

# Ring Opening Polymerization and Copolymerization for Polyester and Polycarbonate Formation by a Diamino-bis(phenolate) Chromium(III) Catalyst

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## ABSTRACT

The diamino-bis(phenolate) chromium(III) complex, CrCl[L], **1** where [L] = dimethylaminoethylamino-*N,N*-bis(2-methylene-4,6-*tert*-butylphenolate) when pre-contacted with cocatalyst, bis(triphenylphosphine)iminium chloride, formed the bis(triphenylphosphine)iminium chromium(III) dichloride ate complex, **2**. Complex **2** shows good activity for the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) and  $\epsilon$ -caprolactone ( $\epsilon$ -CL), ring-opening copolymerization (ROCOP) of cyclohexene oxide (CHO) and phthalic anhydride (PA), ROCOP of epoxides and CO<sub>2</sub>, and synthesis of terpolymers containing polylactide or polycaprolactone, polycarbonate, and polyester segments. For example, polyester-*b*-polycarbonates can be obtained through controlled ROCOP of PA and CHO giving, moderate molecular weight polymers with narrow dispersity (e.g.  $M_n = 8.7 \text{ kg mol}^{-1}$  and  $D = M_w/M_n = 1.14$ ),

followed by addition of CO<sub>2</sub> to generate polycarbonate chains and an increase in  $M_n$  to 17.6 kg mol<sup>-1</sup> with  $D = 1.13$ .

## INTRODUCTION

The ring-opening polymerization (ROP) of cyclic esters to aliphatic polyesters has been explored extensively and identified as a desirable process for making polymers from renewable sources, such as lactide obtained from corn and other bio-derived sources.<sup>1-4</sup> While ROP of these cyclic monomers can be highly controlled, the thermal properties of these materials, such as low glass-transition temperatures, limits their commercial applications.<sup>5-12</sup> The ring-opening copolymerization (ROCOP) of epoxides and anhydrides is another promising method of polymer synthesis. It is versatile as it allows use of a broad range of epoxides and anhydrides to yield polyesters that can potentially be obtained from renewable sources.<sup>12-17</sup> The ROCOP of epoxides with CO<sub>2</sub> further expands the potential to generate polymers from potentially renewable feedstocks and brings with it access to polycarbonates with potentially higher glass-transition temperatures dependent upon the epoxide used.<sup>8,12</sup> Terpolymerization reactions that combine cyclic ester ROP with ROCOP can produce polymers resulting in mixed polyester or polyester-polycarbonate chains. The monomers can be incorporated as random insertions during ROP or ROCOP steps, or as blocks from stepwise or selective polymerization of individual monomers. Control of these processes can result in formation of polymers with tunable thermal properties.

A variety of metal complexes have been used as catalysts for the preparation of polyesters, polycarbonates and terpolymers from ROCOP of epoxides with cyclic anhydrides. Complexes of salen-type ligands have been particularly effective with metals including Al, Cr, Mn, Fe, Co and Zn.<sup>8,12,18</sup> Chromium systems have been shown to show exceptional activity, such as the trimetallic

Cr(III) salen complexes of Lu and co-workers.<sup>19</sup> Chromium(III) complexes of amino-tris(phenolate) ligands have also been used for copolymerization of cyclohexene oxide with phthalic, naphthalic and maleic anhydrides. Limonene oxide was shown to only form copolymer with phthalic anhydride.<sup>20</sup>

Williams and co-workers reported catalytic systems that can polymerize a variety of cyclic monomers forming co- and terpolymers possessing tunable physical properties. Using dizinc macrocyclic complexes they were able to perform ROP of  $\epsilon$ -decalactone initiated using *trans*-1,2-cyclohexane diol (CHD) followed by ROCOP using an established Al-(amino)tris(phenolate) catalyst, which polymerized limonene oxide (LO) and CO<sub>2</sub> forming a ABA block copolymer.<sup>21</sup> These polymers exhibited impressive properties, such as the polycarbonate portion (A) having a high glass transition temperature ( $T_g$ ) while the polyester portion (B) having a low  $T_g$ .<sup>21</sup> Williams and co-workers also showed the ability to perform terpolymerization of bio-derived epoxides with CO<sub>2</sub> to form partially unsaturated polycarbonates as well as polyesters containing phthalic anhydride (PA) and the bioderived epoxide.<sup>22</sup> These unsaturated polycarbonates and polyesters formed showed high  $T_g$  values and decomposition temperatures, variability of polymers able to be formed, and potential to further modify the double bond to allow for a potential change in polymer properties.<sup>22</sup>

Lu and co-workers synthesized controllable statistical terpolymers with a single  $T_g$  using a one-pot reaction of  $\beta$ -propiolactone, epoxides, and CO<sub>2</sub> catalyzed by a catalytic system containing a salcyCo(III)OTs (salcy = N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-diaminocyclohexane; OTs = p-toluenesulfonate) catalyst.<sup>23</sup> Ko and co-workers were able to catalyze the synthesis of polycarbonates and cyclic carbonates using a variety of monomers with dinuclear Ni and Co complex catalytic systems, respectively.<sup>24</sup> Others have used Cr(III) catalysts for the ROCOP of

epoxides such as CHO with PA.<sup>25–27</sup> Bester and co-workers used amino-bis(phenolate) Cr(III) complexes with 4-(dimethylamino)pyridine (DMAP) as a co-catalyst.<sup>26</sup> Boggioni used (salen)MCl catalysts, where M = Cr, Al, and Mn, and determined that formation of high molecular weight and  $T_g$  polymers required a pre-contact step between the catalyst and external nucleophilic co-catalyst was required.<sup>25,28</sup> Others have shown the importance of a pre-contact step between Cr catalysts and various co-catalysts.<sup>20,29–31</sup>

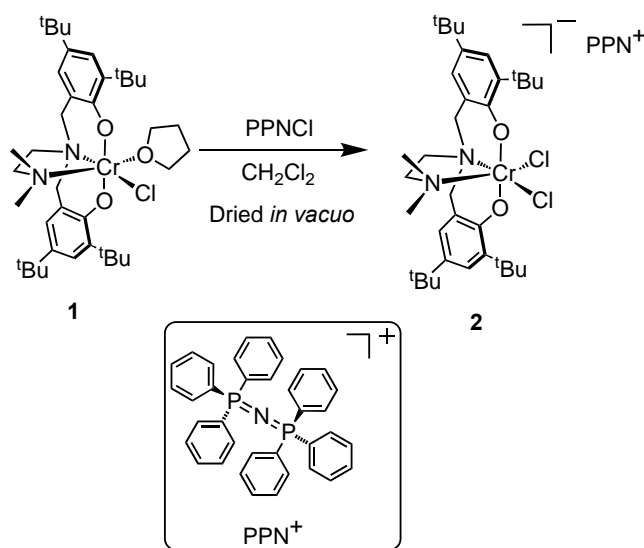
We have previously reported the use of chromium(III) diamino-bis(phenolate) complexes as catalysts for the ring-opening polymerization (ROP) of cyclohexene oxide (CHO) to form polyether under mild conditions.<sup>32</sup> These and related Cr(III) complexes also catalyze ring-opening copolymerization reactions of epoxides and carbon dioxide (CO<sub>2</sub>) giving polycarbonates.<sup>33–39</sup> In order to increase the variability of monomers used with our previously studied catalyst, naturally occurring monomers such as *rac*-lactide (*rac*-LA) were looked into being used for polymerizations. The ROCOP of *rac*-LA with epoxides and CO<sub>2</sub> has also been shown to be capable with a related salenCo(III) catalyst.<sup>40</sup> Herein, we build upon the previous work, using our previous Cr(III) complexes with the assistance of bis(triphenylphosphine)iminium chloride (PPNCl) pre-contacting with the catalyst to form a catalytic system that could be used for ROP and ROCOP reactions to form terpolymers consisting of ester and carbonate linkages.

