- Supporting Information –

One-Step Synthesis of Polylactide Macrocycle from Sparteine-Initiated ROP.

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Experimental section

Materials. L-Lactide (L-LA, GALACTIC, Belgium) was recrystallized twice from dried toluene and stored in a glove box under dry nitrogen atmosphere before use. CH_2Cl_2 was dried over CaH_2 for 48 hours at r.t., distilled under reduced pressure and stored in a glove box under dry nitrogen atmosphere before use. Toluene was dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns. (+)-Sparteine (SP, 97%, ABCR) was dried over BaO, distilled and stored in a glove box. Thiourea has been prepared by addition of cyclohexylamine to 3,5-bis(trifluoromethyl)phenyl isothiocyanate as reported in *Macromolecules 2006, 39, 7863.*

Characterizations. ^{1}H NMR spectra were recorded using a Bruker AMX-500 apparatus at r.t. in $CDCl_3$ (4mg/0.6ml). Size exclusion chromatography (SEC) was performed in THF (with 2% triethylamine added) at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a Marathon autosampler (loop volume = 200 µL, solution conc. = 1 mg/mL), a PL-DRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed-B 10 µm columns (linear columns for separation of MW_{PS} ranging from 500 to 10^6 daltons). Poly(styrene) standards were used for calibration. Polymerization conversions were checked by integration of PLA and LA signals. Matrix-assisted laser desorption ionization-time-of-flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser of 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10 000. The matrix, trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]malonitrile (DCTB), was prepared as a 40 mg/mL solution in chloroform. The matrix solution (1 µL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in chloroform to obtain 1 mg/mL solutions. Then, 1 µL aliquots of these solutions were applied onto the target area (already bearing the matric crystals) and then air-dried. Finally, 1µL of a solution of NaI (2 mg/mL in acetonitrile: water (1:1)) was applied onto the target plate.

Polymerization procedure. In a glove box, a dried vial equipped by a stirrer is charged with L-lactide (0.2 g, 1.4 x 10^{-3} mol) and SP (1 µl, 4.67 x 10^{-6} mol) in 0.49 ml of dry CH_2Cl_2. The sealed vial is then maintained under agitation and several withdrawals were performed to follow the kinetics by SEC.

Figure SI1 – SEC traces evolution

(cfr. Table 1, entry 3 to 7)

