Supporting Information for

Ammonium Betaines: Efficient Ionic Nucleophilic Catalysts for the Ring-Opening Polymerization of L-lactide and Cyclic Carbonates

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    A – Experimental section

    B – Experimental data

    C – References

A − Experimental section

Materials

1-Pyrenemethanol, 1,4-butanediol, THF and $CHCl_3$ were purchased from Aldrich and dried in appropriate conditions. L-LA (Galactic, Belgium) was recrystallized twice from dried toluene and stored in a glove box. α-Methyl, ω-hydroxyl poly(ethylene oxide) (PEO) (Fluka, Mw ~ 5000 g/mol) was dried by three azeotropic distillations of toluene, then dried at 60°C in vacuum overnight and stored in a glove box. ε-Caprolactone was dried 48 hours on CaH_2 before distillation under vacuum. TMC (Pugh&Co) was recrystallized twice from dried toluene and TMC-Bn was synthesized according to the procedure described in the literature[1] and recrytallized twice from dried toluene.

Analytical techniques

^{13}C and ^{1}H NMR spectra were recorded using a Bruker AMX-500 apparatus at r.t. in $CDCl_3$ (4 mg / 0.6 mL). 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 $J.m^{-2}$ 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*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was prepared as 10 mg/mL solution in acetone. The matrix solutions (1 μL) were applied to a stainless steel target and air dried. Polymer samples were dissolved in dichloromethane to obtain 1 mg/mL solutions. 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air dried. Finally, 1 μL of a solution of NaI (2 $mg.mL^{-1}$ 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 1,000 to 10,000 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. Number-average molecular weights and molecular weight distributions ($Đ = M_w/M_n$) values of polymers determined by Size Exclusion Chromatography (SEC) were based on experiments conducted in chloroform at 35 C at a flow rate of 1 mL/min, using an isocratic pump (VE 1122, Viscotek) a set of two PLgel 5 mm MIXED-C ultra high efficiency column and a Shodex SE 61 differential refractive index detector. A volume of 100 μL of sample solution in chloroform (concentration 0.3% w/v) was injected. Polystyrene standards (Polymer Laboratories) with narrow molecular weight distributions were used to generate a calibration curve. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q200 apparatus from T.A. Instruments under nitrogen flow (heating rate: 10°C/min). FT-IR analyses were performed in a solid state by using a Fourier Transform Infra-Red Bruker Tensor 27 Spectrometer (6000–600 cm^{-1}) equipped with a Miracle micro-ATR from Pike.

Procedure for the syntheses of *m*-BE, *o*-BE and *p*-BE. Syntheses were carried out using procedures described in the literature.[2]

Procedures for the ring-opening polymerization

Typical procedure of L-LA polymerization using 1-pyrenemethanol as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with L-LA (0.2 g, $1.39.10^{-3}$ mol), *m*-BE (4.2 mg, $2.78.10^{-5}$ mol), 1-pyrenemethanol (6.4 mg, $2.78.10^{-5}$ mol) and CHCl$_3$ (0.55 ml). The vial is maintained under agitation at room temperature for 1 hour. Finally the polymer is precipitated in methanol.

^{1}H NMR (CDCl$_3$) δ (ppm): 8.4-8.0 (m, aromatic protons of pyrene), 5.9 (dd, pyrene-C*H$_2$*-O), 5.3-5.1 (m, -O-C*H*CH$_3$-CO-), 4.35 (q, -C*H*CH$_3$-OH), 1.6-1.5 (d, -O-CHC*H$_3$*-CO-).

$M_{n,SEC}$ = 12,300 g/mol, Đ = 1.04, yield = 99%.

Typical procedure of TMC polymerization using 1-pyrenemethanol as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with TMC (0.178 g, $1.75.10^{-3}$ mol), *m*-BE (2.7 mg, $1.75.10^{-5}$ mol), 1-pyrenemethanol (4.2 mg, $1.75.10^{-5}$ mol) and CHCl$_3$ (0.8 ml). The vial is maintained under agitation at room temperature for 24 hours. Finally the polymer is precipitated in methanol.

