

UC Berkeley

UC Berkeley Previously Published Works

Title

Mechanism-Inspired Design of Bifunctional Catalysts for the Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides

Permalink

<https://escholarship.org/uc/item/1xm0s04p>

Journal

Journal of the American Chemical Society, 141(32)

ISSN

0002-7863

Authors

Abel, Brooks A
Lidston, Claire AL
Coates, Geoffrey W

Publication Date

2019-08-14

DOI

10.1021/jacs.9b05570

Peer reviewed

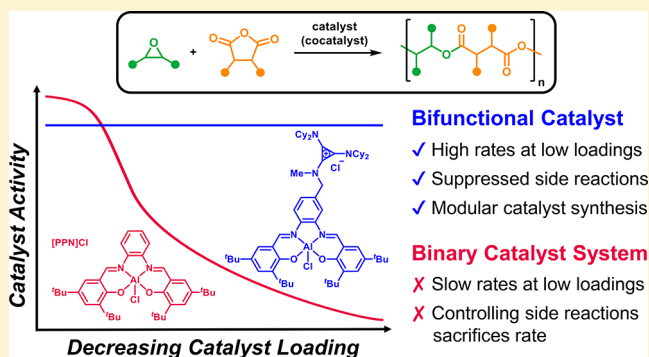
Mechanism-Inspired Design of Bifunctional Catalysts for the Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides

Brooks A. Abel,[‡] Claire A. L. Lidston,[‡] and Geoffrey W. Coates*[‡]

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, United States

Supporting Information

ABSTRACT: Advances in catalysis have enabled the ring-opening copolymerization of epoxides and cyclic anhydrides to afford structurally and functionally diverse polyesters with controlled molecular weights and dispersities. However, the most common systems employ binary catalyst/cocatalyst pairs which suffer from slow polymerization rates at low loadings. Inspired by new mechanistic insight into the function of binary metal salen/nucleophilic cocatalyst systems at low concentrations, we report a bifunctional complex in which the salen catalyst and an aminocyclopropenium are covalently tethered. A modular ligand design circumvents the extended linear syntheses typical of bifunctional catalysts, enabling systematic variation to understand and enhance catalytic activity. The optimized bifunctional aluminum salen catalyst maintains excellent activity for the ring-opening copolymerization of epoxides and cyclic anhydrides at low concentrations (≥ 0.025 mol %), and the aminocyclopropenium cocatalyst suppresses undesirable transesterification and epimerization side reactions, preserving the integrity of the polymer backbone.



INTRODUCTION

Aliphatic polyesters are promising sustainable alternatives to petroleum-based plastics due to their potentially renewable monomers, ease of recycling, and biodegradability.^{1–3} Yet many industrial methods of polyester production employ energy-intensive polycondensation reactions that produce small molecule byproducts,^{4,5} creating a pressing need for more sustainable synthetic routes. The ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides provides a lower-temperature and atom-economical chain-growth approach to aliphatic polyester synthesis, producing materials with controlled molecular weights and low dispersities.^{6,7} Additionally, this strategy enables a wide range of monomer combinations, permitting the synthesis of polyesters with readily tunable renewable content and thermomechanical properties.⁸ Current catalyst/cocatalyst systems for ROCOP (Scheme 1) typically exhibit moderate to poor activities at low catalyst loadings and often fail to prevent deleterious side reactions, such as epoxide homopolymerization, transesterification, or epimerization.

In 1985, Inoue copolymerized propylene oxide (PO) and phthalic anhydride (PA) using an aluminum porphyrin complex in conjunction with a tetraalkylammonium salt.⁹ Subsequent efforts by our group,^{10–14} Darensbourg,¹⁵ Williams,^{16–18} Duchateau,^{19,20} and others have resulted in diverse metal^{21–23} and organocatalysts,^{24–28} the most successful of which are based on the salenMX framework

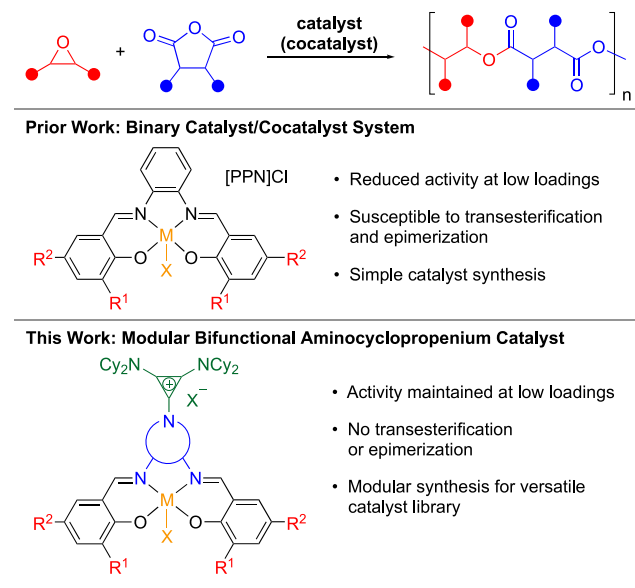
(salen = *N,N'*-bis(salicylidene)ethylenediamine).^{29–32} In these systems, the Lewis acid/nucleophilic cocatalyst pair initiates polymerization, activates epoxide toward ring-opening, and modulates the reactivity of the propagating chain-ends. A mechanistic study by the Tolman, Coates, and Cramer groups demonstrated that a mixed alkoxide/carboxylate intermediate preferentially ring-opens cyclic anhydride to generate a (bis)carboxylate resting state.³³ From this species, epoxide binding at the Lewis acid is fast relative to rate-limiting epoxide ring-opening by a cocatalyst-associated carboxylate (Scheme 2). Therefore, dilution of the catalyst/cocatalyst pair at low loadings is anticipated to inhibit nucleophilic attack by the cocatalyst-associated propagating chain at the metal-bound epoxide. Nevertheless, performing polymerizations at decreased catalyst concentrations is highly desirable to reduce cost, minimize catalyst residue, and access high molecular weight materials.

To subvert the effects of dilution on binary catalyst activity in epoxide/CO₂ copolymerization, Nozaki,³⁴ Lee,^{35–44} Lu,^{45–50} and others^{51–54} have developed highly active cobalt salen catalysts in which the Lewis acid and nucleophilic cocatalyst are covalently tethered. Extending two of these bifunctional systems to terpolymerizations with cyclic anhydrides afforded block⁵¹ and gradient⁴⁴ poly(carbonate-*co*-ester)

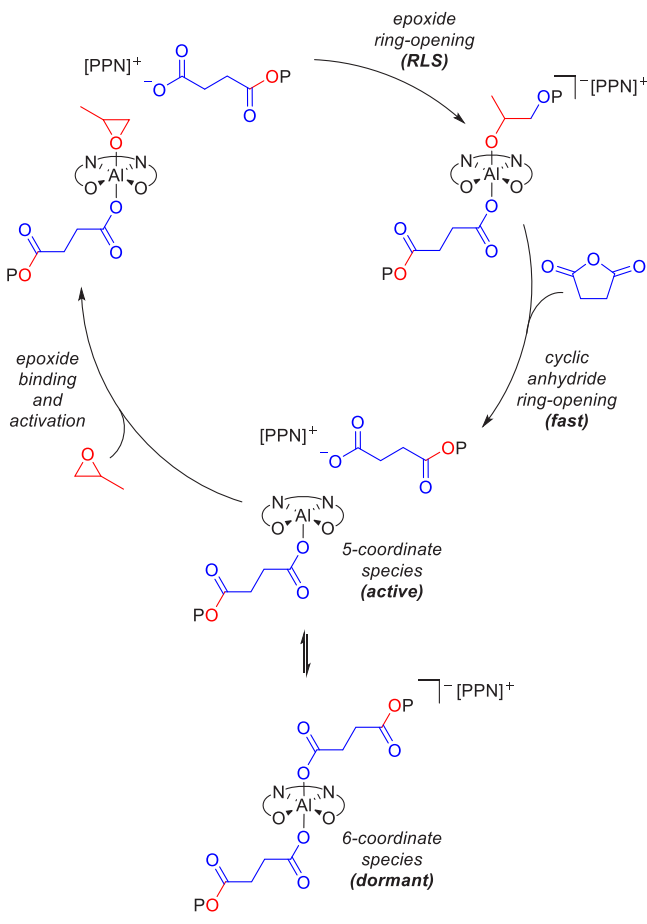
Received: May 24, 2019

Published: August 5, 2019

Scheme 1. Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides Using a Binary Catalyst/Cocatalyst System or Bifunctional Catalyst



Scheme 2. Simplified Mechanism of Epoxide/Cyclic Anhydride Copolymerization in the Binary System³³



copolymers with attenuated activity at increasing ratios of anhydride:CO₂. In their terpolymerization report, Lee and co-workers use a cobalt salen complex bearing four quaternary ammonium substituents in the absence of CO₂. While they

