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

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ABSTRACT: Ring-opening polymerization is used to prepare polyesters with precisely controlled molecular weights, molecular weight distributions, and tacticities. Herein, we report a 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 cationic[1] 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
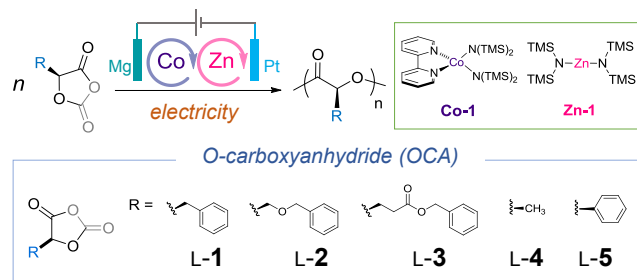
- *High-MW polymers (>140 kDa)* · *Living polymerization (Đ <1.1)*
- *No epimerization · Simple setup in mild reaction conditions*
- *Electrochemically stereoselective ring-opening polymerization*

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 (MW$_{cal}$, 118.5 kDa), and a narrow Đ of 1.04 (Đ =

Table 1. Optimization of Conditions for Electrochemical Ring-Opening Polymerization of *O*-Carboxyanhydrides [a]
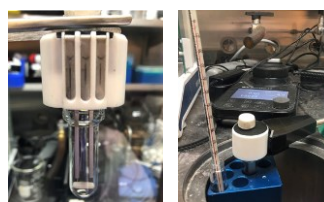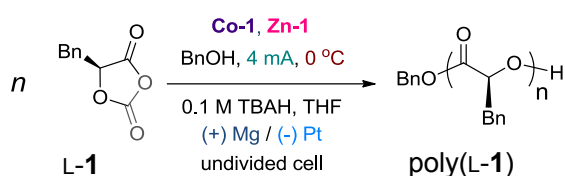
Entry	Conditions	FR	Temp (°C)	Time (h)	Conv (%) [b]	M_n (kDa) [c]	MW$_{cal}$ (kDa)	MW$_{theo}$ (kDa)	$Đ$ [c]
1	As shown	700	0	2	100	103.5	103.7	103.7	1.06
2	As shown	900	0	2	100	135.1	133.3	133.3	1.02
3	As shown	900	r.t.	2	100	69.2	133.3	133.3	1.04
4	No Co-1	700	0	2	53	52.5	103.7	55.0	1.22
5	No Zn-1	700	0	2	33	65.8	103.7	34.3	1.74
6	No BnOH	700	0	2	42	34.4	103.7	43.6	1.44
7	No current	700	0	4	35	49.6	103.7	36.4	1.21
8	Recycled Mg anode [d]	700	0	2	100	105.7	103.7	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); MW$_{theo}$, molecular weight calculated on the basis of 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
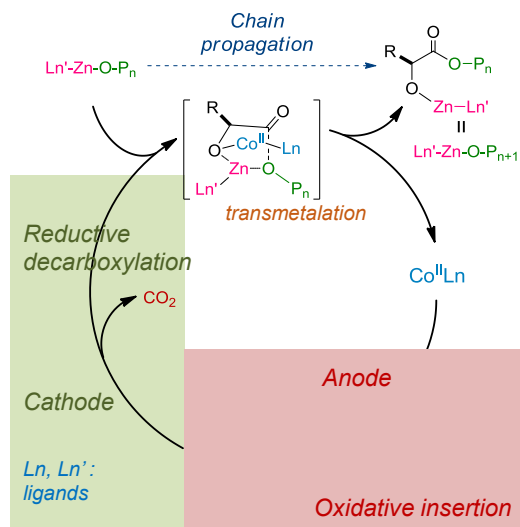
The success of the Co/Zn-mediated photoredox ROP at 0 °C (compared with -15 °C for Ni/Ir/Zn system) without exogenous Ir- or Ru-based polypyridyl photocatalysts inspired us to explore whether this reaction could be modulated electrochemically. Indeed, the cyclic voltammogram (CV) of **Co-1** exhibited 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*-(carbobenzyloxy)-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
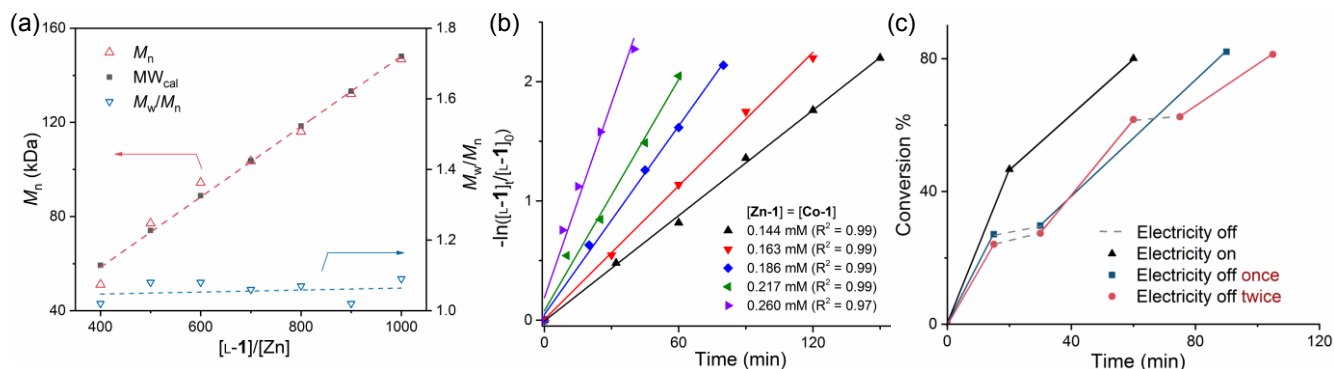
Figure 1. Electrochemically controlled polymerization of L-**1** ([**Co-1**]/[**Zn-1**]/[BnOH] = 1/1/1, [L-**1**] = 130.2 mM in all studies; all reactions are performed at 0 °C using Mg(+)/Pt(-) electrodes and 4mA current). (a) Plots of M_n and MW distribution (M_w/M_n) of poly(L-**1**) versus [L-**1**]/[**Zn-1**] 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 Đ 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, Đ = 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:

