## Supplemental Information

to

## Polycondensations and Cyclization of Poly(L-lactide) Ethyl Esters in the Solid State

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**Figure S1**: MALDI-TOF mass spectra of PLAs prepared by co-polycondensation of ELA in bulk T=150 °C/6 d: (A) with SnCl<sub>2</sub> (1, Table1), (B) with BuSnPhF (7, Table 1)



**Figure S2** GPC elution curve of a PLA prepared with BuSnPhF at 140 °C and annealed for 1 d, with indication of fractions (4BX, Table 2)



**Figure S3** MALDI TOF mass spectra of 4 GPC fractions recorded from the PLA prepared with BuSnPhF at 140 °C/ 1 d (4BX, Table 2, GPC elugram see Figure S2)



**Figure S4** MALDI-TOF mass spectra (segments) of PLAs annealed at 140 °C for 28 d: (A) SnOct<sub>2</sub>, (B) SnCl<sub>2</sub>, (C) BuSnPhCl and (D) BuSnOPF



Figure S5 GPC elution curve of a PLA prepared with  $SnCl_2$  at 140 °C/28 d (2D, Table 2) with indication of fractions taken for MALDI TOF MS







**Figure S7** MALDI TOF mass spectra of 5 GPC fractions recorded from the fractionated PLA (see Figure S6) prepared with BuSnPhF (4D, Table 2)



**Figure S8** MALDI TOF mass spectrum of a ELA-initiated PLA equilibrated with BuSnPhF (LA/Cat = 400/1) in anisole at 140°C/28d



Figure S9 GPC elution curve of an ELA-initiated PLA equilibrated with BuSnPhF (LA/Cat = 400/1) in anisole at 140 °C/28d



**Figure S10** SAXS curves of PLAs prepared at 140 °C with SnCl<sub>2</sub>: (A) after 1 d (2B, Table 2), (B) after 28 d (2D, Table 2)



Figure S11 ESI TOF mass spectra of PLAs annealed with  $SnOct_2$ : (A) at 140 °C/7d (1C, Table 2), (B) at 160 °C/6d (1B, Table 3)

$$R^{1}-C^{\downarrow O}_{OR^{2}} \xrightarrow{+H^{+}}_{-H^{+}} R^{1}-C^{\downarrow O}_{OHR^{2}}$$

$$+R^{3}-OH \downarrow$$

$$R^{1}-C^{\downarrow O}_{OR^{3}} \xrightarrow{-H^{+}}_{-R^{2}-OH} R^{1}-C^{-}-OR^{2}_{H-O^{-}-R^{3}}$$

$$\xrightarrow{(H^{+})}_{(H^{+})} R^{1}-C^{-}-OR^{2}_{H-O^{-}-R^{3}}$$

Scheme S1 Proton-catalyzed esterification of a carboxylic acid



Scheme S2 SnOct<sub>2</sub>-catalyzed alcoholytic transesterification



Scheme S3 SnOct<sub>2</sub> catalyzed ester-ester interchange reaction



Scheme S4 Schematic illustration of the "wandering loop mechanism".