

## Supporting information

### Cooperative effects in Schiff base binuclear zinc complexes for the synthesis of aliphatic and semi-aromatic polyesters.

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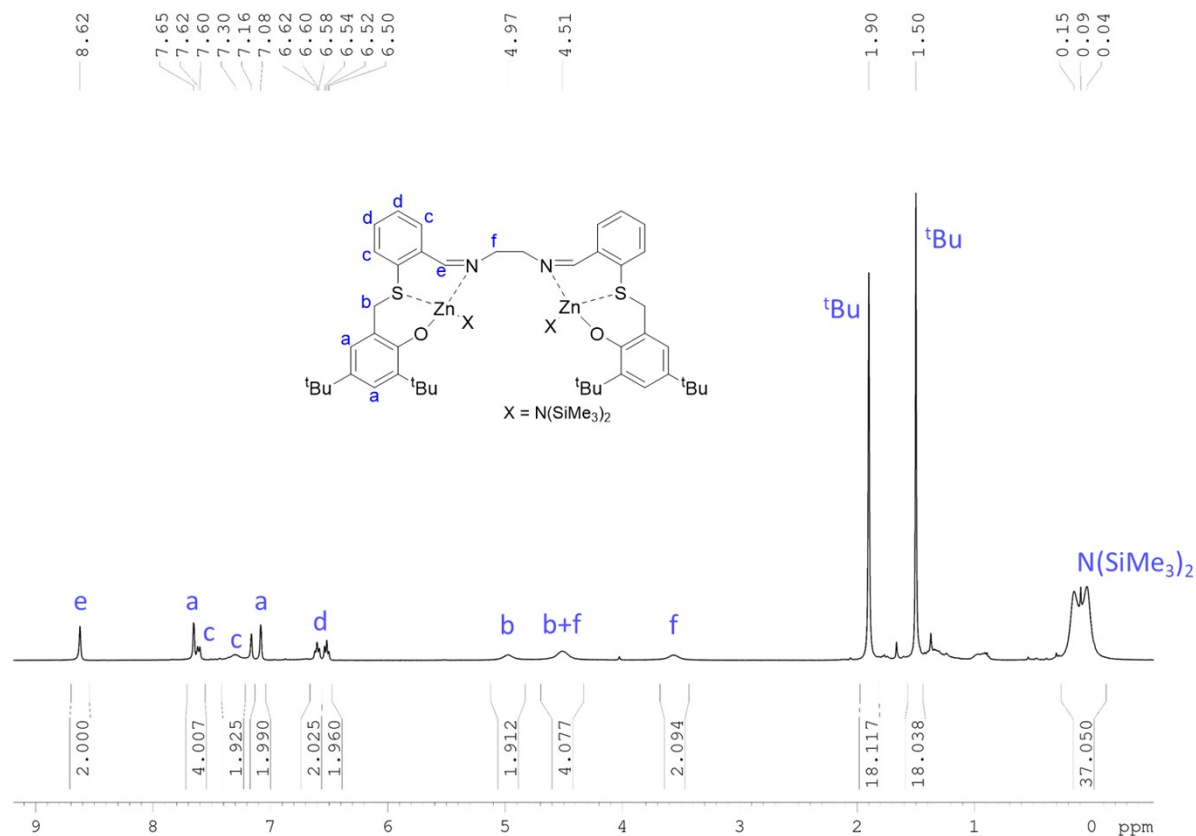
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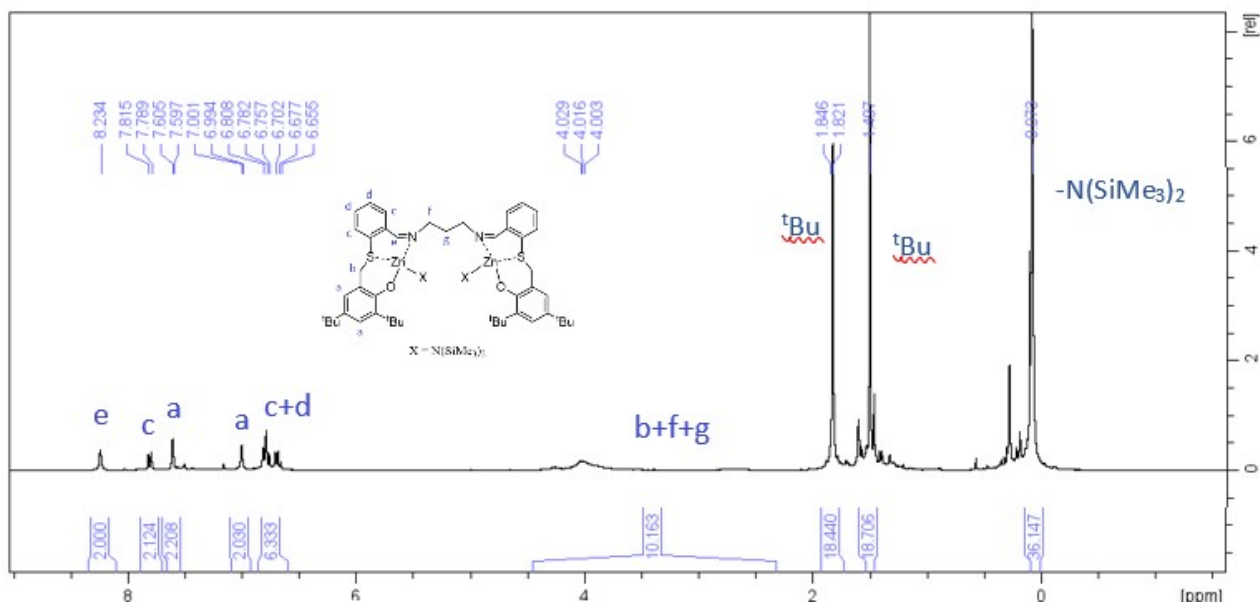
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## Characterization of complexes



