Supplementary Information for

Effects of Lewis Acidity and Size of Lanthanide Salts for Ring-Opening Copolymerization

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1. Proposed Mechanistic Insight



Fig. S1 Proposed metal species for the ROCOP of epoxides and cyclic anhydrides with trichloride rare earth metal (Ln) salts pre-catalysts and [PPN]Cl cocatalyst. [PPN] cocatalyst and protonated chain ends are omitted for clarity. Four chain ends per metal center is due to three chloride initiators on the lanthanide salt and one chloride initiator associated with the PPN cation.



Fig. S2 Proposed catalytic cycle for the ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides in the presence of multiple monomers.



Fig. S3 Hypothesis of why steric repulsions causes monomer epoxide ring opening with a CPMA chain end to favor larger metals (left) and why a less bulky pair of monomers (such as BO/GA) can favor smaller metals (right).

2. General Considerations

All polymerization reactions were set up on a benchtop under atmospheric conditions. Protio and deuterated chloroform were purchased from commercial suppliers and used as received. 1-Butene oxide (BO) and cyclohexene oxide (CHO) were dried over CaH₂ for at least 24 hours, then filtered and stored under atmospheric conditions. Carbic anhydride (CPMA) was recrystallized from hot 30:70 ethyl acetate/hexanes and dried under reduced pressure for 24 h prior to use. Phthalic anhydride (PA), and succinic anhydride (SA) were sublimed prior to use. Glutaric anhydride (GA), and diglycolic anhydride (DGA) were purchased from commercial suppliers and used as received. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) was recrystallized from CH₂Cl₂/diethyl ether and dried under reduced pressure for 24 h prior to use. All rare earth hydrate salts were purchased from commercial suppliers and stored in a desiccator prior to use.

2.1. Methods

¹H NMR spectra were recorded on a Varian 400-MR 2-Channel, Varian Mercury 400 2-Channel, and Varian VNMRS-600 3-Channel spectrometers referenced against residual protio solvent resonances. ¹³C NMR spectra were recorded on a Varian VNMRS-600 3-Channel spectrometer referenced against residual protio solvent resonances. Polymer molar masses and dispersities were determined using a SEC-MALS instrument equipped with an Agilent 1260 Infinity II HPLC System and autosampler, 2 Agilent PolyPore

columns (both 5 micron, 4.6 mm ID) in sequence, a Wyatt DAWN HELEOS-II light scattering detector, and a Wyatt Optilab T- rEX refractive index detector. The columns were eluted with HPLC grade THF at 30 °C at a flow rate of 0.3 mL/min, and polymer samples were dissolved in this solvent and filtered through a 0.2 micron PTFE membrane before dRI analyses. dn/dc values were calculated from the RI signal by using the 100% mass recovery method in the Astra software and a known sample concentration.

3. General Procedures for Polymerization

On the benchtop, $LnCl_3 \cdot xH_2O$ (x = 6 or 7) (1 equiv), [PPN]Cl (1 equiv), anhydride, epoxide and a stir bar were charged into a 2 dram vial equipped with a Teflon-lined cap. Example reaction for **Fig. 3**: YCl₃·6H₂O (1 equiv, 2.98 mg, 0.010 mmol), [PPN]Cl (1 equiv, 5.64 mg, 0.010 mmol), CPMA (400 equiv, 644.5 mg, 3.9 mmol), and CHO (2000 equiv, 2 mL, 19.6 mmol). The vial was closed and then taped with electrical tape and placed inside a Chemglass high throughput tray that was preheated to 110 °C for at least 1 h. After the desired time, the vial was cooled to room temperature and the resulting mixture was dissolved in 1 mL of chloroform. Hexanes was added in excess until the polymer started to precipitate out. The precipitate was allowed to settle, and the supernatant was pipette away. The isolated polymer was then dried under reduced pressure at 80 °C overnight. Conversions were calculated via analysis of crude ¹H NMR spectra in CDCl₃.