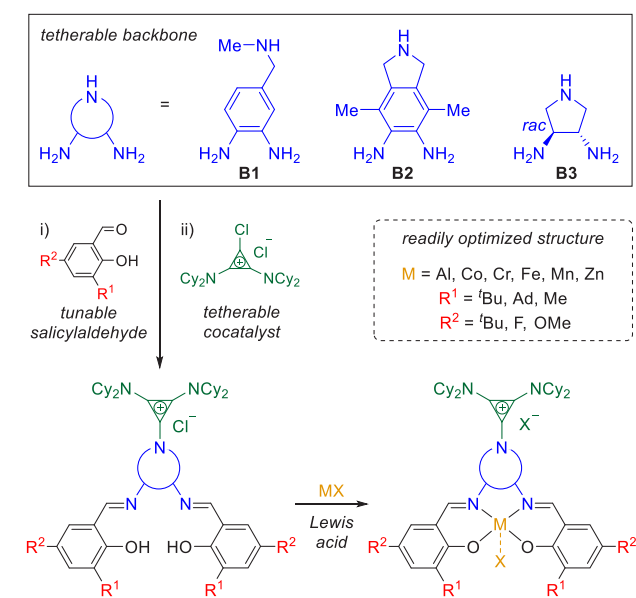
initially obtain turnover frequencies (TOFs) as high as 1600 h⁻¹ at 80 °C ([Co]₀:[PA]₀:[PO]₀ = 1:6400:85000), the catalytic activity decreases with prolonged reaction times. This single report suggests the potential efficacy of the bifunctional strategy for the ROCOP of epoxides and cyclic anhydrides at low catalyst loadings. However, it is unclear from these experiments whether the high polymerization rates were due to the covalent anchor, the catalyst:cocatalyst stoichiometry, or the inherent activity of the cobalt salen unit.

To better understand the effects of the covalent tether on catalytic activity, we have developed a modular bifunctional catalyst system that can be directly compared to binary analogues. With this approach, we hope to identify which catalyst features influence activity, control selectivity, and impact the polymerization mechanism at various catalyst loadings. Applying this strategy, we developed an aminocyclopropenium-tethered aluminum salen complex that maintains excellent activity under the same dilute conditions that render the binary system inactive (Scheme 1). Kinetic studies provide mechanistic justification for employing a bifunctional catalyst system at low catalyst concentrations. Serendipitously, the novel aminocyclopropenium cocatalyst suppresses transesterification and epimerization side reactions commonly observed in previous systems, ultimately preventing degradation of the polymer backbone.

RESULTS AND DISCUSSION

Modular Bifunctional Catalyst Strategy. Existing bifunctional systems tether the cocatalyst by functionalizing the salicylidene moiety. This approach requires extended linear syntheses that impede optimization and systematic study.^{35,36,45,48} We therefore sought a parallel synthetic route in order to independently tune the individual catalyst components (Scheme 3). We reasoned that tethering the cocatalyst via the diamine backbone of the salen ligand would allow us to systematically vary the electronic properties and steric profile of the catalyst through the many commercially available or readily synthesized salicylaldehydes. We envisioned reacting an alkyl halide-functionalized cocatalyst with a

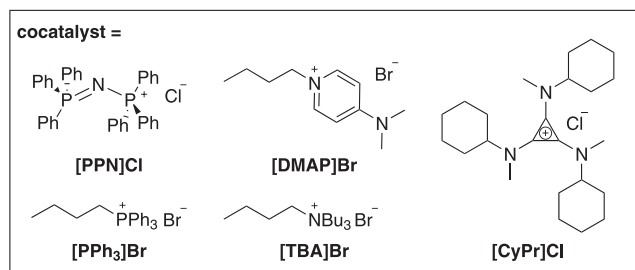
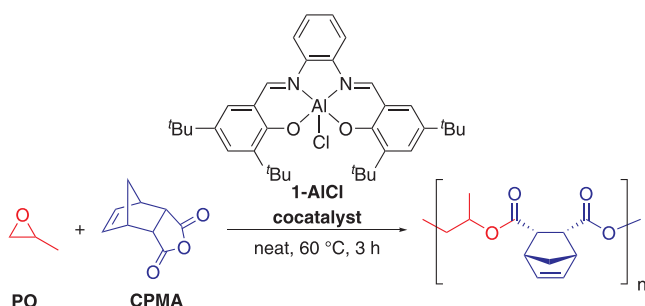
Scheme 3. Modular Synthesis of Bifunctional Catalysts



secondary amine pendant to the salen backbone as the final step in ligand synthesis (Scheme 3).

Cocatalyst Optimization. Onium salts derived from weakly coordinating ion pairs, such as widely used bis-(triphenylphosphine)iminium chloride ([PPN]⁺Cl⁻), are highly effective nucleophilic cocatalysts for ROCOP.²⁰ Cocatalysts such as 4-(dimethylamino)pyridine (DMAP), tetraalkylammonium, and phosphonium salts have also been used successfully in binary^{9,20} and bifunctional^{35,45,51,52} ROCOP systems. PO and carbic anhydride (CPMA) were copolymerized using **1-AICI** and a series of onium salts. Of these cocatalysts, [PPN]⁺Cl⁻ (Table 1, entry 1) achieved the highest catalytic activity and gave marginally lower dispersities as compared to the other onium salts (Table 1, entries 2–4).

Table 1. Cocatalyst Optimization in the Binary 1-AICI System^a



entry	cocatalyst	conv (%) ^b	TOF (h ⁻¹) ^c	M _n (kDa) ^d	Đ ^d
1	[PPN]Cl	84	112	23.6	1.09
2	[DMAP]Br	46	61	13.5	1.12
3	[PPh ₃]Br	36	48	10.1	1.16
4	[TBA]Br	45	59	13.2	1.14
5	[CyPr]Cl	86	114	23.8	1.09

^a[1-AICI]₀: [cocatalyst]₀: [CPMA]₀: [PO]₀ = 1:1:400:2000. ^bDetermined by ¹H NMR analysis of the crude reaction mixture. ^cTOF = Turnover frequency, mol anhydride consumed × mol 1-AICI⁻¹ × h⁻¹. ^dDetermined by GPC in THF, calibrated with polystyrene standards.

We therefore sought to develop a cocatalyst of similar activity to [PPN]⁺Cl⁻ that could be easily tethered to the ligand backbone. Recently, Lambert and co-workers demonstrated that tris(dialkylamino)cyclopropenium (TDAC) salts catalyze the coupling of epoxides with CO₂ or acyl chlorides to give cyclic carbonates or chlorohydrin esters, respectively.⁵⁵ TDAC derivatives also promote the ring-opening polymerization of lactones through H-bond donor/acceptor cooperative catalysis.⁵⁶ The ion pair strain^{57,58} exhibited by aminocyclopropenium ion pairs gives rise to the increased anion reactivity required for ring-opening, prompting our interest in TDAC salts. Furthermore, TDACs can be prepared on >10 g scale by coupling chlorobis(dialkylamino)cyclopropenium chlorides

with secondary amines, affording a facile route to install TDACs on secondary amine-containing salen backbones.

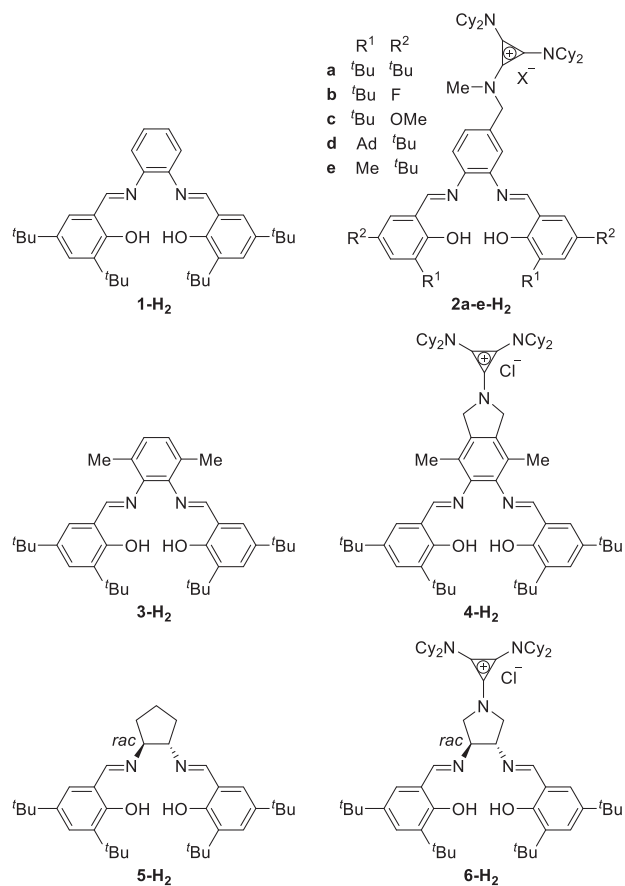
Tris(methylcyclohexylamino)cyclopropenium chloride ([CyPr]⁺Cl⁻) was synthesized as a representative TDAC, and its activity was compared to PO/CPMA copolymerizations cocatalyzed by [PPN]⁺Cl⁻. With **1-AICI**, [PPN]⁺Cl⁻ and [CyPr]⁺Cl⁻ cocatalysts afford polymers with low dispersities and nearly identical TOF values of 112 h⁻¹ and 114 h⁻¹, respectively (Table 1, entries 1 and 5). However, copolymerizations of PO and CPMA mediated by **1-AICI**/[PPN]⁺Cl⁻ run past full anhydride conversion undergo extensive transesterification and epimerization due to the formation of persistent alkoxide chain-ends. To our surprise, transesterification and epimerization were not observed in polymerizations with **1-AICI**/[CyPr]⁺Cl⁻ after CPMA was fully consumed (*vide infra*). This result demonstrates that cocatalysts with similar catalytic activities can produce markedly different copolymers due to the counterion's influence on side reactions.