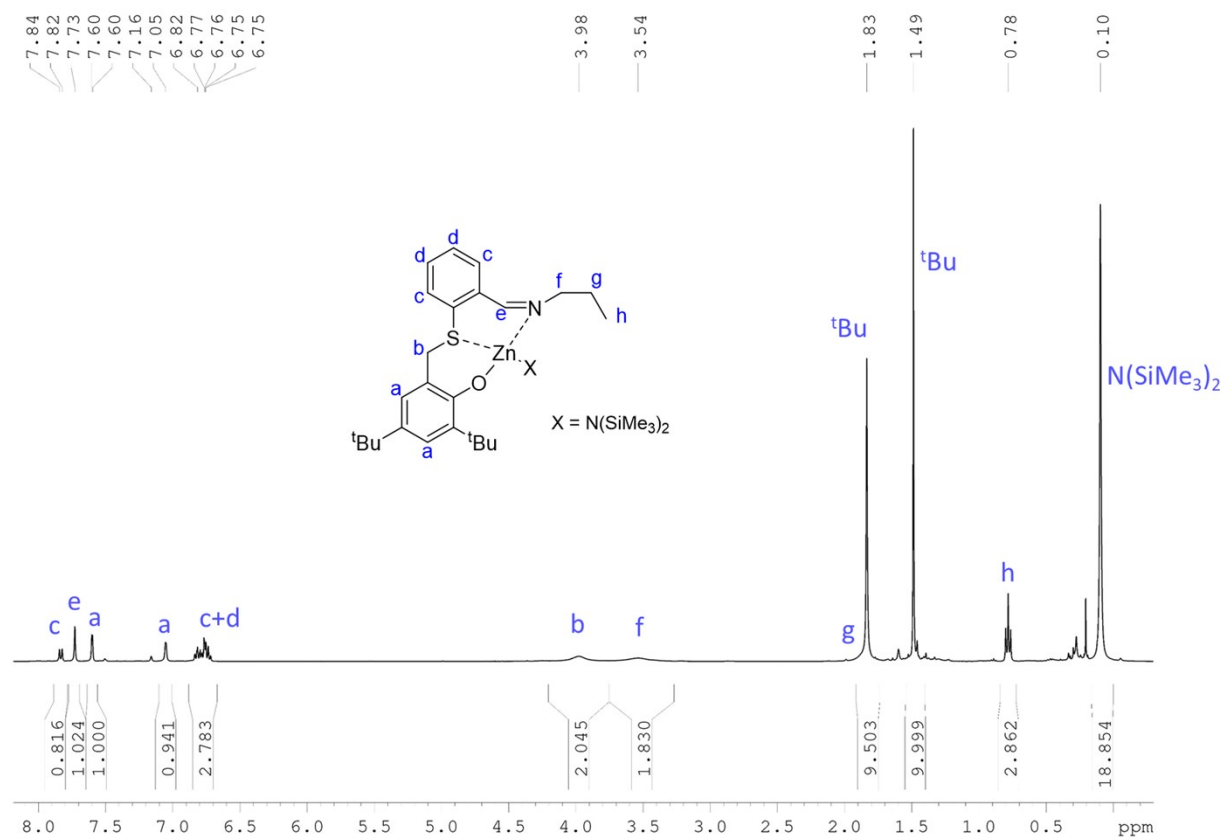
**Figure S1.**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 298 K, 400 MHz) of complex **1**

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  8.62 (s, 2H, CH=N), 7.63 (d,  $J=2.53$  Hz, 2H, Ar-H), 7.60 (d,  $J=7.88$  Hz, 2H, Ar-H), 7.29 (br, 2H, Ar-H), 7.08 (d,  $J=2.48$  Hz, 2H, Ar-H), 6.58 (t, 2H, Ar-H), 6.49 (t, 2H, Ar-H), 4.98 (br, 2H, N-CH<sub>2</sub>), 4.51 (br, 4H, S-CH<sub>2</sub>), 3.57 (br, 2H, N-CH<sub>2</sub>), 1.90 (s, 18H, CCH<sub>3</sub>), 1.50 (s, 18H, CCH<sub>3</sub>), 0.14 (br, 36H, Si(CH<sub>3</sub>)<sub>3</sub>).



**Figure S2.**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 298 K, 400 MHz) of complex **2**

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  8.24 (s, 2H, CH=N), 7.80 (d,  $J=7.92$  Hz, 2H, Ar-H), 7.60 (d,  $J=2.50$  Hz, 2H, Ar-H), 6.80 (d,  $J=2.15$  Hz, 2H, Ar-H), 6.76 (m, 4H, Ar-H), 6.66 (t, 2H, Ar-H), 4.25 (br, 4H, S- $\text{CH}_2$ ), 4.00 (br, 4H, N- $\text{CH}_2$ ), 1.82 (s, 18H,  $\text{CCH}_3$ ), 1.50 (s, 18H,  $\text{CCH}_3$ ), 0.10 (s, 36H,  $\text{Si}(\text{CH}_3)_3$ ).



**Figure S3.** <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 298 K, 400 MHz) of complex **3**

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.84 (d, J = 7.90 Hz 2H, Ar-H), 7.73 (s, 1H, CH=N), 7.59 (s, 1H, Ar-H), 7.05 (s, 1H, Ar-H), 6.75 (m, 3H, Ar-H), 3.98 (br, 2H, S-CH<sub>2</sub>), 3.54 (br, 2H, N-CH<sub>2</sub>), 1.83 (s, 9H, CCH<sub>3</sub>), 1.49 (s, 9H, CCH<sub>3</sub>), 0.78 (t, 3H, CH<sub>3</sub>), 0.10 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>).

