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Electronic Supplementary Information for

Synthesis and characterizations of guanidinate tin(II) complexes for ring-opening polymerizations of cyclic esters

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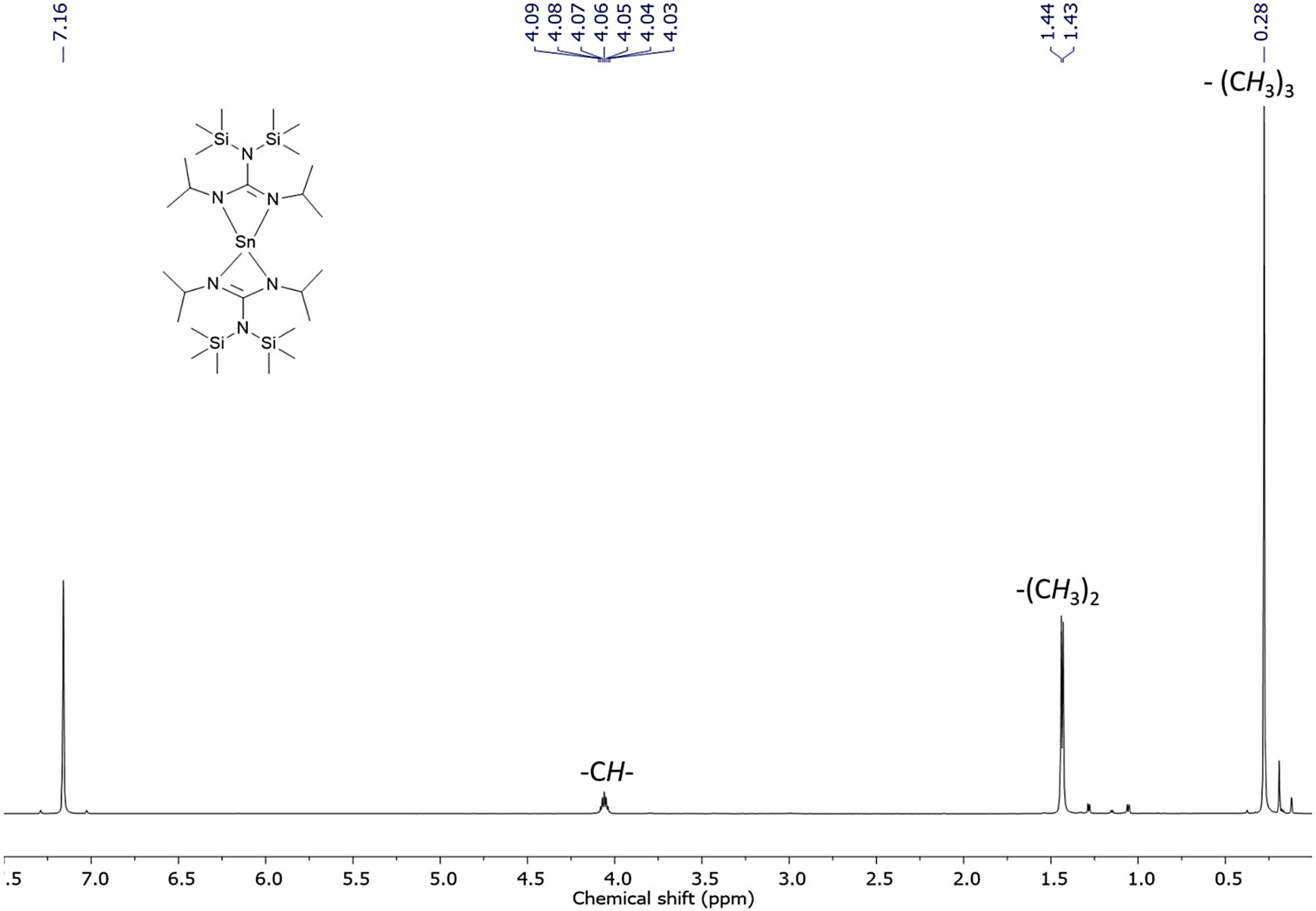

Figure S1. ^{1}H NMR spectra of **1** (600 MHz, C_6D_6, 30 °C).

