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Mechanism of the Polymerization of rac-Lactide by Fast Zinc **Alkoxide Catalysts**

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Supporting Information

ABSTRACT: The ring-opening transesterification polymerization (ROTEP) of rac-lactide (rac-LA) using $L^{X}Zn$ catalysts (L^{X} = ligand having phenolate, amine, and pyridine donors with variable para substituents X on the bound phenolate donor; X = NO₂, Br, t-Bu, OMe) was evaluated through kinetics experiments and density functional theory, with the aim of determining how electronic modulation of the ligand framework influences polymerization rate, selectivity, and control. After determination that zinc-ethyl precatalysts required 24 h of reaction with benzyl alcohol to convert to active alkoxide complexes, the subsequently formed species proved to be active and fairly selective, polymerizing up to 300 equiv of rac-LA in 6–10 min while yielding isotactic ($P_{\rm m} = 0.72-0.78$) polylactide (PLA) with low dispersities: D = 1.06 - 1.17. In contrast to previous work with aluminum catalysts for which electronic effects of ligand substituents were significant (Hammett $\rho = +1.2-1.4$), the L^XZn systems exhibited much less of an effect ($\rho =$ +0.3). Density functional calculations revealed details of the initiation and



propagation steps, enabling insights into the high isotacticity and the insensitivity of the rate on the identity of X.

INTRODUCTION

New catalytic synthetic methods are needed for the development and broader implementation of sustainable polymers that are both derived from biorenewable feedstocks and readily degraded after use.^{1,2} Understanding the mechanisms by which existing catalysts operate is a key prerequisite for addressing this goal. As a privileged class of bioderived monomers, cyclic esters undergo ring-opening transesterification polymerization (ROTEP) to yield useful sustainable materials, with catalysis by metal alkoxide complexes being a pervasive route.³ There is wide agreement that these systems follow a coordinationinsertion mechanism involving initial binding of the monomer to the catalyst followed by nucleophilic attack and ring-opening by an alkoxide ligand. However, purposeful catalyst design is hindered by a general lack of knowledge of many details of the process, including the nature of the coordination and insertion steps and the fundamental reasons for changes in rates and selectivities observed upon varying the supporting ligand and/ or metal ion.

Significant insights into these issues have been obtained from kinetics studies of ROTEP of lactide (LA) or ε -caprolactone (CL) by aluminum alkoxide (AlOR) complexes.⁴⁻¹³ Such catalysts exhibit high molecular weight control and modest rates that are convenient for monitoring by NMR spectroscopy and typically feature easily synthesized supporting Schiff-base ligands that are readily structurally modified so that steric, overall geometric, and electronic influences may be evaluated.^{14,15} Notably, previous studies of AlOR systems have revealed significant rate changes upon variation of the electronwithdrawing/-donating power of substituents on otherwise identical supporting ligands. For example, electron-withdrawing substituents in salen-AlOR catalysts were found to enhance the rate of ROTEP of CL (for the insertion rate constant k_i Hammett $\rho \approx +1.3$, $\Delta \Delta G^{\ddagger} = 1.6-2.6$ kcal/mol between systems with NO₂ and OMe substituents).^{4,5} Analysis by density functional theory (DFT) pointed to changes in the bonding in the insertion transition state as being responsible for the rate differences (greater electron withdrawal shortens the Al–O(carbonyl) and C(carbonyl)–O(alkoxide) interactions). On the other hand, other AlOR catalysts exhibit the reverse trend, where ROTEP is inhibited by electron-withdrawing groups and enhanced by electron-donating substituents.^{12,13}

While these and other results from studies of the wellcontrolled but relatively slow AlOR catalysts ($k \approx 10^{-2} \text{ s}^{-1}$) provide useful insights, it is unclear whether they are transferable to catalysts that perform ROTEP at much faster rates. A notable example of the latter is 1 (Figure 1), which was found to polymerize up to 500 equiv of *rac*-LA in under 5 min at room temperature ($k_p = 2.2 \text{ M}^{-1} \text{ s}^{-1}$).¹⁶ However, this system only produced atactic PLA with moderate polydispersities (1.3-1.4), and the fact that it exists predominantly as a

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Figure 1. Zn complexes used for the polymerization of LA.

dimer renders mechanistic analysis challenging. Recently, a modified version of the ligand in 1 incorporating a pyridyl group was found to yield exclusively monomeric L^XZn (2, X = *t*-Bu), which is a fast, controlled, and selective precatalyst for the polymerization of *rac*-LA using a benzyl alcohol initiator, reaching >95% conversion in ~30 min at ambient temperature with high isotacticity ($P_m = 0.7-0.8$).¹⁷