## DOSY-NMR experiments details

A measurement of diffusion has been carried out by observing the attenuation of the NMR signals during a pulsed field gradient experiment using the double stimulated echo pulse sequence. In particular, 2D DOSY PGSE NMR spectra were performed on a Bruker Avance 600 spectrometer at 298 K without spinning. Tetramethylsilane (TMS) was added as the internal standard. The dependence of the resonance intensity ( $I$ ) on the gradient strength ( $G$ ) is described by the following equation:

$$I(G) = I_0 \exp[-D \gamma^2 G^2 \delta^2 (\Delta - \delta/3)]$$

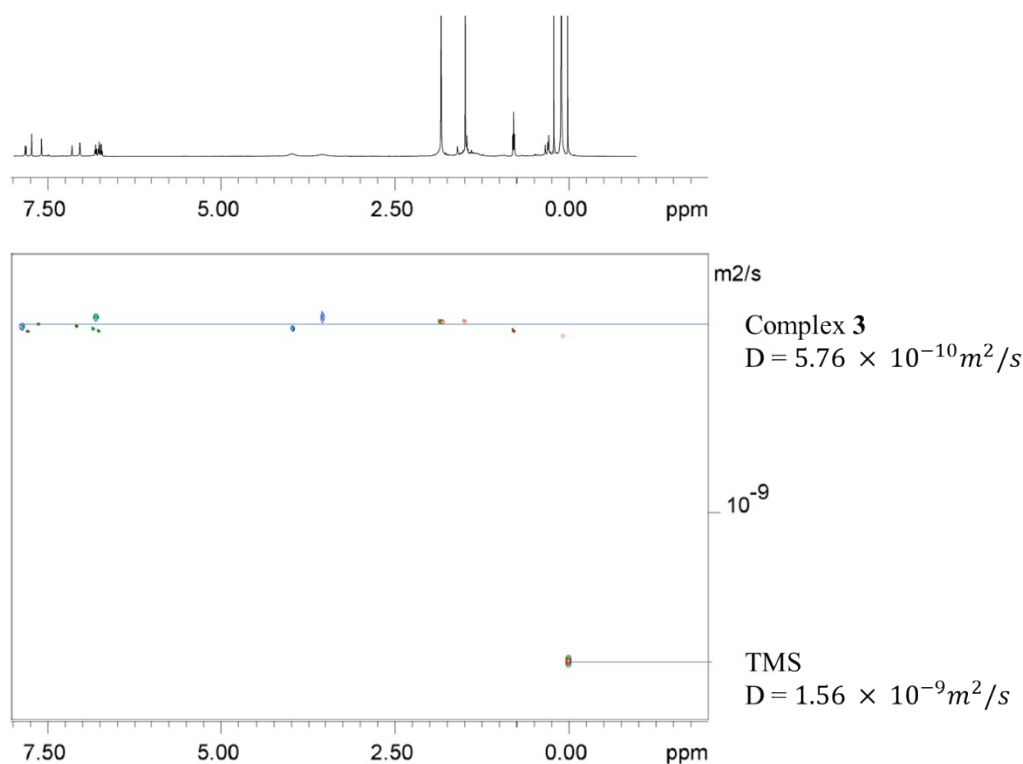
where  $I$  is the observed intensity (attenuated signal intensity),  $I_0$  is the reference intensity (unattenuated signal intensity),  $D$  is the diffusion coefficient,  $\gamma$  is the nucleus gyromagnetic ratio,  $G$  is the gradient strength,  $\delta$  is the gradient duration, and  $\Delta$  is the diffusion delay. The parameters  $\delta$  and  $\Delta$  were kept constant during the experiments (1800  $\mu$ s and 0.15 s, respectively) whereas  $G$  varied from 5 to 95% in 100 steps.

A nonlinear regression on  $I$  and  $G^2$  data gave the coefficients  $D$  for the samples and the corresponding internal standard signals ( $D_{\text{sample}}$  and  $D_{\text{TMS}}$ , respectively).

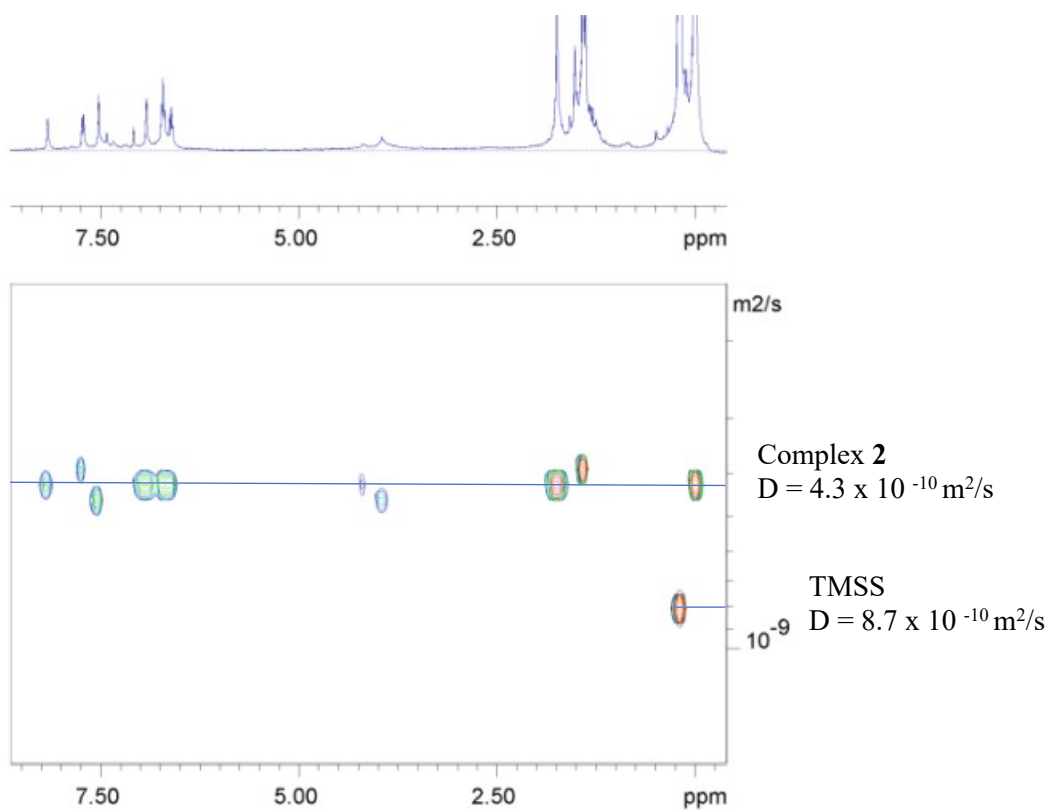
The molecular masses in solution ( $MM$ ) were simply estimated using Graham's law of diffusion:  $D = K(T/MM)^{1/2}$ , where the constant  $K$  depends on geometric factor. By assuming the same  $K$  for both species in solution and a constant temperature, the relative diffusion rate of the sample and the TMS is given by

$$D_{\text{sample}}/D_{\text{TMS}} = (MM_{\text{TMS}}/MM_{\text{sample}})^{1/2}$$

This allows the calculation of an unknown molecular mass. This method is useful when a highly accurate value is not required for the molecular mass.