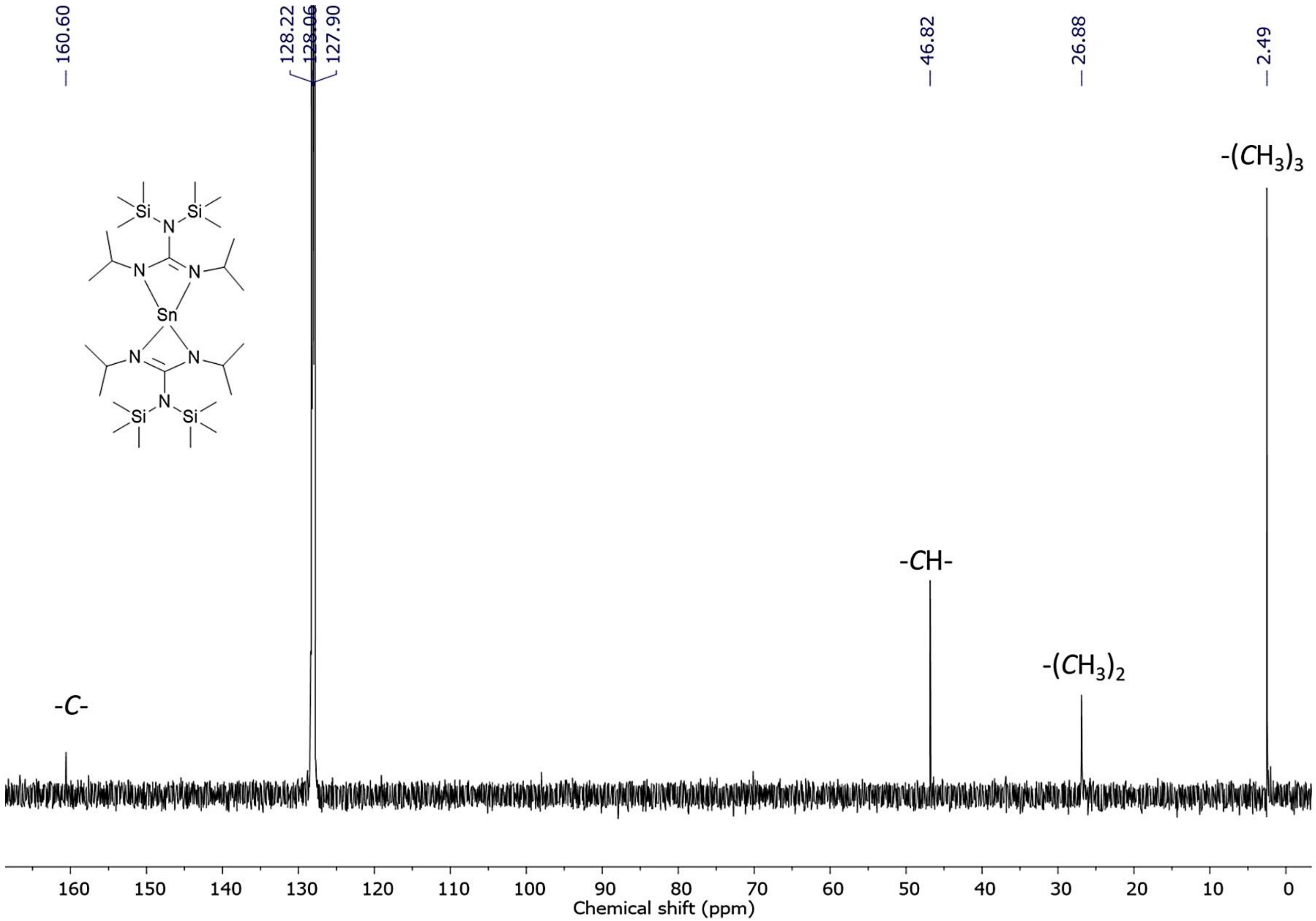

Figure S2. $^{13}C\{^1H\}$ NMR spectra of **1** (150 MHz, C_6D_6, 30 °C).