Intrigued by these initial results, we sought to investigate the effects of varying the electron-donating propensities of substituents X in 2 on the ROTEP kinetics and stereocontrol. We report the synthesis and characterization of new variants with $X = NO_2$, Br, OMe and a full experimental kinetic analysis of their ROTEP of *rac*-LA by all four derivatives. Key findings include discoveries that preconditioning of the complexes with BnOH results in very high ROTEP rates, that all catalysts yield PLA with similar isotacticity, and that the polymerization rates are *insensitive* to the nature of X, in contrast to what is observed with AlOR catalysts. We evaluated the bases for these results through analysis of the reaction pathway by DFT calculations, which provided insights into the high isotacticity of the system and a rationalization for the lack of significant rate changes upon varying X.

RESULTS AND DISCUSSION

Synthesis of Complexes. Using the same method reported previously for the synthesis of the proligand and complex 2 (X = t-Bu),¹⁷ the respective proligands and complexes 2 (X = Br, NO₂) were prepared by coupling the appropriate bromomethylphenol with the pyridyl-amine fragment followed by treatment with ZnEt₂ (Figure 2). A different route was found to be necessary to produce the proligand with X = OMe, involving reductive amination of the indicated aldehyde. Each ligand was fully characterized by ¹H, ¹³C, COSY, and HSQC NMR spectroscopy, as well as highresolution electrospray ionization mass spectrometry (HR-ESI-MS; details provided in the Supporting Information). Complexes 2 were obtained as crystalline solids in good yields (85-93%), and were characterized by ¹H, ¹³C, COSY, and HSQC NMR spectroscopy, CHN analysis, HR-ESI-MS, and, for 2 (X = Br), X-ray crystallography. Similar to other reported structures with analogous ligands,¹⁷ the complex is mononuclear with a distorted-square-pyramidal geometry characterized by $\tau_5 = 0.24$ ($\tau_5 = 0$ is square pyramidal and $\tau_5 = 1$ is trigonal bipyramidal).¹

Polymerization Kinetics: ¹H NMR Monitoring. Polymerization of *rac*-LA was initially monitored by ¹H NMR spectroscopy with fixed concentrations of *rac*-LA (0.9 M < $[LA]_0 < 1.2$ M), precatalyst **2** (3 mM < $[2]_0 < 4$ mM), and benzyl alcohol (3 mM < $[BnOH]_0 < 4$ mM) in CD₂Cl₂, using 1,4-bis(trimethylsilyl)benzene (8.33 mM) as an internal standard. In the experiments, benzyl alcohol was added last, at which point data collection was initiated. Upon inspection of the ¹H NMR data for the polymerization of *rac*-LA by **2** (X = NO₂) we found evidence of an induction period near the



Figure 2. Synthesis of proligands and complexes and a representation of the X-ray crystal structure of **2** (X = Br), showing all non-hydrogen atoms as 50% thermal ellipsoids. Selected distances (Å) and angles (deg): Zn1–O1, 2.0473(11); Zn1–N1, 2.1407(14); Zn1–N2, 2.4348(14); Zn1–N3, 2.1999(15); Zn1–C1, 2.0059(17); C1–Zn1–O1, 114.67(6); C1–Zn1–N1, 113.30(7); C1–Zn1–N2, 104.29(6); C1–Zn1–N3, 116.42(7); O1–Zn1–N1, 87.43(5); N1–Zn1–N2, 73.24(5); N2–Zn1–N3, 76.93(5); N3–Zn1–O1, 88.89(5); O1–Zn1–N2, 140.84(5); N1–Zn1–N3, 126.62(5).

beginning of the polymerization array (Figure 3; note the overall sigmoidal form of the curves). It had been previously suggested that, once the benzyl alcohol initiator was introduced, rapid exchange between the zinc's ethyl substituent and the benzyl alcohol occurred to yield a L^X ZnOBn complex (2') which initiated ROTEP. To explain the apparent induction period observed under the aforementioned reaction conditions, however, we hypothesized that the conversion of 2 to 2' was in fact slow and that the overall rate observed under these conditions (>95% conversion in 2.5 h) was in fact slower than that if formation of 2' was instantaneous.