## RESULTS AND DISCUSSION

### *Catalyst Synthesis*

The Cr(III) diamino-bis(phenolate) complex **1** was afforded via a similar route to that previously reported by us and others for preparation of Cr(III) amino-bis(phenolate) complexes.<sup>25,32–38</sup> The process involves reacting the proligand H<sub>2</sub>L with sodium hydride (NaH) in

THF at  $-78\text{ }^{\circ}\text{C}$ , and a subsequent reaction with  $\text{CrCl}_3(\text{THF})_3$  in THF at  $-78\text{ }^{\circ}\text{C}$  to afford a pink solid. This pink catalyst **1** was reacted with  $\text{PPNCl}$  in  $\text{CH}_2\text{Cl}_2$  and stirring for 1 h at  $22\text{ }^{\circ}\text{C}$  produced a purple solution that was dried *in vacuo* to give the purple bis(triphenylphosphine)iminium salt, **2**. (Scheme 1). Complex **1** was previously fully characterized including in the solid state by single crystal X-ray diffraction.<sup>35</sup> Complex **2** was previously identified spectroscopically using MALDI-TOF MS.<sup>34</sup>



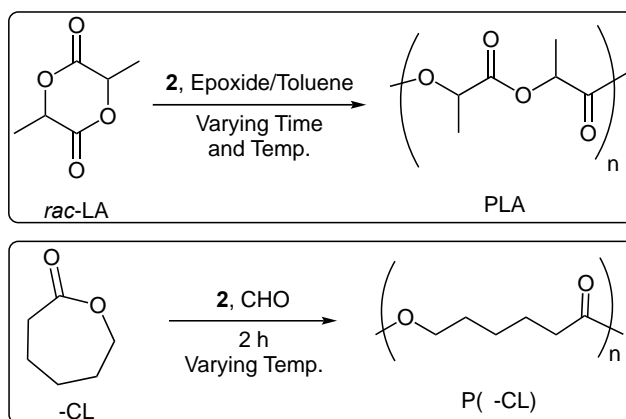
**Scheme 1.** Synthesis of the bis(triphenylphosphine)iminium salt, **2**, from the addition of bis(triphenylphosphine)iminium chloride to **1**.

### ***Ring opening polymerization reactions of *rac*-LA and $\epsilon$ -CL***

The ring-opening polymerization reactions of *rac*-LA to polylactide (PLA) (Table 1, entries 1 – 10) were catalyzed using either the precursor catalyst **1** by itself, the co-catalyst  $\text{PPNCl}$  by itself, or  $\text{PPN}[\text{CrCl}_2\text{L}]$ , **2**. (Scheme 2) The reactions were conducted in dry toluene or in an epoxide, CHO or propylene oxide (PO). Use of only  $\text{PPNCl}$  (Table 1, entries 1 and 2) displayed

very little conversion of *rac*-LA to PLA in either CHO or toluene. Complex **1** with no added PPNCI also showed no conversion of *rac*-LA to PLA in toluene or mixtures of CHO and toluene (Table 1, entries 3 and 4). Using **2**, excellent conversions of *rac*-LA could be obtained at 60 °C or higher temperatures, but only poor conversions at 40 °C (Table 1, entries 5 – 10). A 1.0 mol% loading of **2** of *rac*-LA in CHO at 80 °C gave high conversions within 2 h (Table 1, entries 7 – 9). The isolated polymer showed lower than expected molecular weights but with narrow dispersity (Table 1, entry 8). When these conditions were performed at 100 °C (Table 1, entry 9) much lower molecular weights were obtained than expected suggesting increase chain transfer events, likely due to CHO being contaminated with cyclohexene diol even after reduced-pressure distillation. When performed at 60 °C, a similarly high conversion of *rac*-LA to PLA was observed, but very low isolated yield of polymer was obtained preventing mass and dispersity determination (Table 1, entry 7). Using PO as solvent at 40 °C showed excellent conversion in 1 h yielding good molecular weights but with broader dispersity compared to when CHO was used (Table 1, entry 10).

The ring-opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) was performed in CHO using **2** at 80 °C and 100 °C, showing improved conversion with increasing temperature. Conversion of 31%  $\epsilon$ -CL to poly( $\epsilon$ -CL) was observed at 80 °C (Table 1, entry 11), with very low isolated yield again preventing mass and dispersity determination. At 100 °C, the conversion improved to 64% of  $\epsilon$ -CL to poly( $\epsilon$ -CL) with 31% (79 mg) isolated yield allowing for GPC analysis. The observed  $M_n$  was slightly lower than the calculated value with  $D = 1.61$ . (Table 1, entry 12).



**Scheme 2.** Catalyzed synthesis of PLA and poly( $\epsilon$ -CL) from *rac*-LA and  $\epsilon$ -CL, respectively.

**Table 1.** Ring opening polymerization of *rac*-LA and  $\epsilon$ -CL catalyzed by **1** and **2**.<sup>a</sup>

Entry	Cat/solvent	[I]:[Monomer]: [Solvent]	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%) <sup>b</sup>	<i>M</i> <sub>n,calc</sub> / <i>M</i> <sub>n</sub> (kDa) <sup>c,d</sup>	<i>D</i> <sup>d,e</sup>
1 <sup>f</sup>	PPNCl/CHO	1:100:1000	80	2	7	1.0/-	-
2 <sup>f</sup>	PPNCl/ Toluene	1:100:1000	80	2	5	0.7/-	-
3 <sup>g</sup>	<b>1</b> /Toluene	1:100:1000	80	24	2	0.3/-	-
4 <sup>g,h</sup>	<b>1</b> /CHO/Toluene	1:100:2000	80	24	4	0.6/-	-
5	<b>2</b> /CHO	1:100:500	40	1	15	2.2/-	-
6	<b>2</b> /CHO	1:100:500	40	2	15	2.2/-	-
7	<b>2</b> /CHO	1:100:500	60	2	92	13.2/-	-
8	<b>2</b> /CHO	1:100:500	80	2	94	13.5/4.9	1.16
9	<b>2</b> /CHO	1:100:500	100	2	82	11.9/1.3	1.20
10	<b>2</b> /PO	1:100:500	40	1	100	14.4/7.4	1.64
11	<b>2</b> /CHO	1:100:500	80	2	31	3.5/-	-
12	<b>2</b> /CHO	1:100:500	100	2	64	7.3/5.8	1.61

<sup>a</sup> Entries 1 – 10 monomer = *rac*-LA, entries 11 and 12 monomer =  $\epsilon$ -CL. <sup>b</sup> Conversion to polyester product determined by <sup>1</sup>H NMR spectroscopy. All produced polymers had < 5% ether linkage formation as determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>  $M_{n,calc} = (M \text{ of monomer} \times [\text{Monomer}]/[\text{I}] \times \text{conv.} (\%))$ , [I] = initiator/catalyst. <sup>d</sup> Determined via universal calibration with triple detection gel permeation chromatography (GPC) in THF. <sup>e</sup>  $D = M_w/M_n$ . <sup>f</sup> Only PPNCl was used as catalyst for these reactions. <sup>g</sup> Only **1** was used with no PPNCl. <sup>h</sup> Both CHO and toluene used as solvents for this reaction, each in 1000 equiv. (2000 in total) compared to the catalyst.

