

## Supporting Information

### Insights into the mechanism for ring-opening polymerization of lactide catalyzed by $\text{Zn}(\text{C}_6\text{F}_5)_2$ /organic superbase Lewis pairs

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#### Experimental section

##### Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out on a dual-manifold Schlenk line or in an inert gas ( $\text{N}_2$ ) filled glovebox. *L*-lactide (*L*-LA) and 4-dimethylaminopyridine (DMAP) was recrystallized three times from ethyl acetate and dried under in a vacuum at 40 °C prior to use. Toluene and dichloromethane were purified by Solvent Purification System. Bis(pentafluorophenyl)zinc was purchased from Sigma-Aldrichinc., stored in a glovebox and used without further purification. 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (<sup>Mes</sup>NHC) was purchased from Strem Chemicals Inc. and used without further purification. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 7-methyl-1,5,7-triazabicyclo[4.4.0] decane-5-ene (MTBD) were purchased from Adamas-Beta and J&K Chemical respectively, dried over molecular sieves 4 Å.  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$  and toluene- $d_8$  were also dried over molecular sieves 4 Å.

##### Instrumentation and characterization

**NMR analysis.** <sup>1</sup>H NMR Spectra were recorded in  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$  or  $\text{C}_7\text{D}_8$  on a Bruker Advance III 400 MHz instrument at room temperature. Monomer conversion was determined by the integration of methine protons of the monomer vs those of the polymers.

**In situ <sup>1</sup>H NMR experiments.** *In situ* <sup>1</sup>H NMR Spectra were also recorded in  $\text{C}_7\text{D}_8$  on a Bruker Advance III 400 MHz instrument. The typical procedure is as follows:

(1) A NMR tube was charged with  $\text{Zn}(\text{C}_6\text{F}_5)_2$  (1 equiv.) and DMAP (2 equiv.) or MTBD (1 equiv.). Toluene- $d_8$  (0.5 mL) was added to dissolve the reactants. The NMR tube was shaken slightly until all solids were fully dissolved. *In situ* <sup>1</sup>H NMR experiments were carried out at variable temperature,

at 25, 40, 60 and 80 °C, respectively.

(2) A NMR tube was charged with *L*-LA (5 equiv.), Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1 equiv.) and MTBD (1 equiv.). Toluene-d<sub>8</sub> (0.5 mL) was added to dissolve the reactants. The NMR tube was shaken slightly until all solids were fully dissolved. Then the NMR tube was heated at 80 °C for 10 min. *In situ* <sup>1</sup>H NMR experiments were carried out at room temperature in CD<sub>2</sub>Cl<sub>2</sub>. The reaction condition of <sup>13</sup>C NMR sample is similar to the <sup>1</sup>H NMR sample, but the concentration is more higher (70 mg/mL).

(3) A NMR tube was charged with *L*-LA (5 equiv.), Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1 equiv.) and MTBD (1 equiv.). Toluene-d<sub>8</sub> (0.5 mL) was added to dissolve the reactants. Two same samples were prepared. The NMR tube was shaken slightly until all solids were fully dissolved. Then the NMR tubes were heated at 80 °C for 15 min and 30 min respectively. *In situ* <sup>1</sup>H NMR experiments were carried out at room temperature.

**GPC analysis.** The number-average molar masses ( $M_n$ ) and molar mass distributions ( $M_w/M_n$ ) of the polymers samples were determined by gel permeation chromatography (GPC). Gel permeation chromatographic (GPC) measurements were carried out using a Waters instrument (515 HPLC pump) equipped with a Wyatt interferometric refractometer, eluted with THF at 35°C at 1 mL/min. The molecular weights of polymer samples were calibrated against polystyrene standards.