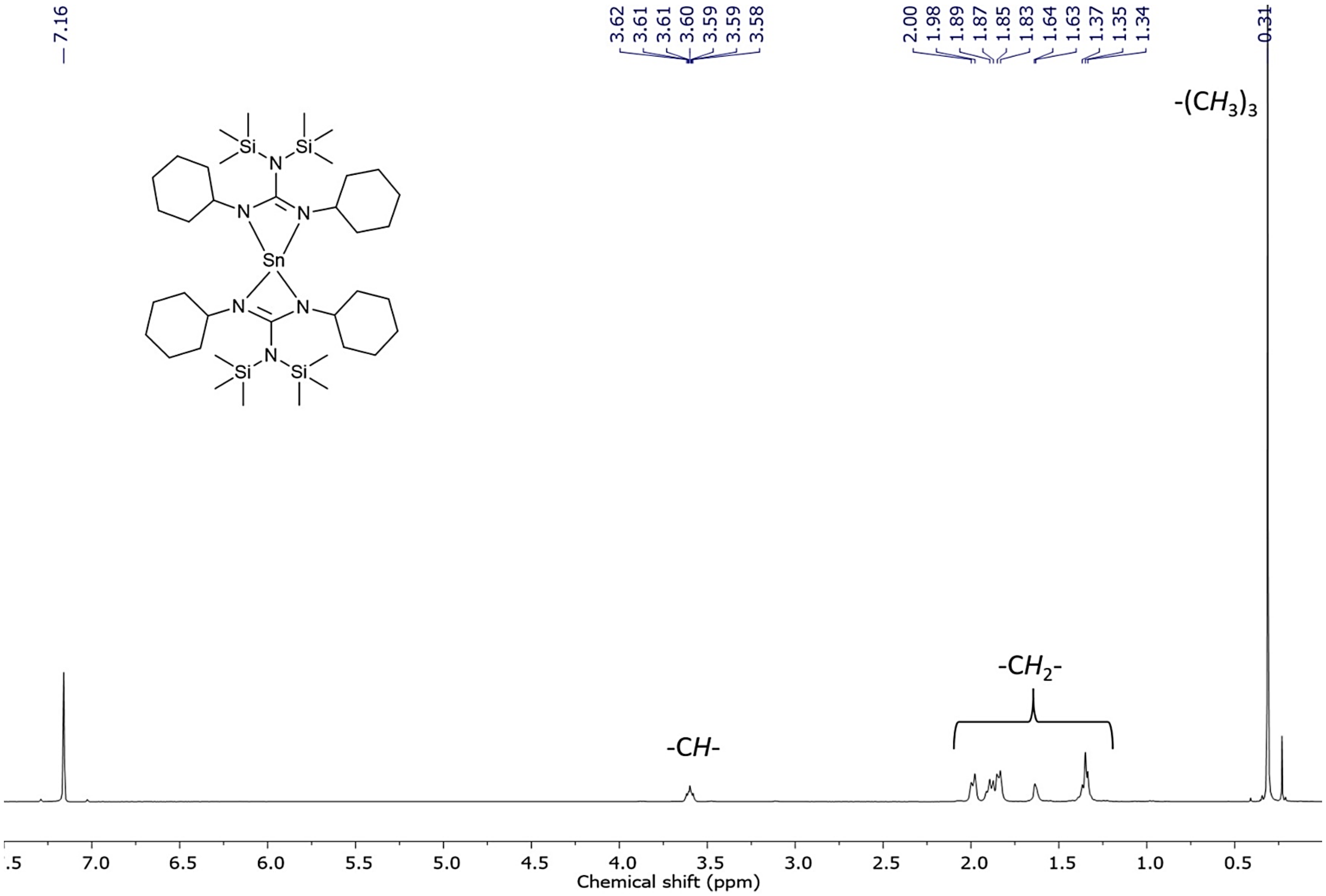

Figure S3. ^{1}H NMR spectra of **2** (600 MHz, C_6D_6, 30 °C).