**Figure S4.** DOSY spectrum ( $C_6D_6$ , 298 K, 600 MHz) of complex 3 ( $D = 5.76 \cdot 10^{-10} m^2/s$ ) in the presence of TMS as standard ( $D = 1.56 \cdot 10^{-9} m^2/s$ ).



**Figure S5.** DOSY spectrum ( $\text{C}_6\text{D}_6$ , 298 K, 600 MHz) of complex **2** ( $D = 4.3 \times 10^{-10} \text{ m}^2/\text{s}$ ) in the presence of TMSS as standard ( $D = 8.7 \times 10^{-10} \text{ m}^2/\text{s}$ ). (Molecular weight of TMSS = 320.84 Da; estimated mass for complex **2** = 1300; Molecular weight for complex **2** = 1200.67 Da).

## Ring-Opening Polymerization of lactides

**Table S1.** Ring-opening polymerization of L-lactide by complexes 1-3

<sup>a</sup> Run	Cat	[LA] <sub>0</sub> /[Zn] <sub>0</sub> / [iPrOH] <sub>0</sub>	Temp (°C)	Time (h)	<sup>b</sup> Conv (%)	<sup>c</sup> M <sub>n</sub> <sup>th</sup> (×10 <sup>3</sup> )	<sup>d</sup> M <sub>n</sub> <sup>GPC</sup> (×10 <sup>3</sup> )	<sup>d</sup> Đ
1	1	200:2:0	25	2	0			
				4	5			
				7	11			
				24	76	21.9	21.1	1.17
2	2	200:2:0	25	2	0			
				4	7			
				7	20			
				24	69	19.9	21.0	1.27
3	3	100:1:0	25	2	8			
				4	20			
				7	40			
				9	61	8.8	34.4	1.34
4	1	200:2:0	60	2	57			
				3	74			
				4	86	24.8	28.8	1.24
5	2	200:2:0	60	2	85	24.6	24.7	1.23
6	3	100:1:0	60	0.5	50			
				1	82	11.8	31.3	1.47

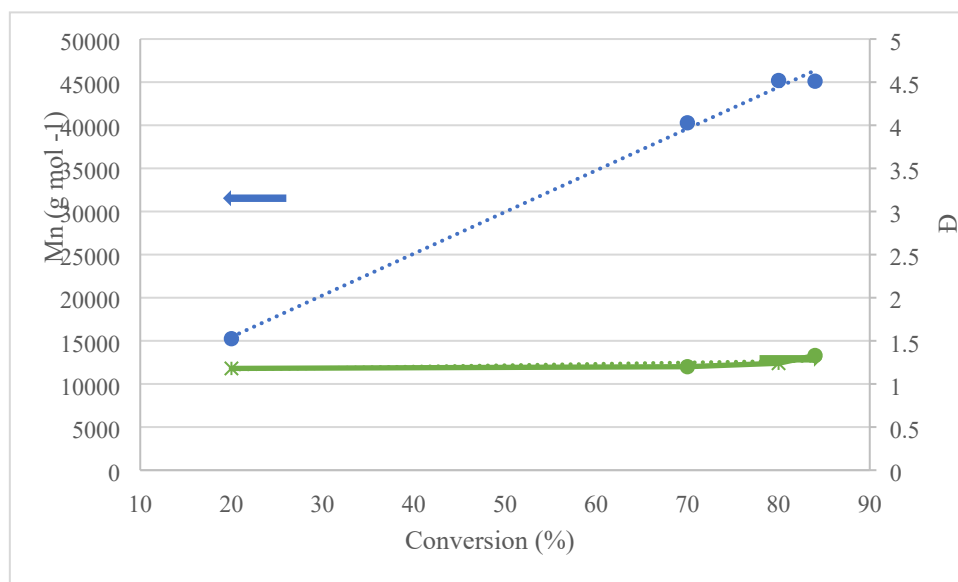
General conditions: All reactions were carried out in 1 mL of THF. [1]<sub>0</sub>-[2]<sub>0</sub> = 5.0 10<sup>-6</sup> mol; [3]<sub>0</sub> = 1.0 10<sup>-5</sup> mol, (i.e. [Zn]<sub>0</sub> = 1.0 10<sup>-2</sup> M). [L-LA] = 1.0 M). <sup>a</sup>Determined by <sup>1</sup>H NMR spectral data. <sup>b</sup>M<sub>n</sub><sup>th</sup> (g mol<sup>-1</sup>) 144,13 x ([L-LA]<sub>0</sub>/[Cat]<sub>0</sub>) x L-LA conversion (for entries 1-6). <sup>c</sup>Experimental M<sub>n</sub> (in g mol<sup>-1</sup>) and M<sub>w</sub>/M<sub>n</sub> (Đ) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.58.



**Table S2.** Polymerization of L-LA by complex **2**

Time (h)	<sup>a</sup> Conv. (%)	<sup>b</sup> $M_n^{\text{th}}$ ( $\times 10^3$ )	<sup>c</sup> $M_n^{\text{GPC}}$ ( $\times 10^3$ )	<sup>c</sup> $\bar{D}$
6	20	5.8	8.8	1.18
16	70	20.2	23.4	1.20
20	80	23.1	26.2	1.24
24	84	24.2	26.2	1.33