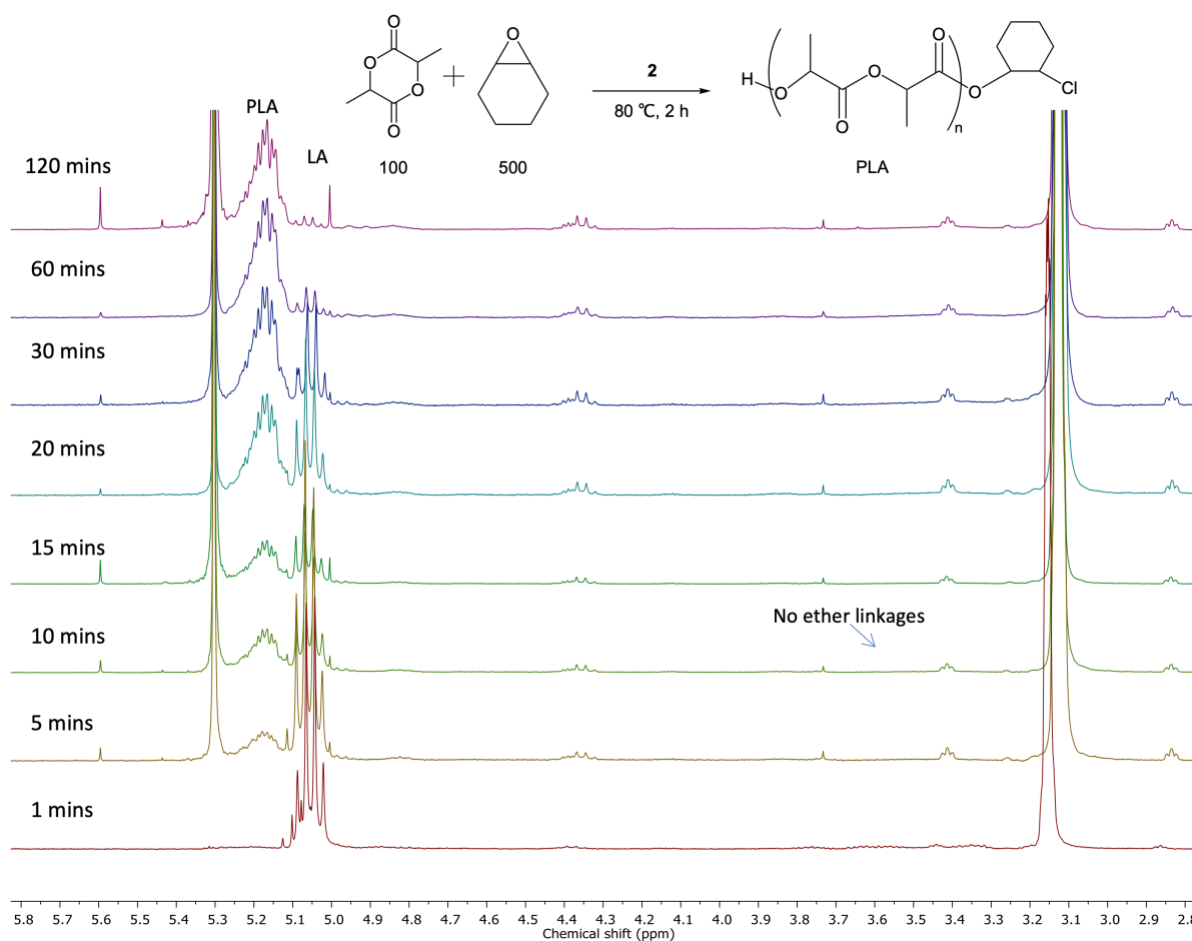
The results obtained in this study can be compared to the polymerization activity of related M(III) catalysts. Jones and co-workers described iron(III) chloride salalen complexes performing

ROP of *rac*-LA in PO. Conversions of 62 to 80% were observed over periods of days, giving low molecular weight polymers with narrow dispersity.<sup>41</sup> Indium alkoxide phosphosalen complexes of Buchard, Williams and co-workers for the ROP of *rac*-LA and  $\epsilon$ -CL could achieve conversions of over 90% in 40 min in THF without the use of a co-catalyst or chain-transfer agent.<sup>42</sup> Similarly they observed higher conversion of  $\epsilon$ -CL to poly( $\epsilon$ -CL) (82 – 99%) at room temperature in only minutes.<sup>42</sup> Rieger and co-workers use indium alkoxide salen catalysts for the ROP of *rac*-LA and  $\epsilon$ -CL with activity exceeding this work, also obtaining high conversion of  $\epsilon$ -CL to poly( $\epsilon$ -CL) (72 – 82%) at room temperature in under 2 min.<sup>43</sup> Previous work from our group using amino-bis(phenolate) complexes of Li, Na, and K showed high activity for ROP of *rac*-LA.<sup>44</sup> In both toluene and solvent-free under melt conditions, the ROP of *rac*-LA was performed in under an hour with full conversion.<sup>44</sup>

The ROP of *rac*-LA to PLA was monitored over the course of 2 h by <sup>1</sup>H NMR spectroscopy (Figure 1) according to the conditions of Table 1, entry 8. The spectra show most of the *rac*-LA is converted to PLA in the first hour. The <sup>1</sup>H NMR spectrum displays PLA formation as the multiplet at ~5.15 – 5.30 ppm corresponding to the polymer methine region grows as the reaction proceeds while the quartet at ~5.00 – 5.15 ppm corresponding to the unreacted *rac*-LA decreases. The spectra over time show the absence of resonances in the ~3.30 – 3.60 ppm region attributed to internal ether linkages in the polymer.<sup>32,45–47</sup> The presence of the CHO initiator is not observed in the <sup>1</sup>H NMR spectrum, but end group analysis using MALDI-TOF MS that will be discussed below promotes the idea of the ROP of *rac*-LA being initiated by CHO. Using PO as initiator and solvent rather than CHO showed full conversion of *rac*-LA to PLA after 1 h at 40 °C as determined by <sup>1</sup>H NMR spectroscopy (Table 1, entry 10 and Figure S2). The resulting polymer had a higher dispersity than those performed in CHO at higher temperatures. Similar reactions done in CHO at



40 °C (Table 1, entries 5 and 6) showed much lower conversion of *rac*-LA to PLA, with no polymer able to be isolated for further mass and dispersity determination. Polymerizations performed at 80 °C in CHO (Table 1, entry 8) showed a higher conversion of *rac*-LA than at 100 °C (Table 1, entry 9) as determined by <sup>1</sup>H NMR spectroscopy (Figure S1), giving higher molecular weights but with similar molecular weight dispersities. The polymerization follows first-order kinetics with respect to lactide concentration (Figure S6). Characterization of the resulting PLA by MALDI-TOF MS will be discussed below.

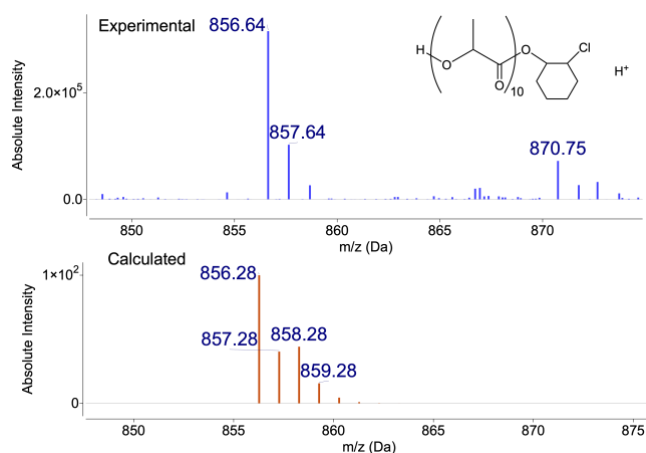


**Figure 1.** Time dependent <sup>1</sup>H NMR spectra (300 MHz in CDCl<sub>3</sub>) of aliquots from the ROP of *rac*-LA in CHO using **2** as an initiator. Conditions as in Table 1, entry 8, [*rac*-LA]<sub>0</sub>:[CHO]<sub>0</sub>:[**2**]<sub>0</sub> = 100:500:1, 80 °C. Conversion is taken from integration of the methine region of the polymer and the monomer. Ether linkages are monitored from resonances in the range of 3.50 – 3.70 ppm.