$M_{n,SEC}$ = 12,800 g/mol, Đ = 1.04, yield = 97%.

Typical procedure of TMC-Bn polymerization using 1-pyrenemethanol as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with TMC-Bn (0.437 g, $1.75.10^{-3}$ mol), *m*-BE (13 mg, $8.75.10^{-5}$ mol), 1-pyrenemethanol (4.5 mg, $1.75.10^{-5}$ mol) and CHCl$_3$ (0.5 ml). The vial is maintained under agitation at room temperature for 144 hours.

$M_{n,SEC}$ = 600 g/mol, Đ = 1.2.

Typical procedure of ε-CL polymerization using 1-pyrenemethanol as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with ε-CL (0.2 g, $1.75.10^{-3}$ mol), *m*-BE (27 mg, $17.5.10^{-5}$ mol), 1-pyrenemethanol (8.4 mg, $3.5.10^{-5}$ mol) and CHCl$_3$ (0.75 ml). The vial is maintained under agitation at room temperature for 144 hours. Finally the polymer is precipitated in heptane.

$M_{n,SEC}$ = 600 g/mol, Đ = 1.22

Typical procedure of L-LA polymerization using 1,4-butanediol as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with L-LA (0.2 g, $1.39.10^{-3}$ mol), *m*-BE (2.1 mg, $1.39.10^{-5}$ mol), 1,4-butanediol (1.2 mg, $1.39.10^{-5}$ mol) and CHCl$_3$ (0.48 ml). The vial is maintained under agitation at room temperature for 3 hours. Finally the polymer is precipitated in methanol.

$M_{n,SEC}$ = 19,100 g/mol, Đ = 1.16, yield = 99%.

Typical procedure of L-LA polymerization using PEO-OH as initiator and *m*-BE as catalyst. In a glove box, a dried vial equipped with a stirrer is charged with L-LA (0.2 g, $1.39.10^{-3}$ mol), *m*-BE (2.1 mg, $1.39.10^{-5}$ mol), PEO-OH (5,000 g.mol^{-1}, Đ = 1.03, 70 mg, $1.39.10^{-5}$ mol) and CHCl$_3$ (0.48 ml). The vial is maintained under agitation at room temperature for 3 hours. Finally the polymer is

precipitated in methanol.

^{1}H NMR (CDCl$_3$) δ (ppm): 8.4-8.0 (m, aromatic protons of pyrene), 5.9 (dd, pyrene-CH_2-O), 5.3-5.1 (m, -O-CHCH$_3$-CO-, P(L-LA)), 4.3 (q, -CHCH$_3$-OH, P(L-LA)), 3.6 (t, -O-CH_2-CH_2-O- PEO), 3.4 (s, -CH$_2$-O-CH_3 PEO) 1.6-1.5 (d, -O-CHCH_3-CO-, P(L-LA)).

$M_{n,SEC}$ = 26,800 g/mol, Đ = 1.06, yield = 99%.

Methodology for the molecular modelling study. Molecular mechanics (MM) and molecular dynamics (MD) simulations have been performed within the Materials Studio 6.0 package[3] to get insights into the polymerization mechanism. All calculations are based on the Dreiding force field[4] with ESP charges taken out from MP2/6-31g(d,p) optimized isolated compounds. To reduce computational efforts, methanol has been used as the initiator and put in close contact with the oxygen atom of m-BE to allow for hydrogen bonding. In addition, three different starting geometries have been considered for the L-LA monomer: (i) with one carbonyl group pointing to the positively charged trimethylammonium group; (ii) on top of the betaine molecule; and (iii) in close contact with the carbon atom in the para position of the nitrogen atom of BE. After an initial optimization, these systems have been introduced in a simulation box (30 Å x 30 Å x 30 Å) containing chloroform molecules (density = 1.48 g/cm³). In all simulations, the box has been replicated using periodic boundary conditions to generate an infinite system. 5 ns-long equilibration MD runs (NVT, T = 298 K) have been performed on each system while keeping the position of m-BE fixed as well as the distances between the hydrogen of the alcohol group and the oxygen of m-BE and between the oxygen atom of the carbonyl group of L-LA and the nitrogen atom of m-BE. After this equilibration stage, all constraints have been removed and the geometries of the systems optimized. The latter have then been used as starting point of a second 5 ns-long MD (NVT, T = 298K) from which snapshots of the systems have been saved every 5 ps for further analysis.