To test the above hypothesis and determine the mixing time required for full formation of 2', exchange experiments were performed, in which a solution of $2 (X = NO_2, 3.33 \text{ mM})$ in CD_2Cl_2 was placed in an NMR tube with an equimolar amount of benzyl alcohol (Figure 5) and the decay of the ethyl peaks



Figure 3. Concentration versus time plot for polymerization of *rac*-LA (300 equiv, 1 M) by **2** ($X = NO_2$, 1 equiv, 3.33 mM) and BnOH (1 equiv, 3.33 mM) as monitored by ¹H NMR spectroscopy. Data collection was begun soon after addition of BnOH.

associated with 2 (X = NO₂) was monitored. Total disappearance of the Et peaks from the NMR of the L^XZnEt + BnOH mixture signifying complete conversion to the ZnOBn complex occurred after stirring for 24 h (Figure S9 in the Supporting Information). Although the slow reaction of 2 with the BnOH was unexpected, there is literature precedent for slow Zn alkyl and alcohol exchanges.¹⁹ While NMR data support the formulation of 2' (X = NO₂), efforts to isolate it have not been successful. It is likely mononuclear in solution, as indicated by the results of diffusion ordered spectroscopy (DOSY) experiments; hydrodynamic radii r_H for 2 and 2' (X = NO₂) were found to be 6.22 and 6.98 Å, respectively (Figure S10 in the Supporting Information).

With the knowledge that conversion to a zinc alkoxide was slow, we "preconditioned" the catalysts by first stirring 2 with BnOH for 24 h to fully convert it to 2' before adding rac-LA. Subsequent ROTEP was then monitored via ¹H NMR spectroscopy using the same fixed conditions as described above. Significantly faster polymerizations were observed; with pure 2' $(X = NO_2, Br) > 95\%$ conversion was reached in just under 400 s (~ 6 min), with the same conversion reached with 2' (X = t-Bu, OMe) in ~8 and ~10 min, respectively. These enhanced rates in comparison to the previously monitored polymerizations support the hypothesis that slow conversion from 2 to 2' underlies the induction period and that full conversion to the active zinc alkoxide catalyst is necessary for rapid ROTEP. However, these new polymerization rates rendered monitoring of the polymerizations by traditional ¹H NMR spectroscopy methods much more challenging, and so we turned to an alternative methodology.

Polymerization Kinetics: React-IR Monitoring. In view of the fast overall conversions observed for the ROTEP reactions performed by first allowing 2 to react 24 h with BnOH, we used in situ IR monitoring by React-IR to obtain accurate and precise kinetic data. Kinetic measurements of the ring-opening polymerization of LA using $Sn(oct)_2$ were previously measured with React-IR using single-wavelength analysis.²⁰⁻²² In preliminary experiments using this method we obtained variable and inconsistent results depending on the IR peak selected. This problem was avoided by using spectral deconvolution and global fitting in the 1900–900 cm⁻¹ region to obtain relative amounts of rac-LA and PLA per spectrum collected. Known issues with nonlinear absorption response versus analyte concentration 20,23 were addressed by use of calibration curves for both rac-LA and PLA (~50 kDa average $M_{\rm w}$), which established correlation of integrated area under the 1900–900 cm⁻¹ region of interest to known concentrations (Figure S12 in the Supporting Information).

Polymerizations of *rac*-LA to PLA were performed in triplicate and monitored by React-IR at fixed concentrations of LA (0.5 M < $[LA]_0 < 1.5$ M) and 2' (1 mM < $[2']_0 < 4$ mM). The series of spectra (illustrative data shown in Figure 4) were separated into two components, *rac*-LA and PLA, through spectral deconvolution analysis.²⁴ Relative concentrations of *rac*-LA and PLA versus time as well as absolute concentration (using the calibration curves) versus time data were fit with COPASI software.²⁵ Excellent agreement with a first-order fit by all 2' species showed that the polymerizations follow a pseudo-first-order rate expression: rate law = $k_{obs}[LA]$ where $k_{obs} = k_p[2']$ (Figures S13 and S14 in the Supporting Information; illustrative data are shown in Figure 5). The spectral data were also fit to a pseudo-first-order rate law by the Olis GlobalWorks spectral fitting software.²⁶ Comparison of the



Figure 4. Stacked IR spectra at 30 s intervals for polymerization of LA (black) to PLA (red) to >95% conversion using 2' (X = NO₂; intermediate spectra in gray).



