa; $\bar{D}$: 1.13

M_n : 75.9 kDa; $\bar{D}$: 1.05

M_n : 66.9 kDa; $\bar{D}$: 1.06

M_n : 68.4 kDa; $\bar{D}$: 1.05

M_n : 69.9 kDa; $\bar{D}$: 1.04

M_n : 48.1 kDa; $\bar{D}$: 1.03

M_n : 72.0 kDa; $\bar{D}$: 1.05

M_n : 81.5 kDa; $\bar{D}$: 1.04

M_n : 80.5 kDa; $\bar{D}$: 1.05

M_n : 81.7 kDa; $\bar{D}$: 1.05

M_n : 86.2 kDa; $\bar{D}$: 1.05

M_n : 89.6 kDa; $\bar{D}$: 1.05

Conversion: 33%

M_n : 79.6 kDa; $\bar{D}$: 1.04

M_n : 85.7 kDa; $\bar{D}$: 1.03

Conversion 76%

M_n : 73.3 kDa; $\bar{D}$: 1.06

M_n : 69.4 kDa; $\bar{D}$: 1.11

M_n : 82.7 kDa; $\bar{D}$: 1.05

Figure S1. Screening of Co complexes and Co(HMDS)₂ ligands for photoredox ring-opening polymerization of L-1. The photoredox polymerization reaction was performed at an $[L-1]/[Zn-1]/[Co]/[BnOH]$ ratio of 600/1/1/1 at room temperature with light irradiation for 2 hours. The data in red indicates the less controlled reactions.

Figure S2. Cyclic voltammetry of (a) various reagents including OCA monomers, **Zn-1** and amino acids comparing to **Co-1**, (b) **Co-1** and the ring-opening reaction mixtures (1 equiv. of each) and (c) eROP of **L-1** at 0 °C mediated by **Co-1/Zn-1** ($[\text{L-1}]/[\text{Co-1}]/[\text{Zn-1}]/[\text{BnOH}] = 400/1/1/1$). Scan rate: 50 mV/s; solvent: 0.1 M TBAH in THF.

Discussion:

As our polymerization reactions were performed in THF, we did not choose acetonitrile, which is commonly used in the literature, as the solvent for CV studies. CV data in (a) suggested that **Zn-1**, $\text{Co}(\text{HMDS})_2$ and OCA monomer alone did not have strong redox properties. Our data in (b) agrees well with the literature that also showed the reduction potentials of $\text{Co}^{\text{IV}}/\text{Co}^{\text{III}}$ and $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$,¹⁵ while the reduction potential of $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ often negative vs SCE.^{15c, 15d} The results in (c) indicated that the redox reaction (more obviously, oxidation) of $\text{Co}^{\text{IV}}/\text{Co}^{\text{III}}$ occurred in the early stage of the reaction, whereas peaks of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ (~ 1 V) showed up in the late stage, which eventually resulted in the dominant $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ peaks (~ 0.5 V) in the equivalent mixture of OCA monomer and metal complexes in (b).

Figure S3. Screen of electrode materials for electrochemical polymerization of L-1. (a) Screen of anodes when using Pt as the cathode in the electrolysis at room temperature with 4 mA current for 2 hours ($[L-1]/[Co-1]/[Zn-1] = 700/1/1$). (b) Screen of the Cathode when selecting Ni, Zn and Mg as the anodes based on results in (a) ($[L-1]/[Co-1]/[Zn-1] = 700/1/1$). Note that the best results are represented in dark blue (high monomer conversion) and small circle (low $\bar{D}$).

Discussion:

Based on the results in Figure S3, we found that Mg and Ni were optimal for the anode (working electrode) at a $[L-1]/[Zn-1]$ ratio of 700/1. However, at a $[L-1]/[Zn-1]$ ratio of 900/1 at 0 °C, reaction using Mg as the anode (100% in 2 hours) was faster than that using Ni as the anode (90% in three hours). Thus we decide to use Mg as the anode for the eROP of OCAs.

Figure S4. The GPC traces of poly(L-1) at different [L-1]/[Zn-1] ratios (left column, both light-scattering and refractive index detector traces) and differential molecular weight distribution analysis (right column) of the GPC data in Figure 1a, obtained from Wyatt ASTRA software. For the differential molecular weight distribution analysis, the ASTRA software looks at the ratio of scattered light (from light scattering detector) to concentration in each and every data “slice” (from refractive index detector) and calculates a molecular weight. A “slice” of data is determined by a 0.5 second (default value) interval during the data acquisition. The differential weight molar mass distribution (right column red line) reflects the exact molar mass distribution information, based on the data from both detectors. All data showed the monodispersed and narrow molecular weight distributions for all polymers.