3.1 General Procedure for Anhydride Reactivity Ratio Reactions

On the benchtop, $LnCl_3 \cdot xH_2O$ (x = 6 or 7) (1 equiv), [PPN]Cl (1 equiv), 2 anhydrides of choice (each 50 equiv, 0.49 mmol), epoxide (500 equiv.) and a stir bar were charged into a 2 dram vial equipped with a Teflon-lined cap. Example reaction for **Fig. 4**, $LaCl_3 \cdot 6H_2O$ (1 equiv, 3.6 mg, 0.010 mmol), [PPN]Cl (1 equiv, 5.6 mg, 0.010 mmol), DGA (50 equiv, 57.0 mg, 0.49 mmol), PA (50 equiv, 72.7 mg, 0.49 mmol), CHO (500 equiv, 0.50 mL, 4.91 mmol) and a stir bar were charged into a vial equipped with a Teflon-lined cap. The Vial is placed inside a Chemglass high throughput tray that was preheated to 110 °C for at least 1 h. Aliquots, which were then dissolved in CDCl₃, were then taken at selected times for each reaction to monitor monomer conversion by ¹H NMR (**Fig. S29-S34**).

4. Single-Point Polymer Conversion Data

4.1. Polymerizations with CPMA for Single-Point Turnover Frequency (TOF)

 Table S1 Tabulated polymerization data for ROCOP of BO/CPMA catalyzed by lanthanide hydrate salts.^a

Catalyst	Run 1 %	Run 2 % conversion ^b	Stdv.
	conversion ^b		
LaCl ₃ ·7H ₂ O	84	78	4
CeCl ₃ ·6H ₂ O	82	79	2
NdCl ₃ ·6H ₂ O	78	72	4
SmCl ₃ ·6H ₂ O	67	64	2
GdCl ₃ ·6H ₂ O	57	61	3
YCl ₃ ·6H ₂ O	63	66	2
HoCl ₃ ·6H ₂ O	62	62	0
TmCl ₃ ·6H ₂ O	61	63	1

^{*a*}[BO]:[CPMA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 3 hrs. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer.

Table S2 Tabulated polymerization data for ROCOP of CHO/CPMA catalyzed by lanthanide hydrate salts.^{*a*}

Catalyst	Run 1 % conversion ^b Run 2 % conversion		Stdv. ^c
LaCl ₃ ·7H ₂ O	65	69	3
CeCl ₃ ·6H ₂ O	73	70	2
NdCl ₃ ·6H ₂ O	64	71	5
SmCl ₃ ·6H ₂ O	64	73	6
GdCl ₃ ·6H ₂ O	60	66	4
YCl ₃ ·6H ₂ O	64	71	5
HoCl ₃ ·6H ₂ O	66	61	4
TmCl ₃ ·6H ₂ O	53	64	8

^{*a*}[CHO]:[CPMA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 2 hrs. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer. ^{*c*}Standard deviation based on conversion of duplicate runs.

4.2 Polymerizations with GA for Single-Point TOF

Catalyst	Run 1 % conversionRun 2 % conversion		Stdv.
LaCl ₃ ·7H ₂ O	53	53	0
CeCl ₃ ·6H ₂ O	65	66	1
NdCl ₃ ·6H ₂ O	69	69	0
SmCl ₃ ·6H ₂ O	83	73	7
GdCl ₃ ·6H ₂ O	78	73	4
YCl ₃ ·6H ₂ O	86	81	4
HoCl ₃ ·6H ₂ O	86	76	7
TmCl ₃ ·6H ₂ O	75	75	0

Table S3 Tabulated polymerization data for ROCOP of BO/GA catalyzed by lanthanide hydrate salts.^a

^{*a*}[BO]:[GA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 3 hrs. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer.

-	Catalyst	Run 1 % conversion ^b	Run 2 % conversion ^b	Stdv.
-	LaCl ₃ ·7H ₂ O	52	50	1
	CeCl ₃ ·6H ₂ O	68	60	6
	NdCl ₃ ·6H ₂ O	79	78	1
	SmCl ₃ ·6H ₂ O	89	84	3
	GdCl ₃ ·6H ₂ O	88	66	15
	YCl ₃ ·6H ₂ O	93	93	1
	HoCl ₃ ·6H ₂ O	90	90	0
	TmCl ₃ ·6H ₂ O	82	88	4

Table S4 Tabulated polymerization data for ROCOP of CHO/GA catalyzed by lanthanide hydrate salts.^a

^{*a*}[CHO]:[GA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 2 hrs. ^{*b*}Determined using ¹H NMR sepctra of crude reaction mixtures, comparing conversion of anhydride to polymer.

