

Supporting Information

Imidazole-based organocatalyst designed for bulk polymerization of lactide isomers: inspiration from Nature

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Materials. L-lactide (L-LA) and D-lactide (D-LA) (GALACTIC, Belgium) were recrystallized from dried toluene and stored in a glove box. Benzyl alcohol (VWR) was dried over CaH₂ for 48 hours prior to its distillation under reduced pressure and stored in a glove box. Poly(ethylene oxide), α -methyl, ω -hydroxyl (Fluka, Mw ~ 2000 g/mol) was dried by three azeotropic distillations of toluene, then dried at 60°C in vacuo overnight and stored in a glove box. Imidazole (VWR), trifluoroacetic acid (Sigma Aldrich), benzimidazole (Sigma Aldrich), benzoic acid (Sigma Aldrich), lithium diisopropylamide (Sigma Aldrich) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride were used as received. After their preparation salts (1)-(5) were dried at 80°C in vacuo overnight and stored in a glove box.

Characterizations. ¹H NMR spectra were recorded using a Bruker AMX-500 apparatus at r.t. in CDCl₃ (4mg/0.6ml). The molecular mass measurements as well as the end-groups determinations were performed on a Waters QToF2 mass spectrometer equipped with an orthogonal electrospray (ESI) source (Z-spray) operated in positive ion mode. Sample was dissolved in acetonitrile in order to approximately achieve 10⁻⁴ M concentrations, as estimated from the molar mass determined by GPC analysis. The solution was infused into the ESI source at a rate of 5 μ l.min⁻¹ with a Harvard syringe pump. Typical ESI conditions were: Capillary Voltage : 3.1 kV ; Cone Voltage : 80 V ; Source

Temperature : 80°C and Desolvation Temperature : 120 °C. Dry nitrogen was used as the ESI gas. The quadrupole was set to pass ions from m/z 100 to 7000 and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass-analyzed with a 1 sec integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m² delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analysis were performed in the reflectron mode at a resolution of about 10 000. The matrix - *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) - was prepared as 10 mg/mL solution in acetone. The matrix solutions (1 μ L) were applied to a stainless steel target and air dried. Polymer samples were dissolved in dichloromethane to obtain 1mg/mL solutions. 1 μ L aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air dried. Finally, 1 μ L of a solution of NaI (2 mg/mL in acetonitrile: water (1:1)) was applied onto the target plate. For the recording of the single-stage MALDI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from m/z 1000 to 10000, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. Gel permeation chromatography (GPC) was performed in a tetrahydrofuran (THF)/triethylamine (NEt₃, 2wt%) mixture on a Waters chromatograph equipped with four 5 μ m Waters columns (300 mm x 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10⁵, 10⁶ Å). Polystyrene samples of known molecular weight were used as calibration standards. A Waters 410 differential refractometer and 996 photodiode array detector were employed. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q200 apparatus from T.A. Instruments under nitrogen flow (heating and cooling rate 10°C /min) from r.t. to 300°C.

Preparation of salts (1) to (4) – general procedure illustrated for the preparation of (1). In a 50ml flask, the imidazole base (0.1 g, 1.47x10⁻³ mol) is solubilized in 10 ml of chloroform. After cooling down to 0°C, trifluoroacetic acid (167 mg, 1 eq.) is slowly added. After 24 hours of agitation, the precipitated salt is filtered out and dried under vacuum at 80°C for 12 hours. Yield ~ 90%. Melting temperature = 127.2°C. Degradation temperature = 170°C.

Preparation of salt (5). In a 50ml flask, the lithium diisopropylamide (0.17 g, 5.9x10⁻⁴ mol) is solubilized in 10 ml of water. After cooling down to 5°C, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.2 g, 1 eq.) is slowly added. After 30 minutes of agitation, the precipitated salt is filtered out and dried under vacuum at 30°C for 12 hours. Yield ~ 87%. Melting temperature = 135.4°C.

General 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), BzOH (2.1 μ g, 1.98 x 10⁻⁵ mol) and (1) (8 mg, 1.0 x 10⁻⁴ mol). Out of

the box, the sealed vial is maintained under agitation in a 140°C oil bath for 2 hours. GPC analysis of the crude medium reveals a conversion^{ref.1.} of 60%, a M_n GPC of 11400 g/mol (uncorrected value) and a D_M of 1.14.

Ref.1. See for example: O. Coulembier, Ph. Dubois, “4-Dimethylaminopyridine-based Organoactivation: from Simple Esterification to Lactide Ring-Opening “Living” Polymerization”, *Journal of Polymer Science: Part A: Polymer Chemistry*, **2012**, 50, 1672-1680.