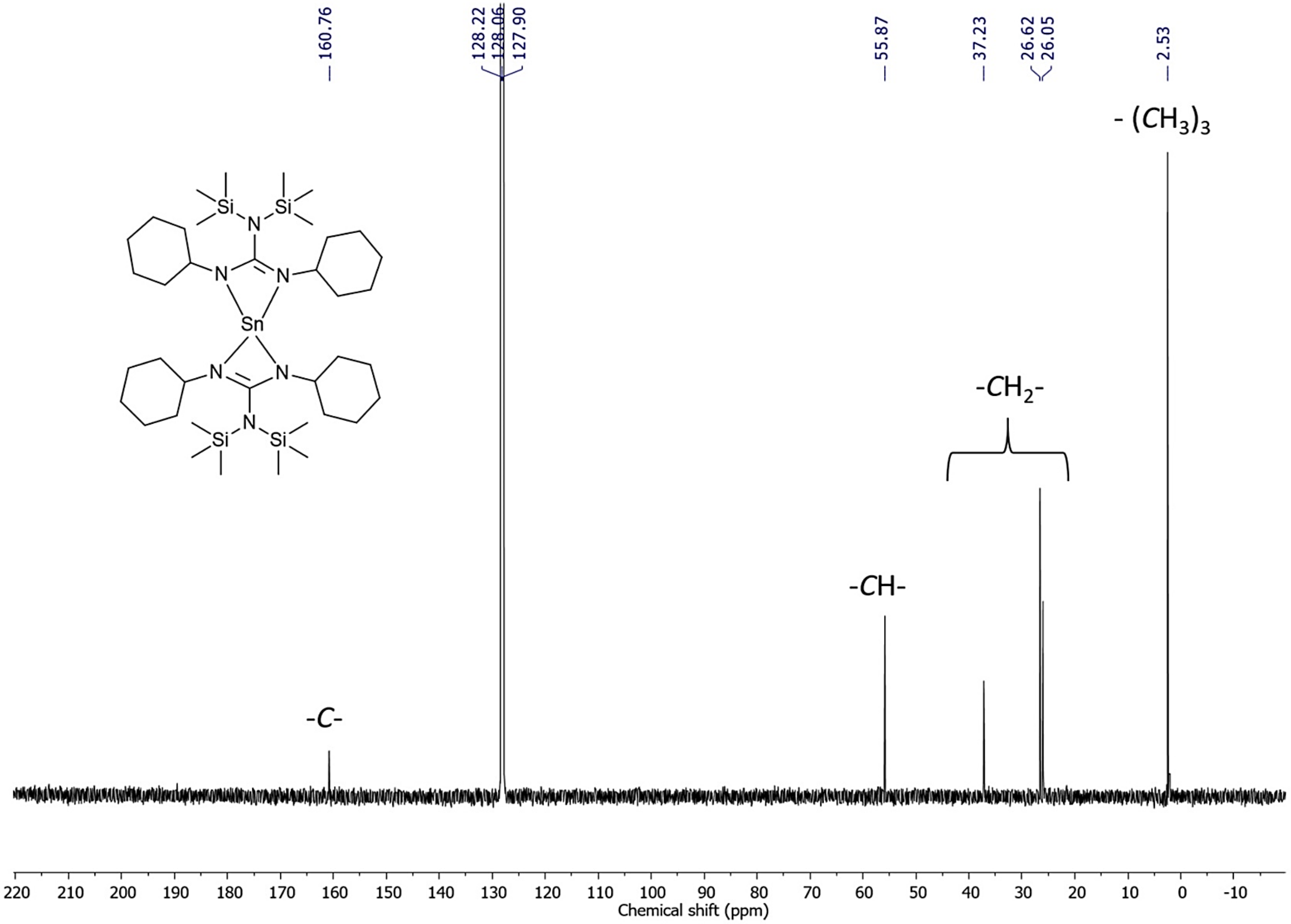

Figure S4. $^{13}C\{^1H\}$ NMR spectra of **2** (150 MHz, C_6D_6, 30 °C).