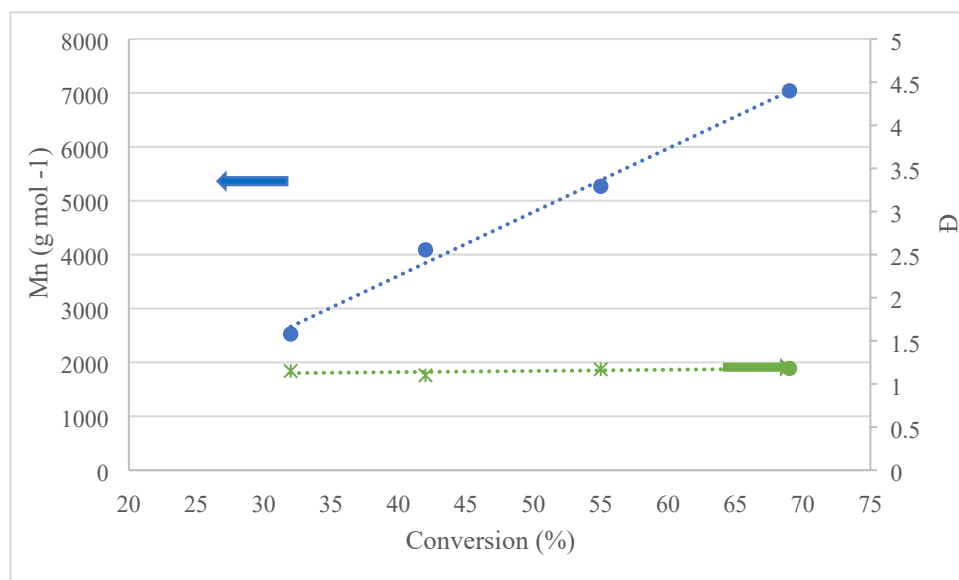
The polymerization was carried out in 1 mL of THF.  $[2]_0 = 5.0 \times 10^{-6}$  mol.  $[L\text{-LA}] = 1.0$  M.  $[L\text{-LA}]_0:[2]_0:[i\text{PrOH}]_0 = 200:2:0$ . <sup>a</sup>Determined by <sup>1</sup>H-NMR spectral data. <sup>b</sup> $M_n^{\text{th}}$  ( $\text{g mol}^{-1}$ ) =  $144.13 \times ([L\text{-LA}]_0/[2]_0) \times \text{L-LA conversion}$ . <sup>c</sup> $M_n^{\text{GPC}}$  (in  $\text{g mol}^{-1}$ ) and  $M_w/M_n$  ( $\bar{D}$ ) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.58.

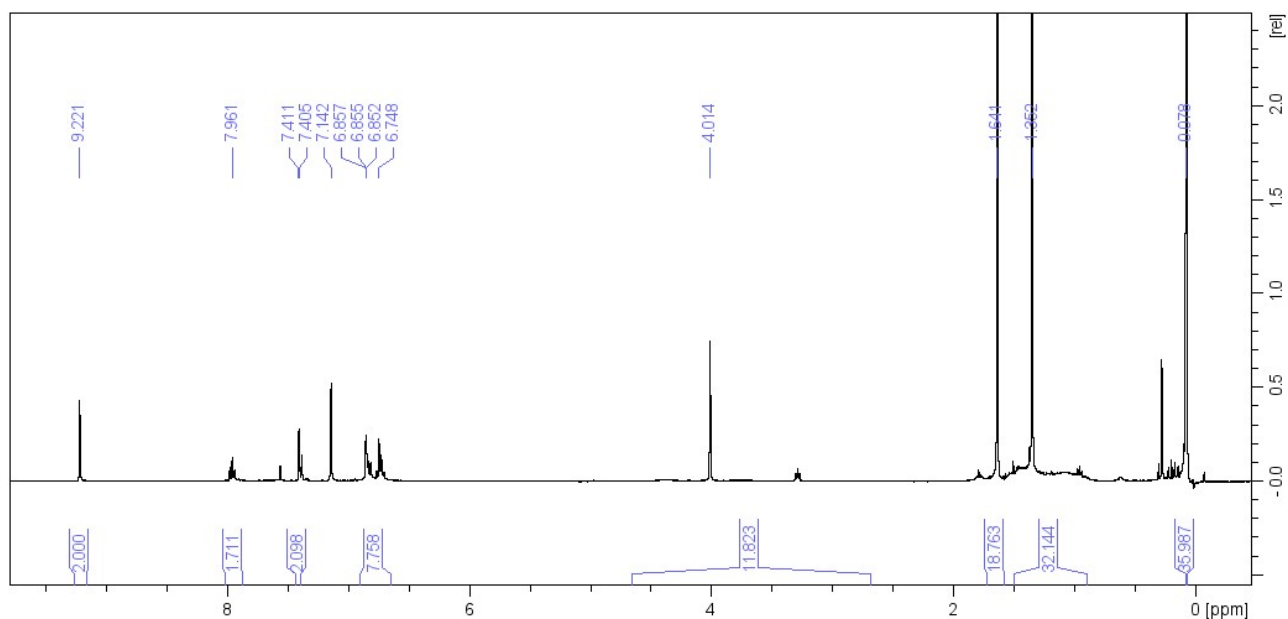
**Figure S6.** Molecular weights and molecular weights distribution (determined by GPC analysis) in function of the conversion for the polymerization experiment detailed in Table S2 ( $[L\text{-LA}]_0:[2]_0 = 200:2$  in THF as solvent).

