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Development of Highly Active and Regioselective Catalysts for the Copolymerization of Epoxides with Cyclic Anhydrides: An Unanticipated Effect of Electronic Variation

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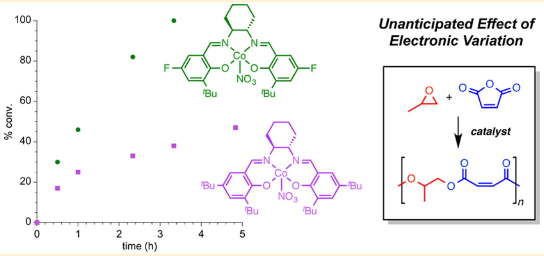
Supporting Information

ABSTRACT: Recent developments in polyester synthesis have established several systems based on zinc, chromium, cobalt, and aluminum catalysts for the ring-opening alternating copolymerization of epoxides with cyclic anhydrides. However, to date, regioselective processes for this copolymerization have remained relatively unexplored. Herein we report the development of a highly active, regioselective system for the copolymerization of a variety of terminal epoxides and cyclic anhydrides. Unexpectedly, electron withdrawing substituents on the salen framework resulted in a more redox stable Co(III) species and longer catalyst lifetime. Using enantiopure propylene oxide, we synthesized semicrystalline polyesters via the copolymerization of a range of epoxide/anhydride monomer pairs.



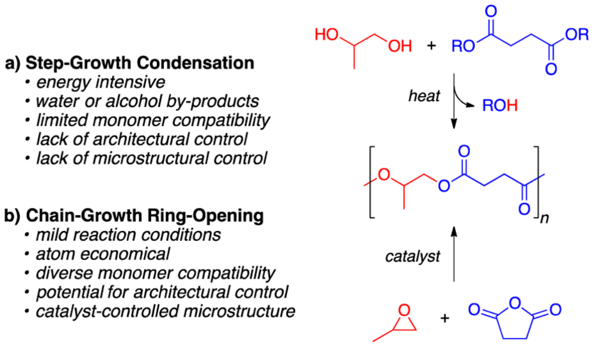
INTRODUCTION

Polyethylene (PE) and isotactic polypropylene (iPP) are key industrial polymers because of their low cost and superior performance, supported by robust manufacturing methods.[1] The thermal properties of PE and iPP materials can be tuned by adjusting their percent crystallinity, facilitating easy processing and diverse applications. For PE, semicrystallinity results from a linear backbone structure, whereas for iPP, it results from high stereo- and regioregularity.[2] Recent advances in catalyst performance have enabled the development of new systems that create polyolefins in which stereo- and regiochemistry are precisely controlled, along with advanced systems that create polymers of defined molecular weight and with block morphologies.[3] These key technologies diversify the utility of polyolefins in manufacturing; however, one remaining limitation is the difficulty of incorporating polar monomers.[4]

Polyesters are good candidates for a new class of functionally diverse material to compliment semicrystalline PE and iPP;[5] however, comparable catalyst systems to control stereo- and regiochemistry are required.[2b,6] Most commodity polyesters are prepared industrially via the step-growth copolymerization of diols and diesters (Scheme 1a).[5a] Although a wide range of diol and diester monomers are available, this process is energy-intensive, and controlling polymer microstructure and molecular weight are difficult.[5a,7] For example, unsymmetrically substituted monomers are randomly enchained by step-growth mechanisms to create regioirregular, usually amorphous polymers.

Alternatively, polyesters can be synthesized via the chain-growth ring-opening polymerization of lactides and lactones.[8] In this atom-economical process, regiochemistry is inherent to the monomers, which ring-open in the same manner every time. Poly(lactide) and poly(hydroxybutyrate) are examples of semicrystalline polyesters prepared with this method; however, their utility is in some cases restricted by their poor thermal properties and limited functional diversity.