The ROP of  $\epsilon$ -CL to poly( $\epsilon$ -CL) was monitored by  $^1\text{H}$  NMR through sampling aliquots of the reaction mixture over the course of 2 h at 100 °C and quenching the removed aliquots by exposure to air (Figure S7). Similarly, aliquots were also taken for the less reactive 80 °C  $\epsilon$ -CL reaction (Figure S8). No ether linkages were observed for the poly( $\epsilon$ -CL) synthesis indicating selectivity of **2** for ROP of  $\epsilon$ -CL over ring-opening (and polymerization) of epoxide. The mechanism of polymerization is expected to be like for *rac*-LA polymerization, where ring-opening of the CHO via nucleophilic attack generates an alkoxide, which in turn initiates ROP of  $\epsilon$ -CL. Ether linkages potentially form upon insertion of an epoxide unit instead of a cyclic ester monomer. The polymerization follows first-order kinetics with respect to  $\epsilon$ -CL concentration at 100 °C (Figure S10), as for the polymerization of *rac*-LA observed at 80 °C. The conversion of  $\epsilon$ -CL to poly( $\epsilon$ -CL) observed after 2 h was 64%, which was significantly lower than PLA production. However, the ability of **2** to polymerize both monomers indicates a versatility of this catalyst system for ROP of cyclic esters as well as for the previously reported ROCOP of epoxides with  $\text{CO}_2$ .<sup>34,35,38</sup>

### ***MALDI-TOF MS characterization of PLA***

MALDI-TOF MS has been used for the end-group analysis of polymers including PLA.<sup>14,22,32–34,38,44,48–60</sup> For the PLA prepared according to Table 1, entry 8, MALDI-TOF MS showed the formation of linear PLA with peak separation of 72  $m/z$  corresponding to the repeating unit of half of a lactide molecule (Figure S39). End-group analysis supports polymerization is initiated by a chlorinated cyclohexene oxide and termination via protonation of an alkoxide chain-end. Cationization is via protonation from the 2,5-dihydroxybenzoic acid (DHB) matrix. A comparison of the experimentally obtained peak at 856.64  $m/z$  matches closely with the calculated pattern for an appropriate oligomer containing the expected end-groups (Figure 3).



**Figure 3.** MALDI-TOF mass spectrum for the polymerization of *rac*-LA in CHO at 80 °C for 2 h using **2** (Table 1, Entry 8). Comparison of the experimental mass spectrum (top) and the calculated isotopic pattern (bottom) for the expected end-groups. Oligomer chain peaks were calculated with exact masses for  $C_6H_{10}O + Cl + (C_3H_4O_2)_n + 2H^+ = 98.07 + 34.97 + (72.02)_n + 2(1.01)$  Da.

The ability of catalyst **2** to perform ROP of *rac*-LA and  $\epsilon$ -CL led us to investigate polymerization or copolymerization of other monomers. In previous reports we described the use of **1** with various nucleophilic co-catalysts for the ROCOP of  $CO_2$  with CHO<sup>34,35</sup> and PO.<sup>37</sup> The ROCOP of epoxides with phthalic anhydride was, therefore, attempted.

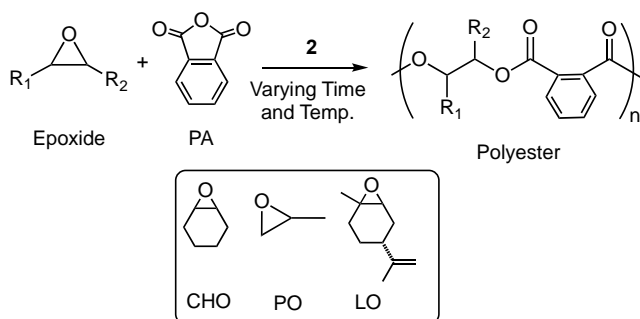
### ***Ring opening copolymerization reactions of epoxides and phthalic anhydride***

The ring opening copolymerization reactions of the epoxides CHO, PO, and LO with the cyclic anhydride of phthalic anhydride (PA) were catalyzed by **2** (Scheme 3). The alternating poly(PA-*alt*-CHO) polymers formed (Table 2, entries 1 – 4) all showed 100% conversion of PA into polyester with  $M_n$  values ranging from 8 – 12 kg mol<sup>-1</sup> and dispersities below 1.2. Side products such as 1,2-benzene dicarboxylic acid were not observed during the conversion of PA to polyester. Performing the reaction in toluene and using equimolar ratios of CHO to PA and 1 mol% **2** gave full conversion of PA to polyester in 1 h rather than 2 h at 100 °C for toluene-free conditions (Table 2, entries 1 and 2). Polymer molecular weights increased modestly from 7.3 to 8.1 kg mol<sup>-1</sup>

when performed in toluene compared to in CHO alone with little change in dispersity. When the reaction is run in CHO under more concentrated conditions (2:PA:CHO of 1:100:500) at 100 °C complete conversion of PA is achieved in 15 min (Table 2, entry 3) with molecular weights nearing 14 kg mol<sup>-1</sup> with narrow dispersity. Lowering the temperature to 80 °C does not significantly decrease activity as quantitative conversion of PA is achieved after 20 min. The reactions were monitored by <sup>1</sup>H NMR spectroscopy over time for entries 3 and 4 (Figures S11 and S14, respectively) showing consumption of PA was rapid. Under the conditions in entry 3, polymer molecular weight increases over time (Figure S12) and conversion vs. time through sampling of reaction aliquots shows nearly complete consumption of PA in 10 min (Figure S13). The polymerization shows a linear growth in  $M_n$  vs. % PA conversion to polyester with narrow dispersity remaining below 1.1 (Figure 4a). The lower molecular weights observed for reactions performed over longer times at 100 °C (Table 2, entries 1 and 2) could indicate that chain transfer reactions (possibly due to adventitious water) may be occurring upon consumption of PA monomer. The linearized plot of  $[PA]_0 - [PA]_t$  vs time demonstrates a zero-order dependence on PA concentration (Figure 4b). The polymers obtained show  $\leq 5\%$  ether linkage formation in their <sup>1</sup>H NMR spectra (Figures S3, S11 and S14), suggesting anhydride reaction is rapid and epoxide ring opening polymerization is not competitive.

Reactions using PO as the epoxide were limited by its lower boiling point. At 40 °C 74% conversion of PA was observed after 90 min showing good control of molecular weight and dispersity (Table 2, entry 5). Reactions with LO as the epoxide required longer reaction times and higher temperatures giving oligomeric polyesters with narrow dispersity (Table 2, entry 6). An attempt was made to generate an alkoxide species of **2** in situ by adding a pre-contact step with PO, followed by removal of excess PO with the CH<sub>2</sub>Cl<sub>2</sub> in vacuo (Table 2, entry 7). This showed

the full conversion of PA to polyester in 1 h compared to the previous reaction that had 93% of PA conversion to polyester after 3 h. The increased activity is most likely caused by the PO pre-activation occurring, similar to what was observed in our previous work where alkoxide-containing anions formed when **1** and PPNCI or PPNN<sub>3</sub> were mixed with CHO prior to polycarbonate formation as per ESI-MS analysis.<sup>34</sup> The reactions using LO showed very good selectivity for polyester formation with approximately 5% ether linkage formation observed by <sup>1</sup>H NMR spectroscopy (Figure S4). An additional reaction was performed of **2** mixed with LO in a concentration ratio of 1:500 and then placed in the pressure vessel using 40 bar CO<sub>2</sub> at 60 °C for 24 h. The crude <sup>1</sup>H NMR sample showed 0% conversion into polymer of any kind. Use of temperatures above 80 °C are known to favor cyclic carbonate formation,<sup>35</sup> therefore no further studies were done regarding the polycarbonate, polyester, or terpolymer formation using LO.