Backbone Optimization. Metal salens containing chiral backbones such as (*R,R*)- or (*S,S*)-1,2-diaminocyclohexane (salcy-type ligands) have been used to synthesize stereoregular polyesters, whereas metal salens incorporating achiral planar 1,2-phenylenediamine backbones (salph-type ligands) have achieved some of the highest activities in aluminum salen-catalyzed ROCOP of epoxides and cyclic anhydrides. Mimicking those geometries, we synthesized several 1,2-diamino backbones with pendant secondary amines (**B1**, **B2**, and **B3**) that could orthogonally react with salicylaldehydes and a tetherable aminocyclopropenium cocatalyst (Scheme 3).

Using this strategy, we prepared tethered ligands **2a-H₂**, **4-H₂**, and **6-H₂** (Chart 1) from the sequential reaction of backbones **B1**, **B2**, and **B3**, respectively, with 3,5-di-*tert*-butylsalicylaldehyde and chlorobis(dicyclohexylamino)cyclopropenium chloride (see Supporting Information for synthetic details). Ligands **1-H₂**, **3-H₂**, and **5-H₂** (Chart 1) were prepared as binary catalyst controls to deconvolute the influences of backbone geometry and the covalently tethered cocatalyst on catalytic activity. Metalation with diethylaluminum chloride afforded the associated aluminum-salen catalysts (see Supporting Information for metalation conditions).

Catalyst activities for the copolymerization of PO and CPMA were evaluated at 60 °C; [PPN]⁺Cl⁻ was used as a cocatalyst with binary systems **1-AICI**, **3-AICI**, and **5-AICI** (Table 2). All catalyst systems afforded perfectly alternating copolymers with low dispersities, indicative of controlled polymerization behavior. As anticipated, the bifunctional catalysts **2a-AICI**, **4-AICI**, and **6-AICI** maintained their activities at low catalyst loadings, whereas their binary analogues slowed significantly (Table 2, *vide infra* discussion of polymerization kinetics). The salph-inspired bifunctional catalysts **2a-AICI** and **4-AICI** exhibited higher polymerization rates (TOFs of 93 and 64 h⁻¹, respectively) than the *trans*-pyrrolidine catalyst **6-AICI** (TOF = 14 h⁻¹). A similar trend in activity was also observed for polymerizations catalyzed by the corresponding binary catalysts **1-AICI** (TOF = 112 h⁻¹), **3-AICI** (TOF = 57 h⁻¹), and **5-AICI** (TOF = 28 h⁻¹) (Table 2, entries 1, 3, and 5, respectively), indicating that backbone geometry is primarily responsible for the relative activities of the bifunctional catalysts. These results are consistent with previous reports that salenAlX complexes with distorted ONNO equatorial ligand planes produce slower rates due to disrupted epoxide binding and activation.²⁰

Chart 1. Binary and Bifunctional Ligands Synthesized and Screened with Various Lewis Acids To Optimize Activity and Selectivity for Alternating Epoxide/Cyclic Anhydride Copolymerization



Although the salph backbone is conserved across catalysts **1-AICl** to **4-AICl**, *ortho*-substituted **3-AICl** and **4-AICl** exhibited notably slower rates than unsubstituted **1-AICl** and **2a-AICl**. Cort and co-workers have shown that *o*-Me substitution of atropisomeric salphUO₂ complexes significantly reduces the rate of enantiomer interconversion due to steric destabilization of the intermediate planar conformer.⁵⁹ We hypothesize that steric interference from the imine protons and proximal *o*-Me

substituents in **3-AICl** and **4-AICl** results in out-of-plane twisting of the C=N moieties, disrupting planarity and reducing catalytic activity. Attempts to crystallize **4-AICl** for X-ray structural validation have been unsuccessful but are ongoing. Nonetheless, the unsubstituted and easily synthesized phenylenediamine backbone (**B1**) imparts high catalytic activity and was therefore selected for further optimization.

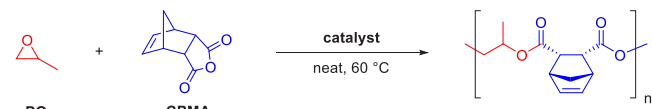
Lewis Acid Optimization. Extensive ROCOP catalyst development has demonstrated that the choice of Lewis acid significantly influences polymerization rates and selectivities. Consistent with previous comparisons of Lewis acids employed in binary salph⁶⁰ and salcy⁶¹ systems, Cr, Co, and Al derivatives of **2a-H₂** exhibited the highest activities (TOFs = 111, 376, and 93 h⁻¹, respectively; Table 3, entries 1, 4, and 6). By contrast, the Mn, Fe, and Zn bifunctional catalysts only achieved modest conversions in 16 h (Table 3, entries 2, 3, and 5); indeed, previous reports employed temperatures above 100 °C to access moderate TOFs (42 and 57 h⁻¹) using Fe⁶² and Mn⁶⁰ binary salph analogues, respectively. While **2a-CoOAc** initially appeared promising, efforts to apply this catalyst at low loadings resulted in catalyst deactivation as evidenced by nonlinear conversion vs time plots (Figure S21) that deviate from the expected first-order catalytic kinetic behavior. Further study revealed that prolonged heating of **2a-CoOAc** under dilute reaction conditions resulted in the formation of a paramagnetic species whose ¹H NMR spectrum matched that of the **2a-Co(II)** synthetic precursor. This observation is consistent with previous reports detailing the thermally induced reduction of active salenCo(III)X complexes to inactive Co(II) species.^{63–67} While the chromium catalyst **2a-CrCl** is slightly faster than the aluminum analogue **2a-AICl**, salenCr(III)X complexes are known to homopolymerize epoxides via a bimetallic mechanism,^{68,69} which may be a concern at high catalyst loadings or high conversions of anhydride. For this reason, the diamagnetic aluminum catalyst **2a-AICl** was chosen for further ligand optimization due to its high activity and selectivity toward ROCOP, relative ease of synthesis and characterization, and use of an earth-abundant nontoxic metal.

Salicylidene Optimization. The salicylidene moiety of the salen ligand provides an additional opportunity to tune the Lewis acidity and steric environment of the metal center. Our group previously demonstrated that electron-withdrawing para-substituents enhance the Lewis acidity of salphAl(III)Cl

Table 2. Effect of Backbone Geometry on Catalyst Activity in the Binary and Bifunctional Catalyst Systems

entry	catalyst	cocatalyst	1:400:2000 ^a						1:2000:10000 ^b				
			time (h)	conv (%) ^c	TOF (h ⁻¹) ^d	M _n (kDa) ^e	Đ ^e	time (h)	conv (%) ^c	TOF (h ⁻¹) ^d	M _n (kDa) ^e	Đ ^e	
1	1-AICl	[PPN]Cl	3	84	112	23.6	1.09	48	53	22	36.2	1.18	
2	2a-AICl	^f	3	70	93	18.3	1.13	20	87	87	67.6	1.18	
3	3-AICl	[PPN]Cl	5	71	57	18.6	1.10	72	45	13	24.6	1.19	
4	4-AICl	^f	5	80	64	21.0	1.10	36	44	24	30.0	1.16	
5	5-AICl	[PPN]Cl	12	84	28	24.2	1.12	72	29	8	15.4	1.17	
6	6-AICl	^f	12	43	14	9.0	1.21	36	22	12	14.9	1.17	

^a[catalyst]₀: [CPMA]₀: [PO]₀ = 1:400:2000, entries 1, 3, and 5, [catalyst]₀: [PPNCl]₀ = 1:1. ^b[catalyst]₀: [CPMA]₀: [PO]₀ = 1:2000:10000, entries 1, 3, and 5, [catalyst]₀: [PPNCl]₀ = 1:1. ^cDetermined by ¹H NMR analysis of crude reaction mixture. ^dTOF = Turnover frequency, mol anhydride consumed × mol catalyst⁻¹ × h⁻¹. ^eDetermined by GPC in THF, calibrated with polystyrene standards. ^fNo exogenous cocatalyst was used.