Scheme 1. Copolymerization Routes for the Synthesis of Polyesters: (a) Step-Growth Condensation and (b) Chain-Growth Ring-Opening



The ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides is another promising route to structurally diverse polyesters (Scheme 1b).[9] β-Diiminate zinc (BDI)Zn(II)[9a,b] and *N*,*N*′-bis(salicylidene)ethylenediimine chromium (salen)Cr(III)[9c−h,j] type complexes can catalyze the formation of highly alternating polyesters from a variety of cyclic anhydrides and epoxides. To date, most monometallic systems yield regioirregular polyesters, and only one report of a bimetallic Cr complex by Lu[9k] et al. showed up to 99% regioregular head-to-tail linkages for the copolymerization of

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maleic anhydride (MA) with (*S*)-phenyl glycidyl ether. Considering the similar mechanisms for the copolymerization of epoxides with CO_2, we drew upon examples from this field in pursuit of developing robust regioselective catalysts for the reaction of epoxides with cyclic anhydrides with hopes that the more Lewis acidic cobalt metal center would impart selectivity to epoxide ring-opening.[10]

(BDI)Zn and (salen)Cr-type catalysts exhibit low regioselectivity in the ring-opening copolymerization of terminal epoxides and CO_2.[11] However, we and others have observed that *N,N′*-bis(salicylidene)cyclohexanediimine cobalt (salcy)-Co(III)-type catalysts produce highly regioregular polycarbonates.[12] Therefore, we investigated the ROCOP of epoxides and cyclic anhydrides catalyzed by (salcy)Co(III)-type complexes and addressed the low activity described for these systems in previous publications.[9c,d,f]

Herein we report the effects of complex preparation, addition of cocatalysts, and ligand electronics[9o,w] on the activity and selectivity of (salcy)Co(III) catalysts for the copolymerization of various epoxides and cyclic anhydrides. Epoxide electronics distinctly influence copolymerization rates with MA, in which the most electron-poor epoxides produce the most active [turnover frequency (TOF) > 300 h^{-1}] systems. A variety of other cyclic anhydrides can be copolymerized with terminal epoxides to yield high-molecular-weight polyesters with good activity at low catalyst concentrations. The high regioselectivity of this system allows the creation of semicrystalline stereoregular polyesters when using enantiopure propylene oxide (PO). Semicrystallinity is unique to polyesters, since the copolymerization of enantiopure PO with CO_2 yields exclusively amorphous polycarbonate, emphasizing the potential for polyesters as a platform for a new class of semicrystalline materials.[12]

■ EXPERIMENTAL SECTION

Representative Copolymerization Procedure. In a glovebox, the metal salcy complex (0.010 mmol), PPN cocatalyst (0.010 mmol), and MA (**2a**, 98.0 mg, 1.00 mmol) were measured into a flame-dried 4.0 mL vial equipped with a Teflon-coated stir bar. PO (**1a**, 0.14 mL, 2.0 mmol) was added via syringe, washing all solids into the base of the vial. The vial was sealed with a Teflon-lined cap, removed from the glovebox, and placed in an aluminum heat block preheated to 30 °C. After the reaction became viscous or all visible anhydride monomer disappeared, the vial was removed from the heat block, the mixture was dissolved in CH_2Cl_2, and a small aliquot was analyzed for conversion using ^1H NMR spectroscopy. The CH_2Cl_2 polymer mixture was then precipitated into an excess of hexanes, and the process repeated until no residual monomer was detected in the ^1H NMR spectrum of the product. For polyesters containing phthalic anhydride, methanol was used as a nonsolvent instead of hexanes. After several rounds of precipitation, the material was collected and dried in vacuo.

■ RESULTS AND DISCUSSION

Several studies report low activity for the Co-catalyzed copolymerization of epoxides with cyclic anhydrides.[9c,f] In agreement with these findings, the results of our previous publication show lower yields for the reaction of PO and MA catalyzed by *rac*-(salcy)$CoO_2CC_6F_5$ compared with *rac*-(salcy)-CrCl.[9d] However, the poly(propylene maleate) (PPM) synthesized by the Co catalyst is more regioregular than that produced by the similar Cr catalyst (Figure 1).[9d] Intrigued by these results, we focused our efforts on improving the activity of the regioselective Co copolymerization system.