**Table S3.** Polymerization of L-LA by complex **2** and *i*PrOH

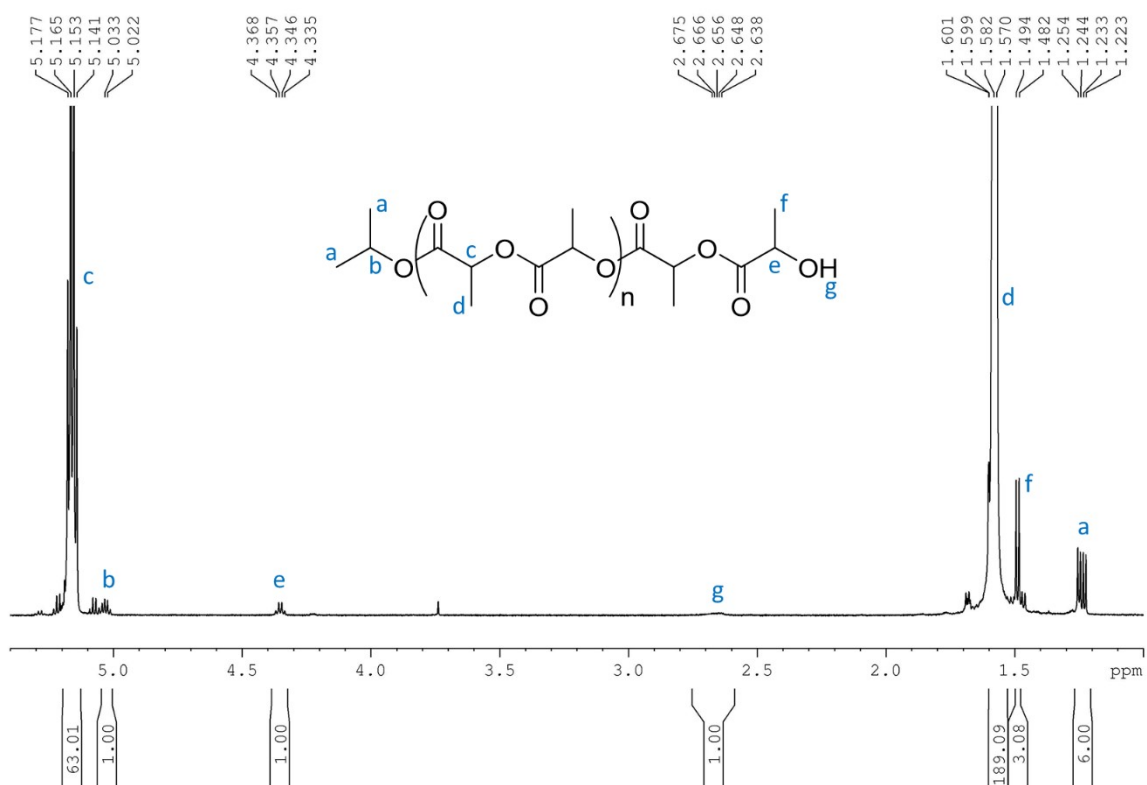
Time (h)	<sup>a</sup> Conv. (%)	<sup>b</sup> $M_n^{\text{th}}$ (x 10 <sup>3</sup> )	<sup>c</sup> $M_n^{\text{GPC}}$ (x 10 <sup>3</sup> )	<sup>c</sup> $\mathcal{D}$
0.5	32	4.6	2.5	1.15
1	42	6.1	4.1	1.10
1.5	55	7.9	5.3	1.17
2	69	9.9	7.0	1.18

The polymerization experiment was carried out in 1 mL of THF.  $[\mathbf{2}]_0 = 5.0 \times 10^{-6}$  mol.  $[\text{L-LA}] = 1.0$  M.  $[\text{L-LA}]_0:[\mathbf{2}]_0:[i\text{PrOH}]_0 = 200:2:2$ . <sup>a</sup>Determined by <sup>1</sup>H-NMR spectral data. <sup>b</sup> $M_n^{\text{th}}$  (g mol<sup>-1</sup>) = 144.13 x  $([\text{L-LA}]_0/[i\text{PrOH}]_0)$  x L-LA conversion. <sup>c</sup> $M_n^{\text{GPC}}$  (in g mol<sup>-1</sup>) and  $M_w/M_n$  ( $\mathcal{D}$ ) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.58.

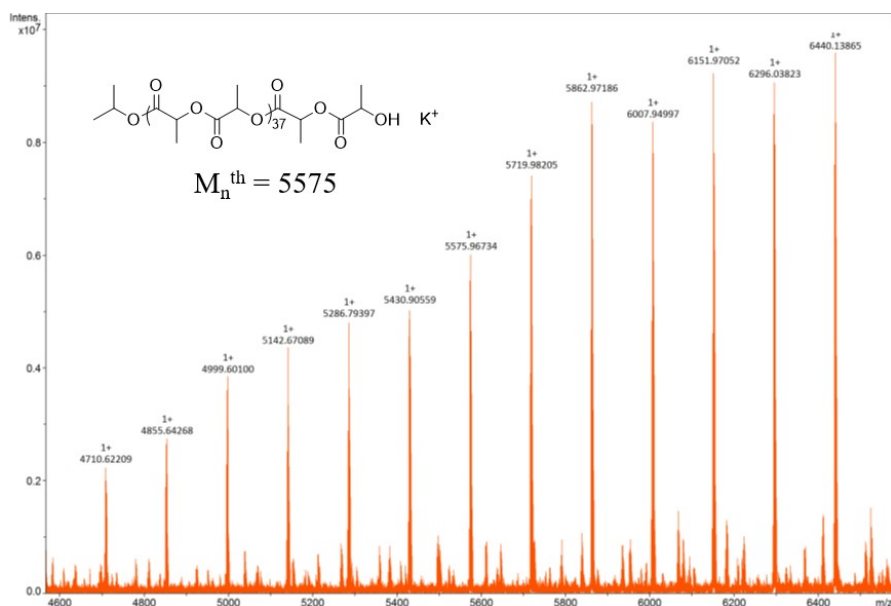
**Figure S7.** Molecular weights and molecular weights distribution (determined by GPC analysis) in function of the conversion for the polymerization experiment detailed in Table S3 ( $[\text{L-LA}]_0:[\mathbf{2}]_0:[i\text{PrOH}]_0 = 200:2:2$  in THF as solvent).



**Figure S8.** <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 298 K, 400 MHz) of the reaction mixture composed by complex **2** and 2 equivalents of isopropanol.



**Figure S9.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 298K) of a PLA sample (run 10 in Table 1).

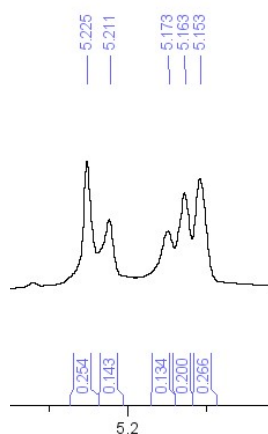


**Figure S10.** MALDI-FT-ICR spectrum of a PLA sample (run 10, Table 1).

**Table S4.** Ring-opening polymerization of *rac*-lactide by complexes **1** and **2**.

<sup>a</sup> Run	Cat	[L-LA] <sub>0</sub> /[Zn] <sub>0</sub> / [ <sup>i</sup> PrOH] <sub>0</sub>	<sup>b</sup> Conv (%)	<sup>c</sup> M <sub>n</sub> <sup>th</sup> (×10 <sup>3</sup> )	<sup>d</sup> M <sub>n</sub> <sup>GPC</sup> (×10 <sup>3</sup> )	<sup>d</sup> Đ
S1	<b>1</b>	200:2:0	66	19.0	16.3	1.41
S2	<b>2</b>	200:2:0	77	22.2	25.6	1.43