Table 3. Effect of Steric and Electronic Perturbations on Bifunctional Catalyst Activity^a


entry	catalyst	R ¹	R ²	time (h)	conv (%) ^b	TOF (h ⁻¹) ^c	M _n (kDa) ^d	D ^d
1	2a-CrCl	^t Bu	^t Bu	3	83	111	19.3	1.23
2	2a-MnOAc	^t Bu	^t Bu	16	9	2	n.d. ^e	n.d. ^e
3	2a-FeCl	^t Bu	^t Bu	16	9	2	n.d. ^e	n.d. ^e
4	2a-CoOAc	^t Bu	^t Bu	1	94	376	19.2	1.11
5	2a-ZnCl	^t Bu	^t Bu	16	37	9	15.3	1.18
6	2a-AlCl	^t Bu	^t Bu	3	70	93	18.3	1.13
7	2b-AlCl	^t Bu	F	9	56	25	6.9	1.24
8	2c-AlCl	^t Bu	OMe	9	96	43	15.9	1.17
9	2d-AlCl	Ad	^t Bu	9	36	16	4.1	1.27
10	2e-AlCl	Me	^t Bu	9	56	25	7.2	1.24

^a[catalyst]₀:[CPMA]₀:[PO]₀ = 1:400:2000. ^bDetermined by ¹H NMR analysis of the crude reaction mixture. ^cTOF = Turnover frequency, mol anhydride consumed × mol catalyst⁻¹ × h⁻¹. ^dDetermined by GPC in THF, calibrated with polystyrene standards. ^en.d. = not determined.

complexes, suppressing side reactions but also reducing catalyst activity.⁷⁰ Consistent with this observation, the *p*-F-substituted catalyst **2b-AlCl** polymerized PO and CPMA at slower rates than the *p*-^tBu catalyst **2a-AlCl** (Table 3, entries 6 and 7). Interestingly, the *p*-OMe variant **2c-AlCl** was also less active; its attenuated Lewis acidity likely disfavors epoxide binding and activation (Table 3, entry 8). The *ortho* position of the salicylidene moiety can be used to adjust the steric environment surrounding the active site. The Lee group has observed that *o*-Me substituents enhanced rates of epoxide/CO₂ copolymerization.³⁶ However, both *o*-Ad- and *o*-Me-substituted catalysts (**2d-AlCl** and **2e-AlCl**, respectively) exhibited reduced reaction rates relative to the *o*-^tBu catalyst (**2a-AlCl**) (Table 3, entries 6, 9, and 10). The increased steric projection of the adamantyl group likely distorts the backbone from the most active planar geometry. We therefore selected the 3,5-di-*tert*-butyl-substituted bifunctional catalyst **2a-AlCl** for further investigation.

Polymerization Kinetics in the Binary and Bifunctional Catalyst Systems. To understand the effect of covalently tethering the cocatalyst and Lewis acid, we compared the kinetic behavior of the optimized bifunctional catalyst **2a-AlCl** with that of the binary system **1-AlCl**/[PPN]Cl. We varied the concentrations of **1-AlCl** and [PPN]Cl concurrently, maintaining a 1:1 stoichiometry, and monitored the consumption of cyclic anhydride. Burés's time-normalized method was used to determine the reaction order in the **1-AlCl**/[PPN]Cl catalyst pair.⁷¹ At high catalyst loadings ([**1-AlCl**]₀: [PPNCl]₀: [CPMA]₀: [PO]₀ = 1:1:200:1000–1:1:800:4000), excellent overlay was obtained using a time normalization of $t \times [\mathbf{1-AlCl} \cdot \text{PPN}]$ (Figure 1, left), consistent with the previously reported first-order dependence on the concentration of the catalyst pair.²⁴ However, as the catalyst loading was reduced, the time-normalized reaction profiles began to deviate from the first-order fit (Figure S17). At low catalyst loadings ([**1-AlCl**]₀: [PPNCl]₀: [CPMA]₀: [PO]₀ = 1:1:1200:6000–1:1:4000:20000), the reaction profiles overlay when a second-order time normalization of $t \times [\mathbf{1-AlCl} \cdot \text{PPN}]^2$ was applied (Figure 1, right). Varying the epoxide concentration (3.5–14.3 M) revealed that the first-order dependence on [PO] is maintained at low catalyst loadings ([**1-AlCl**]₀:

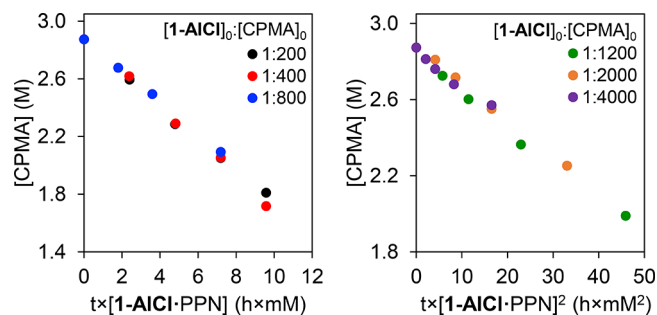


Figure 1. Anhydride decay versus normalized time scale showing a change in the reaction order in the binary catalyst pair **1-AlCl**/[PPN]Cl. First-order fit applied when [**1-AlCl**]₀: [PPNCl]₀: [CPMA]₀: [PO]₀ = 1:1:200:1000–1:1:800:4000 (left). Second-order fit applied when [**1-AlCl**]₀: [PPNCl]₀: [CPMA]₀: [PO]₀ = 1:1:1200:6000–1:1:4000:20000 (right).

[PPNCl]₀: [CPMA]₀ = 1:1:1200) (Figure S18). The experimental rate law $k[\text{PO}][\mathbf{1-AlCl}][\text{PPN}]$ is consistent with a pre-equilibrium kinetic model in which epoxide binding is fast relative to subsequent ring-opening (Scheme 2). Polymerization kinetics using **1-AlCl**/[CyPr]Cl afforded excellent agreement with those performed using [PPN]Cl (Figure S20), indicating that the change in reaction order at low loadings is a shared feature of binary catalyst systems.

We anticipated that covalently tethering the Lewis acid catalyst and nucleophilic cocatalyst would facilitate intramolecular epoxide ring-opening and eliminate the second-order dependence on catalyst pair concentration observed in the binary system at low loadings. Accordingly, a series of polymerization kinetics experiments was performed in which the catalyst concentration was varied from 0.7–14.3 mM ([**2a-AlCl**]₀: [CPMA]₀: [PO]₀ = 1:200:1000–1:4000:20000). A linear dependence of the rate of cyclic anhydride consumption on catalyst concentration was observed, which is consistent with a first-order dependence on [**2a-AlCl**]. A time normalization of $t \times [\mathbf{2a-AlCl}]$ afforded excellent overlay of the reaction profiles at all catalyst loadings studied, providing further support for first-order behavior (Figure 2). As in the binary system,³³ the ROCOP of PO and CPMA catalyzed by **2a-AlCl** is first-order in [PO] prior to the onset of saturation kinetics and zero-order in [CPMA] (Figures S22 and S23,

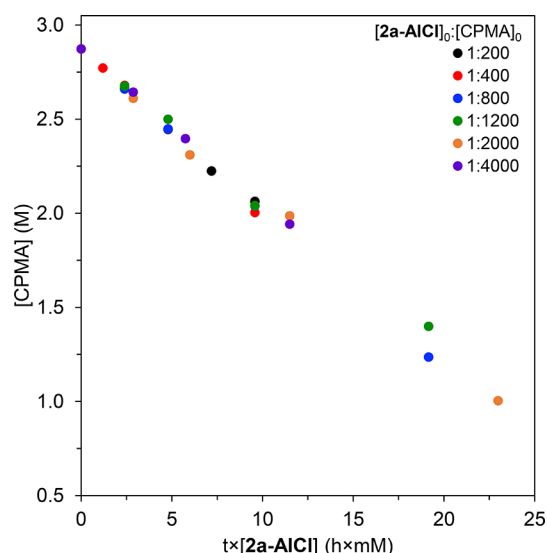


Figure 2. Anhydride decay versus normalized time scale showing first-order behavior in bifunctional catalyst **2a-AICl** at a variety of catalyst loadings $[2a-AICl]_0:[CPMA]_0:[PO]_0 = 1:200:1000-1:4000:20000$.

respectively). Taken together, these kinetic results are consistent with a bis-carboxylate resting-state from which epoxide binding is fast relative to intramolecular ring-opening.