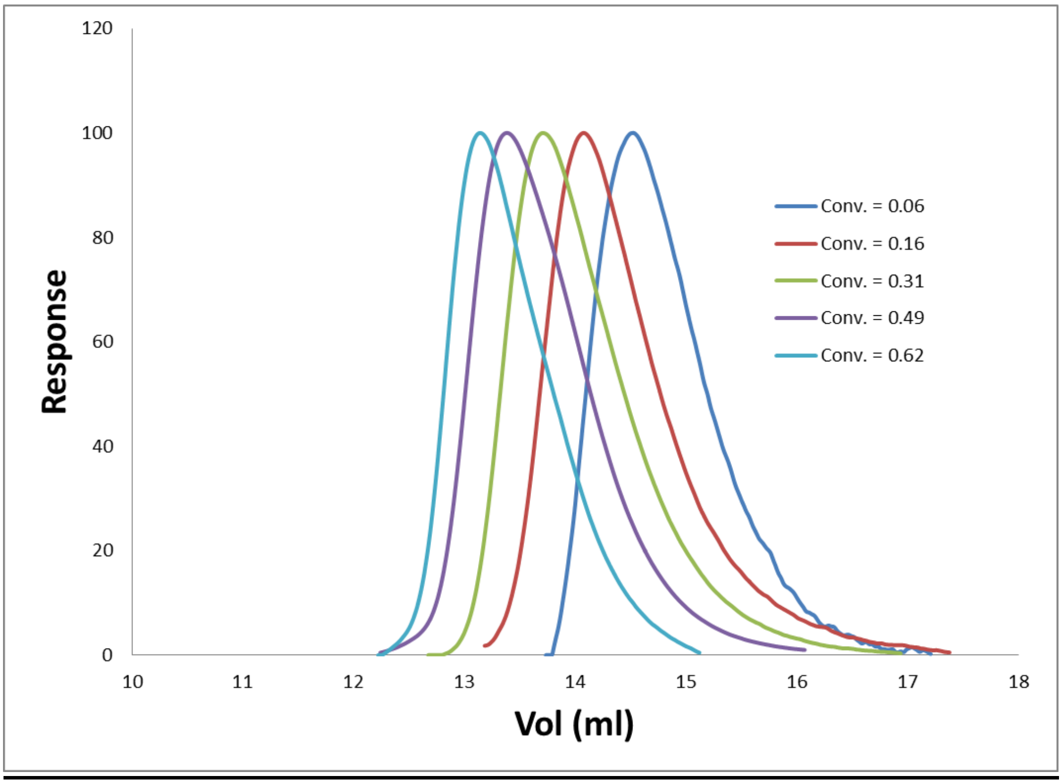


Figure SI2

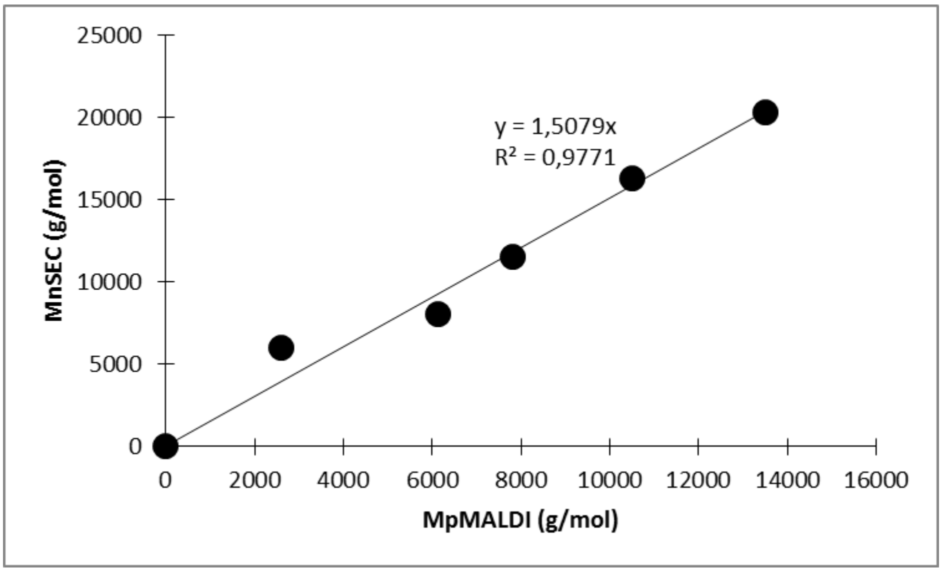


Figure SI3 – ^{1}H NMR

(cfr. Table 1, entry 5: crude medium)