**MALDI-TOF MS analysis.** MALDI-TOF MS mass spectrum was conducted on a Autoflex III smart beam mass spectrometry (Bruker company). The scanning mode is positive ion linear model. The typical procedure is as follows:

(1) The cyclic PLA samples for MALDI-TOF MS analysis were obtained by quenching the polymerization run at low monomer conversion. The polymerization condition was as followed: the concentration of *L*-LA was 0.36 M, the ratio of [*L*-LA]<sub>0</sub>: [Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>0</sub>: [PMP]<sub>0</sub> was 25:1:1, the reaction was carried out in toluene at 80 °C and quenched after 60 min. The obtained polymer was purified by dissolution-precipitation cycle in CH<sub>2</sub>Cl<sub>2</sub> and cold ether and dried under in a vacuum at 40 °C prior to tested. Then the samples were compounded as 2 mg/mL solution in chloroform and 1 μL solution was extracted for detection. The delay extraction time of the ions is 200 ns and the matrix is 2,5-dihydroxybenzoic acid (DHB).

(2) The samples of reactive species for MALDI-TOF MS analysis were obtained by unquenching the polymerization run at low monomer ratio. The polymerization condition was as followed: the concentration of *L*-LA was 0.018 M, the ratio of [*L*-LA]<sub>0</sub>: [Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>0</sub>: [MTBD]<sub>0</sub> was 5:1:1, the reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and the solvent was eliminated by vacuum pumping after 180 min. The obtained sample was compounded as 2 mg/mL solution in chloroform and 1 μL solution was extracted for detection. The delay extraction time of the ions is 200 ns and the matrix is trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

## Ring opening polymerization of lactide

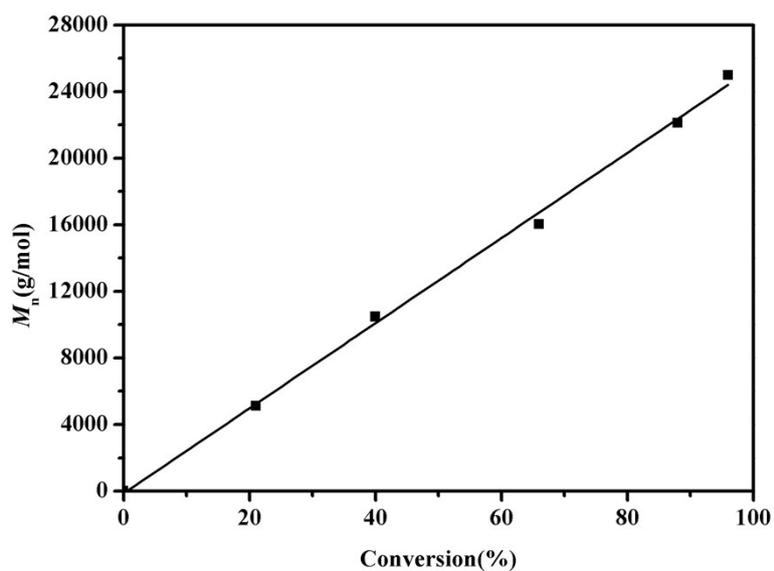
The typical polymerization procedure is as follows. All glassware used for polymerizations was oven-dried. In the glovebox, a Schlenk tube was charged with *L*-LA (50 equiv.). Toluene (5 mL) was added to dissolve the monomer.  $\text{Zn}(\text{C}_6\text{F}_5)_2$  (1 equiv.) and Lewis base (1 equiv.) were added to the solution and reaction was stirred at 80 °C. After stirring to the prescribed time, the polymerization was quenched by adding  $\text{HCl}/\text{Et}_2\text{O}$  (5 equiv.). An aliquot was withdrawn from the reaction by pipette and solvent was evaporated under vacuum. The crude material was analyzed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  to determine the monomer conversion. Cold ether was further added into the flask and the polymer was precipitated. The white polymer was obtained by vacuum filtration. The crude polymer was further purified by dissolution-precipitation cycle in  $\text{CH}_2\text{Cl}_2$  and cold ether. The polymer was filtrated, washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and dried under vacuum at 40 °C for 24 h.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 1.41–1.61 ppm (m, 6H,  $2\text{CH}_3$  backbone, PLA), 5.06–5.10 ppm (m, 2H, 2CH, backbone, PLA).