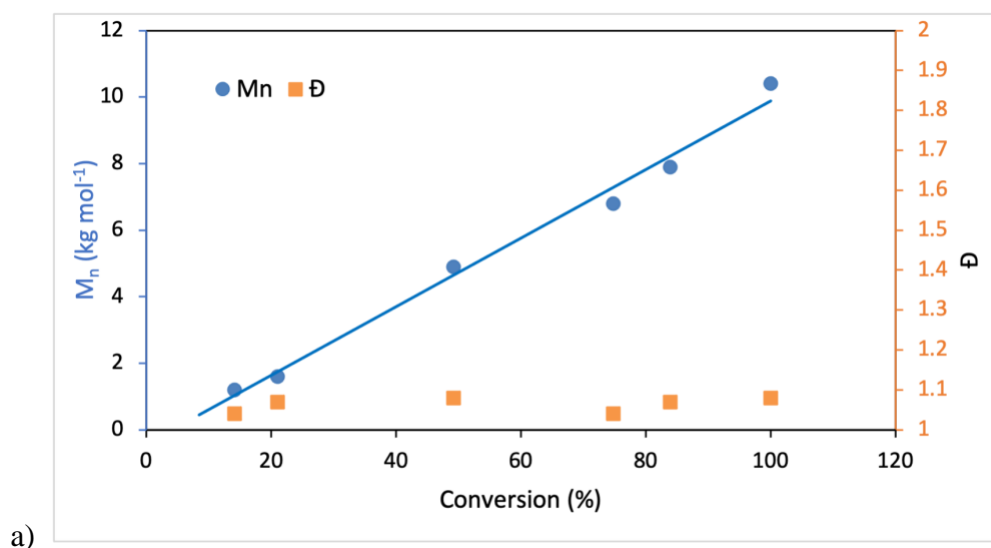


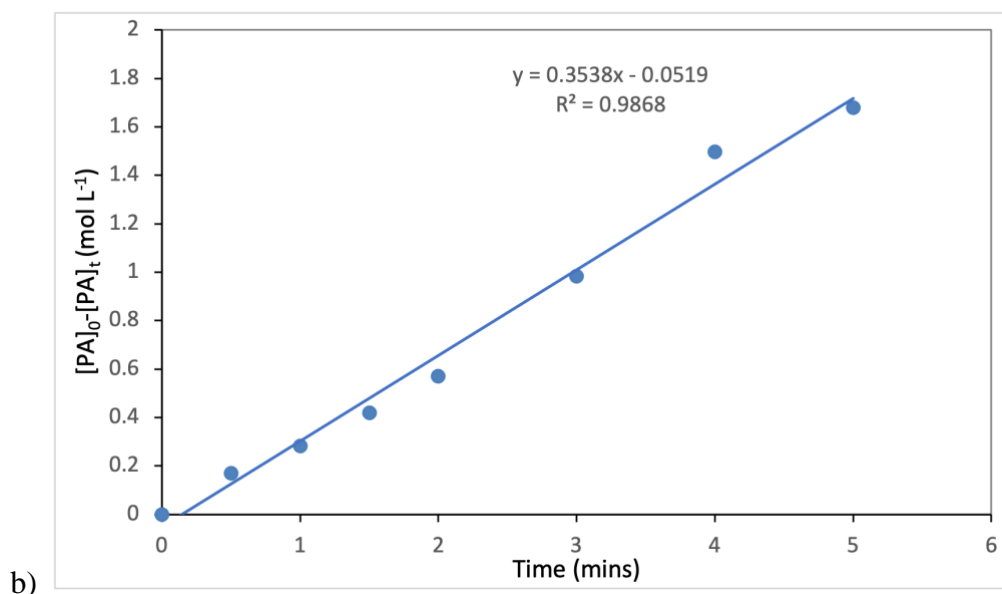
**Scheme 3.** Catalyzed synthesis of polyesters from phthalic anhydride and epoxides.

**Table 2.** Ring opening copolymerization reactions of phthalic anhydride and epoxides catalyzed by **2**

Entry	Epoxide	[ <b>2</b> ]:[PA]: [Epoxide]	<i>T</i> (°C)	<i>t</i> (h)	PA Conversion (%) <sup>a</sup>	Ester:Ether linkages <sup>b</sup>	<i>M<sub>n,calc</sub></i> (kDa) <sup>c</sup>	<i>M<sub>n</sub></i> (kDa) <sup>d</sup>	<i>D</i> <sup>d,e</sup>
1	CHO	1:100:800	100	2	100	>99	24.6	7.3	1.08
2 <sup>f</sup>	CHO	1:100:100	100	1	100	>99	24.6	8.1	1.12
3	CHO	1:100:500	100	0.25	100	97:3	24.6	13.8	1.08
4	CHO	1:100:500	80	0.33	100	97:3	24.6	11.4	1.06
5	PO	1:100:500	40	1.5	74	97:3	15.3	13.6	1.03
6	LO	1:100:500	130	3	93	95:5	27.9	4.6	1.25
7 <sup>g</sup>	LO	1:100:500	130	1	100	95:5	30.0	4.7	1.23

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy, comparing aromatic proton signals of PA to polyester. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy of dry purified product, comparing methine signals from polyester to methine signals from ether linkages. <sup>c</sup>  $M_{n,calc} = (148.11 \text{ g mol}^{-1} + M \text{ of epoxide}) \times [\text{PA}]/[\mathbf{2}] \times \text{conv.} (\%)$  <sup>d</sup> Determined via triple detection gel permeation chromatography (GPC) in THF. <sup>e</sup>  $D = M_w/M_n$  <sup>f</sup> Reaction conducted in 0.4 mL toluene. <sup>g</sup> Reaction conducted using 0.5 mL of PO with the CH<sub>2</sub>Cl<sub>2</sub> during catalyst prep, then removed *in vacuo* before LO and PA were added to generate the alkoxide *in situ* prior to the copolymerization.





**Figure 4.** a) Plot of  $M_n^{\text{GPC}}$  and  $\bar{D}$  against conversion for the ROCOP of PA and CHO using **2** as catalyst.  $[\text{PA}]_0:[\text{CHO}]_0:[\mathbf{2}]_0 = 100:500:1$ , 100 °C (Table 2, Entry 3).  $M_n$  and  $\bar{D}$  are calculated from triple detection GPC in THF. b) Zero-order plot for the ROCOP of PA and CHO using **2**. Line represents best fit. Conversion of PA to polyester is taken from integration of the aromatic protons of the polymer and the monomer.

The results seen here using **2** can be compared to those of Boggioni and co-workers who used salen chromium complexes and varying co-catalysts to form polyesters from CHO and PA.<sup>25,28</sup> In that work, the chromium catalyst with a PPnCl co-catalyst in a 1:1 molar ratio achieved 78% conversion of PA to polyester with a low  $M_n$  of 1.8 kg mol<sup>-1</sup> and high  $\bar{D}$  of 3.0 after 0.3 h, while also having a high degree of ether linkages.<sup>25</sup> By employing a "pre-contact step" where the chromium complex and PPnCl, which is poorly soluble in CHO, were combined in toluene to give a soluble species (as was used by us to prepare complex **2**) more controlled polymerizations were attained ( $M_n = 9.4$  kg mol<sup>-1</sup>,  $\bar{D} = 1.10$  after 1 h).<sup>25</sup> Further work was done using these catalyst systems on the copolymerization of LO or vinylcyclohexene oxide with PA.<sup>28</sup> Here, the chromium catalyst with PPnCl co-catalyst in a 1:1 mixture following pre-contact under similar reaction conditions produced polyesters of LO and PA giving similar  $M_n$  and  $\bar{D}$  observed to those in this

work ( $M_n = 5.7 \text{ kg mol}^{-1}$ ,  $\bar{D} = 1.2$  after 3 h compared to Table 2, entry 6  $M_n = 4.6 \text{ kg mol}^{-1}$  and  $\bar{D} = 1.25$  after 3 h).<sup>28</sup>

Comparing the conversion vs. time plots for the activity of **2** for the ROP of *rac*-LA and  $\epsilon$ -CL, and the ROCOP of PA with CHO reveals the relative rates of polymerization and the effect of temperature (Figure S16). The rate for the ROCOP of PA/CHO at both 80 °C and 100 °C occurs much faster than the ROP of  $\epsilon$ -CL and *rac*-LA. The ROP of *rac*-LA at 80 °C, in turn, proceeds faster than the ROP of  $\epsilon$ -CL.