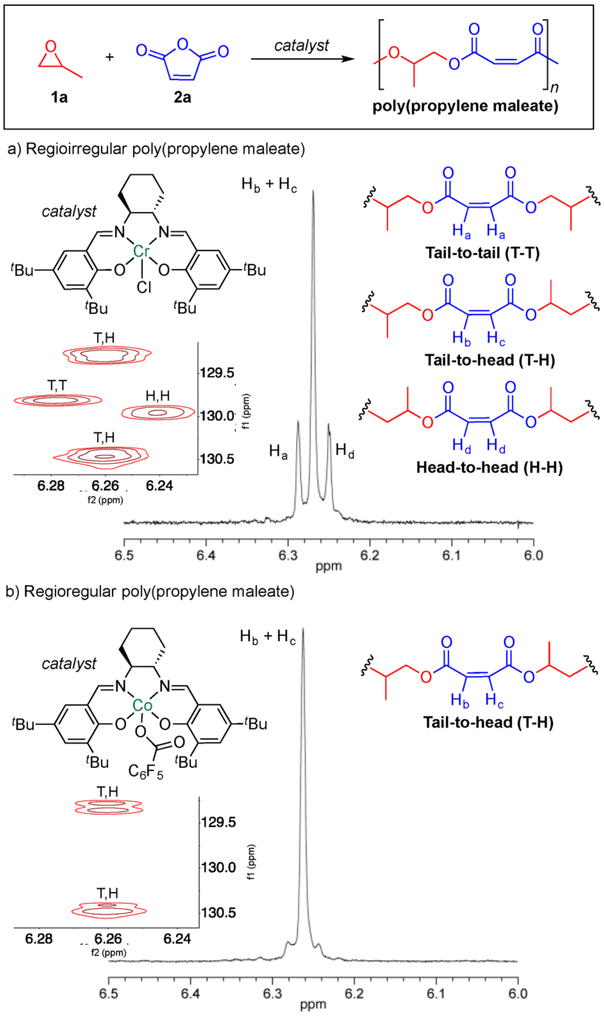
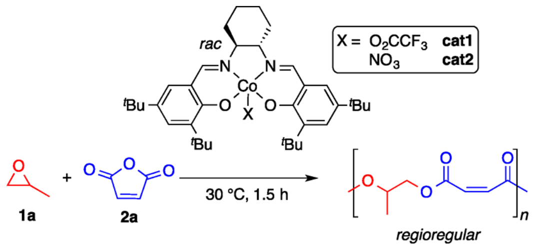


Figure 1. Analysis of regiochemistry using ^1H and band selective gradient HSQC NMR spectroscopy of poly(propylene maleate) (PPM): (a) alkene region of the spectrum of regioirregular PPM produced by *rac*-(salcy)CrCl; (b) alkene region of the spectrum of regioregular PPM produced by *rac*-(salcy)$CoO_2CC_6F_5$.

Many salcy complexes open epoxides regioselectively,[13] and because of their particular success in polycarbonate polymerizations, we chose to study variations of (salcy)Co(III) catalysts.[12] We initially measured the activity of complexes with different initiators and cocatalysts synthesized using two separate methods (Table 1). Catalyst **cat1** was prepared via metalation of *rac*-(salcy)H_2 with $Co(OAc)_2$ and subsequent oxidation of the isolated *rac*-(salcy)Co(II) complex with trifluoroacetic acid in air to give *rac*-(salcy)CoO_2CCF_3.[14] This complex is representative of several complexes with acetate and perfluoroacetate and benzoate counteranions, which yielded comparable results. Catalyst **cat2** was prepared via a one-pot metalation of (salcy)H_2 with $Co(NO_3)_2{\cdot}6H_2O$ and in situ oxidization with HNO_3 (formed during the reaction) in air to obtain *rac*-(salcy)$CoNO_3$.[15]

Due to the tendency of (salcy)Co(III) complexes to reduce in situ at high temperatures,[12a,13,14] **cat1** and **cat2** were screened neat at 30 °C with racemic PO (**1a**) and MA (**2a**; see Table 1). In the absence of ionic cocatalysts, both systems formed polyesters that contained polyether linkages (from consecutive enchainment of epoxide, entries 1 and 3). This finding contrasts with our previous results using *rac*-(salcy)-

Table 1. Initiators and Cocatalysts Evaluated for the Regioselective Copolymerization of PO (1a)/MA (2a) with (salcy)Co(III)-Type Catalysts[a]



entry	catalyst	cocatalyst	% conv[b]	% ether linkages[c]	M_n^{theo} (kDa)	M_n^{obs} (kDa)[d]	PDI[d]
1	**cat1**		19	22	3.2	3.0	1.16
2	**cat1**	[PPN][O_2CCF_3]	25	<1	2.0[e]	1.8	1.10
3	**cat2**		42	16	6.9	3.4	1.22
4	**cat2**	[PPN][NO_3]	52	<1	4.1[e]	2.6	1.18