Figure 5. Illustrative plot of experimental data (circles) and corresponding COPASI fit (red line) for the ROTEP of LA by 2' (X = NO₂). See Figures S13 and S14 in the Supporting Information for all other such data plots.

three fitting methods revealed results in close agreement (within 20%; Table S1 in the Supporting Information); we arbitrarily chose to provide in Table 1 those obtained by COPASI fitting to calibrated data.

Table 1. Rate Constants and PLA Characterization Data

complex	$k_{\rm obs} (s^{-1})^a$	$M_{\rm w} {\rm (kDa)}^{b}$	$M_{\rm n}~({\rm kDa})$	Đ	$P_{\rm m}$
$2' (X = NO_2)$	0.014(1)	63.1	53.8	1.17	0.72
2 ' (X = Br)	0.010(1)	70.4	61.4	1.15	0.76
$2' \ (\mathbf{X} = t - \mathbf{Bu})$	0.0102(8)	40.8	35.5	1.15	0.78
2' (X = OMe)	0.006(1)	41.6	39.2	1.06	0.75
^{<i>a</i>} Conditions: [LA °C. ^{<i>b</i>} theoretical <i>1</i>	$[A]_0 = 1 M: [2]_M_w = 43.3 kI$	2′] ₀ = 3.33 ml Da.	M (300:1) in	n CH ₂ C	l ₂ at 25

Comparison of the k_{obs} values as a function of para substituent (Table 1) reveals a negligible trend, as illustrated by only ~2-fold difference in rate constants. Also, a small ρ value of +0.3 is seen in a Hammett plot of the log k_p values (black line, Figure 6). This finding differs from that seen for ROTEP of CL by salen-AlOR catalysts (red and blue lines), which exhibited $\rho = +1.2$ or +1.5, respectively (where k_p refers to the catalytic rate constant k_2 in the Michaelis–Menten expression applicable for these catalysts because they exhibited saturation kinetics). In addition, the polymerization rates for the Al catalysts (also at 293 K) varied by approximately 1 order



Figure 6. Hammett plots of log k_p vs σ_{para} for 2' (X = NO₂, Br, *t-Bu*, OMe; black data and linear fit, R = 0.825), with data and fits reported previously for ROTEP of CL by AlOR catalysts supported by salen ligands with a three-carbon backbone (red, R = 0.995) or a two-carbon backbone (blue; R = 0.999) at 298 K. The slopes of the lines corresponding to the Hammett ρ values are shown.

of magnitude $(NO_2 > Br > OMe)$.⁴ In a later section, we turn to DFT calculations in order to better understand why a significantly less pronounced trend in rate as a function of phenolate substituent was observed for the Zn catalysts in comparison to the previously studied salen-AlOR systems.

Polymer Characterization. Kinetic experiments were exposed to air to quench the polymerization reaction within \sim 30 min of completion, and PLA was precipitated by addition to cold methanol, collected, and dried under reduced pressure for 48 h. Size exclusion chromatography (SEC) using a dynamic light scattering detector was used to determine the

average molecular weight (M_w) and dispersity (\mathcal{D}) of the resulting polymers (Table 1). Even at the rapid polymerization rates observed by the **2**' species, polymerization control is maintained, which is indicated by narrow polymer dispersities $(\mathcal{D} = 1.06-1.17)$. A sample of dry PLA from each kinetic experiment was dissolved in CDCl₃ and used to determine the polymer's isotacticity (P_m) via homonuclear-decoupled ¹H NMR. Isotactic preference for PLA by all catalysts studied was also maintained with P_m values reaching as high as 0.78 (Table 1).

Density Functional Theory Calculations. Quantum chemical modeling, which has previously offered important insights into the metal-catalyzed ROTEP of lactide in other systems,²⁷ was undertaken to (i) offer insight into the observed isotacticity in the polymer product and (ii) rationalize the insensitivity of the reaction rate to para substitution of the phenoxide moiety in the catalyst. In particular, a detailed survey of stereodistinct isomers for relevant insertion and ring-opening transition-state structures in the parent system was done using the M06 family of density functionals (see Calculation Details in the Supporting Information for details), and the reaction coordinate shown in Figure 7 was found to have the lowest barriers for the initiation step of the proposed polymerization mechanism. The ring-opening transition state (TS4-5) was predicted to be rate limiting for both enantiomers of rac-LA, with the S,S enantiomer having a significantly higher barrier than the R,R enantiomer (16.1 vs 14.0 kcal/mol, respectively) for the catalyst configuration used. While we note that the flexibility of the growing polymer chain, together with the structural similarity of isopropoxide to the portion of the growing polymer chain coordinated to the metal, suggests that similar differential energetics may be expected for subsequent