$$-d[\text{L-}\mathbf{1}]/dt = k_p [\mathbf{Co\text{-}1}] [\mathbf{Zn\text{-}1}] [\text{L-}\mathbf{1}] \tag{1}$$

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 blade[9] 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 Đ 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 Đ values (Figure S14).

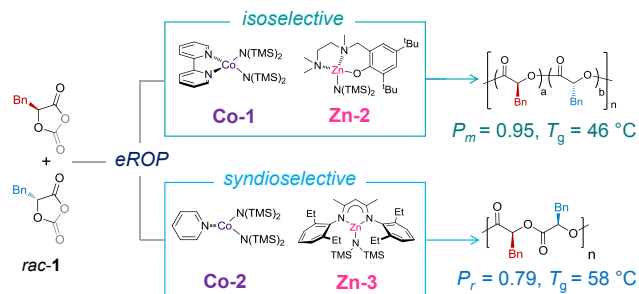**Scheme 3. Co/Zn Complex-Mediated Stereoselective Electrochemical Ring-Opening Polymerization of *rac*-1**

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)	Đ [c]	P_m [d]
1	rac-**1** (300)	Co-1/ Zn-2	100	67.6	44.5	1.05	0.95
2	rac-**1** (300)	Co-2/ Zn-3	100	46.2	44.5	1.07	0.21 [e]
3	rac-**3** (200)	Co-1/ Zn-2	100	34.7	44.1	1.04	0.98
4	rac-**4** (300)	Co-1/ Zn-2	100	32.2	21.7	1.08	0.90

| 5 | rac-**4** (300) | Co-2/ Zn-3 | 100 | 49.6 | 21.7 | 1.07 | 0.89 |

[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; $Đ$, 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 ^{13}C NMR spectroscopy. [e] $P_r = 1 − P_m = 0.79$, where P_r 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 $Đ$ (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 syndioselective 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 $Đ$ of 1.07 (entry 2), and a decent P_r (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 ^{1}H and ^{13}C NMR spectra, DSC data and CV curves.

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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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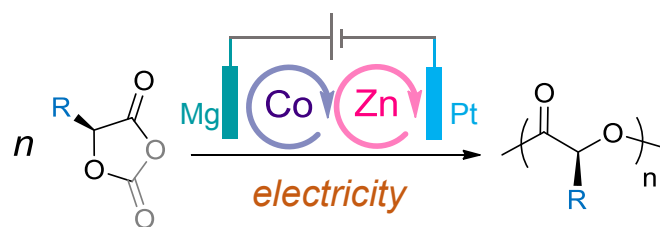
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TOC

✓ *High-MW polymers (>140 kDa)*
✓ *Living polymerization (Đ <1.1)*
✓ *No epimerization*
✓ *Simple setup in mild reaction conditions*
✓ *Electrochemically stereoselective polymerization*