4.3 Polymerizations with PA for Single-Point TOF

-	Catalyst	Catalyst Run 1 % conversion ^b Run 2 %		Stdv.
-	LaCl ₃ ·7H ₂ O	52	55	2
	CeCl ₃ ·6H ₂ O	58	53	4
	NdCl ₃ ·6H ₂ O	51	70	14
	SmCl ₃ ·6H ₂ O	48	48	0
	GdCl ₃ ·6H ₂ O	42	40	1
	YCl ₃ ·6H ₂ O	43	51	5
	HoCl ₃ ·6H ₂ O	57	52	3
	TmCl ₃ ·6H ₂ O	56	38	13

Table S5 Tabulated polymerization data for ROCOP of BO/PA catalyzed by lanthanide hydrate salts.^a

^{*a*}[BO]:[PA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 100 minutes. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer.

Table S6 Tabulated polymerization data for ROCOP of CHO/PA catalyzed by lanthanide hydrate salts.^a

Catalyst	Run 1 % conversionRun 2 % conversion		Stdv.
LaCl ₃ ·7H ₂ O	51	48	2
CeCl ₃ ·6H ₂ O	61	52	6
NdCl ₃ ·6H ₂ O	60	51	6
SmCl ₃ ·6H ₂ O	49	51	1
$GdCl_3 \cdot 6H_2O$	49	54	4
YCl ₃ ·6H ₂ O	69	61	6
HoCl ₃ ·6H ₂ O	48	49	1
TmCl ₃ ·6H ₂ O	52	60	6

^{*a*}[CHO]:[PA]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C for 30 minutes. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer.

5. Full Conversion Polymerization Data for ¹H NMR and SEC Analysis

Table S7 Tabulated polymerization data for ROCOP of different monomer pairs catalyzed by lanthanide hydrate salts.^{*a*}

Monomer	Metal	%	% ester ^c	%	$M_{\rm n}({\rm exp.})^d$	D^d
Pair	Catalyst	Conversion ^b		epim ^e		
	LaCl ₃ ·7H ₂ O	>99	94	52	-	-
BO/CPMA	NdCl ₃ ·6H ₂ O	98	96	7	-	-
	GdCl ₃ ·6H ₂ O	88	96	9	10.3	1.2
	CeCl ₃ ·6H ₂ O	>99	75	11	6.8	1.5
CHO/CPMA	GdCl ₃ ·6H ₂ O	>99	72	13	4.6	1.3
	TmCl ₃ ·6H ₂ O	>99	70	16	5.6	1.3
	LaCl ₃ ·7H ₂ O	70	>99	-	3	1.0
BO/GA	GdCl ₃ ·6H ₂ O	98	>99	-	5.8	1.1
	YCl ₃ ·6H ₂ O	98	>99	-	5.0	1.2
	LaCl ₃ ·7H ₂ O	98	>99	-	3.6	1.2
CHO/GA	NdCl ₃ ·6H ₂ O	98	>99	-	3.9	1.1
	YCl ₃ ·6H ₂ O	98	>99	-	3.1	1.2
	NdCl ₃ ·6H ₂ O	95	>99	-	5.9	1.1
BO/PA	SmCl ₃ ·6H ₂ O	92	>99	-	4.5	1.1
	GdCl ₃ ·6H ₂ O	83	>99	-	5.5	1.1
	CeCl ₃ ·6H ₂ O	90	>99	-	2.9	1.1
CHO/PA	YCl ₃ ·6H ₂ O	97	>99	-	3.5	1.1
	HoCl ₃ ·6H ₂ O	85	>99	-	3.2	1.1

^{*a*}[epoxide]:[cyclic anhydride]:[rare earth chloride hydrate]:[[PPN]Cl] was 2000:400:1:1 at 110 °C. ^{*b*}Determined using ¹H NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer. ^{*c*}Determined using ¹H NMR of purified polymers, comparing the polyether signal to a polyester signal. ^{*d*}Identified by gel permeating chromatography (GPC), using a Wyatt MALS detector. ^{*e*}Determined using ¹H NMR spectra of purified polymers: % Epim. = $\{2 \ge A_{2.7 \text{ ppm}}/(A_{6.0-6.5 \text{ ppm}})\} \ge 100$.