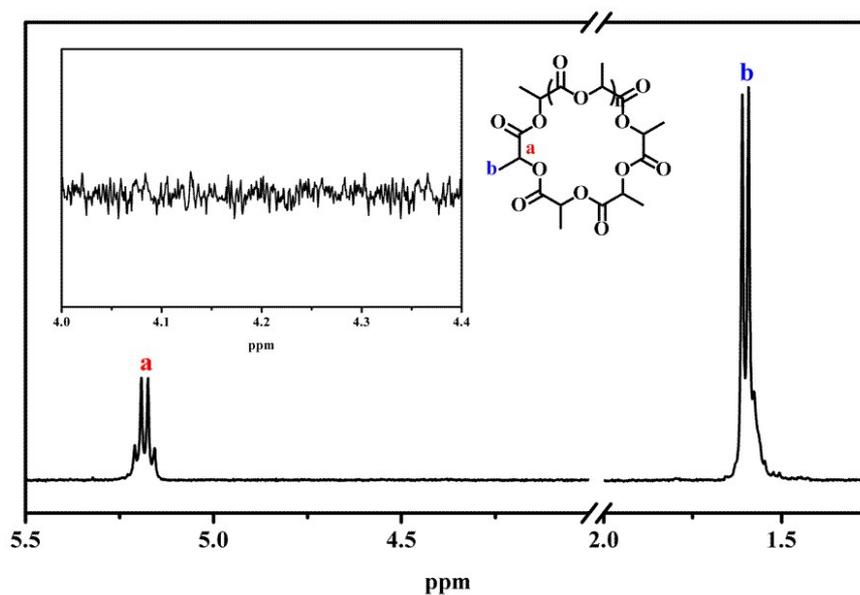
**Table S1** Ring-opening polymerization of CL with  $\text{Zn}(\text{C}_6\text{F}_5)_2$  or amine alone.<sup>a</sup>

Run	Mono.	base	solvent	T (°C)	<i>t</i> (h)	conv. <sup>b</sup> (%)	$M_n$ , calcd <sup>c</sup> (kg/mol)	$M_n$ <sup>d</sup> (kg/mol)	PDI <sup>d</sup>
1	<i>L</i> -LA	DMAP	Toluene	80	12	0	–	–	–
2	<i>L</i> -LA	<sup>IMes</sup> NHC	Toluene	80	12	68	4.9	17.6	1.52
3	<i>L</i> -LA	DBU	Toluene	80	12	94	6.8	19.8	1.46
4	<i>L</i> -LA	MTBD	Toluene	80	12	95	6.9	26.3	1.33
5	<i>L</i> -LA	–	Toluene	80	12	29	2.1	5.1	1.17
6	<i>L</i> -LA	–	$\text{CH}_2\text{Cl}_2$	40	12	2	–	–	–

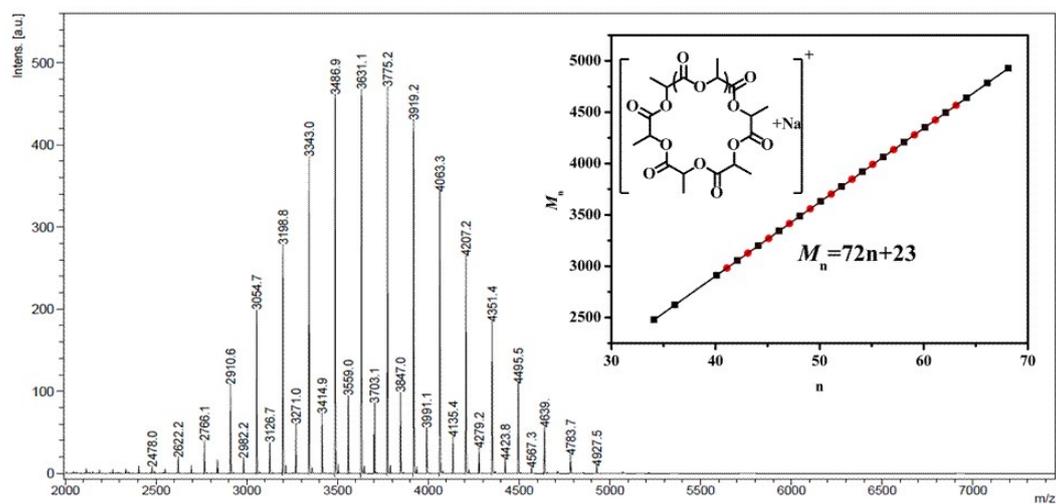
<sup>a</sup> Unless otherwise stated, the reactions was carried out with  $[\text{L-LA}]_0 = 0.36$  M,  $[\text{L-LA}]_0:[\text{Zn}]_0$  or  $[\text{L-LA}]_0:[\text{Base}]_0 = 50:1$ . <sup>b</sup> The conversion was determined by  $^1\text{H}$  NMR. <sup>c</sup> Calculated based on the assumption that each Lewis pair initiate one polymer chain,  $M_n = [\text{M}]_0/[\text{Zn}] \times \text{Monomer conversion} \times M_{\text{mono}}$ . <sup>d</sup> Determined by GPC analysis vs PS standard and corrected by the equation:  $M_n = 0.58 M_{n(\text{GPC})}$  for PLA.