[a] General conditions: **1a**/**2a**/**cat**/cocat = 200:100:1:1. [b] Calculated using ^{1}H NMR spectroscopy based on **2a** as the limiting reagent. [c] Determined with ^{1}H NMR spectroscopy of crude reaction mixture. [d] Polydispersity index (PDI) measured using gel-permeation chromatography relative to polystyrene standards eluted at 0.3 mL/min with THF at 30 °C. [e] Calculated based on the assumption of two initiating groups.

$CoO_2CC_6F_5$ in the absence of a cocatalyst, in which no measurable polyether linkages formed; however, the previous reaction was conducted at higher temperatures under more dilute conditions.[9d] Based on reports of activity and selectivity increases for (salcy)M(III)-catalyzed (M = Cr, Co) epoxide/CO_2 copolymerizations, we added nucleophilic cocatalysts such as bis(triphenylphosphine)iminium salts ([PPN][X]).[12a]

In the presence of [PPN][X], both catalysts yielded exclusively alternating, regioregular polyesters, as determined by ^{1}H NMR spectroscopy (entries 2 and 4). Catalyst **cat2** showed higher activity than **cat1** in both the presence and absence of a cocatalyst and exhibited a smaller amount of reduced *rac*-(salcy)Co(II) [visually indicated by a bright brick-red color vs the green-brown color of the Co(III) species]. Therefore, derivatives of **cat2** were selected for further study with 1 equiv of [PPN][NO_3]. Despite optimizations, the molecular weights of MA copolymers were generally lower than predicted and are the subject of ongoing investigations.

We next examined the electronic effects of salcy ligand substituents, expecting the electronic nature of the ligand to influence the Lewis acidity of the cobalt center and thereby affect the reaction rate.[13,16] Additionally, phenolate ligands reportedly influence the redox properties of coordinated metals, where the redox stability affects catalyst activity.[17] Five additional *rac*-(salcy)$CoNO_3$ complexes with electron-donating (OMe, Me) or electron-withdrawing (F, Cl, NO_2) substituents at the 5-positions of the salicylidene moieties were prepared and tested for activity in the copolymerization of **1a** with **2a** (Figure 2a). Electron-withdrawing ligands resulted in more active catalysts as measured by average TOF (mol monomer · mol cat^{-1} · h^{-1}). Notably, **cat5** produced the highest TOF of 38 h^{-1} (entry 4). However, activity did not improve linearly with increasingly electron-withdrawing ligands, suggesting that Lewis acidity is not the only contributor to overall activity.