Figure S5. NMR spectra of poly(L-1) in CDCl₃ (Table 1, entry 2). (a) ¹H NMR spectrum; (b) Homodecoupling ¹H NMR spectrum; (c) ¹³C NMR spectrum. Note that the small shoulder peak in (b) is due to the NMR instrument. Both the well-split peak of α-proton in (a) and single peak in α-methine in (c) support that no epimerization occurs during the polymerization.

(a) TBAH

(b) TBAH / THF
electrolysis,
4mA, 1h

Figure S6. ^1H NMR spectra of (a) TBAH and (b) The mixture after electrolysis of 0.1 M TBAH in THF solution using the electrochemical polymerization condition ($\text{Mg}(+)/\text{Pt}(-)$, 4mA, 1 hour) without adding the OCA monomer. Solvent: CDCl_3 .

Figure S7. Kinetic plots of the electrochemical ROP of **L-1** with variation of catalysts' concentrations at 0 °C using Mg(+)/Pt(-) electrodes and 4mA current. [**L-1**] = 130.2 mM in all studies. (a) [**Co-1**]/[**Zn-1**]/[BnOH] = 1/1/1. (c, e, g) only the noted catalyst's concentration was changed and the rest is fixed at 0.186 mM in THF. (b, d) Plot of $-\ln(k_{app})$ versus $-\ln[\text{catalyst}]$ for eROP of **L-1**. The slope of which suggests the reaction orders.

Discussion:

We fixed the Co/Zn ratio at 1/1 in the kinetic studies and found the reaction order was 2.16 ± 0.13 (Figure S7b). This value is close to the sum of the individual reaction order of **Co-1** (0.90 ± 0.12 , Figure S7d) and **Zn-1** (1.10 ± 0.10 , Figure S7f), which also suggested no formation of Co-Zn complex during the polymerization (supported by Figure S20). The propagation rate independence of BnOH indicates that BnOH only involved in the chain initiation (Figure S7g). These results suggest that the kinetics of eROP of **L-1** can be described by the equation:

$$-d[\text{L-1}]/dt = k_p [\text{Co-1}]^{0.90} [\text{Zn-1}]^{1.10} [\text{L-1}]^1$$

We listed reaction order as integers in the paper. Note that a few kinetic studies with fitted lines had y-intercept larger than zero, presumably due to the rapid kinetics and experimental error in the early time points (especially for reaction rates at 5 min and 10 min). For higher feeding ratio reactions, the y-intercept values are zero.

(e)	Conv. 60 min (%)	Conv. 120 min (%)	Mg Anode
L-1 (FR = 700, Original Mg)	80.2	100
L-1 (FR = 700, 1 st recycle)	78.4	100
L-1 (FR = 700, 3 rd recycle)	81.5	100
L-1 (FR = 700, 5 th recycle)	82.1	100

Figure S8. Characterizations of electrode surfaces before and after electrochemical polymerization, and after cleaning. (a) Mg electrodes after electrochemical polymerization and after cleaning. The deposited salt in the Mg electrode surfaces can be scraped and cleaned. Scanning electron microscopies of (b) Mg, (c) Ni and (d) Pt electrode surfaces in the conditions of no reaction, after eROP and scraping/cleaning of the surface. (e) Repetitive recycling / cleaning of Mg anode does not affect polymerization kinetic rates.

Figure S9. Energy-dispersive X-ray spectroscopies analysis of the elements on the electrode surfaces that are shown in **Figure S8**. Three conditions correspond to no reaction (b1), after electrochemical polymerization (b2) and after scraping/cleaning of the surface (b3) in Figure S8. The results confirmed that majority of TBAH salt can be removed from Mg anode surface as F atom% decreased from 52.89 % to 2.81 %, accompanied by the absence of P and C after cleaning. The 8.59 atom% of F may suggest the possible diffusion of Mg from anode to cathode surface. Both Pt and Mg electrodes can be recycled for repetitive polymerization studies without affecting the polymerization results (see Table 1 entry 8).

Figure S10. NMR spectra of poly(L-2) in CDCl_3 . (a) ^1H NMR spectrum; (b) Homodecoupling ^1H NMR spectrum; (c) ^{13}C NMR spectrum.

Figure S11. NMR spectra of poly(L-3) in CDCl₃. (a) ¹H NMR spectrum; (b) Homodecoupling ¹H NMR spectrum; (c) ¹³C NMR spectrum.

Figure S12. NMR spectra of poly(L-4) in CDCl_3 . (a) ^1H NMR spectrum; (b) Homodecoupling ^1H NMR spectrum; (c) ^{13}C NMR spectrum.

Figure S13. NMR spectra of poly(L-5) in CDCl₃. (a) ¹H NMR spectrum; (b) ¹³C NMR spectrum.