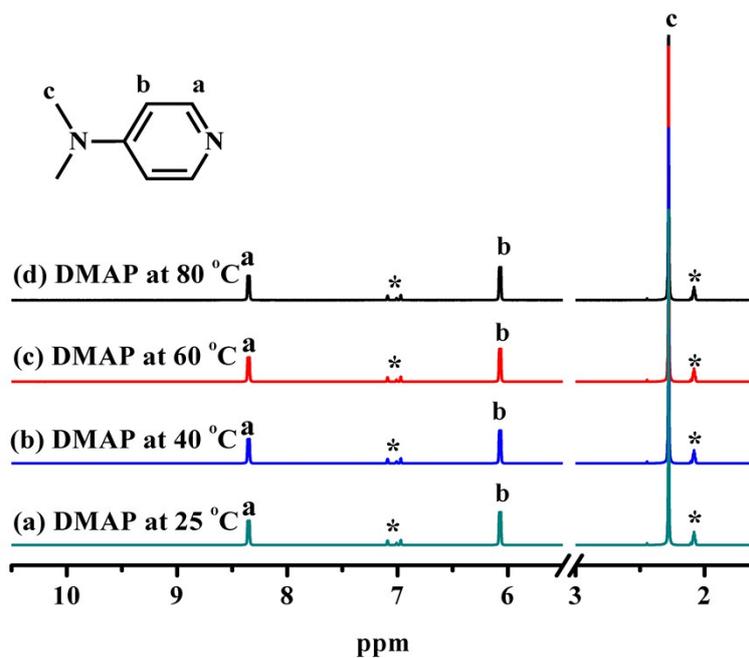
**Fig. S1** Plots of experimental  $M_n$  vs monomer conversion.  
 (Reaction condition:  $[L-LA]_0:[Zn(C_6F_5)_2]_0:[DBU]_0 = 50:1:1$ ,  $[L-LA]_0 = 0.36$  M,  $CH_2Cl_2$ ,  $40^\circ C$ )



**Fig. S2**  $^1H$  NMR spectrum ( $CDCl_3$ , 400 MHz) of a cyclic polylactide sample obtained by polymerization of L-lactide (L-LA) with  $Zn(C_6F_5)_2/DBU$  system. ( $[L-LA]_0:[Zn(C_6F_5)_2]_0:[DBU]_0 = 25:1:1$ ,  $[L-LA]_0 = 0.36$  M, Toluene,  $80^\circ C$ , 10 min)



**Fig. S3** Positive ion MALDI-TOF mass spectrum of cyclic PLA. Illustration shows the relationship of  $M_n$  vs  $n$  (the number of  $1/2$   $L$ -LA). ( $[L-LA]_0:[Zn(C_6F_5)_2]_0:[DBU]_0 = 25:1:1$ ,  $[L-LA]_0 = 0.36$  M, Toluene,  $80^\circ\text{C}$ , 10 min)