The first-order dependence on catalyst concentration is a common feature of the three modular bifunctional systems, independent of backbone geometry. Polymerization rates depended linearly on $[6-AICl]$ at all catalyst loadings studied (Figure S28). Similarly, polymerizations performed with bifunctional catalyst **4-AICl** exhibited a first-order rate dependence on $[4-AICl]$ for catalyst concentrations above $[4-AICl]_0:[CPMA]_0:[PO]_0 = 1:1200:6000$ (Figure S28). At lower concentrations of **4-AICl**, the polymerization rate slowed over extended reaction times, and the reaction mixtures darkened from yellow to brown, which may indicate catalyst decomposition. The apparent first-order dependence on catalyst concentration across the bifunctional systems further supports that the covalent tether is responsible for maintaining high activities at low loadings.

The mechanistic disparity between the binary and bifunctional catalyst systems is particularly apparent when comparing their respective TOFs as the catalyst loading is reduced (Figure 3). Though faster than the bifunctional system at high loadings, the binary catalyst systems **1-AICl**/[PPN]Cl and **1-AICl**/[CyPr]Cl rapidly decelerate with decreasing concentration (TOFs decrease from 115 to 9 h^{-1}). In contrast, the bifunctional system **2a-AICl** maintains excellent activity (TOF $\cong 90\text{ h}^{-1}$) even at extremely low catalyst loadings ($[2a-AICl]_0:[CPMA]_0:[PO]_0 = 1:4000:20000$), further validating the bifunctional approach. Covalently tethering the cocatalyst and Lewis acid affords catalysts that are immune to dilution effects, enabling polymerizations at low catalysts loadings without sacrificing activity.

Transesterification and Epimerization with [PPN]Cl and [CyPr]Cl Cocatalysts. At high monomer conversions, ROCOPs of epoxides and cyclic anhydrides catalyzed by salen complexes often undergo undesirable side reactions that degrade the polymer backbone and change polymer properties. Reactions performed using excess epoxide are particularly prone to transesterification and epimerization due to persistent alkoxide chain-ends that form after full consumption of the

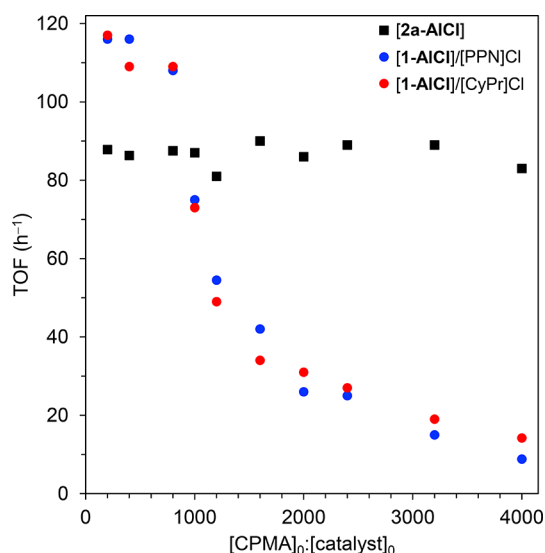
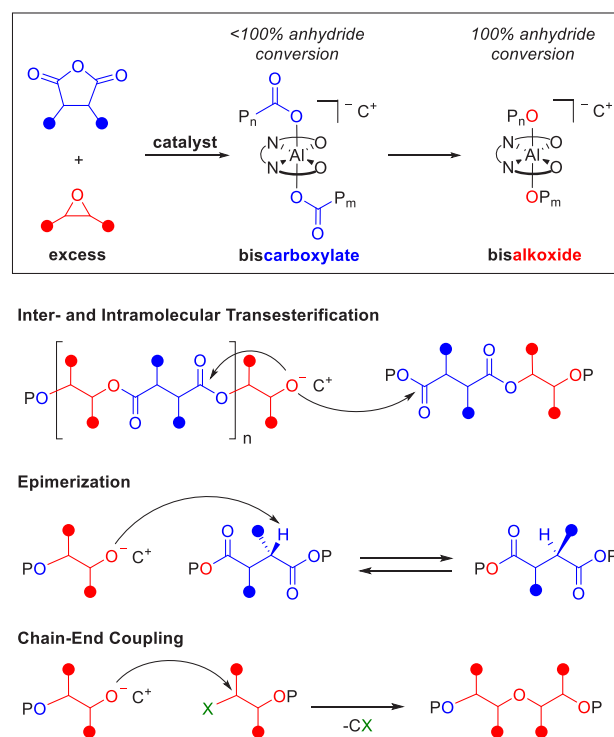


Figure 3. Turnover frequency as a function of catalyst loading showing attenuated polymerization activity in the binary catalyst system (**1-AICl**) and maintained activity in the bifunctional catalyst system (**2a-AICl**), $[catalyst]_0:[CPMA]_0:[PO]_0 = 1:200:1000-1:4000:20000$. For polymerizations performed using **1-AICl**, $[catalyst]_0:[cocatalyst]_0 = 1:1$. TOF = Turnover frequency, mol anhydride consumed \times mol catalyst $^{-1} \times$ h $^{-1}$.

cyclic anhydride (Scheme 4). In 2016, Coates and co-workers reported that installing an electron-withdrawing *p*-F group on the salicylidene of an aluminum salph complex suppresses transesterification and epimerization for up to 6 h beyond full conversion of CPMA.⁷⁰ The authors proposed that the enhanced Lewis acidity of the *p*-F catalyst relative to **1-AICl** promotes formation of a hexacoordinate aluminate complex,

Scheme 4. Side Reactions Commonly Observed at High Cyclic Anhydride Conversion



preventing the alkoxide chain-ends from degrading the polymer backbone. Unfortunately, the *p*-F substituted catalyst also exhibited retarded rates of polymerization relative to **1-AICI** (TOFs 49 and 88 h⁻¹, respectively, in THF at 60 °C).

We investigated whether the most active bifunctional catalyst in this report, *p*-^tBu-substituted **2a-AICI**, was similarly prone to deleterious side reactions as its previously studied binary analogue **1-AICI**. Polymerizations with **2a-AICI** performed in excess neat epoxide were allowed to run beyond full conversion of anhydride (~4 h to 100% conversion). Aliquots were analyzed by gel permeation chromatography (GPC) to identify transesterification by observing increased dispersities and ¹³C NMR to quantify *cis*-diester content (Figure 4). Gratifyingly, no significant transesterification or

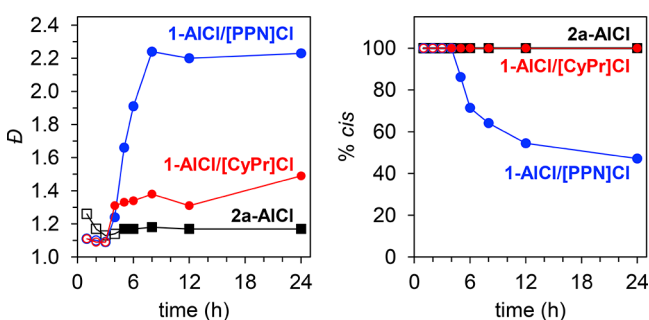


Figure 4. Effect of cocatalyst identity on polyester dispersity (left) and diester stereochemistry (right) in the binary systems **1-AICI**/[PPN]Cl and **1-AICI**/[CyPr]Cl and the bifunctional system **2a-AICI**. Open circle = copolymerization quenched prior to reaching full conversion of CPMA determined by ¹H NMR analysis. Closed circle = polymerization quenched after reaching full conversion of CPMA determined by ¹H NMR analysis.

epimerization were observed with **2a-AICI**, as evidenced by low dispersities (1.10–1.20) and high *cis*-diester content (>99%) preserved even at 24 h. As reported previously,⁷⁰ reactions catalyzed by **1-AICI**/[PPN]Cl were subject to extensive transesterification and epimerization immediately after the cyclic anhydride was fully consumed (Figure 4).