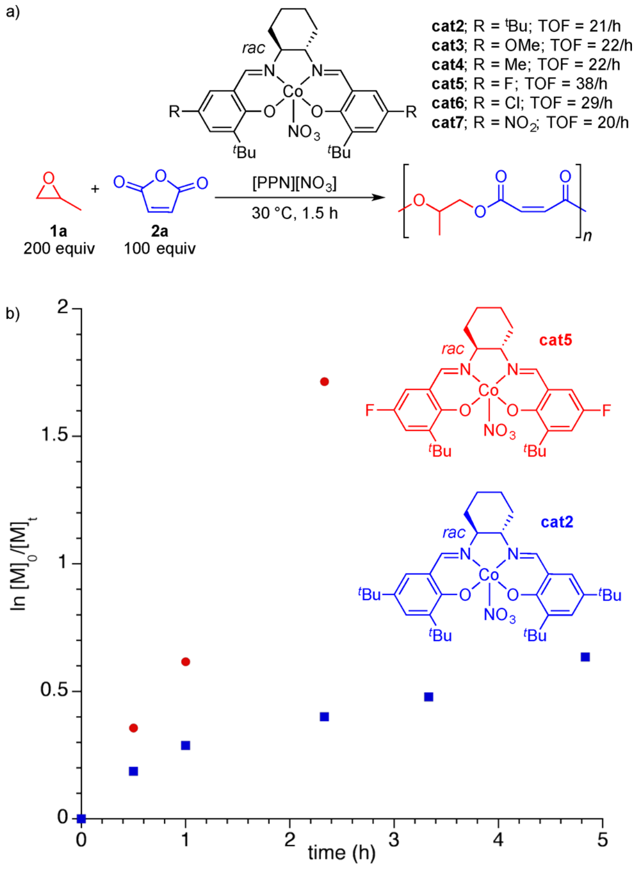


Figure 2. Impact of ligand electronics on the copolymerization behavior of *rac*-(salcy)$CoNO_3$/[PPN][NO_3] catalyst systems: (a) Average turnover frequency (TOF) {(RPU)[(cat)·h]$^{-1}$} of each catalyst for the copolymerization of **1a**/**2a** measured at t_{rxn} = 1.5 h; (b) first order plot of conversion versus time for the **cat2**- and **cat5**-catalyzed copolymerization of **1a**/**2a**.

To better understand the observed activity differences, copolymerizations of PO and MA catalyzed by **cat2** (R = ^{t}Bu) and **cat5** (R = F), respectively, were studied in detail spectroscopy. Addition of **cat2**/[PPN][NO_3] to a PO/MA mixture immediately produced a paramagnetic species as determined by ^{1}H NMR spectroscopy, preventing measurement of polymerization kinetics and suggesting the formation of a Co(II) complex. In contrast to this, **cat5**/[PPN][NO_3] remained diamagnetic, allowing direct monitoring of polymerization progress and suggesting the presence of a stable, octahedral (salcy)Co(III) species. Time-lapse aliquots of each polymerization reflected the activity and stability (or lack thereof) of each system (Figure 2b). The activity of **cat2** diminished over time, reaching only 40% conversion of MA in

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5 h. This result suggests that the paramagnetic species may contribute to catalyst deactivation. Conversely, the activity of **cat5** remained constant, achieving 100% conversion of MA in 4 h.

We next characterized the electrochemical properties of each catalyst using cyclic voltammetry and rotating disk electrode voltammetry to directly investigate how ligand electronics affect the redox stability of cobalt in (salcy)Co(III). The CV curves of **cat2** and **cat5** each exhibited three redox events: one metal-centered couple near −100 mV representing the Co(III)/Co(II) transition and two ligand-centered couples at potentials of >600 mV (Figure 3). These curves matched well with literature reports of similar compounds.[17a] Under representative copolymerization conditions, both catalysts retained all signature redox couples. However, the electrochemical behaviors of the metal centers with respect to the potential required for a Co(III)/Co(II) transition were dependent on ligand identity.[18] The cyclic voltammetry results suggest that thermodynamically, **cat5** reduces to Co(II) more easily. In addition, rotating disk voltammetry shows that kinetically **cat5** is also reduced more quickly than **cat2**.[18] While these results contradict the higher activity observed for polymerizations with **cat5**, Lu and co-workers[19] recently proposed a mechanism for hydrolytic kinetic resolution in which reduction of Co(III) to Co(II) involves a Co(IV) intermediate. We propose that because **cat2** is more easily oxidized than **cat5**, it can more readily undergo this transition to Co(IV), which ultimately produces Co(II). This series of redox events results in a less stable catalyst for the polymerization of **1a** with **2a**.[18] Consistent with this mechanistic proposal, both catalysts maintain activity in the presence of oxygen but produce low molecular weight polymers due to chain transfer to adventitious atmospheric water.

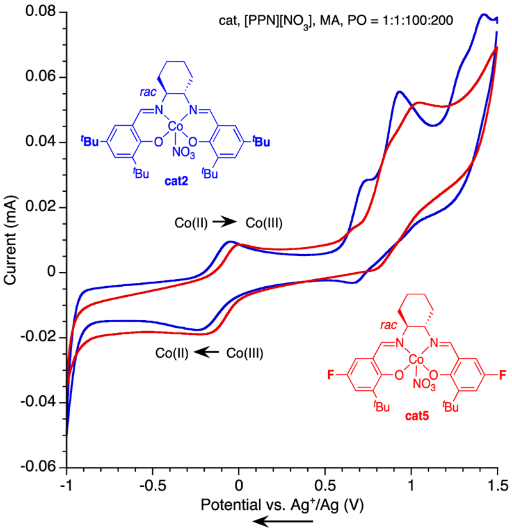
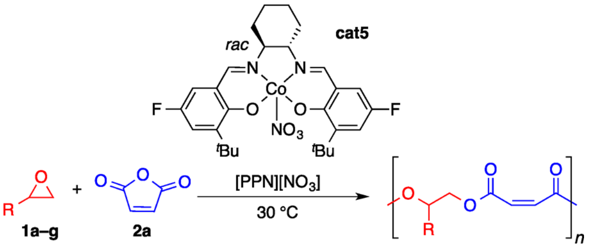
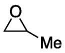
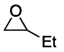
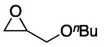
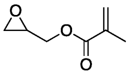
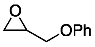
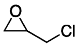
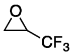