**Fig. S4**  $^1\text{H}$  NMR spectra of DMAP at variable temperature in  $\text{toluene-d}_8$ .

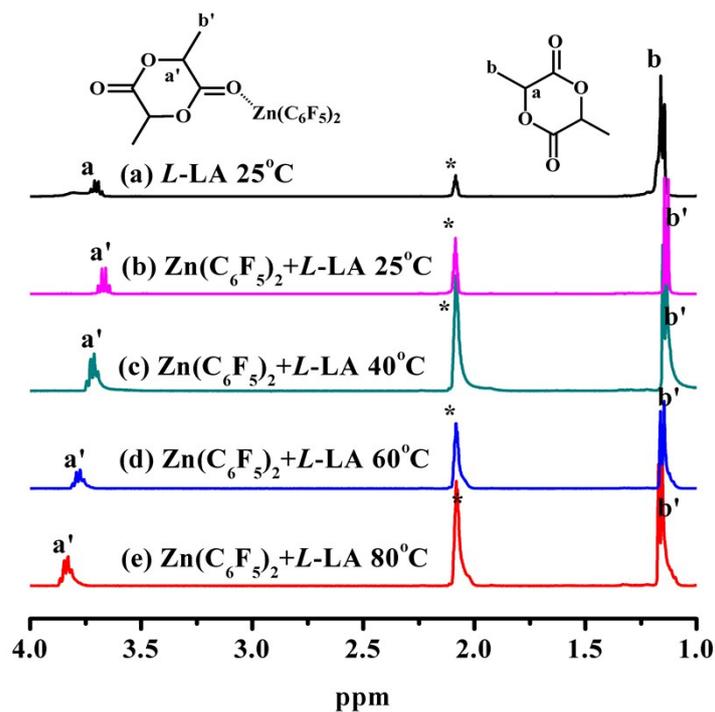


Fig. S5  $^1\text{H}$  NMR spectra of  $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{L-LA}$  (1:1) at variable temperature in  $\text{toluene-d}_8$ .