B – Experimental data

(a)

(b)
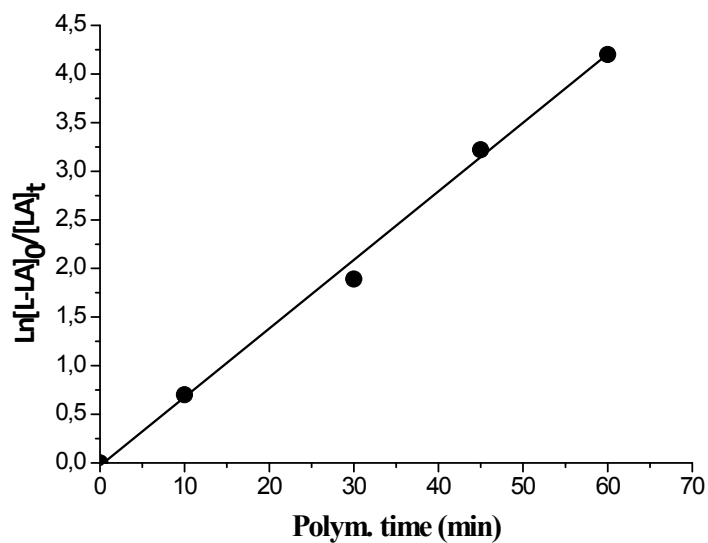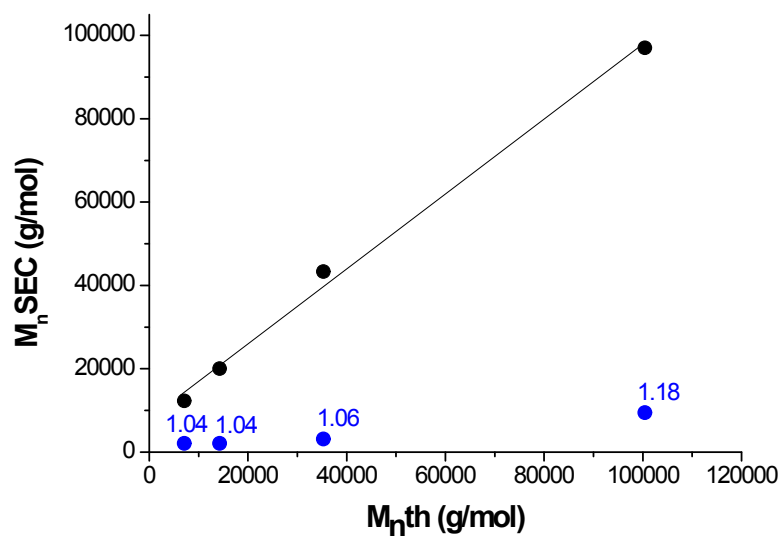
Figure SI1. (a) Ln($[M]_0/[M]$) *versus* polymerization time calculated by SEC in CHCl$_3$ experiment for