Figure S14. NMR spectra of poly(L-**1**-*b*-L-**3**) in CDCl₃. (a) ¹H NMR spectrum; (b) ¹³C NMR spectrum; (c) ¹H – DOSY (diffusion ordered spectroscopy) spectrum, which confirms the formation of block copolymer.

Figure S15. ^{13}C NMR spectra overlay of electrochemical stereoselective ring-opening polymerization of *rac*-1. Note that we used ^{13}C NMR spectra for P_m calculation as the homodecoupled ^1H NMR spectra did not present good resolution for polymers with P_m values lower than 0.9.

Figure S16. Plots of monomer conversion in polymerization reactions of (a) L-1 ([L-1]/[Zn-2]/[Co-1]/[BnOH] = 500/1/1/1), D-1 ([D-1]/[Zn-2]/[Co-1]/[BnOH] = 500/1/1/1), and *rac*-1 ([L-1]/[D-1]/[Zn-2]/[Co-1]/[BnOH] = 250/250/1/1/1), [1] = 130.2 mM; (b) L-1 ([L-1]/[Zn-3]/[Co-2] = 500/1/1), D-1 ([D-1]/[Zn-3]/[Co-2] = 500/1/1), and *rac*-1 ([L-1]/[D-1]/[Zn-3]/[Co-2] = 250/250/1/1), [1] = 130.2 mM.

Discussion:

The results in (b) showed that the polymerization of *rac*-1 mediated by **Co-2/Zn-3** had more rapid polymerization rate than that of each enantiomer, which indicated the syndiospecific polymerization of *rac*-1. On the other hand, for isoselective polymerization mediated by **Co-1/Zn-2**, the copolymerization rate was significantly slower than that of each enantiomer.

Based on Figures S15 and S16, we conclude that Co/Zn-mediated stereoselective eROPs are likely exerted by chain end control mechanism. For eROPs of *rac*-1 and *rac*-4 mediated by **Co-1/Zn-2**, our reported work on **Zn-2**¹⁴ suggested the isoselective chain end control mechanism. For eROP of *rac*-1 mediated by **Co-2/Zn-3**, *rmr* peak area is larger than that of *rmm* or *mmr*, suggesting the syndiospecific chain end control mechanism.

We also calculated the average sequence length in poly(*sb*-1) mediated by **Co-1/Zn-2** using Randall's equation:

$$n(m) = (I_{rrr} + 1/2I_{rrm} + 2I_{rmr} + 3/2I_{mmr} + I_{mmm}) / (I_{rrr} + 1/2I_{rrm} + I_{rmr} + 1/2I_{mmr})$$

where I_{mmr} , I_{mmm} , and so on are the respective NMR areas.¹⁶ The poly(*sb*-1) contained an average of 11 units ($n(m)$) of enantiomerically pure **1**. Similarly, we also calculated the average syndiotactic sequence length in poly(*sd*-1) mediated by **Co-2/Zn-3**, following $n(r) = 1 / (1 - P_r)$, where assuming Bernoullian chains. The poly(*sd*-1) contained an average of 5 units ($n(r)$) of racemic **1**.

Figure S17. DSC thermograms of polyesters with various microstructures. Details of polymers' MWs and Ds are shown, respectively, in (a) Table 2, entry 1; (b) Table 2, entry 2; (c) Table S8 entry 10; (d) Table 2, entry 3; (e) Table 2, entry 4; (f) Table 2, entry 5.

Discussion:

Note that our previous studies showed that poly(**L-1**) had a T_g of $50\text{ }^{\circ}\text{C}$, and poly(*rac*-1) had a T_g of $51\text{ }^{\circ}\text{C}$.¹⁴ Neither polymer has a T_m . The T_m peak exhibited in poly(**L-5**) indicated the stereoregularity and no epimerization occurred during the polymerization. Poly(*sb*-4) synthesized

by **Co-1/Zn-2** had a T_m peak of 146 °C, which was absent in that by **Co-2/Zn-3**, presumably due to the difference in their P_m values (see Table S9). Note that both had same T_g values.

Figure S18. ^{13}C NMR spectra overlay of electrochemical isoselective ring-opening polymerization of *rac*-4.

Figure S19. NMR spectra of poly(*sb-3*) in CDCl_3 prepared by **Co-1/Zn-2** (Table 2 entry 3). (a) ^1H NMR spectrum; (b) ^{13}C NMR spectrum.

(a) **Zn-1**

(b) **Co-1**

(c) **Zn-1 / Co-1**

Figure S20. ^{13}C NMR spectra of **Co-1**, **Zn-1** and their mixture (1/1) in toluene- d_8 . The results indicate no interaction between Co and Zn complexes.

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