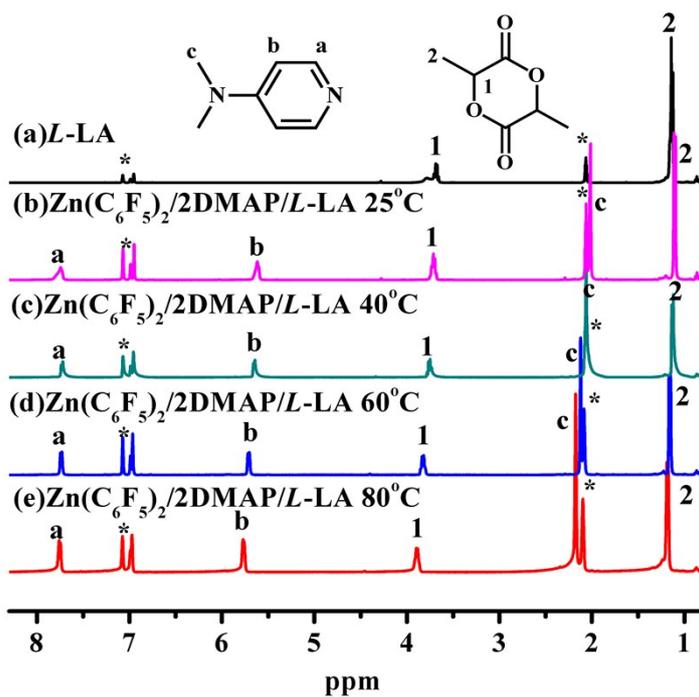
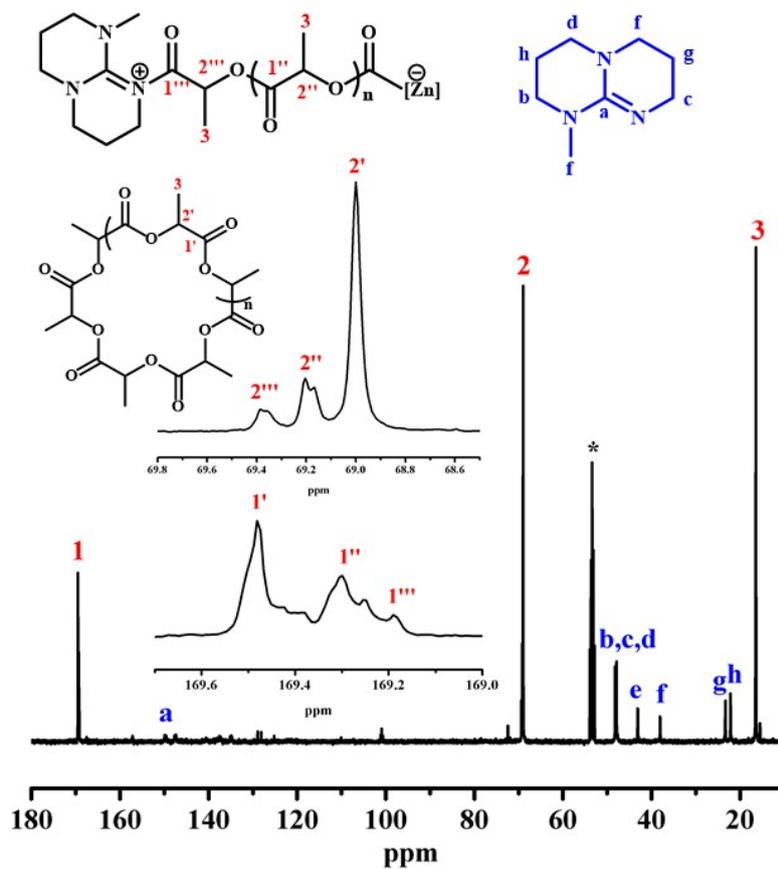
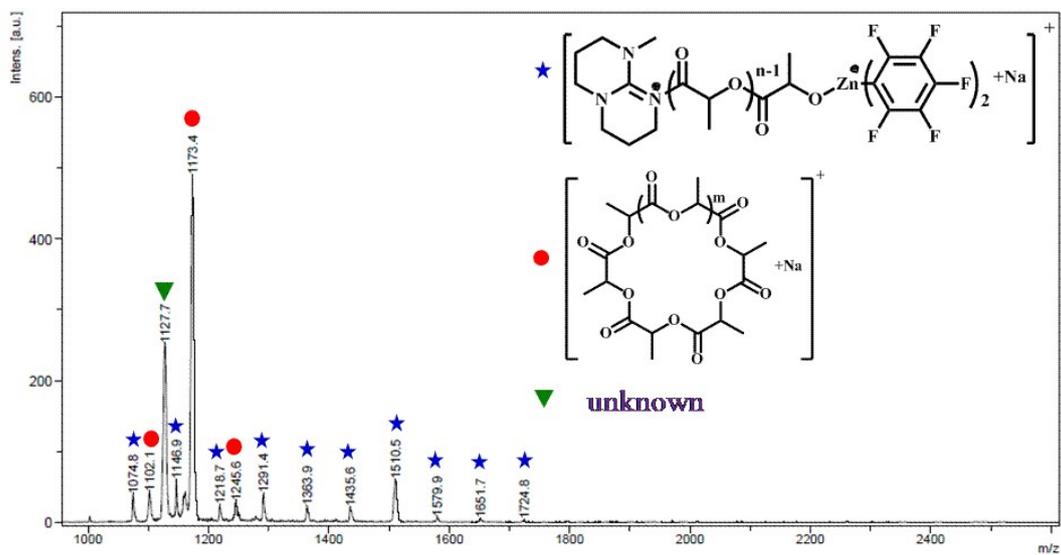