P(L-LA) at $M_{n,th}$ = 7,430 g.mol^{-1}. (b) M_nSEC *versus* M_nth and dispersity obtained by means of SEC for P(L-LA) catalyzed by m-BE.
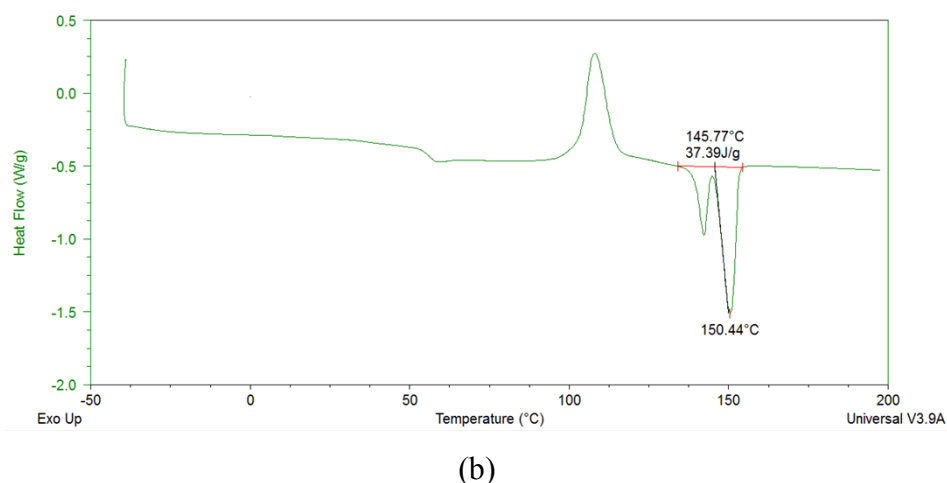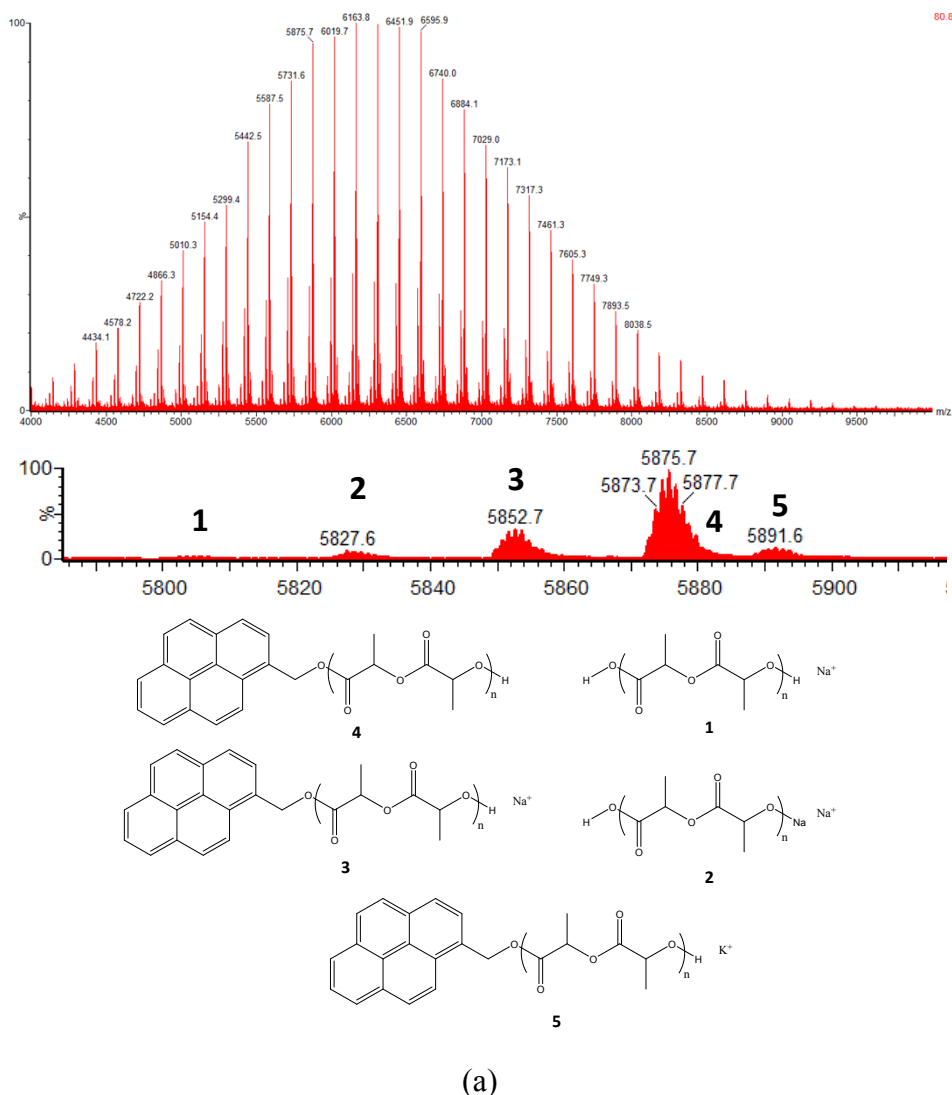
(a)