Figure 7. M06-2X//M06-L reaction coordinate standard-state free energies for lactide opening (kcal/mol) relative to separated species with line drawings of relevant stationary points. Results for pathways involving both *S,S*-lactide (green dotted line) and *R,R*-lactide (black solid line) are shown with adoption of a particular configuration at Zn in the precatalyst differentiating these two paths.

propagation steps, we also recognize that some degree of chainend control of polymer stereochemistry likely occurs and is not addressed by our calculations.²⁸ Working under the assumption that site control is important, we hypothesize that the difference in activation free energies between the two LA enantiomers is one key determinant of the isotacticity observed in the polymer (noting that changing the configuration at Zn requires a quite high-energy dissociation/recoordination of the growing polymer chain from the metal center). The origin of this 2.1 kcal/ mol energy difference is associated with the boat-like geometry of the six-membered lactide ring in this ring-opening TS structure (Figure S22 in the Supporting Information). The boat is preferred because it permits both methyl groups of the lactide to be pseudoequatorial while their corresponding geminal hydrogen atoms are pseudoaxial (the planarity of the ester linkages that comprise the other four atoms of the ring also contribute to stabilizing the boat ring form in this TS structure). For the specific L^XZn catalyst configuration chosen, the alternative boats have differing steric interactions. For the S,S case, a methyl group of the lactide ring is close to and clashes with the tert-butyl group of the aryloxy ring and the alkylamino portion of the ligand linker, whereas these interactions are lessened considerably for the R,R isomer. Moreover, the methyl group from the alkylamino portion of the ligand linker points directly toward the unperturbed ester linkage of the lactide ring for the S,S case, whereas these interactions are absent in the R,R variant. We hypothesize that these differences in steric interactions and/or unfavorable changes in electronic interactions associated with geometry relaxation to ameliorate the steric clash underlie the TS energies and are at least partially responsible for the observed isotacticity in the polymerization.

To assess substitution effects, all of the stationary points in Figure 7 were substituted at the para position (cf. Figure 3). Relative energetics for TS4-5, along with CM5 charges on the Zn atom, are shown in Table 2 for all of the reaction

Table 2. DFT Predicted Free Energies of Activation and Zn Charges in TS4-5

	R,R-lactide		S,S-lactide			
substituent	$\Delta G^{\ddagger} (\text{kcal/mol})^{a}$	Q _{Zn,CM5}	$\Delta G^{\ddagger} (\text{kcal/mol})^{a}$	Q _{Zn,CM5}		
$-NO_2$	13.3	0.733	15.4	0.722		
-Br	12.9	0.728	16.9	0.718		
-H	14.0	0.729	16.1	0.717		
− <i>t</i> -Bu	14.0	0.727	16.9	0.716		
-OMe	14.0	0.726	16.9	0.715		
$-N(Me)_2$	14.6	0.725	17.0	0.714		
^{<i>a</i>} Computed as $G_{TS4-5} - G_4$ using M06-2X//M06-L free energies.						

coordinates (again, taking the specific configuration at Zn that favors R_rR reactivity). Slightly lower reaction barriers were predicted for electron-withdrawing substituents in comparison to those for H or electron-donating substituents, in good agreement with experimental observations, but the overall sensitivity to para substitution is predicted to be slight. Consistent with this observation is the very small variation in Zn CM5 charges that is predicted over the range of substituents. Thus, from p-N(Me)₂ to p-NO₂, there is an increase in the Zn charge of only 0.008 au: i.e., its Lewis acidity is modulated very little by para substitution of the phenol. It is not entirely trivial, of course, to explain why something does *not* happen, but we speculate that the extensive nitrogen functionality about Zn buffers the phenol para substitution effect so that its influence is more limited than it might otherwise be expected to be.