ESI-MS Analysis Details. The ESI-ToF mass spectrum of the product obtained after 0.3h (entry 5, Table 1) has been recorded at two different values of the cone voltage (CV) (Figure SI1). Increasing the CV value can enhance the intensity of the signals in the mass spectra by increasing the transmission of the ions from the ion source to the vacuum of the mass analyzer.^{Ref.2.} Heavy ions generally require a high CV value to be nicely transmitted. Nevertheless, increasing the CV can also induce ion decompositions following high energetic collisional events with the residual gas molecules. The ESI-ToF mass spectrum recorded with a CV of 30 volts points in particular to the presence of low mass polymer chains of cyclic nature (Figure SI1a). This of course seems in contradiction with the corresponding GPC data. However by increasing the CV to 190 V, the mass spectrum is considerably modified and higher mass polymer ions are observed with the mass distribution spreading up to m/z 6000 revealing the generation of fragment ions from larger polymer chains (Figure SI1b).

Ref.2: J. De Winter, M. Vachaudez, O. Coulembier, Ph. Dubois, R. Flammang and P. Gerbaux, *e-Polymers*, 2010, **103**, 1.

Figure SI1.

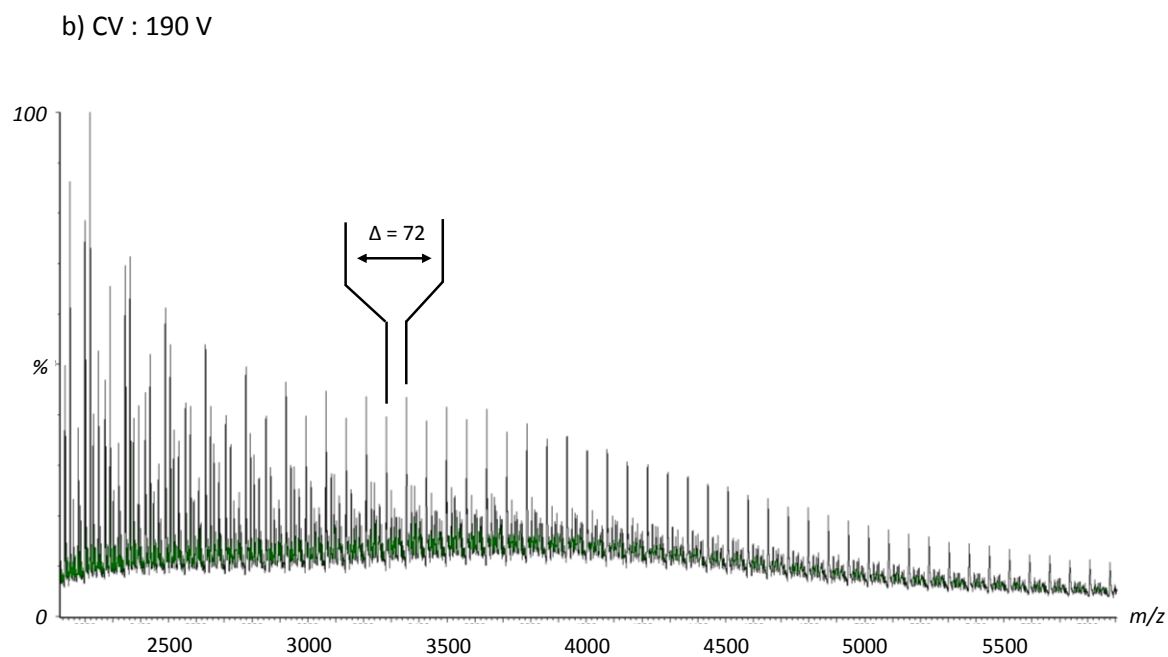
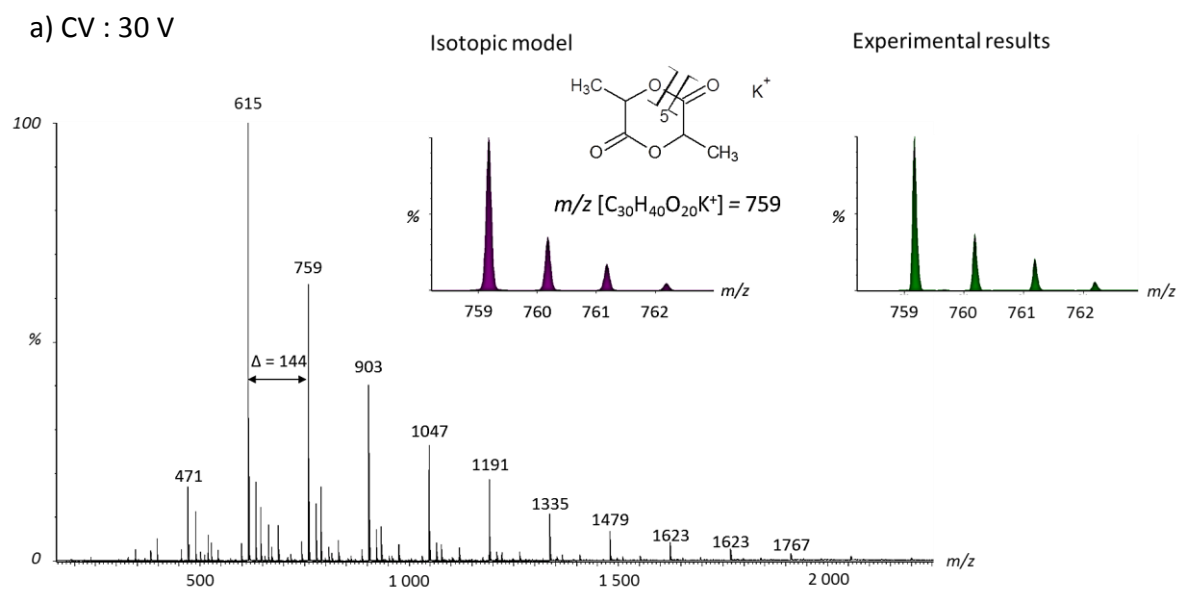