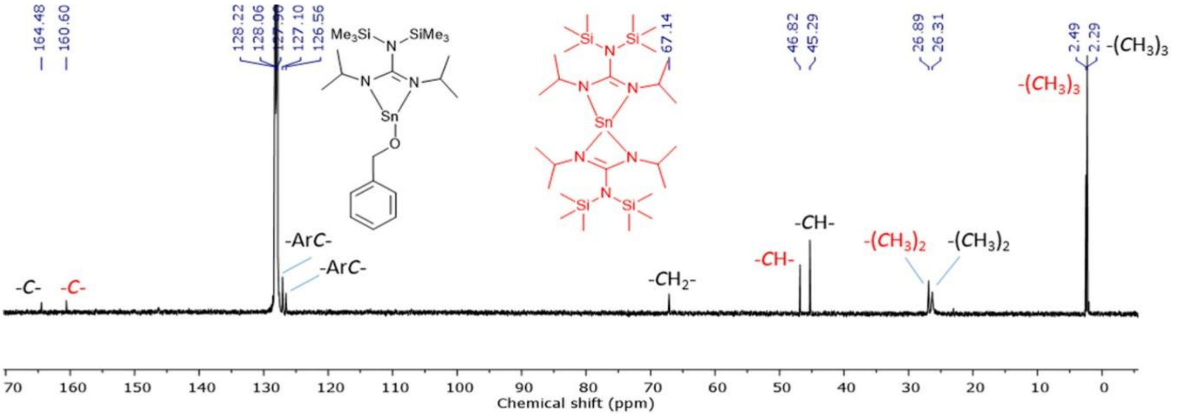

Figure S5. $^{13}C\{^1H\}$ (150 MHz, C_6D_6, 30 °C) of **5** upon standing at room temperature for 3 h (600 MHz, C_6D_6, 30 °C).

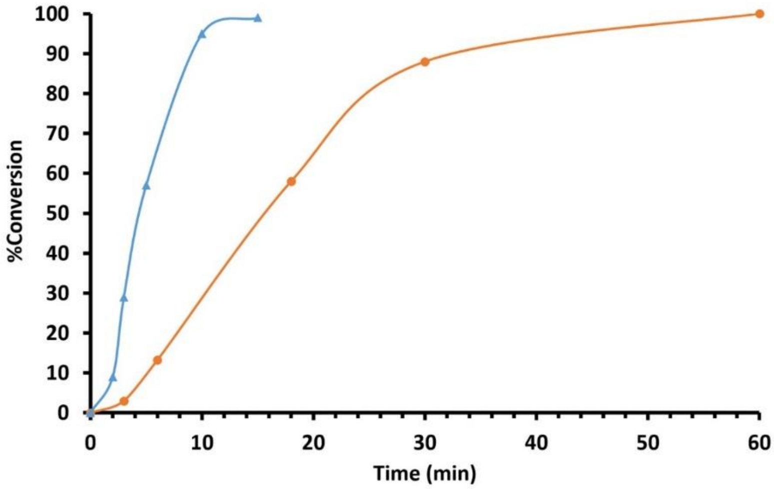

Figure S6. Neat polymerization at 120 °C.; ▲ = using *Ɛ*-CL: **1** molar ratio of 200: 1, ● = using *Ɛ*-CL: **2** molar ratio of 200: 1 (Table 2, entries 4-5).