Figure 3. Cyclic voltammetry curves collected from 1.5 to −1.0 V for 1.0 mM solutions of **cat2** (blue) and **cat5** (red) in 0.1 M tetrabutylammonium perchlorate/acetonitrile with 1 equiv of [PPN][NO$_3$], 100 equiv of maleic anhydride (MA), and 200 equiv of propylene oxide (PO).

With a more robust cobalt catalyst system in hand, we evaluated copolymerization scope and regioselectivity. **Cat5**/[PPN][NO$_3$] was tested for the ROCOP of MA with a variety of epoxides (Table 2). NMR spectroscopic analysis of the polyester products revealed highly regioregular structures.[9n] Electron-rich epoxides (entries 1 and 2) were slower to copolymerize, whereas glycidyl ethers with electron-withdrawing substituents (entries 3−5) exhibited enhanced polymerization rates. Electron-poor epoxides (entries 6 and 7) were faster and yielded polyesters with higher molecular weights and narrower polydispersity indices. Epoxides with orthogonally reactive groups such as methyl methacrylates (**1d**) and primary alkyl chlorides (**1f**; entries 4 and 6) readily polymerized without side reactions to afford polyesters capable of postpolymerization modifications.

Table 2. Ring-Opening Alternating Copolymerization of Maleic Anhydride (2a) with Terminal Epoxides (1a−g) Using cat5/[PPN][NO$_3$]^a



Entry	Epoxide	Time (h)	% Conv. 2a^b	TOF^c (h^{-1})	% Ether^d	M_n^{theo} (kDa)^e	M_n^{obs} (kDa)^f	PDI^f	T_g (°C)
1	 **(1a)**	1.5	65	43	<1	5.1	3.4	1.21	21
2	 **(1b)**	1.5	37	25	<1	3.2	2.2	1.19	9
3	 **(1c)**	1.5	40	27	<1	4.6	3.3	1.26	-18
4	 **(1d)**	0.83	91	109	<1	10.9	6.3	1.24	-6^g
5	 **(1e)**	0.67	71	140	<1	8.8	4.8	1.27	36
6	 **(1f)**	0.25	77	308	<1	7.3	5.5	1.17	26
7	 **(1g)**	0.67	88	131	<1	9.2	5.2	1.13	25

^{a}General conditions: **1**/**2**/**cat5**/[PPN][NO$_3$] = 200:100:1:1. ^{b}Calculated using ^{1}H NMR spectroscopy based on **2a** as the limiting reagent. ^{c}Turnover frequency. ^{d}Determined with ^{1}H NMR spectroscopy of crude reaction mixture. ^{e}Calculated based on the assumption of two initiating groups. ^{f}Measured using gel-permeation chromatography relative to polystyrene standards eluted at 0.3 mL/min with THF at 30 °C. ^{g}Measured using differential scanning calorimetry; values reported are from the second heat. ^{h}After rigorous drying, this polymer cross-linked; thus the differential scanning calorimetry measurement reflects the cross-linked product.