(b)

Figure SI2. (a) MALDI-ToF spectrum of P(L-LA) (Table 1, entry 1) (top) initiated by 1-pyrenemethanol, catalyzed by *m*-BE. Zoom of the MALDI-ToF spectrum with the different structures of P(L-LA) (bottom). (b) DSC thermogram of P(L-LA) (Table 1, entry 1) obtained in the presence of *m*-BE in CHCl₃ and as initiated by 1-pyrenemethanol. The analysis reveals the presence of two melting temperatures potentially attributed to polymorphic P(L-LA)s (α- and α'-form crystals) possibly formed during the DSC process.[5]
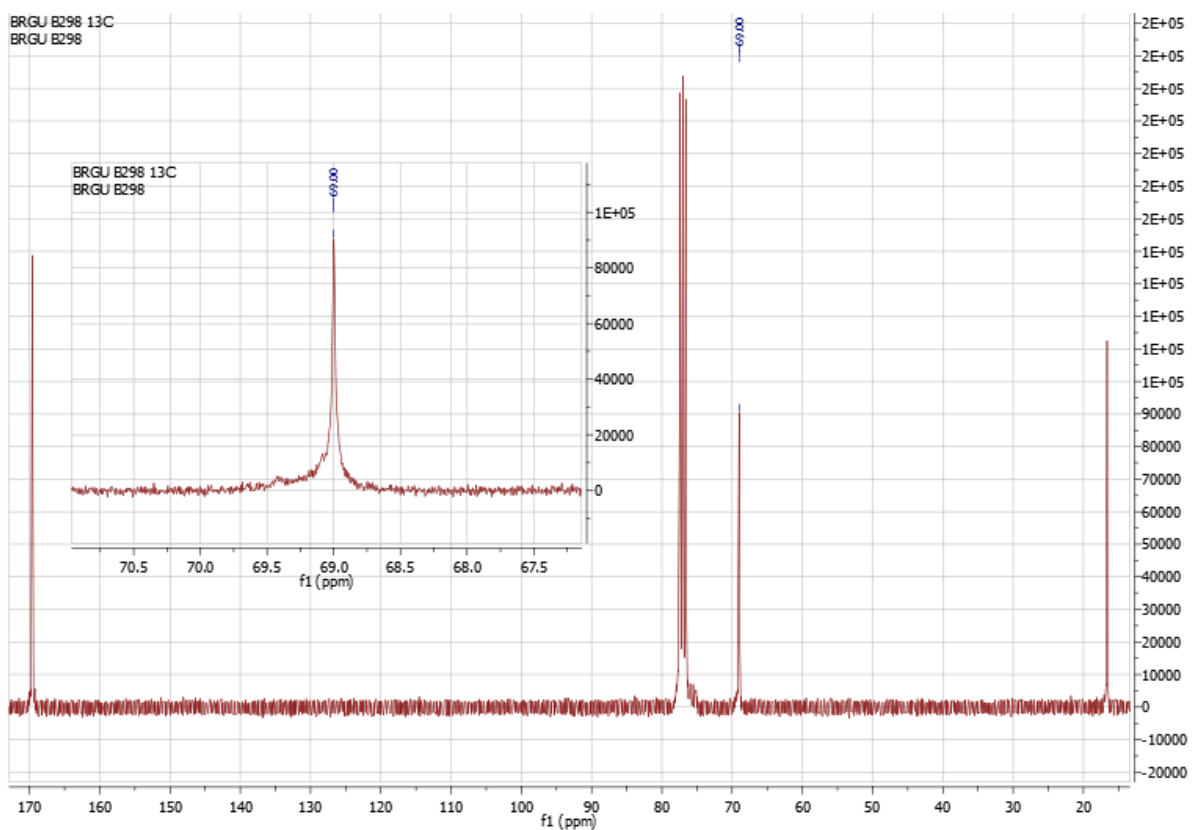
Figure SI3. ^{13}C NMR and zoom of P(L-LA) in CDCl$_3$ obtained in the presence of *m*-BE in CHCl$_3$ and as initiated by 1-pyrenemethanol (entry 2, Table 1).