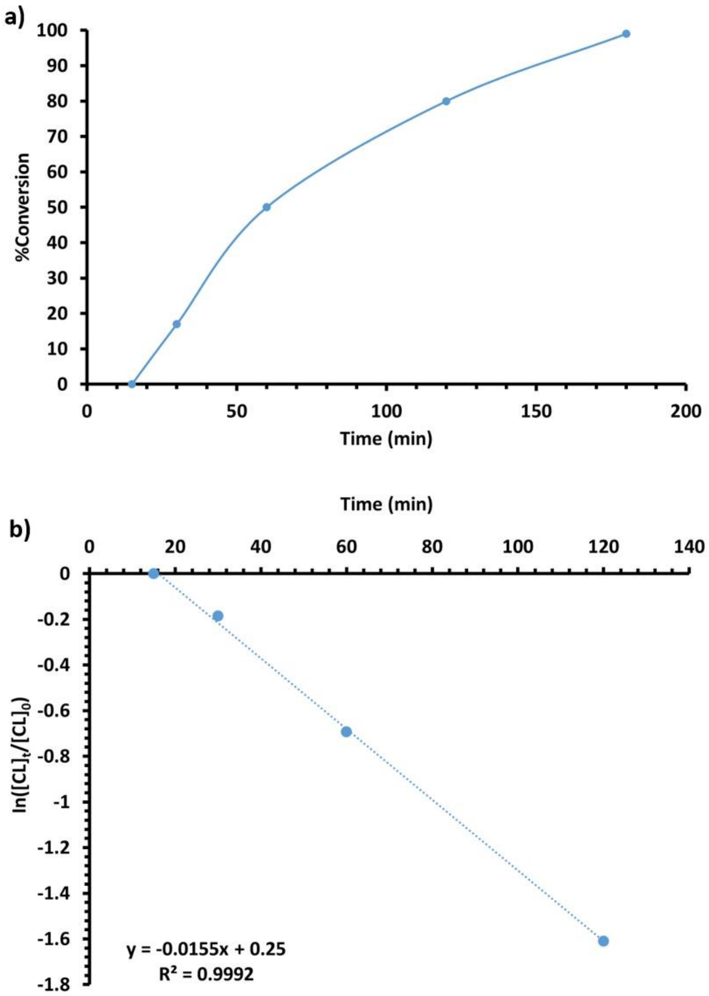

Figure S7. Solution polymerization using ε-CL: **1** molar ratio of 100: 1 at 100 °C in toluene (Table 2, entry 8); a) plots of conversion *vs.* time, b) linear plots of $\ln([\varepsilon\text{-CL}]_t/[\varepsilon\text{-CL}]_0)$ *vs.* time.

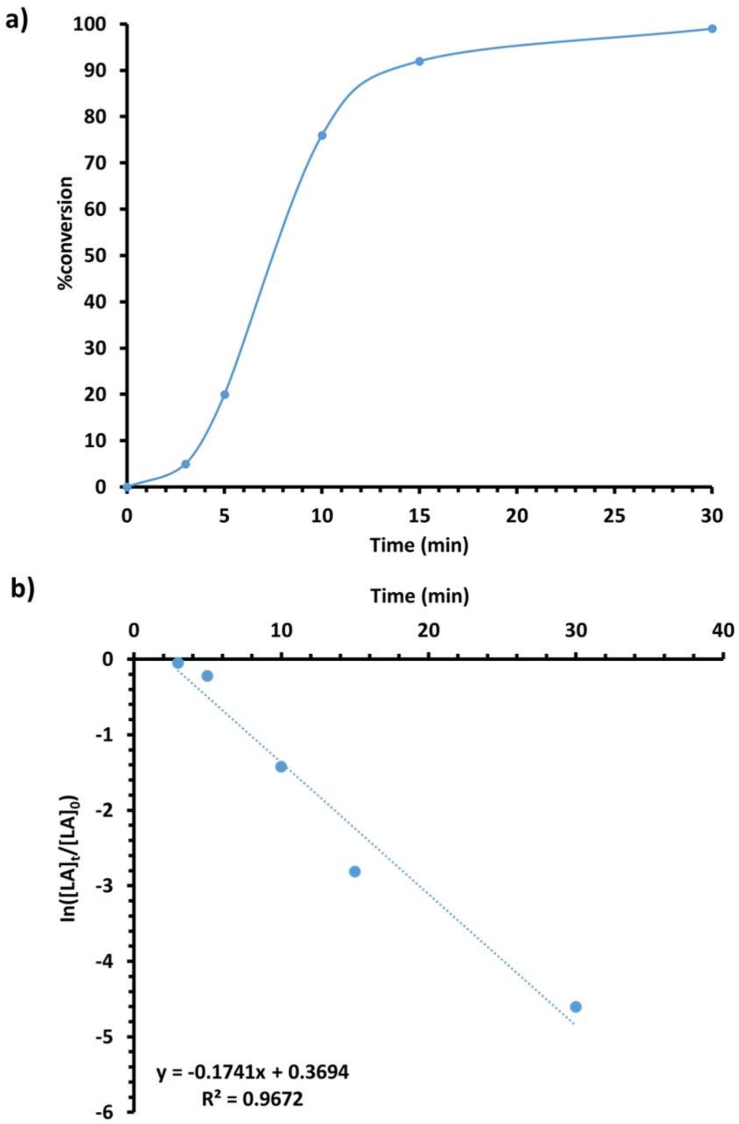

Figure S8. Solution polymerization using *L*-LA: **1** molar ratio of 100: 1 at 100 °C in toluene (Table 2, entry 11); a) plots of conversion *vs.* time, b) linear plots of ln($[LA]_t/[LA]_0$) *vs.* time.