<sup>a</sup>Reactions were carried out in 1 mL of solvent (THF), complexes **1-2** = 5.0 10<sup>-6</sup> mol; *rac*-lactide was used as monomer. Temperature = 25 °C; time = 24 h. <sup>b</sup>Determined by <sup>1</sup>H NMR spectral data. <sup>c</sup>M<sub>n</sub><sup>th</sup> (g mol<sup>-1</sup>) = 144,13 x ([LA]<sub>0</sub>/[<sup>i</sup>PrOH]<sub>0</sub>) x LA conversion. <sup>d</sup>Experimental M<sub>n</sub> (in g mol<sup>-1</sup>) and M<sub>w</sub>/M<sub>n</sub> (Đ) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.58.



**Figure S11.** Methine region of the homonuclear decoupled <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 298K, 400K) of P(*rac*-LA) (run S1 in Table S4).

## Statistical analysis of a PLA sample obtained by *rac*-LA

**Table S5.** Tetrad probabilities based on Bernoullian Statistics (Th) and experimental values (Exp) as obtained by NMR analysis of polymeric sample obtained in entry S1 of Table S4.

Tetrad	Formula	Th	Exp
[ <i>rrmm</i> ]	$P_m^2/2$	0.254	0.254
[ <i>rrmm</i> ]	$P_r P_m/2$	0.102	0.143
[ <i>mrrr</i> ]	$P_r P_m/2$	0.102	0.134
[ <i>mmmm</i> ]	$P_r^2 + P_r P_m/2$	0.185	0.200
[ <i>mrrm</i> ]	$(P_m^2 + P_r P_m)/2$	0.356	0.266

**Table S6.** Tetrad probabilities based on Enantiomorphic Site Control Statistics (Th) and experimental values (Exp) as obtained by NMR analysis of polymeric sample obtained in entry S1 of Table S4.

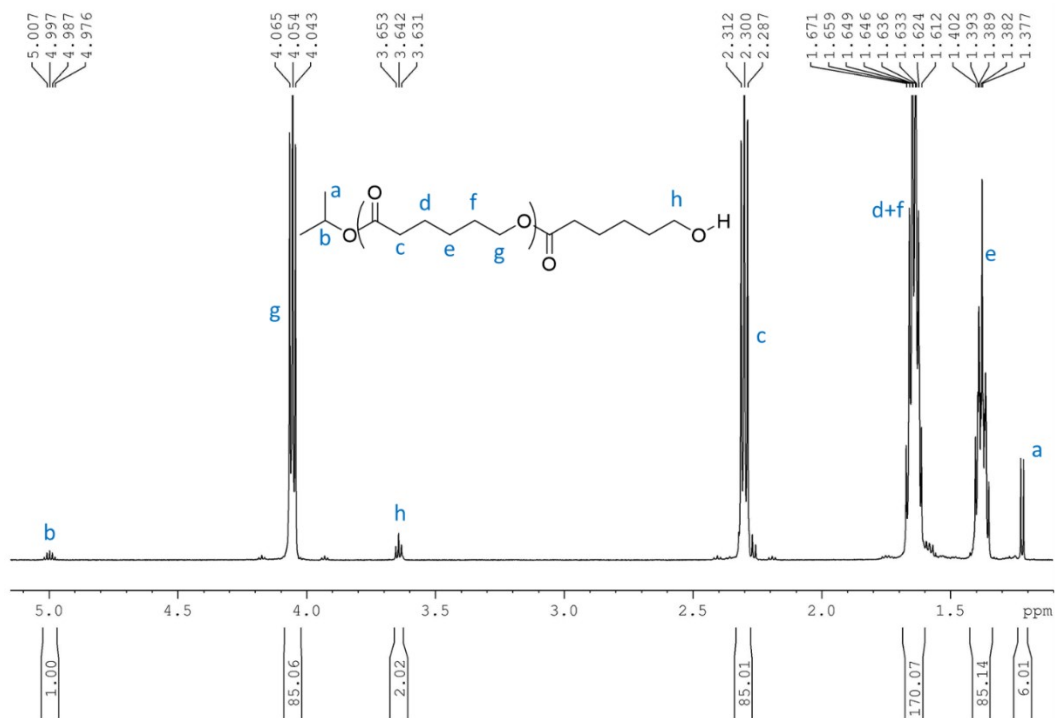
Tetrad	Formula	Th	Exp
[ <i>rrmm</i> ]	$[\alpha^2(1-\alpha) + \alpha(1-\alpha)^2]/2$	0.113	0.254
[ <i>rrmm</i> ]	$[\alpha^2(1-\alpha) + \alpha(1-\alpha)^2]/2$	0.113	0.143
[ <i>mrrr</i> ]	$[\alpha^2(1-\alpha) + \alpha(1-\alpha)^2]/2$	0.113	0.134
[ <i>mmmm</i> ]	$[\alpha^2 + (1-\alpha)^2 + \alpha^3 + (1-\alpha)^3]/2$	0.435	0.200
[ <i>mrrm</i> ]	$[\alpha(1-\alpha) + \alpha(1-\alpha)]/2$	0.226	0.266