6. Alternative Representation of Polymerization TOF Comparisons



Fig. S4 Differences in catalytic activity between $LnCl_3 \cdot XH_2O$ (X= 6, 7) salts for chosen monomer pairs. All TOFs are in reference to the slowest catalyst. Error bars represent one standard deviation, calculated from duplicate measurements, * = smallest TOF.

7. Reactivity Ratio Data

7.1 Calculation of reactivity ratios

Due to the rate-determining step of the ROCOP of epoxides and cyclic anhydrides involving only epoxide ring opening, turn-over frequency data from individual ROCOP reactions does not allow accurate predictions of polymer sequence in the presence of multiple anhydrides. Therefore, a non-terminal compositional drift copolymerization kinetics model was employed to determine the reactivity ratios of multiple anhydride pairs.¹⁻³ Following the experimental procedure described in section 2.1, Equations 1 and 2 were used to calculate the reactivity ratios of a mixture of two anhydrides. For these equations, p_A and p_B are the respective conversions of A and B monomers with $p_A = 1$ - (A(t)/A₀). The calculated reactivity ratios are then fit to the experimental data as shown in **Fig. S5-S10**.

$$p_{AB}(p_A) = 1 - n_A(1 - p_A) - (1 - n_A)(1 - p_A)^{r_B}$$
(1)

$$p_{AB}(p_B) = 1 - (1 - n_A)(1 - p_B) - n_A(1 - p_B)^{r_A}$$
⁽²⁾

7.2 Reactivity Ratio Plots



Fig. S5 Differences in reactivity ratios for the polymerization of CHO/DGA/PA with LaCl₃·7H₂O/[PPN]Cl at 110 °C.



Fig. S6 Differences in reactivity ratios for the polymerization of CHO/PA/SA with LaCl₃·7H₂O/[PPN]Cl at 110 °C.



Fig. S7 Differences in reactivity ratios for the polymerization of CHO/SA/GA with LaCl₃·7H₂O/[PPN]Cl at 110 °C.



Fig. S8 Differences in reactivity ratios for the polymerization of CHO/GA/CPMA with $LaCl_3 \cdot 7H_2O/[PPN]Cl at 110 \ ^{\circ}C.$



Fig. S9 Differences in reactivity ratios for the polymerization of CHO/DGA/CPMA with $LaCl_3 \cdot 7H_2O/[PPN]Cl at 110 \ ^{\circ}C.$



Fig. S10 Differences in reactivity ratios for the polymerization of CHO/SA/CPMA with $YCl_3 \cdot 6H_2O/[PPN]Cl$ (faded) and $LaCl_3 \cdot 7H_2O/[PPN]Cl$ (dark) at 110 °C.





Fig. S11 ¹H NMR (CDCl₃, 400 MHz) of aliquot of BO-alt-CPMA catalyzed with GdCl₃·6H₂O.



Fig. S12 ¹H NMR (CDCl₃, 400 MHz) of aliquot of CHO-alt-CPMA catalyzed with CeCl₃·7H₂O.



Fig. S13 ¹H NMR (CDCl₃, 400 MHz) of aliquot of BO-alt-GA catalyzed with LaCl₃·7H₂O.





Fig. S15 ¹H NMR (CDCl₃, 400 MHz) of aliquot of BO-alt-PA catalyzed with NdCl₃·6H₂O.



Fig. S16 ¹H NMR (CDCl₃, 400 MHz) of aliquot of CHO-alt-PA catalyzed with CeCl₃·7H₂O.