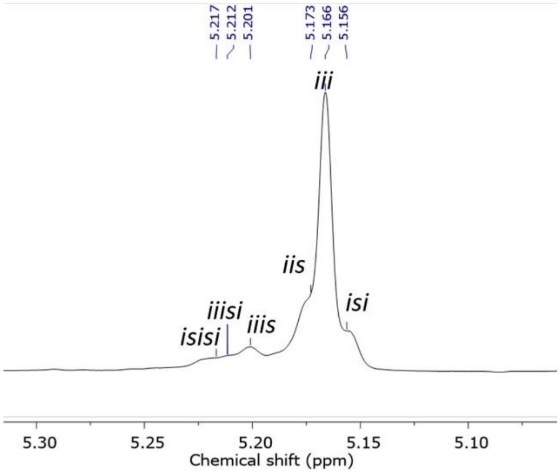

Figure S9. Homonuclear decoupled ^{1}H NMR spectra of PLAs obtained from *L*-LA (600 MHz, $CDCl_3$, 30 °C). NMR signals were assigned according to literature.[1,2]

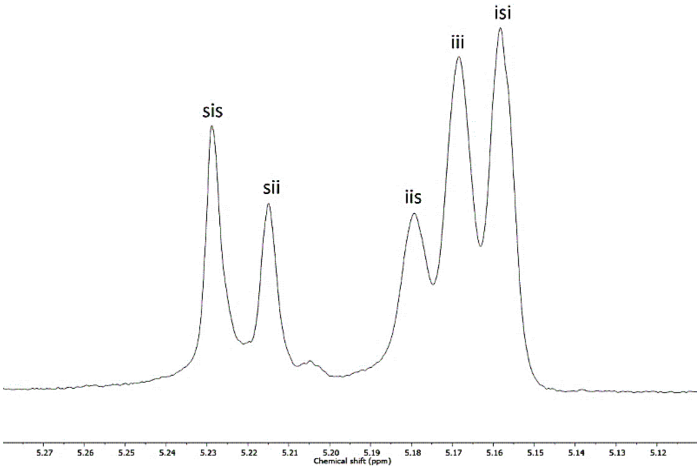

Figure S10. Homonuclear decoupled ^{1}H NMR spectra of PLAs obtained from *rac*-LA (600 MHz, $CDCl_3$, 30 °C). NMR signals were assigned according to literature.[3] The probability of racemic enchainment (P_r) was calculated as shown below.

The determination of probability of racemic enchainment (P_r)

Generally, the atactic PLA shows five tetrads in its homonuclear decoupled ^{1}H NMR spectra including [*sis*], [*sii*], [*iis*], [*iii*], and [*isi*]. According to tetrad probabilities based on Bernoullian statistics[4], The P_r value can be calculated using following equation;

$$[sis] = P_r^2/2 \tag{1}$$

$$2[sis] = P_r^2 \tag{2}$$

$$P_r = \sqrt{2[sis]} \tag{3}$$

$$P_m = 1 - P_r \tag{4}$$

Where P_m equals the probability of *meso* enchainment.

[*sis*] value equals the integrated intensity ratio of *sis* tetrads divided by that of total methine proton region. For heterotactic PLAs, the P_r value is close to 1, on the other hand the P_r value of isotactic PLAs is close to 0. For atactic PLAs, the P_r value is 0.5.