**Table S7.** Ring-opening polymerization of L-lactide by complex **2**, using different solvents.

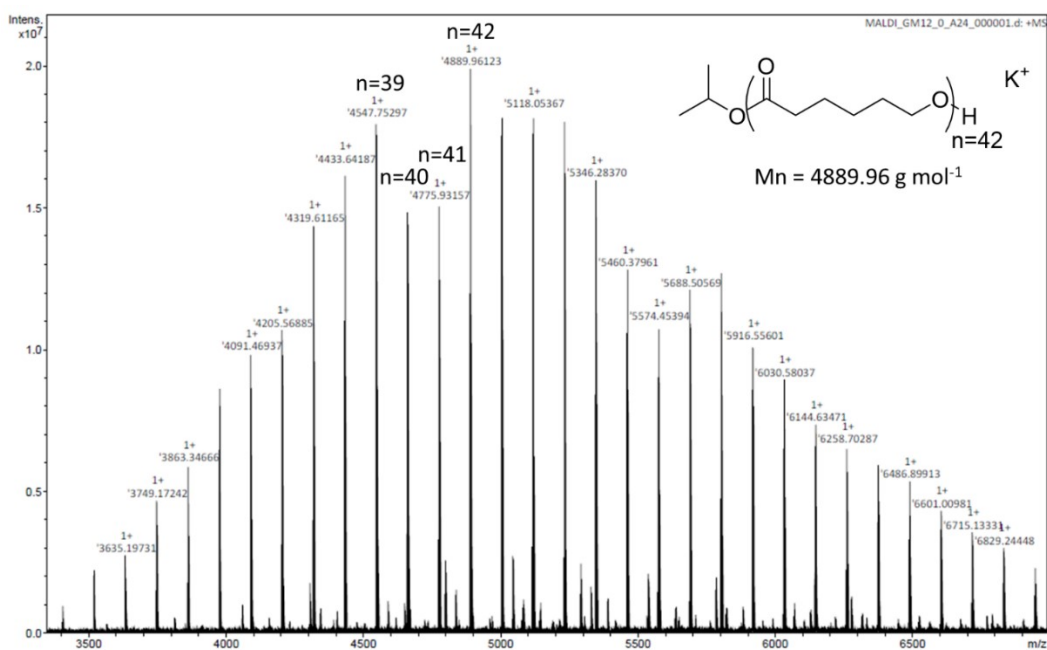
<sup>a</sup> Run	Solvent (V, mL)	Temp (°C)	Time (h)	<sup>b</sup> Conv (%)
2	THF (1 mL)	25	24	69
S3	DCM (1 mL)	25	24	74
5	THF (1 mL)	60	2	85
S4	Toluene (1 mL)	60	1	36
			2	59
S5	Toluene (2.5 mL)	60	1	24
			2	37
			4	63
			6	77
S6	THF (2.5 mL)	60	1	20
			2	39
			4	57
			6	75

<sup>a</sup>All reactions were carried out with complex **2** =  $5.0 \cdot 10^{-6}$  mol;  $i\text{PrOH}$  =  $1.0 \cdot 10^{-5}$  mol; L-LA =  $1.0 \cdot 10^{-3}$  mol (200 eq, i.e. 100 eq/Zn). <sup>b</sup>Determined by <sup>1</sup>H NMR spectral data.

## Ring-Opening Polymerization of $\epsilon$ -caprolactone

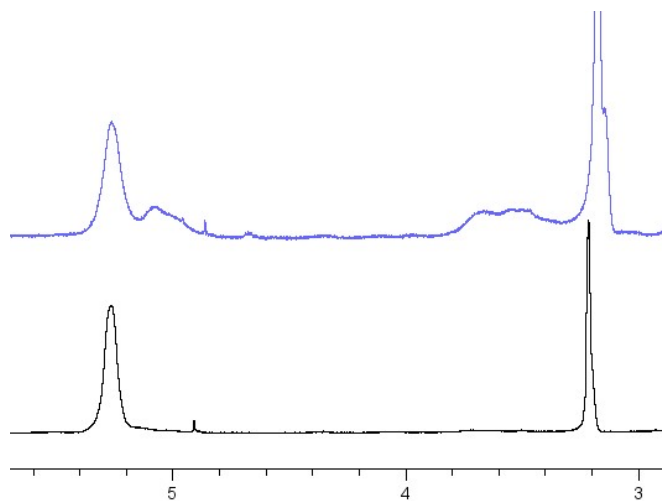


**Figure S12.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ , 298K) of PCL (run 17 in Table 2).

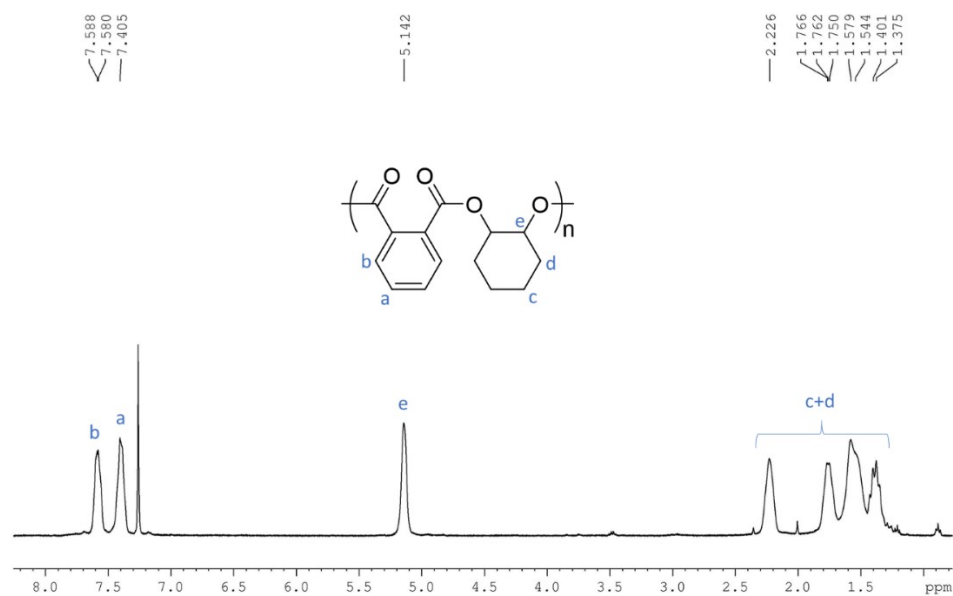


**Figure S13.** MALDI-FT-ICR spectrum of PCL (run 17, Table 2).

## Ring-Opening COPolymerization of phthalic anhydride and cyclohexene oxide



**Figure S14.** <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>, 298K) of the sampling of the reaction mixtures during two CHO/PA ROCOP experiments (blue spectrum: run 20 in Table 3, black spectrum: run 22 in Table 3).



**Figure S15.** <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 298K) of a P(CHO-PA) isolated sample (run 24 in Table 3).