Bester and co-workers reported use of chromium complex **1** and related complexes for PA/CHO ROCOP. They observed that in the absence of a co-catalyst the Cr complex itself gave only 2% conversion of PA to polyester with a high degree of ether linkages.<sup>26</sup> However, upon addition of Lewis bases such as triphenylphosphine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1-butylimidazole or DMAP, PA to polyester conversions up to 42% were obtained using equimolar amounts of catalyst to Lewis base and equimolar amount of PA to CHO in 0.5 mL of toluene at 110 °C and 1 h reaction time.<sup>26</sup> Reaction times of 4 h for the Cr complex with DMAP gave higher PA conversions of 95% with low ether linkages, molecular weights up to  $12.6 \text{ kg mol}^{-1}$  and dispersities of 1.21. Comparing these results to our catalyst system (Table 2 entry 2) the use of PPNCl obtains full conversion of PA to polyester within the same time frame with a  $M_n$  of  $8.1 \text{ kg mol}^{-1}$  and  $\bar{D}$  of 1.12.

### ***Terpolymerization reactions involving copolymerization featuring the incorporation of CO<sub>2</sub>***

We have previously reported the use of the combination of **1** and PPNCl (under pre-contact conditions giving **2**, [PPN][CrCl<sub>2</sub>L]) for the ROCOP of epoxides with CO<sub>2</sub> to give polycarbonates.<sup>34,35,38</sup> We investigated terpolymerizations of epoxides with cyclic anhydrides under CO<sub>2</sub> (Scheme 4). Most of the terpolymerizations involved a ROP or ROCOP reaction



occurring under a nitrogen atmosphere followed by charging the mixture with CO<sub>2</sub> in an autoclave to pressures of 40 bar CO<sub>2</sub> at 60 °C.

Polymerization of  $\epsilon$ -CL in CHO at 100 °C (Table 3, entry 1) for 2 h followed by exposure to CO<sub>2</sub> for 22 h at 60 °C showed the formation of poly( $\epsilon$ -CL-*b*-CHC), where CHC is cyclohexene carbonate (Figure S18). GPC was performed on the polymer obtained prior to, and after, CO<sub>2</sub> addition showing an increase in molecular weight while maintaining narrow dispersity after polycarbonate formation (Figures S36 – S38). <sup>1</sup>H DOSY NMR spectroscopy (Figure S19) confirms the existence of a single species in solution and not individual polycarbonates and polyesters. Performing the reaction at 60 °C with immediate exposure to CO<sub>2</sub>, however, (Table 3, entry 2) shows only polycarbonate formation with a 97% conversion of CHO and a 98% selectivity for PCHC with 2% ether linkages with no polymerization of  $\epsilon$ -CL (Figure S17). This lack of activity towards  $\epsilon$ -CL ROP at 60 °C allowed for high conversions of epoxide to PCHC as the  $\epsilon$ -CL acts as a solvent rather than a comonomer for polymerization.

Epoxide initiated ROP of *rac*-lactide was found to give oligomers as described above, and when performed under CO<sub>2</sub> produced terpolymers that contained low molecular weight mixtures of ester, carbonate and ether linkages (Table 3, entry 3). Conducting the CO<sub>2</sub>/epoxide ROCOP step at 80 °C for 22 h (increased from 60 °C and 18 h for entry 3) gave an oligomer, with a relatively high dispersity, that was dominated by ester linkages and low CO<sub>2</sub> incorporation into carbonate units (Table 3, entry 4). We previously showed this catalyst system produces cyclic cyclohexene carbonate competitively with polycarbonate at temperatures above 80 °C,<sup>35</sup> which may explain the poorer performance towards polymerization at these conditions. This is reflected in the in situ FTIR spectra (Figure S24), which shows the growth of a peak at 1825 cm<sup>-1</sup> (appearing as a shoulder and partially obscured by the presence of ester and carbonate carbonyl peaks in that region) and

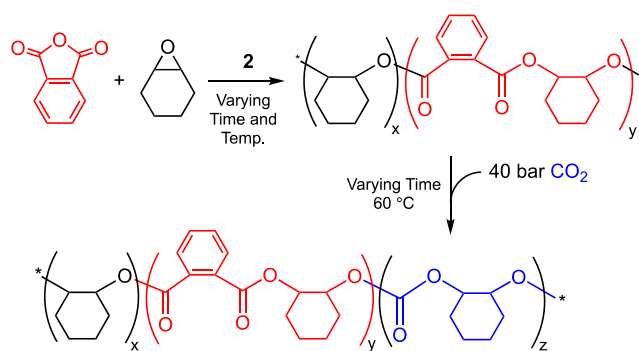
$^1\text{H}$  NMR spectra of the produced polymer (Figure S25) showing the presence of cyclohexene carbonate (CHC). Terpolymer formation is supported by  $^1\text{H}$  DOSY NMR showing one set of translational diffusions (Table 3, entry 3, Figure S23). The MALDI-TOF mass spectra of the produced polymer (Figure S41) show fragmentation from both LA and CHC repeating units observed in the low  $m/z$  range of the spectrum while only PCHC linkages are observed at the higher  $m/z$  range.

The diminished PCHC incorporation into the *rac*-LA terpolymer at 80 °C (Table 3, entry 4) caused a large reduction in the  $M_n$  obtained by GPC analysis of the polymer. The resulting 1.1 kDa value obtained by GPC is in a similar region to the peaks corresponding to PLA fragments in MALDI-TOF MS of the more successful reaction (Table 3, entry 3, Figure S41C). Furthermore, analysis by  $^1\text{H}$  NMR and in situ FTIR monitoring of the reaction (Figures S24 and S25) showed low conversion of CHO to both PCHC and ether linkages, as well as a lower PLA conversion compared to the earlier entry. Therefore, the PLA dominated polymer with low PCHC incorporation, formed at a higher temperature during  $\text{CO}_2$  incorporation, having a low  $M_n$  value agrees with our previous results in Table 1 where PLA formed primarily oligomers.

The tacticity of the PLA observed in the block polymer of PLA-*b*-PCHC produced by **2** in neat CHO (Table 3, entry 3) was determined by  $^1\text{H}$  NMR analysis at 600 MHz and deconvolution of the methine region between 5.12 and 5.24 ppm (Figures S21 and S22).<sup>44,49,61–63</sup> The probability of *meso* linkages was determined as  $P_m = 0.62$ , indicating atactic polymer is obtained during the terpolymerization reaction with CHO and  $\text{CO}_2$ .

The terpolymers of PA, CHO, and  $\text{CO}_2$  (Table 3, entries 5 and 6) show full conversion of PA to produce polyester prior to addition of the  $\text{CO}_2$  as determined by  $^1\text{H}$  NMR spectroscopy (Figure S26). This allowed for the block polymer formation of poly(PA-*alt*-CHO)-*b*-PCHC to

occur upon addition of CO<sub>2</sub>, and was confirmed by <sup>1</sup>H NMR and DOSY NMR of the polymer produced in Table 3, entry 5 (Figures S26 and S27). The lower *M<sub>n</sub>* seen in entry 6 compared to entry 5 could indicate transesterification occurring at the lower temperature and longer initial reaction time prior to CO<sub>2</sub> addition, as previously it was determined that using the same molar ratio and temperature full conversion of PA to polyester was observed after 1 h (Table 2, entry 4). This could also be occurring in entry 5, but to a lesser extent as previously the same reaction conditions prior to CO<sub>2</sub> addition were shown to have full conversion of PA to polyester after 15 min and resulted in a slightly higher *M<sub>n</sub>* obtained (Table 2, entry 3) compared to the one seen before CO<sub>2</sub> addition here. The reduction in time after addition of CO<sub>2</sub> seen in entry 6 compared to entry 5 may be another reason for the overall lower incorporation of PCHC into the terpolymer, which in turn could be the reason behind the significantly reduced *M<sub>n</sub>* with a higher *D* obtained from GPC analysis of the resulting polymer after reaction with CO<sub>2</sub>.