Figure SI2.

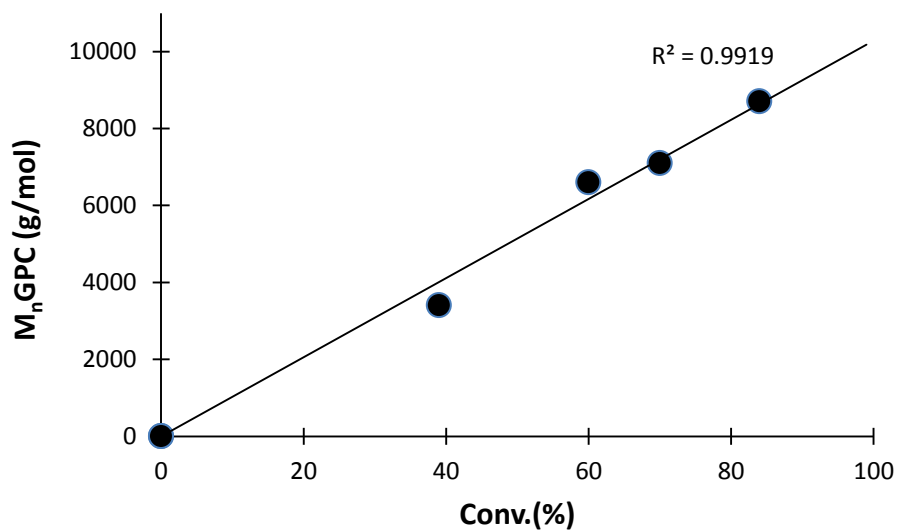


Figure SI3. (Semilog. vs time plots associated to L-LA polymerizations initiated from Imidazole/BzOH (●) and (1)/BzOH (◆) systems)

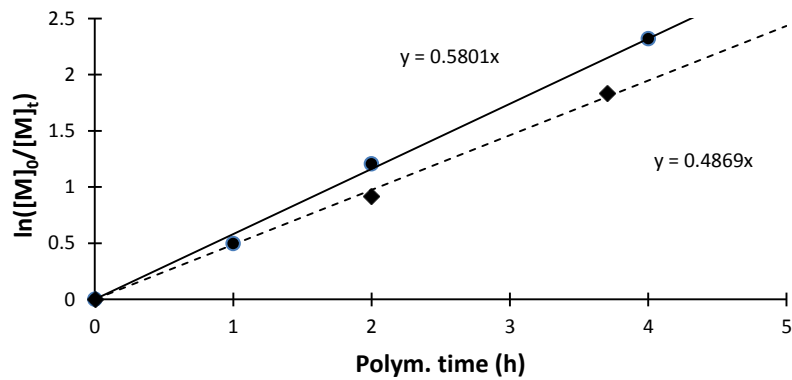


Figure SI4.