Additional insights into the basis for the ligand substitution effects may be obtained by comparing the transition-state structures calculated here to those previously reported for the (salen)Al system with the two-carbon backbone (Figure 8).⁴ As



Figure 8. Optimized transition-state (TS) structure geometries, with selected atoms identified: (a) previously reported TS structure for nucleophilic attack on CL by coordinated alkoxide for (salen)Al catalyst analogous to the Zn catalysts reported here; (b) TS structure for nucleophilic attack on *R*,*R*-lactide with (salan)Zn catalyst (**TS2-3**); (c) ring-opening TS structure for the tetrahedral intermediate in the *R*,*R*-lactide/(salan)Zn system (**TS4-5**). Geometric details are recorded in Table 3 and Tables S3–S5 in the Supporting Information, with fully labeled structures shown in Figures S16–S19 in the Supporting Information.

illustrated for selected bond distances (Table 3; complete data are provided in Tables S3–S5 in the Supporting Information),

Table 3. Selected Bond Lengths (Å) and Bond Length Variations in Calculated TS Structure for Nucleophilic Attack on ε -Caprolactone or R,R-LA by Coordinated Alkoxide as a Function of Para Substitution of the Phenolate Group(s)^{*a*}

bond	NO_2	Br	Н	OMe	range			
(salen)Al								
Al-O1	1.893	1.912	1.927	1.929	0.036			
Al-O2	1.900	1.900	1.905	1.904	0.005			
O1-C1	1.302	1.295	1.289	1.291	0.013			
O2-C1	1.744	1.769	1.801	1.784	0.057			
L ^X Zn								
Zn-O1	2.245	2.283	2.291	2.285	0.046			
Zn-O2	2.061	2.067	2.065	2.076	0.015			
O1-C1	1.255	1.253	1.252	1.252	0.003			
O2-C1	1.874	1.870	1.876	1.879	0.009			

^aBond labels refer to structures in Figure 8a,b, respectively. Data for Al bonds are taken from ref 4. Complete computed bond distances for structures in Figure 8 are given in Tables S3–S5 and Figures S19–S21 in the Supporting Information.

the largest change in TS structure bond lengths for the (salen) Al system is found for the O_2-C_1 bond, which is the bond that is forming in this mechanistic insertion step (0.057 Å; O2 is the alkoxide oxygen nucleophilically attacking the carbonyl carbon of CL, C1). Given such a large change in the position of the TS, it is not particularly surprising that a significant variation in activation free energy (ΔG^{\ddagger}) is also observed for polymerization in this system (Figure 6, blue), presumably reflecting the influence of the varying basicity of the phenolates in the ligand (of which there are two). In contrast, for the L^XZn system, there is quite little variation in the lengths of the key bonds being made or broken as a function of para substitution in the single phenol ring in these catalysts (0.009 Å for O2-C1 in the insertion step, TS2-3, Table 3). The variation is similarly small for O5-C1 in the ring-opening step (0.013 Å, TS4-5, Table S5 in the Supporting Information). Interestingly, in both TS structures, there are significant variations in heteroatom-Zn bond distances associated with para substitution of the L^X phenolate, but these do not seem to significantly influence the reacting partners (consistent with the observed lack of much charge variation at the Zn center described above). We postulate that these findings derive from the fact that (i) there is only a single phenol in the L^XZn system in comparison to the two in the (salen)Al system and/or (ii) the Zn-O bonds are intrinsically about 0.2 Å longer than analogous Al-O bonds, thereby making Zn less sensitive to substitution effects than Al simply from the r^{-1} dependence of purely electrostatic effects.

CONCLUSIONS

In this work we prepared and characterized a series of complexes 2 akin to previously reported efficient ROTEP catalysts,¹⁷ but here featuring para substituents with variable electronic influences. We found that preconditioning with BnOH to yield putative alkoxide species 2' led to fast and reproducible rates of ROTEP of rac-LA (>95% in 6-10 min, depending on catalyst). Analysis of kinetic data acquired using in situ React-IR revealed a pseudo-first-order rate expression, with the reaction yielding highly isotactic polymer. In contrast to previous work on Al systems which showed that variation of the electronic influences of para phenolate substituents has a significant effect on ROTEP rate,^{4,5} the effects were found to be significantly attenuated for the Zn catalysts studied herein. DFT calculations shed important light on the reasons for the high isotacticity and the lack of sensitivity of the ROTEP rate on the nature of para substituents X. Key findings were (a) the ringopening transition state TS4-5 is rate-determining, and its energy is significantly different for opening the R,R and S,S isomers of LA as a result of multiple steric interactions, thus helping to explain the observed isotacticity of the product polymer and (b) the attenuated effect of para substituent variation is reproduced and attributed to lesser charge variation at Zn and small differences in key interatomic distances in the TS structures relative to those seen for Al systems.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02544.

Experimental data, concentration versus time plots, crystallographic information, and calculations (PDF)

Accession Codes

CCDC 1577971 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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