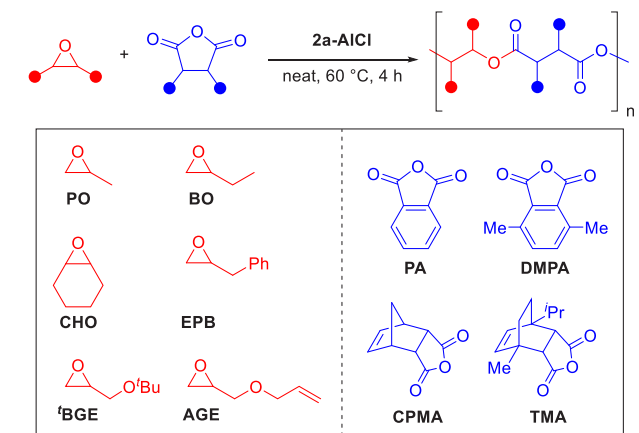
Because the salph ligand is conserved across binary and bifunctional catalysts **1-AICI** and **2a-AICI**, we sought to determine whether the cocatalyst identity (PPN vs CyPr) or covalent tether is responsible for suppressed side reactions in the bifunctional system. Polymerizations using **1-AICI**/[CyPr]Cl were therefore run beyond full conversion of CPMA. No change in the *cis*-diester content was observed using **1-AICI**/[CyPr]Cl, but the dispersity increased slightly (Figure 4). The absence of epimerization suggests that the persistent alkoxide chain-ends are not sufficiently basic to deprotonate the polymer backbone. While dispersity increases uniformly in the **1-AICI**/[PPN]Cl binary system, **1-AICI**/[CyPr]Cl-catalyzed polymerizations revealed an enlarged high molecular weight shoulder and tailing (Figures S3 and S4, respectively). The continued increase in molecular weight beyond full anhydride conversion is consistent with chain-end coupling at the end of the reaction. We propose that the ion pair strain exhibited by TDAC salts enhances the nucleophilicity of the persistent alkoxide, allowing S_N2-type chemistry at the chloride chain-ends.

Notably, we observe only minimal chain-end coupling using the bifunctional **2a-AICI** system at extended reaction times (Figure S5). Side reactions were also suppressed at 80 and 100

°C while catalyst activity increased markedly with temperature (TOFs 186 and 466 h⁻¹ at 80 and 100 °C, respectively, Table S5). We hypothesize that covalently linking the cocatalyst to the Lewis acid keeps alkoxide chain-ends close to the metal center and favors the inert hexacoordinate aluminate species (Scheme 4). The proximity enforced by the covalent anchor therefore prevents chain-end coupling, while the amino-cyclopropenium cocatalyst suppresses transesterification and epimerization. Ongoing efforts are focused on fully elucidating the mechanism of chain-end coupling and developing strategies to completely suppress it. Nevertheless, bifunctional **2a-AICI** achieves excellent chain-end control, suppressing deleterious side reactions without sacrificing polymerization rate.

Monomer Scope. ROCOP is an attractive approach to polyester synthesis, as it is applicable to a large library of structurally and functionally diverse monomers. Moreover, recent efforts have elucidated synthetic routes to several aromatic and tricyclic anhydrides from biorenewable sources.^{8,72} Bifunctional catalyst **2a-AICI** was applied to copolymerizations of a variety of epoxides and cyclic anhydrides (Table 4). In all cases, perfectly alternating polyesters were

Table 4. Comonomer Variants Polymerized by **2a-AICI**^a



entry	comonomers	conv (%) ^b	TOF (h ⁻¹) ^c	M _n (kDa) ^d	Đ ^d
1	PO/PA	>99	>100	22.1	1.14
2	PO/DMPA	88	88	21.9	1.08
3	PO/TMA	35	35	12.3	1.08
4	PO/CPMA	95	95	23.4	1.14
5	BO/CPMA	53	53	16.0	1.12
6 ^e	CHO/CPMA	51	34	8.2	1.24
7	EPB/CPMA	42	42	9.2	1.11
8	BGE/CPMA	19	19	5.5	1.18
9	AGE/CPMA	54	54	12.7	1.16

^a[**2a-AICI**]₀:[anhydride]₀:[epoxide]₀ = 1:400:2000. ^bDetermined by ¹H NMR analysis of the crude reaction mixture. ^cTOF = Turnover frequency, mol anhydride consumed × mol **2a-AICI**⁻¹ × h⁻¹. ^dDetermined by GPC in THF, calibrated with polystyrene standards. ^ePolymerization run to 6 h.

obtained with controlled molecular weights up to 23.4 kDa and low dispersities (<1.24). As observed previously,⁴³ ring-opening of the sterically hindered cyclic anhydride TMA gave slower polymerization rates (Table 4, entry 3). Cyclohexene oxide (CHO)/cyclic anhydride copolymers have exhibited higher glass transition temperatures than their PO-derived analogues.⁴⁴ Copolymerization of CHO with CPMA

afforded a moderate molecular weight polyester with marginally higher dispersity due to increased water content in the epoxide (Table 4, entry 6). Glycidyl ethers were also readily polymerized with CPMA (Table 4, entries 8 and 9). The various epoxide and cyclic anhydride monomers are also effectively polymerized at low catalyst loadings ($[2a-AlCl]_0$: $[anhydride]_0$: $[epoxide]_0 = 1:1200:6000$, Table S1). The bifunctional catalyst **2a-AlCl** can therefore access a substrate scope comparable to those of existing salen systems, allowing tunable polymer properties and renewable content.

CONCLUSION

We have developed a modular bifunctional aminocyclopropenium-salen catalyst for ROCOP of epoxides and cyclic anhydrides. Anchoring the aminocyclopropenium cocatalyst on the salen backbone permits synthetically facile steric and electronic perturbations to optimize catalytic activity. The aminocyclopropenium cocatalyst not only achieves comparable activity to that observed with traditional iminium salts but also successfully prevents transesterification and epimerization side reactions that are commonly observed in PPN-cocatalyzed systems. Studying the polymerization kinetics with the binary and bifunctional catalysts provided new mechanistic insight into the rate-limiting ring-opening step in the binary system and validated the advantages of the bifunctional design. The covalent linkage between cocatalyst and Lewis acid affords high catalytic activity under conditions that suppress polymerization rates in comparable binary systems, allowing access to extremely low catalyst loadings (≥ 0.025 mol %) to reduce costs, minimize catalyst residue, and increase molecular weights. Ongoing work focuses on further exploring side reactions in aminocyclopropenium-cocatalyzed systems and applying the bifunctional catalyst in conjunction with chain transfer agents at low catalyst concentrations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b05570.

Synthetic procedures, characterization data of all new compounds, polymerization data, and expanded mechanistic data (PDF)

AUTHOR INFORMATION

Corresponding Author

*coates@cornell.edu

ORCID

Brooks A. Abel: 0000-0002-2288-1975

Claire A. L. Lidston: 0000-0002-4541-8190

Geoffrey W. Coates: 0000-0002-3400-2552

Author Contributions

[‡]These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Center for Sustainable Polymers, a National Science Foundation (NSF) Center for Chemical Innovation (CHE-1413862) and Cornell University. C.A.L.L. gratefully acknowledges a graduate fellowship from the National Science Foundation (DGE-1650441). This work

made use of the NMR Facility at Cornell University, which is supported, in part, by the NSF under the award CHE-1531632.

REFERENCES

- (1) Hillmyer, M. A.; Tolman, W. B. Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396.
- (2) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The Path Forward for Biofuels and Biomaterials. *Science* **2006**, *311*, 484–489.
- (3) Gross, R. A.; Kalra, B. Biodegradable Polymers for the Environment. *Science* **2002**, *297*, 803–807.
- (4) Goodman, I. Polyesters. In *Encyclopedia of Polymer Science and Engineering*, Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley-Interscience, New York, 1988; pp 1–75.
- (5) Fakirov, S. *Handbook of Thermoplastic Polyesters*; Wiley: New York, 2002.
- (6) Longo, J. M.; Sanford, M. J.; Coates, G. W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure-Property Relationships. *Chem. Rev.* **2016**, *116*, 15167–15197.
- (7) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-Opening Copolymerization (ROCO): Synthesis and Properties of Polyesters and Polycarbonates. *Chem. Commun.* **2015**, *51*, 6459–6479.
- (8) Yu, X.; Jia, J.; Xu, S.; Lao, K. U.; Sanford, M. J.; Ramakrishnan, R. K.; Nazarenko, S. I.; Hoye, T. R.; Coates, G. W.; DiStasio, R. A., Jr. Unraveling Substituent Effects on the Glass Transition Temperatures of Biorenewable Polyesters. *Nature Commun.* **2018**, *9*, 2880–2888.
- (9) Aida, T.; Inoue, S. Catalytic Reaction on Both Sides of a Metalloporphyrin Plane. Alternating Copolymerization of Phthalic Anhydride and Epoxypropane with an Aluminum Porphyrin-Quaternary Salt System. *J. Am. Chem. Soc.* **1985**, *107*, 1358–1364.
- (10) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. *J. Am. Chem. Soc.* **2007**, *129*, 11330–11331.
- (11) Sanford, M. J.; Van Zee, N. J.; Coates, G. W. Reversible-Deactivation Anionic Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides: Access to Orthogonally Functionalizable Multiblock Aliphatic Polyesters. *Chem. Sci.* **2018**, *9*, 134–142.
- (12) Van Zee, N. J.; Coates, G. W. Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures. *Angew. Chem., Int. Ed.* **2015**, *54*, 2665–2668.
- (13) DiCiccio, A. M.; Longo, J. M.; Rodriguez-Calero, G. G.; Coates, G. W. Development of Highly Active and Regioselective Catalysts for the Copolymerization of Epoxides with Cyclic Anhydrides: An Unanticipated Effect of Electronic Variation. *J. Am. Chem. Soc.* **2016**, *138*, 7107–7113.
- (14) Longo, J. M.; DiCiccio, A. M.; Coates, G. W. Poly(propylene succinate): A New Polymer Stereocomplex. *J. Am. Chem. Soc.* **2014**, *136*, 15897–15900.
- (15) Darensbourg, D. J.; Poland, R. R.; Escobedo, C. Kinetic Studies on the Alternating Copolymerization of Cyclic Acid Anhydrides and Epoxides, and the Terpolymerization of Cyclic Acid Anhydrides, Epoxides, and CO₂ Catalyzed by (salen)Cr^{III}Cl. *Macromolecules* **2012**, *45*, 2242–2248.
- (16) Stöber, T.; Mulryan, D.; Williams, C. K. Switch Catalysis to Deliver Multi-Block Polyesters from Mixtures of Propene Oxide, Lactide, and Phthalic Anhydride. *Angew. Chem., Int. Ed.* **2018**, *57*, 16893–16897.
- (17) Garden, J. A.; Saini, P. K.; Williams, C. K. Greater than the Sum of Its Parts: A Heterodinuclear Polymerization Catalyst. *J. Am. Chem. Soc.* **2015**, *137*, 15078–15081.