Next, the copolymerization of different cyclic anhydrides (**2b−d**) with PO (**1a**) was evaluated using **cat2−cat7**/[PPN][NO$_3$] (Figure 4). In all examples, **cat5**/[PPN][NO$_3$] exhibited the highest activity and was further tested at lower catalyst concentrations (see Table 3). Catalyst degradation even with **cat5** limited molecular weights for the copolymerization of PO (**1a**) with MA (**2a**) and succinic anhydride (SA) (**2b**; entries 1 and 2). By contrast, **cat5**/[PPN][NO$_3$] was highly active and produced high-molecular weight polyesters for the copolymerization of PO with diglycolic (DGA) (**2c**) and phthalic anhydrides (PA) (**2d**; entries 3 and 4). The copolymerization of any of these anhydrides with the electron-poor epoxide epichlorohydrin (**1f**) resulted in higher TOFs and

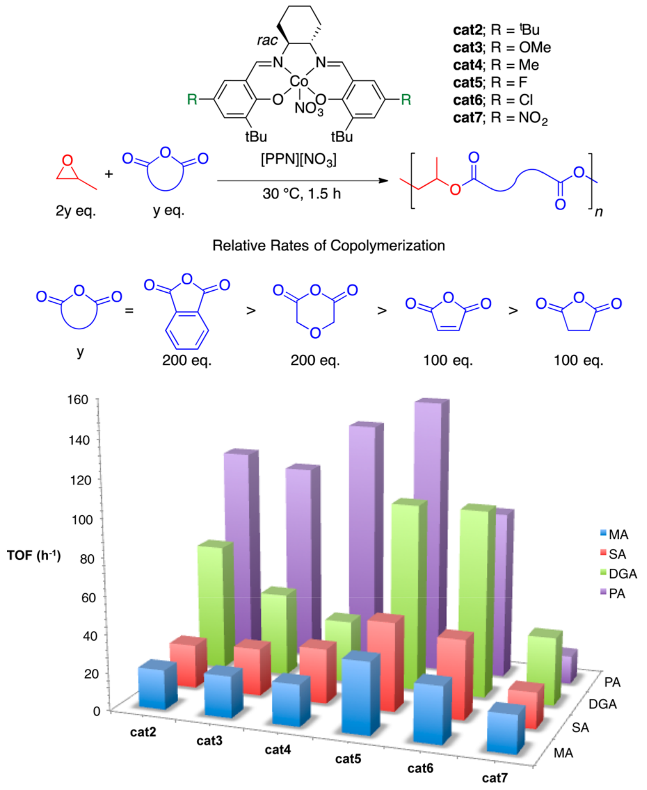


Figure 4. Impact of ligand electronics on catalyst activity for the copolymerization of different cyclic anhydrides with propylene oxide.

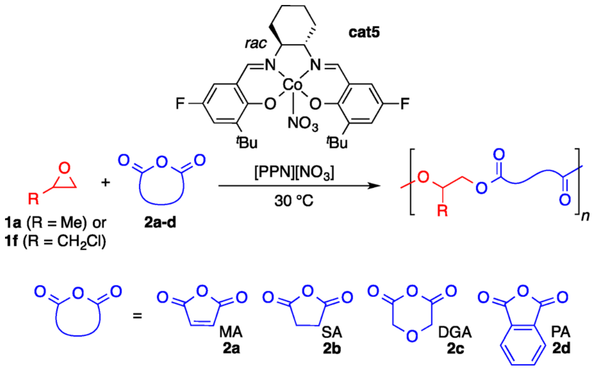
was amenable to changes in reaction stoichiometry (entries 5–8).

Finally, the regioselectivity of this system was quantitatively measured by analyzing the retention of stereochemistry from copolymerizations using enantiopure (*S*)-PO (*S*-**1a**), because ring-opening at the methine instead of the methylene carbon results in both a regioerror and a stereoerror via S_N2-type attack.[9i,n] As we have previously reported, the regioregularity of poly(propylene succinate) was optimized by polymerization with the enantiopure salcy catalyst of opposite absolute stereochemistry of the epoxide.[9n] High regioregularity, in turn, resulted in enhanced crystallinity and higher T_m's of the polymer chains. Therefore, polyesters with anhydrides **2a–d** were synthesized using (*R*,*R*)-**cat5** and (*S*)-PO with an enantiomeric excess (ee) of 99%, and the percentage of regioerrors was determined by measuring the ee of the propylene glycol formed after hydrolysis of the polyester (Figure 5). All anhydrides exhibited high levels of regioregularity (90–99%HT), and DGA (**2c**) and PA (**2d**) were almost exclusively regioregular. Importantly, polyesters formed with MA (**2a**), SA (**2b**), and PA (**2d**) with (*S*)-PO exhibited high melting points (76–152 °C), giving some of the first examples of semicrystalline polyesters synthesized via alternating copolymerization of readily available epoxides and cyclic anhydrides.