**Scheme 4.** Catalyzed synthesis of terpolymers consisting of ether linkages (*x*), ester linkages (*y*), and carbonate linkages (*z*) using an epoxide, CHO, with PA followed by the addition of CO<sub>2</sub>. Terpolymers were also formed with the addition of either *rac*-LA or ε-CL in place of PA using similar conditions.

**Table 3.** Terpolymerization reactions catalyzed by **2**.<sup>a</sup>

Entry	Monomer	t before CO <sub>2</sub> addition (h)	T before CO <sub>2</sub> addition (°C)	t after CO <sub>2</sub> addition (h)	Ether:ester:carbonate linkage x:y:z <sup>b</sup>	M <sub>n</sub> (kDa) <sup>c</sup>	D <sup>c,d</sup>
1	ε-CL	2	100	22	4:65:443	5.2 <sup>e</sup> 11.6 <sup>f</sup>	1.36 <sup>e</sup> 1.23 <sup>f</sup>
2	ε-CL	n/a	n/a	18	11:0:471	14.6	1.14
3	<i>rac</i> -LA	2	80	18	43:96:210	3.3	1.28
4 <sup>g</sup>	<i>rac</i> -LA	2	80	22	13:68:34	1.1	1.96
5	PA	1	100	18	3:100:390	8.7 <sup>e</sup> 17.6 <sup>f</sup>	1.14 <sup>e</sup> 1.13 <sup>f</sup>
6	PA	2	80	16 <sup>h</sup>	5:100:145	4.6	1.56

<sup>a</sup> Reactions conducted neat in CHO using a molar ratio of [**2**]:[Monomer]:[CHO] of 1:100:500 prior to CO<sub>2</sub> addition and using 40 bar CO<sub>2</sub> at 60 °C when CO<sub>2</sub> addition occurred unless stated otherwise. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy of final product, obtained conversion of anhydride/*rac*-LA/ε-CL to polyester (y) and compared conversion of remaining CHO methines to methines in PCHC (z) and ether linkages (x) present. <sup>c</sup> Determined via triple detection gel permeation chromatography (GPC) in THF. <sup>d</sup>  $D = M_w/M_n$  <sup>e</sup> Measured after polyester formation, before addition of CO<sub>2</sub>. <sup>f</sup> Measured after addition of CO<sub>2</sub> when the terpolymer has been formed. <sup>g</sup> 80 °C used instead of 60 °C when CO<sub>2</sub> addition occurred. <sup>h</sup> Temperature was increased from 60 °C to 80 °C in the last 2 h of the reaction during CO<sub>2</sub> addition.

For comparison to other reports of terpolymers formed from the above monomers, DSC was carried out on selected terpolymers. DSC of poly(ε-CL)-*b*-PCHC terpolymer (Table 3, entry 1) was run at both low (-80 °C to 0 °C) and higher (0 °C to 400 °C) temperatures. The polymer showed decomposition above 170 °C. For the poly(ε-CL) product before CO<sub>2</sub> addition no  $T_g$  was observed in the low temperatures between -60 °C and -10 °C where one would expect poly(ε-CL) having a literature  $T_g$  of -60 °C.<sup>58,64–67</sup> However a  $T_m$  was observed at 57 °C (Figure S43) which closely correlates to values seen by Williams.<sup>58</sup> After CO<sub>2</sub> addition to form the terpolymer poly(ε-CL)-*b*-PCHC, a  $T_g$  of 88 °C was obtained (Figure S44). This is significantly higher than the -54 °C from Williams where the ester linkages greatly outnumbered the carbonate linkages in the polymer formed and closely resembles the  $T_g$  values of 70 – 80 °C seen in Zhang's work where

there were a large amount of carbonate linkages present in the terpolymers.<sup>58,68</sup> Furthermore, there is a significant difference between the obtained  $T_g$  and the literature value of PCHC ( $T_g = 135\text{ }^\circ\text{C}$ ) giving further evidence that a block polymer was formed.<sup>58,68-71</sup> The PLA-*b*-PCHC (Table 3, entry 3) gave  $T_g$  between  $65\text{ }^\circ\text{C}$  and  $75\text{ }^\circ\text{C}$  depending on the heating rate (Figures S45 and S46). These temperatures fall in the general range of PLA-*b*-PCHC terpolymers produced in literature using similar reaction conditions and similarly structured catalysts.<sup>57,66,71-75</sup> They also follow the trend towards a slightly higher  $T_g$  obtained with higher PCHC incorporation into the polymer is observed. The  $T_g$  for the PLA-*b*-PCHC with significantly less PCHC incorporation in the structure (Table 3, entry 4) had an expected lower  $T_g$  of  $48\text{ }^\circ\text{C}$  (Figure S45), which is consistent with reported  $T_g$  for terpolymers having fewer carbonate units.<sup>57,66,71-75</sup> The final terpolymer and its precursor polyester analyzed via DSC was poly(CHO-*alt*-PA) and poly(CHO-*alt*-PA)-*b*-PCHC (Table 3, entry 5 before and after CO<sub>2</sub> addition). It was determined to have a  $T_g$  of  $70\text{ }^\circ\text{C}$  for the polyester prior to CO<sub>2</sub> addition (Figure S48) and a  $T_g$  of  $123\text{ }^\circ\text{C}$  after CO<sub>2</sub> addition as the terpolymer (Figure S49). These results can be related to the work by Williams, where similar terpolymerizations of PA, CHO, and CO<sub>2</sub> occurred catalyzed by di-Mg and Zn catalysts but with a 800:100 molar ratio of [CHO]:[PA] compared to the 500:100 used in this work.<sup>59</sup> They report the polyesters had  $T_g$  values of  $57$  and  $83\text{ }^\circ\text{C}$  prior to CO<sub>2</sub> addition with a change to  $104$  and  $97\text{ }^\circ\text{C}$  after CO<sub>2</sub> addition for the Zn and Mg catalysts, respectively.<sup>59</sup> Comparatively, the block polymers formed in this work had more polycarbonate and polyester linkages than their terpolymers formed with both having minimal polyether linkages present. The significantly higher  $T_g$  value obtained in our block polymers could perhaps be a result of the increase in polycarbonate linkages.

## CONCLUSIONS

This study used the pre-contacted mixture of our previously reported chromium(III) complex **1** with PPnCl to form the chromium(III) dichloride "ate" complex, **2**, showing good activity as a catalyst of the ROP of *rac*-LA or  $\epsilon$ -CL and the ROCOP of epoxides and PA to form polyesters. Furthermore, building on our previous work on the ROCOP of epoxides with CO<sub>2</sub> catalyzed by **1** we showed the ability to form terpolymers through the addition of CO<sub>2</sub> after the formation of either PLA, poly( $\epsilon$ -CL), or P(CHO-*alt*-PA) in excess epoxide. The terpolymer formations were confirmed by DOSY NMR, with further support by obtaining  $T_g$  values for the terpolymers that matched closely with previous work on similar ester, carbonate, and ether linkage-containing polymers. The versatility of the polymerization reactions catalyzed by **2** displays is encouraging for the exploration of its application for other copolymerization reactions.