- (18) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. Di-Magnesium and Zinc Catalysts for the Copolymerization of Phthalic Anhydride and Cyclohexene Oxide. *Polym. Chem.* **2014**, *5*, 6068–6075.
- (19) Huijser, S.; Nejad, E. H.; Sablong, R.; de Jong, C.; Koning, C. E.; Duchateau, R. Ring-Opening Co- and Terpolymerization of an Alicyclic Oxirane with Carboxylic Acid Anhydrides and CO₂ in the Presence of Chromium Porphyrinato and Salen Catalysts. *Macromolecules* **2011**, *44*, 1132–1139.
- (20) Nejad, E. H.; van Melis, C. G. W.; Vermeer, T. J.; Koning, C. E.; Duchateau, R. Alternating Ring-Opening Polymerization of Cyclohexene Oxide and Anhydrides: Effect of Catalyst, Cocatalyst, and Anhydride Structure. *Macromolecules* **2012**, *45*, 1770–1776.
- (21) Bernard, A.; Chatterjee, C.; Chisholm, M. H. The Influence of the Metal (Al, Cr and Co) and the Substituents of the Porphyrin in Controlling the Reactions Involved in the Copolymerization of Propylene Oxide and Cyclic Anhydrides by Porphyrin Metal(III) Complexes. *Polymer* **2013**, *54*, 2639–2646.
- (22) Ji, H.-Y.; Wang, B.; Pan, L.; Li, Y.-S. Lewis Pairs for Ring-Opening Alternating Copolymerization of Cyclic Anhydrides and Epoxides. *Green Chem.* **2018**, *20*, 641–648.
- (23) Robert, C.; Ohkawara, T.; Nozaki, K. Manganese-Corrole Complexes as Versatile Catalysts for the Ring-Opening Homo- and Co-Polymerization of Epoxide. *Chem. - Eur. J.* **2014**, *20*, 4789–4795.
- (24) Li, H.; Zhao, J.; Zhang, G. Self-Buffering Organocatalysts Tailoring Alternating Polyester. *ACS Macro Lett.* **2017**, *6*, 1094–1098.
- (25) Li, H.; Luo, H.; Zhao, J.; Zhang, G. Well-Defined and Structurally Diverse Aromatic Alternating Polyesters Synthesized by Simple Phosphazene Catalysis. *Macromolecules* **2018**, *51*, 2247–2257.
- (26) Hu, L.-F.; Zhang, C.-J.; Wu, H.-L.; Yang, J.-L.; Liu, B.; Duan, H.-Y.; Zhang, X.-H. Highly Active Organic Lewis Pairs for the Copolymerization of Epoxides with Cyclic Anhydrides: Metal-Free Access to Well-Defined Aliphatic Polyesters. *Macromolecules* **2018**, *51*, 3126–3134.
- (27) Ji, H.-Y.; Chen, X.-L.; Wang, B.; Pan, L.; Li, Y.-S. Metal-Free, Regioselective and Stereoregular Alternating Copolymerization of Monosubstituted Epoxides and Tricyclic Anhydrides. *Green Chem.* **2018**, *20*, 3963–3973.
- (28) Kummari, A.; Pappuru, S.; Chakraborty, D. Fully Alternating and Regioselective Ring-Opening Copolymerization of Phthalic Anhydride with Epoxides Using Highly Active Metal-Free Lewis Pairs as a Catalyst. *Polym. Chem.* **2018**, *9*, 4052–4062.
- (29) Robert, C.; deMontigny, F.; Thomas, C. M. Tandem Synthesis of Alternating Polyesters from Renewable Resources. *Nat. Commun.* **2011**, *2*, 586.
- (30) Li, J.; Ren, B.-H.; Chen, S.-Y.; He, G.-H.; Liu, Y.; Ren, W.-M.; Zhou, H.; Lu, X.-B. Development of Highly Enantioselective Catalysts for Asymmetric Copolymerization of *meso*-Epoxides and Cyclic Anhydrides: Subtle Modification Resulting in Superior Enantioselectivity. *ACS Catal.* **2019**, *9*, 1915–1922.
- (31) Liu, J.; Bao, Y.-Y.; Liu, Y.; Ren, W.-M.; Lu, X.-B. Binuclear Chromium-Salen Complex Catalyzed Alternating Copolymerization of Epoxides and Cyclic Anhydrides. *Polym. Chem.* **2013**, *4*, 1439–1444.
- (32) Hiranoi, Y.; Nakano, K. Copolymerization of Epoxides with Cyclic Anhydrides Catalyzed by Dinuclear Cobalt Complexes. *Beilstein J. Org. Chem.* **2018**, *14*, 2779–2788.
- (33) Fieser, M. E.; Sanford, M. J.; Mitchell, L. A.; Dunbar, C. R.; Mandal, M.; Van Zee, N. J.; Urness, D. M.; Cramer, C. J.; Coates, G. W.; Tolman, W. B. Mechanistic Insights into the Alternating Copolymerization of Epoxides and Cyclic Anhydrides Using a (Salph)AlCl and Iminium Salt Catalytic System. *J. Am. Chem. Soc.* **2017**, *139*, 15222–15231.
- (34) Nakano, K.; Kamada, T.; Nozaki, K. Selective Formation of Polycarbonate over Cyclic Carbonate: Copolymerization of Epoxides with Carbon Dioxide Catalyzed by a Cobalt(III) Complex with a Piperidinium End-Capping Arm. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274–7277.
- (35) Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y. Two Components in a Molecule: Highly Efficient and Thermally Robust Catalytic System for CO₂/Epoxide Copolymerization. *J. Am. Chem. Soc.* **2007**, *129*, 8082–8083.
- (36) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. A Highly Active and Recyclable Catalytic System for CO₂/Propylene Oxide Copolymerization. *Angew. Chem., Int. Ed.* **2008**, *47*, 7306–7309.
- (37) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, E. S.; Park, J. H.; Lee, B. Y. Immortal CO₂/Propylene Oxide Copolymerization: Precise Control of Molecular Weight and Architecture of Various Block Copolymers. *Macromolecules* **2010**, *43*, 7398–7401.
- (38) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. Elucidation of the Structure of a Highly Active Catalytic System for CO₂/Epoxide Copolymerization; A Salen-Cobaltate Complex of an Unusual Binding Mode. *Inorg. Chem.* **2009**, *48*, 10455–10465.
- (39) Seong, J. E.; Na, S. J.; Cyriac, A.; Kim, B. W.; Lee, B. Y. Terpolymerizations of CO₂, Propylene Oxide, and Various Epoxides Using a Cobalt(III) Complex of Salen-Type Ligand Tethered by Four Quaternary Ammonium Salts. *Macromolecules* **2010**, *43*, 903–908.
- (40) Yoo, J.; Na, S. J.; Park, H. C.; Cyriac, A.; Lee, B. Y. Anion Variation on a Cobalt(III) Complex of Salen-Type Ligand Tethered by Four Quaternary Ammonium Salts for CO₂/Epoxide Copolymerization. *Dalton Trans.* **2010**, *39*, 2622–2630.
- (41) Cyriac, A.; Lee, S. H.; Lee, B. Y. Connection of Polymer Chains Using Diepoxide in CO₂/Propylene Oxide Copolymerizations. *Polym. Chem.* **2011**, *2*, 950–956.
- (42) Cyriac, A.; Jeon, J. Y.; Varghese, J. K.; Park, J. H.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. Unusual Coordination Mode of Tetradentate Schiff Base Cobalt(III) Complexes. *Dalton Trans.* **2012**, *41*, 1444–1447.
- (43) Jeon, J. Y.; Lee, J. J.; Varghese, J. K.; Na, S. J.; Sujith, S.; Go, M. J.; Lee, J.; Ok, M.-A.; Lee, B. L. CO₂/Ethylene Oxide Copolymerization and Ligand Variation for a Highly Active Salen-Cobalt(III) Complex Tethering 4 Quaternary Ammonium Salts. *Dalton Trans.* **2013**, *42*, 9245–9254.
- (44) Jeon, J. Y.; Eo, S. C.; Varghese, J. K.; Lee, B. Y. Copolymerization and Terpolymerization of Carbon Dioxide/Propylene Oxide/Phthalic Anhydride Using a (salen)Co(III) Complex Tethering Four Quaternary Ammonium Salts. *Beilstein J. Org. Chem.* **2014**, *10*, 1787–1795.
- (45) Ren, W.-M.; Liu, Z.-W.; Wen, Y.-Q.; Zhang, R.; Lu, X.-B. Mechanistic Aspects of Copolymerization of CO₂ with Epoxides Using a Thermally Stable Single-Site Cobalt(III) Catalyst. *J. Am. Chem. Soc.* **2009**, *131*, 11509–11518.
- (46) Ren, W.-M.; Zhang, X.; Liu, Y.; Li, J.-F.; Wang, H.; Lu, X.-B. Highly Active, Bifunctional Co(III)-Salen Catalyst for Alternating Copolymerization of CO₂ with Cyclohexene Oxide and Terpolymerization with Aliphatic Epoxides. *Macromolecules* **2010**, *43*, 1396–1402.
- (47) Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Xu, T.-Q.; Darendbourg, D. J. Perfectly Alternating Copolymerization of CO₂ and Epichlorohydrin Using Cobalt(III)-Based Catalyst Systems. *J. Am. Chem. Soc.* **2011**, *133*, 15191–15199.
- (48) Ren, W.-M.; Liu, Y.; Wu, G.-P.; Liu, J.; Lu, X.-B. Stereoregular Polycarbonate Synthesis: Alternating Copolymerization of CO₂ with Aliphatic Terminal Epoxides Catalyzed by Multichiral Cobalt(III) Complexes. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4894–4901.
- (49) Liu, J.; Ren, W.-M.; Liu, Y.; Lu, X.-B. Kinetic Study on the Coupling of CO₂ and Epoxides Catalyzed by Co(III) Complex with an Inter- or Intramolecular Nucleophilic Cocatalyst. *Macromolecules* **2013**, *46*, 1343–1349.
- (50) Ren, W.-M.; Liu, Y.; Xin, A.-X.; Fu, S.; Lu, X.-B. Single-Site Bifunctional Catalysts for COX (X = O or S)/Epoxides Copolymerization: Combining High Activity, Selectivity, and Durability. *Macromolecules* **2015**, *48*, 8445–8450.
- (51) Duan, Z.; Wang, X.; Gao, Q.; Zhang, L.; Liu, B.; Kim, I. Highly Active Bifunctional Cobalt-Salen Complexes for the Synthesis of Poly(ester-block-carbonate) Copolymer via Terpolymerization of