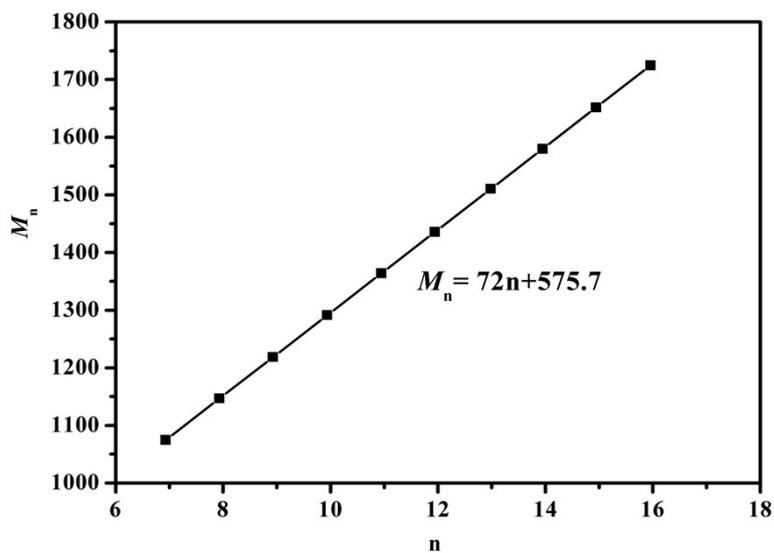
Fig. S6  $^1\text{H}$  NMR spectra of  $\text{Zn}(\text{C}_6\text{F}_5)_2/2\text{DMAP}/\text{L-LA}$  (1:2:1) at variable temperature in  $\text{toluene-d}_8$ .



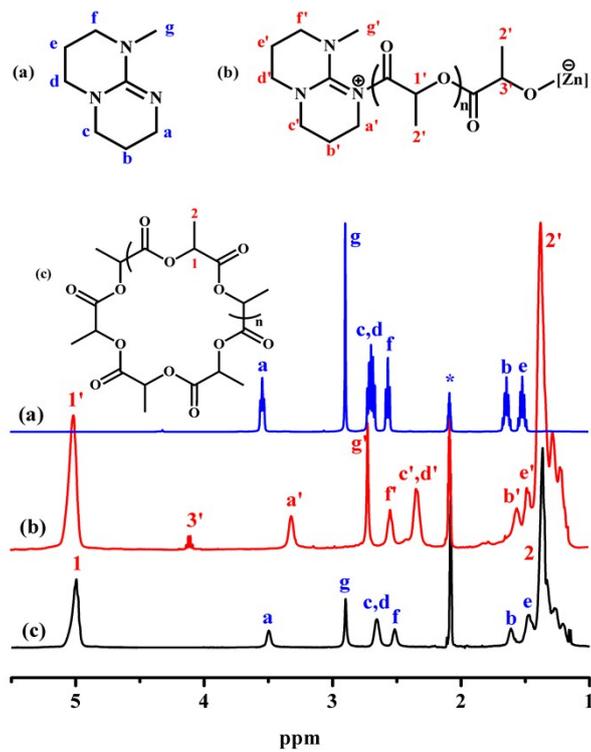
**Fig. S7**  $^{13}\text{C}$  NMR spectra of  $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{MTBD}/5L\text{-lactide}$  (30 °C, 10 min) texted at 25 °C in  $\text{CD}_2\text{Cl}_2$ .



**Fig. S8** MALDI-TOF MS spectra of zwitterionic propagating species.  
 $([L\text{-LA}]_0:[\text{Zn}(\text{C}_6\text{F}_5)_2]_0:[\text{MTBD}]_0 = 5:1:1, [L\text{-LA}]_0 = 0.018 \text{ M}, \text{CH}_2\text{Cl}_2, 180 \text{ min}, \text{unquenched})$



**Fig. S9** Relationship of  $M_n$  vs  $n$  (the number of  $1/2$   $L$ -LA) in MALDI-TOF MS spectra.



**Fig. S10**  $^1\text{H}$  NMR spectra of (a) MTBD alone, (b)  $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{MTBD}/5L$ -lactide ( $80^\circ\text{C}$ , 15 min) and (c)  $\text{Zn}(\text{C}_6\text{F}_5)_2/\text{MTBD}/5L$ -lactide ( $80^\circ\text{C}$ , 30 min) textured at  $25^\circ\text{C}$  in toluene- $d_8$ .