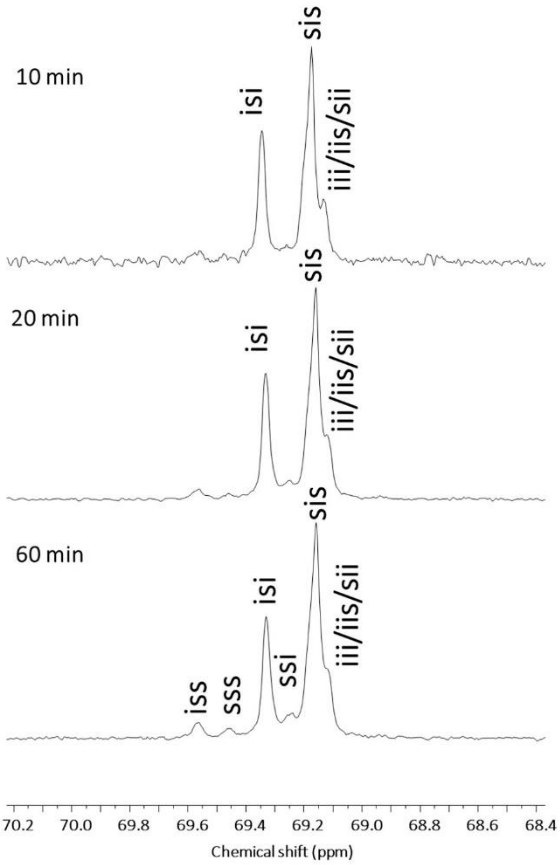

Figure S11. $^{13}C\{^{1}H\}$ spectra (150 MHz, CDCl3, 30 °C) of PLA obtained from the polymerization of *rac*-LA at 10 min (43 % conv.), 20 min (80% conv.), and 60 min (95% conv.).

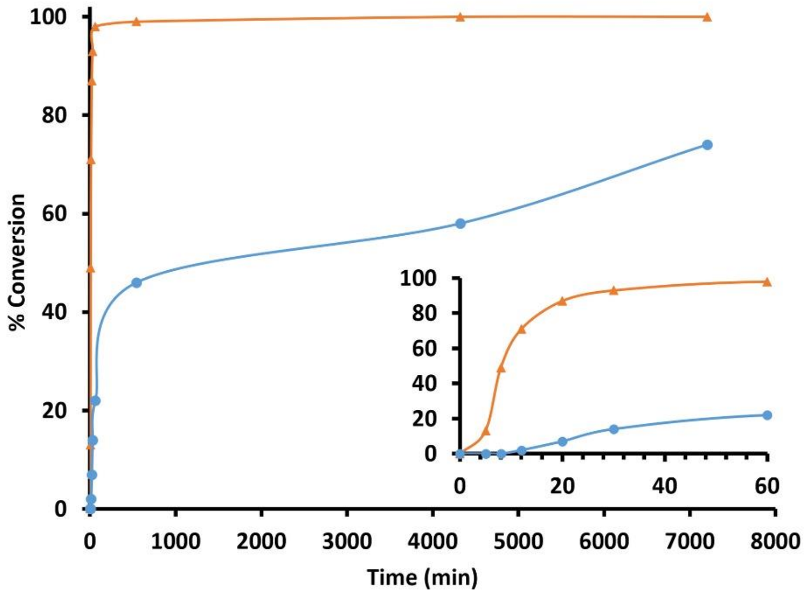

Figure S12. Solution copolymerization of *L*-LA and *Ɛ*-CL using *L*-LA: *Ɛ*-CL: **1** molar ratio of 100: 100: 1 at 100 °C (Table 2, entry 13); ▲ = PLA, ● = PCL.

Determination of average sequence length

For a quantitative analysis according to Bernoulli statistics, $^{13}C\{^1H\}$ NMR spectroscopy was used to analyst the copolymer chains by the integrated intensity ratio of resonance signals. Here in, the transesterification reaction was observed in polymerization using **1** and **Sn(Oct)$_2$** as a catalyst. This phenomenon leads to generate CLC signal which are the second mode of transesterification implying the chains were cut during copolymerization. The experimental-average lengths of lactidyl blocks l_{LL} and l_C can be calculated by the following equation.[5–8]

$$l_{LL} = \frac{1}{2}(LLL + LLC + CLL + CLC)/(CLC + \frac{1}{2}(LLC + CLL)) \quad (1)$$

$$LLL = \frac{1}{2}[CLLLL] + \frac{1}{2}[LLLLC] + \frac{1}{3}[CLLLC] + [LLLLLL] \quad (2)$$

$$LLC = \frac{1}{2}[CLLC] + \frac{1}{2}[LLLLC] + \frac{1}{3}[CLLLC] \quad (3)$$

$$CLL = \frac{1}{2}[CLLC] + \frac{1}{2}[CLLLL] + \frac{1}{3}[CLLLC] \quad (4)$$

$$CLC = [CLC] \quad (5)$$

$$l_C = (LCL + CCL + LCC + CCC)/(LCL + \frac{1}{2}(CCL + LCC)) \quad (6)$$

$$LCL = [LLCLL] + [LLCLC] + [CLCLL] + [CLCLC] \quad (7)$$

$$CCL = [CCLC] + [CCLL] \quad (8)$$

$$LCC = [CLCC] + [LLCC] \quad (9)$$

$$CCC = [CCC] \quad (10)$$

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