Carbon Dioxide, Propylene Oxide, and Norbornene Anhydride Isomer: Roles of Anhydride Conformation Consideration. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 789–795.

(52) Zhu, W.; Du, L.; Qian, S.; Yang, Q.; Song, W. Copolymerization of Carbon Dioxide and Propylene Oxide by Several Metallosalen-based Bifunctional Catalysts. *J. Chin. Chem. Soc.* **2018**, *65*, 841–849.

(53) Sheng, X.; Wang, Y.; Qin, Y.; Wang, X.; Wang, F. Aluminum Porphyrin Complexes via Delicate Ligand Design: Emerging Efficient Catalysts for High Molecular Weight Poly(propylene carbonate). *RSC Adv.* **2014**, *4*, 54043–54050.

(54) Darensbourg, D. J.; Chung, W.-C.; Arp, C. J.; Tsai, F.-T.; Kyran, S. J. Copolymerization and Cycloaddition Products Derived from Coupling Reactions of 1,2-Epoxy-4-cyclohexene and Carbon Dioxide. Postpolymerization Functionalization via Thiol-ene Click Reactions. *Macromolecules* **2014**, *47*, 7347–7353.

(55) Bandar, J. S.; Tanaset, A.; Lambert, T. H. Phase-Transfer and Other Types of Catalysis with Cyclopropenium Ions. *Chem. - Eur. J.* **2015**, *21*, 7365–7368.

(56) Xu, J.; Liu, J.; Li, Z.; Xu, S.; Wang, H.; Guo, T.; Gao, Y.; Zhang, C.; Guo, K.; Zhang, L. Opposite-Charge Repulsive Cation and Anion Pair Cooperative Organocatalysis in Ring-Opening Polymerization. *Polym. Chem.* **2018**, *9*, 2183–2192.

(57) Weiss, R.; Brenner, T.; Hampel, F.; Wolski, A. The Consequences of an Electrostatic “Forced Marriage” between Two Electron-Rich Particles: Strained Ion Pairs. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 439–441.

(58) Weiss, R.; Recharging, M.; Hampel, F.; Wolski, A. Stable 1:1 Adducts from Iodoacetylenes and Iodide Ions: Ion Pair Strain as an Additional Driving Force? *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 441–443.

(59) Dalla Cort, A.; Gasparrini, F.; Lunazzi, L.; Mandolini, L.; Mazzanti, A.; Pasquini, C.; Pierini, M.; Rompietti, R.; Schiaffino, L. Stereomutations of Atropisomers of Sterically Hindered Salophen Ligands. *J. Org. Chem.* **2005**, *70*, 8877–8883.

(60) Nejad, E. H.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R. Catalytic Ring-Opening Copolymerization of Limonene Oxide and Phthalic Anhydride: Toward Partially Renewable Polyesters. *Macromolecules* **2013**, *46*, 631–637.

(61) DiCiccio, A. M.; Coates, G. W. Ring-Opening Copolymerization of Maleic Anhydride with Epoxides: A Chain-Growth Approach to Unsaturated Polyesters. *J. Am. Chem. Soc.* **2011**, *133*, 10724–10727.

(62) Mundil, R.; Hošťálek, Z.; Šeděnková, I.; Merna, J. Alternating Ring-Opening Copolymerization of Cyclohexene Oxide with Phthalic Anhydride Catalyzed by Iron(III) Salen Complexes. *Macromol. Res.* **2015**, *23*, 161–166.

(63) Cohen, C. T.; Chu, T.; Coates, G. W. Cobalt Catalysts for the Alternating Copolymerization of Propylene Oxide and Carbon Dioxide: Combining High Activity and Selectivity. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878.

(64) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. Asymmetric Catalysis with Water: Efficient Kinetic Resolution of Terminal Epoxides by Means of Catalytic Hydrolysis. *Science* **1997**, *277*, 936–938.

(65) Jacobsen, E. N. Asymmetric Catalysis of Epoxide Ring-Opening Reactions. *Acc. Chem. Res.* **2000**, *33*, 421–431.

(66) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. Copolymerization of Cyclohexene Oxide and Carbon Dioxide Using (salen)Co(III) Complexes: Synthesis and Characterization of Syndiotactic Poly(cyclohexene carbonate). *Dalton Trans.* **2006**, 237–249.

(67) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. Asymmetric Catalysis with CO₂: Direct Synthesis of Optically Active Propylene Carbonate from Racemic Epoxides. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733.

(68) Childers, M. L.; Vitek, A. K.; Morris, L. S.; Widger, P. C. B.; Ahmed, S. M.; Zimmerman, P. M.; Coates, G. W. Isospecific, Chain Shuttling Polymerization of Propylene Oxide Using a Bimetallic

Chromium Catalyst: A New Route to Semicrystalline Polyols. *J. Am. Chem. Soc.* **2017**, *139*, 11048–11054.

(69) Morris, L. S.; Childers, I. M.; Coates, G. W. Bimetallic Chromium Catalysts with Chain Transfer Agents: A Route to Isotactic Poly(propylene oxide)s with Narrow Dispersities. *Angew. Chem., Int. Ed.* **2018**, *57*, 5731–5734.

(70) Van Zee, N. J.; Sanford, M. J.; Coates, G. W. Electronic Effects of Aluminum Complexes in the Copolymerization of Propylene Oxide with Tricyclic Anhydrides: Access to Well-Defined, Functionalizable Aliphatic Polyesters. *J. Am. Chem. Soc.* **2016**, *138*, 2755–2761.

(71) Burés, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 2028–2031.

(72) Sanford, M. J.; Pena Carrodeguas, L.; Van Zee, N. J.; Kleij, A. W.; Coates, G. W. Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures. *Macromolecules* **2016**, *49*, 6394–6400.