9. Representative ¹H NMR Data of Purified Polymers

Fig. S17 ¹H NMR (CDCl₃, 600 MHz) of BO-alt-CPMA catalyzed with GdCl₃·6H₂O. Resonance a is assignable to PPN phenyl groups.



Fig. S18 ¹H NMR (CDCl₃, 600 MHz) of CHO-alt-CPMA catalyzed with $CeCl_3 \cdot 7H_2O$. Resonance a is assignable to PPN phenyl groups.



Fig. S19 ¹H NMR (CDCl₃, 600 MHz) of BO-alt-GA catalyzed with LaCl₃·7H₂O. Resonance a is assignable to PPN phenyl groups.



Fig. S20 ¹H NMR (CDCl₃, 600 MHz) of CHO-alt-GA catalyzed with NdCl₃·6H₂O. Resonance a is assignable to PPN phenyl groups.



Fig. S21 ¹H NMR (CDCl₃, 600 MHz) of BO-alt-PA catalyzed with NdCl₃·6H₂O.



Fig. S22 ¹H NMR (CDCl₃, 600 MHz) of CHO-alt-PA catalyzed with CeCl₃·7H₂O. Resonance a is assignable to PPN phenyl groups.

10. Representative ¹³C NMR Data of Purified Polymers



Fig. S23 ¹³C NMR (CDCl₃, 600 MHz) of BO-alt-CPMA catalyzed with GdCl₃·6H₂O.



Fig. S24 ¹³C NMR (CDCl₃, 600 MHz) of CHO-alt-CPMA catalyzed with CeCl₃·7H₂O.



Fig. S25 ¹³C NMR (CDCl₃, 600 MHz) of BO-alt-GA catalyzed with LaCl₃·7H₂O.



Fig. S26¹³C NMR (CDCl₃, 600 MHz) of CHO-alt-GA catalyzed with NdCl₃·6H₂O.



Fig. S27 ¹H NMR (CDCl₃, 600 MHz) of BO-alt-PA catalyzed with NdCl₃·6H₂O.



Fig. S28 ¹H NMR (CDCl₃, 600 MHz) of CHO-alt-PA catalyzed with CeCl₃·7H₂O.

11. Representative ¹H NMR Data for Reactivity Ratios



Fig. S29 ¹H NMR (CDCl₃, 400 MHz) of CHO-alt-DGA-b-CHO-alt-PA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.



Fig. S30 ¹H NMR (CDCl₃, 400 MHz) of CHO-alt-PA-b-CHO-alt-SA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.



Fig. S31 ¹H NMR (CDCl₃, 400 MHz) selected region of CHO-alt-SA-b-CHO-alt-GA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.



Fig. S32 ¹H NMR (CDCl₃, 400 MHz) of CHO-alt-GA-b-CHO-alt-CPMA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.



Fig. S33 ¹H NMR (CDCl₃, 400 MHz) selected region of CHO-alt-DGA-b-CHO-alt-CPMA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.



Fig. S34 ¹H NMR (CDCl₃, 400 MHz) selected region of CHO-alt-SA-b-CHO-alt-CPMA monitored by aliquots. Right side up triangles label monomer decaying, while upside down triangles label polymer growing.

12. Representative SEC Data



Fig. S35 GPC traces (MALS detector left, RI detector right) of BO-alt-CPMA catalyzed with GdCl₃·6H₂O.



Fig. S36 GPC traces (MALS detector left, RI detector right) of CHO-alt-CPMA catalyzed with $CeCl_3$ ·7H₂O.



Fig. S37 GPC traces (MALS detector left, RI detector right) of BO-alt-GA catalyzed with LaCl₃·7H₂O.



Fig. S38 GPC traces (MALS detector left, RI detector right) of CHO-alt-GA catalyzed with NdCl₃·6H₂O.



Fig. S39 GPC traces (MALS detector left, RI detector right) of BO-alt-PA catalyzed with NdCl₃·6H₂O.



Fig. S40 GPC traces (MALS detector left, RI detector right) of CHO-alt-PA catalyzed with CeCl₃·7H₂O.

References

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