■ CONCLUSIONS

We have reported one of the first highly active and regioselective catalyst systems for the ring-opening copolymerization of epoxides and cyclic anhydrides. Through detailed studies of ligand electronics and their impact on catalyst behavior, the fluorine substituted *rac*-(salcy)$CoNO_3$ complex **cat5** was developed as a more stable and active copolymerization catalyst with good substrate scope (Figure 5).

Table 3. cat5/[PPN][NO_3]-Catalyzed Copolymerization of a Variety of Cyclic Anhydrides (2a–d) with PO (1a) or Epichlorohydrin (1f)[a]



entry	reagents	time (h)	% conv 2[b]	TOF (h^{-1})[c]	% ether[d]	M_n^{theo} (kDa)[e]	M_n^{obs} (kDa)[f]	PDI[g]	T_g (°C)[h]
1[h]	**1a**/**2a**	1.5	65	43	<1	5.1	3.4	1.21	21
2[i]	**1a**/**2b**	5.0	85	34	<1	6.7	4.8	1.23	−8
3	**1a**/**2c**	3.0	71	95	<1	24.7	10.7	1.29	2
4	**1a**/**2d**	3.5	70	80	<1	28.8	19.1	1.16	63
5	**1f**/**2a**	6.5	71	44	<1	19.4	16.0	1.26	16
6	**1f**/**2b**	5.0	83	66	<1	31.9	20.0	1.28	7
7	**1f**/**2c**	1.0	97	388	<1	40.4	17.5	1.27	1
8[j]	**1f**/**2d**	2.5	80	128	<1	38.4	21.0	1.13	65

[a] General conditions: **1**:**2**:**cat5**:[PPN][NO_3] = 800:400:1:1. [b] Calculated using ^1H NMR spectroscopy based on **2** as the limiting reagent. [c] Turnover frequency. [d] Determined with ^1H NMR spectroscopy of crude reaction mixture. [e] Calculated based on the assumption of two initiating groups. [f] Measured using gel-permeation chromatography relative to polystyrene standards eluted at 0.3 mL/min with THF at 30 °C. [g] Measured using differential scanning calorimetry; values reported are from the second heat. [h] **1a**:**2a**:**cat5** = 200:100:1. [i] **1a**:**2b**:**cat5** = 200:200:1, [**cat5**] = 0.1 mM benzene. [j] **1f**:**2d**:**cat5** = 400:400:1, [**cat5**] = 0.05 mM THF.

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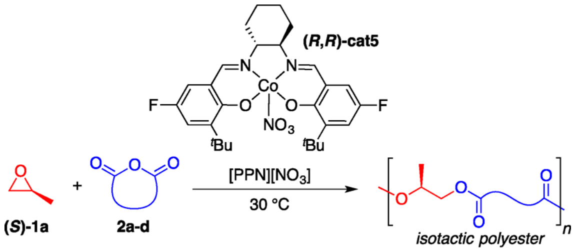

Anhydride	Polyester T_m (°C)	% (S) Stereocenters in Polymer
MA (**2a**)	120	95
SA (**2b**)	76	98
DGA (**2c**)	n.d.	>99
PA (**2d**)	152	>99

Figure 5. Quantitative analysis of regiochemistry for semicrystalline polyesters made with (*S*)-propylene oxide/anhydrides by enantiopure (***R,R***)-**cat5**/[PPN][NO_3] via degradation and % ee analysis of isolated propylene glycol products. MA, maleic anhydride; SA, succinic anhydride; DGA, diglycolic anhydride; PA, phthalic anhydride. All T_m's are reported from first heating cycle due to slow recrystallization kinetics.

Furthermore, we found that enantiopure **cat5** produced very highly regioregular and semicrystalline polyesters. We are incorporating these findings into progressive ligand design with the goal of further improving the activity and molecular weight capabilities of the *rac*-(salcy)$CoNO_3$ system. The stable diamagnetic *rac*-(salcy)Co(III) complex is being used to understand the mechanism of epoxide and cyclic anhydride enchainment and strategize methods for avoiding chain termination. Semicrystalline polyesters from racemic starting materials will be pursued using chiral derivatives of the redox-stabilized ligand architectures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03113.

Additional experimental procedures, characterization data, and spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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