## EXPERIMENTAL SECTION

### *General Experimental Considerations.*

Unless otherwise stated, all materials were used as received and were manipulated under a dry, nitrogen atmosphere using either Schlenk techniques or a MBraun Labmaster DP glovebox. Dry toluene and dichloromethane were acquired from an MBraun Solvent Purification System. CrCl<sub>3</sub>(THF)<sub>3</sub> was prepared according to the reported procedure via Soxhlet extraction of anhydrous CrCl<sub>3</sub> with THF under dry nitrogen.<sup>76</sup>

### *Instrumentation.*

Polymer molecular weight and dispersities were determined by gel permeation chromatography (GPC) using an Agilent 1260 Infinity high-performance liquid chromatograph coupled to a Wyatt Technologies triple detector system (light scattering, viscometer, and refractive index) and

equipped with one Phenogel  $10^3$  Å, 300 mm × 4.60 mm column and one  $10^4$  Å, 300 mm × 4.60 mm column (covering mass ranges of 1000 – 75 000 and 5000 – 500 000 g mol<sup>-1</sup>, respectively). HPLC grade THF was used as the eluent at a flow rate of 0.3 mL min<sup>-1</sup> at 25 °C. Processing of the GPC data were done using the Astra 6 software package. Ring opening polymerization and copolymerization reactions using in situ FTIR spectroscopy were performed using a 100 mL stainless steel Parr 4560 reactor with motorized mechanical stirrer and heating mantle. The reactor was modified to be equipped with a Mettler Toledo SiComp ATR Sentinel sensor connected to a ReactIR 15 base unit using a silver-halide Fiber-to-Sentinel conduit.

<sup>1</sup>H NMR spectra were recorded on Bruker AVANCE III 300 MHz and AVANCE 500 MHz spectrometers with chemical shifts in parts per million (ppm) relative to the residual proton signals in solvent (CDCl<sub>3</sub>). The <sup>1</sup>H diffusion ordered spectroscopy (DOSY) NMR spectra of the purified polymers were recorded using a Bruker AVANCE 500 MHz spectrometer. <sup>1</sup>H{<sup>1</sup>H} NMR spectra for polymer stereochemistry studies were performed on a Bruker AVANCE II 600 MHz spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used without further purification.

MALDI-TOF mass spectrometry on the polymers was performed using a Bruker ultrafleXtreme MALDI TOF/TOF analyzer with a Bruker smartbeam-II laser (up to 2 kHz, operating at 355 nm) for linear and reflectron mode. Mass spectra of 1000 shots were accumulated. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix for polymer analysis where it was dissolved in THF at a concentration of 15 mg mL<sup>-1</sup>. The characterization of **2** by MALDI-TOF MS was done previously using anthracene as a matrix. Repeated analysis for this work gave identical results.<sup>35</sup> A cationizing agent salt solution (sodium trifluoroacetate, NaTFA) in THF was used at a concentration of 1 mol L<sup>-1</sup>. Polymer was dissolved in THF to a concentration of 10 mg mL<sup>-1</sup>, then

combined with the DHBA matrix and NaTFA in a ratio of 3:20:1  $\mu\text{L}$ , respectively. Aliquots of 0.5  $\mu\text{L}$  of these solutions were spotted and the solvent was allowed to evaporate. MALDI-TOF MS data were processed, and images prepared using MestReNova software with the mass analysis plug-in.

### ***Preparation of 2.***

The catalyst was prepared following the previously recorded procedure of reacting  $\text{H}_2[\mathbf{L}]$  with NaH and  $\text{CrCl}_3(\text{THF})_3$  at  $-78\text{ }^\circ\text{C}$  in THF under Schlenk conditions.<sup>35</sup> The  $\text{H}_2[\mathbf{L}]$  proligand was prepared using a modified literature procedure that used water instead of methanol for the reaction medium, and dried over sodium sulfate in THF.<sup>77</sup> The catalyst mixture used for polymerizations was prepared in a 20 mL scintillation vial combining the  $\text{CrCl}[\mathbf{L}]$  base catalyst, **1**, (41 mg, 34  $\mu\text{mol}$ ) in dichloromethane (1 mL) resulting in a pink solution, which was then mixed with PPNCI (39 mg, 68  $\mu\text{mol}$ ) resulting in a purple solution. Dichloromethane was removed under vacuum to obtain the purple bis(triphenylphosphine)iminium-chromium dichloride “ate” complex, **2** (83 mg, 71  $\mu\text{mol}$ ). The characterization of **2** was consistent with that previously reported.<sup>35</sup>

### ***Representative Ring-Opening Polymerization of Cyclic Esters.***

A mixture of purple complex **2** (41 mg, 35.4  $\mu\text{mol}$ ), *rac*-lactide (510 mg, 3.54 mmol), and cyclohexene oxide (1.75 mL, 17.7 mmol) were combined in a microwave vial containing a small magnetic stir bar at  $22\text{ }^\circ\text{C}$  in a glovebox and sealed with a crimped septum cap under  $\text{N}_2$ . The resulting blue solution was stirred magnetically at  $80\text{ }^\circ\text{C}$  until the desired reaction time was reached or became hindered by increased viscosity. The resulting brown solution was exposed to air and quenched by benzoic acid in dichloromethane ( $20\text{ mg mL}^{-1}$ ). An aliquot for  $^1\text{H}$  NMR was taken immediately for determination of conversion. The polymer, now dissolved in dichloromethane,



was precipitated by addition of 5% (v/v with 1 M HCl) acidified methanol. The resulting off-white solid was dried in a vacuum oven at 60 °C overnight.

#### ***Representative Ring-Opening Copolymerization of Epoxides with Phthalic Anhydride.***

A mixture of purple complex **2** (41.0 mg, 35.4  $\mu\text{mol}$ ), phthalic anhydride (518 mg, 3.54 mmol), and cyclohexene oxide (1.75 mL, 17.7 mmol) were combined in a microwave vial containing a small magnetic stir bar at 22 °C in a glovebox and sealed with a crimped septum cap under  $\text{N}_2$ . The resulting green solution was stirred magnetically at 100 °C until the desired reaction time or became hindered by increased viscosity. The dark green solution was exposed to air and quenched by benzoic acid in dichloromethane (20 mg  $\text{mL}^{-1}$ ). An aliquot for  $^1\text{H}$  NMR was taken immediately for determination of conversion. The polymer was precipitated by addition of 5% (v/v with 1 M HCl) acidified methanol. The resulting green-tinted polymer was dried in a vacuum oven at 60 °C overnight. If toluene was used, the product obtained was white instead of green-tinted.

#### ***Representative Terpolymerization Reactions.***

For the reactions that had initial ROP or ROCOP occurring followed by  $\text{CO}_2$  addition: In a glovebox, purple complex **2** (85.1 mg, 71.5  $\mu\text{mol}$ ) was mixed with *rac*-lactide (1.028 g, 7.13 mmol) and cyclohexene oxide (3.5 mL, 35.7 mmol) in a microwave vial containing a small magnetic stir bar at 22 °C giving a pink solution. The vial was sealed with a crimped septum cap under  $\text{N}_2$  and heated for the desired time in the glovebox at desired temperature, after which the reaction was removed from heat and loaded into a syringe for injection into the pressure vessel under vacuum. The vessel was pressurized to 40 bar  $\text{CO}_2$  and heated to 60 °C. The mixture was stirred for the desired time then cooled, vented into a fume hood and opened to reveal a product that was visibly viscous upon exposure to air. The reaction was quenched with benzoic acid in 10 mL

dichloromethane (20 mg mL<sup>-1</sup>). An aliquot for <sup>1</sup>H NMR was taken immediately for determination of conversion. The polymer was precipitated from the viscous brown mixture by addition of 5% (v/v with 1 M HCl) acidified methanol. The gray or off-white polymer product was dried in a vacuum oven at 60 °C overnight. For reactions that used a one-pot approach: in a glovebox under N<sub>2</sub>, **2** (85.9 mg, 72 μmol) and cyclohexene oxide (3.5 mL, 35.7 mmol) were combined in a vial at 22 °C followed by ε-CL (821 mg, 7.2 mmol). No reaction occurs at this temperature. This solution was drawn into a syringe and injected into a purged pressure vessel under vacuum. The vessel was immediately pressurized with 40 bar CO<sub>2</sub>, heated to 60 °C and stirred for 18 h. Upon completion, the work-up of the polymer mixture followed the method as described above.

## ASSOCIATED CONTENT

### *Supporting Information*

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/XXX>. Spectroscopic (NMR, MALDI-TOF MS) and kinetic data, GPC chromatograms, and DSC thermograms (PDF).

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## Notes

The authors declare no competing financial interest.

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