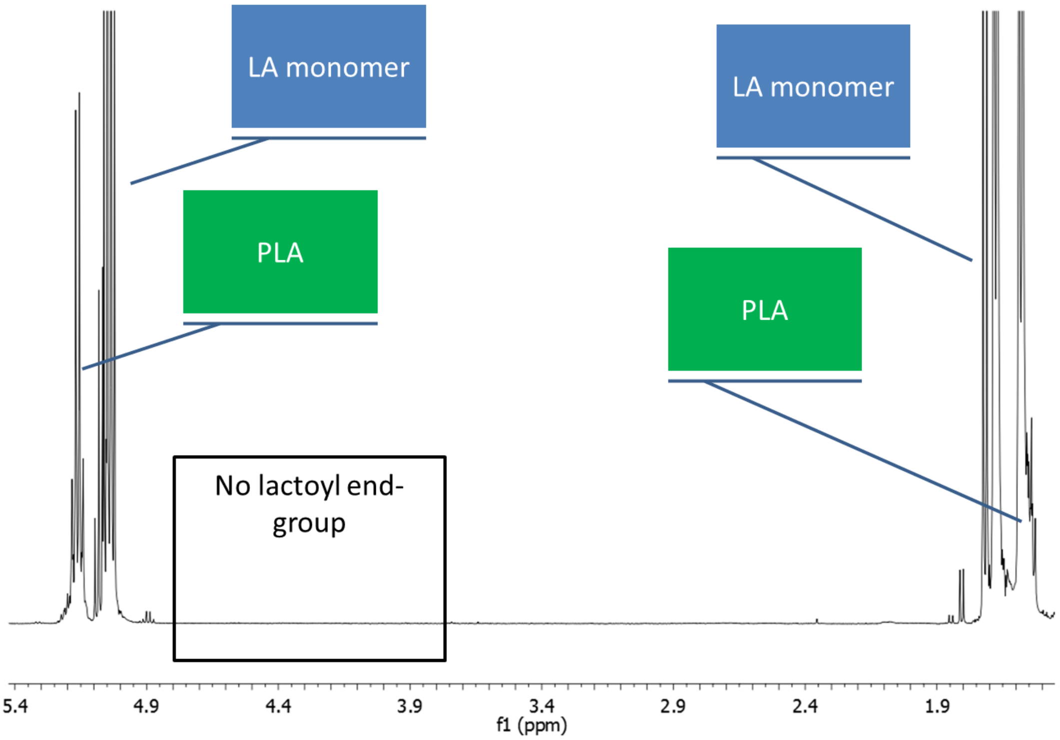
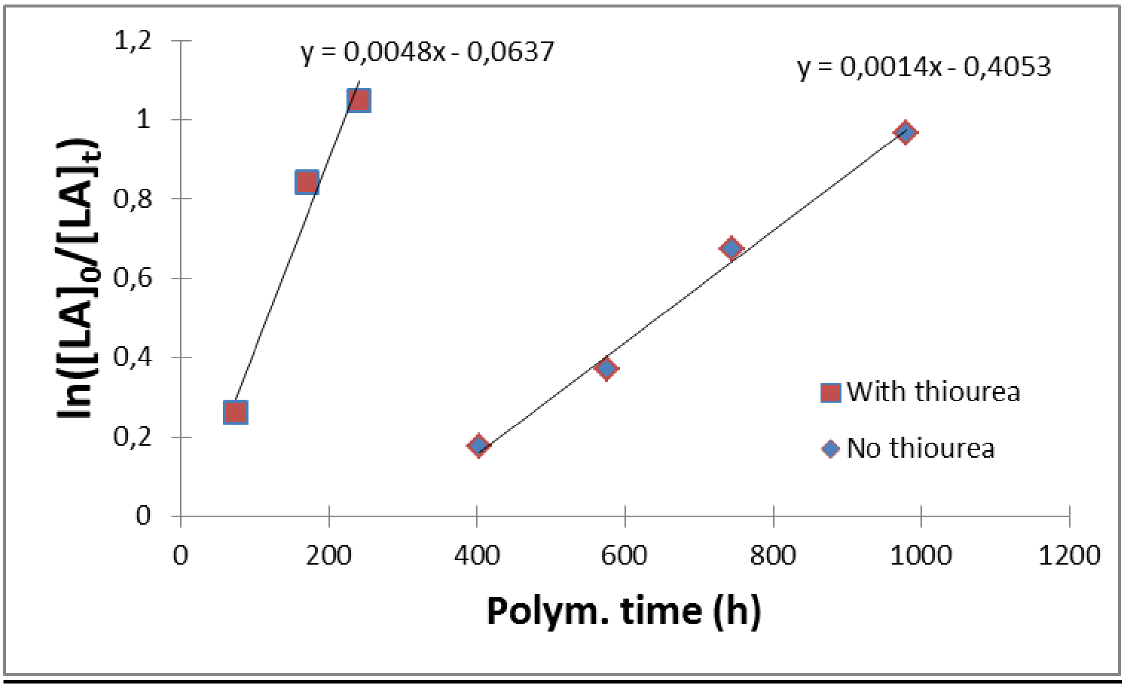
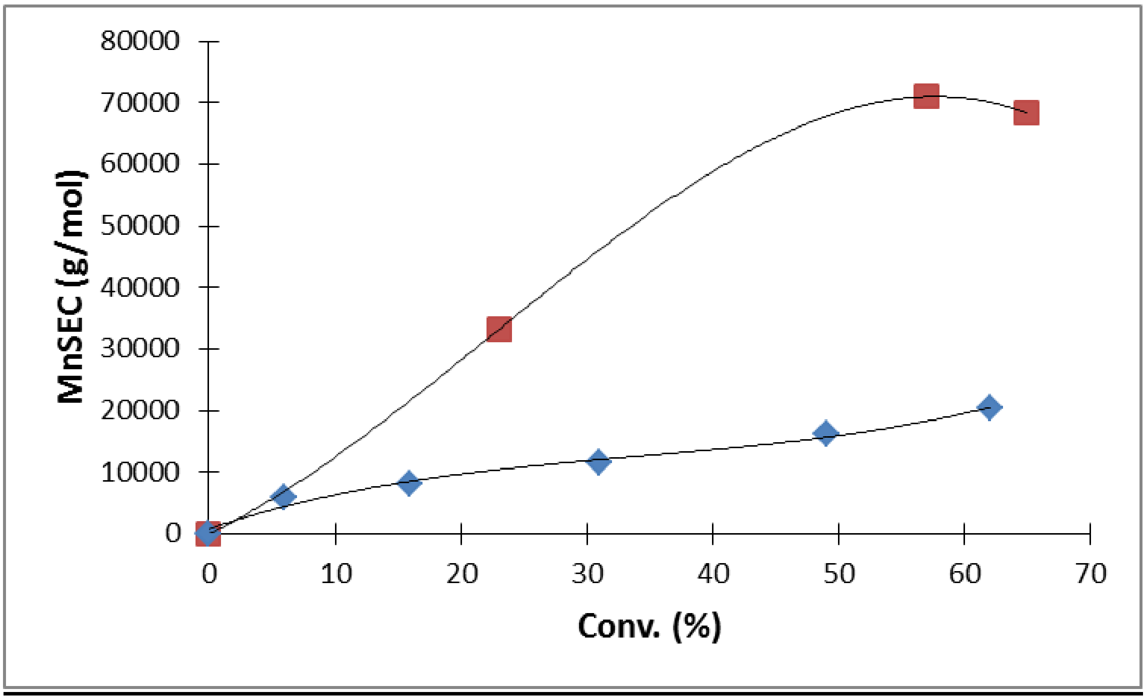


Figure SI4 – Semilog plots and MnSEC evolutions for two polymerization processes realized with and without thiourea ($[LA]_0/[SP]_0 = 300$; ♦ no thiourea; ■ with thiourea, $[SP]_0/[thiourea]_0 = 1$)




80000
70000
60000
50000
40000
30000
20000
10000
0
MnSEC (g/mol)
0
10
20
30
40
50
60
70
Conv. (%)