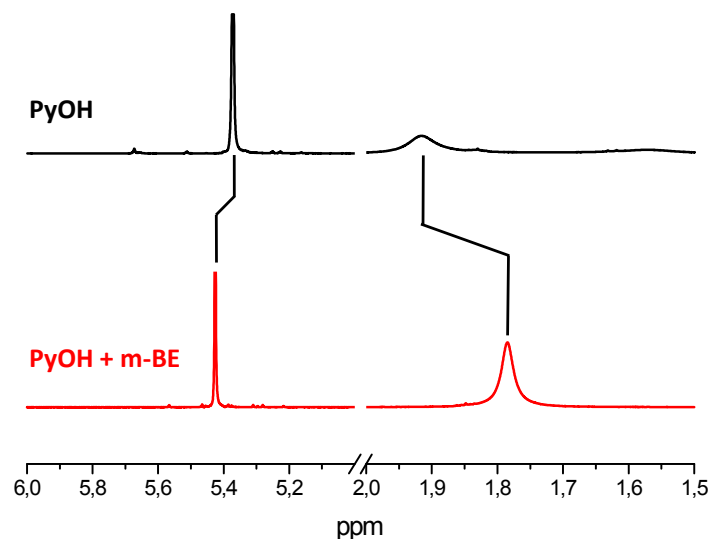
Figure SI4. ^{1}H NMR spectra (CDCl$_3$, 21°C, 500 MHz) of 1-PyOH and a mixture of 1-PyOH and m-BE.
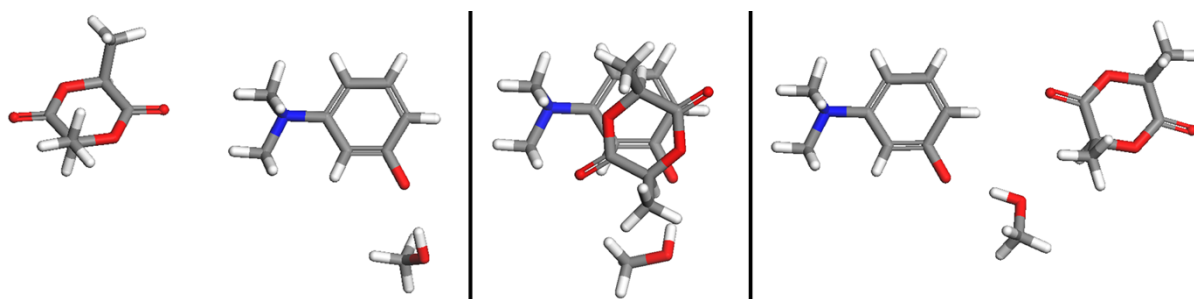

Figure SI5. Representation of the three different starting assemblies of methanol, L-LA, and m-BE considered in the molecular mechanics and dynamics simulations. In all cases, the hydrogen atom of the methanol molecule is close to the oxygen atom of the betaine to allow for hydrogen bonding. In contrast, a carbonyl group of L-LA is either pointing to the nitrogen atom (left) or LLA is located on top of m-BE (middle) or in close contact with the carbon atom in para position of the nitrogen atom.
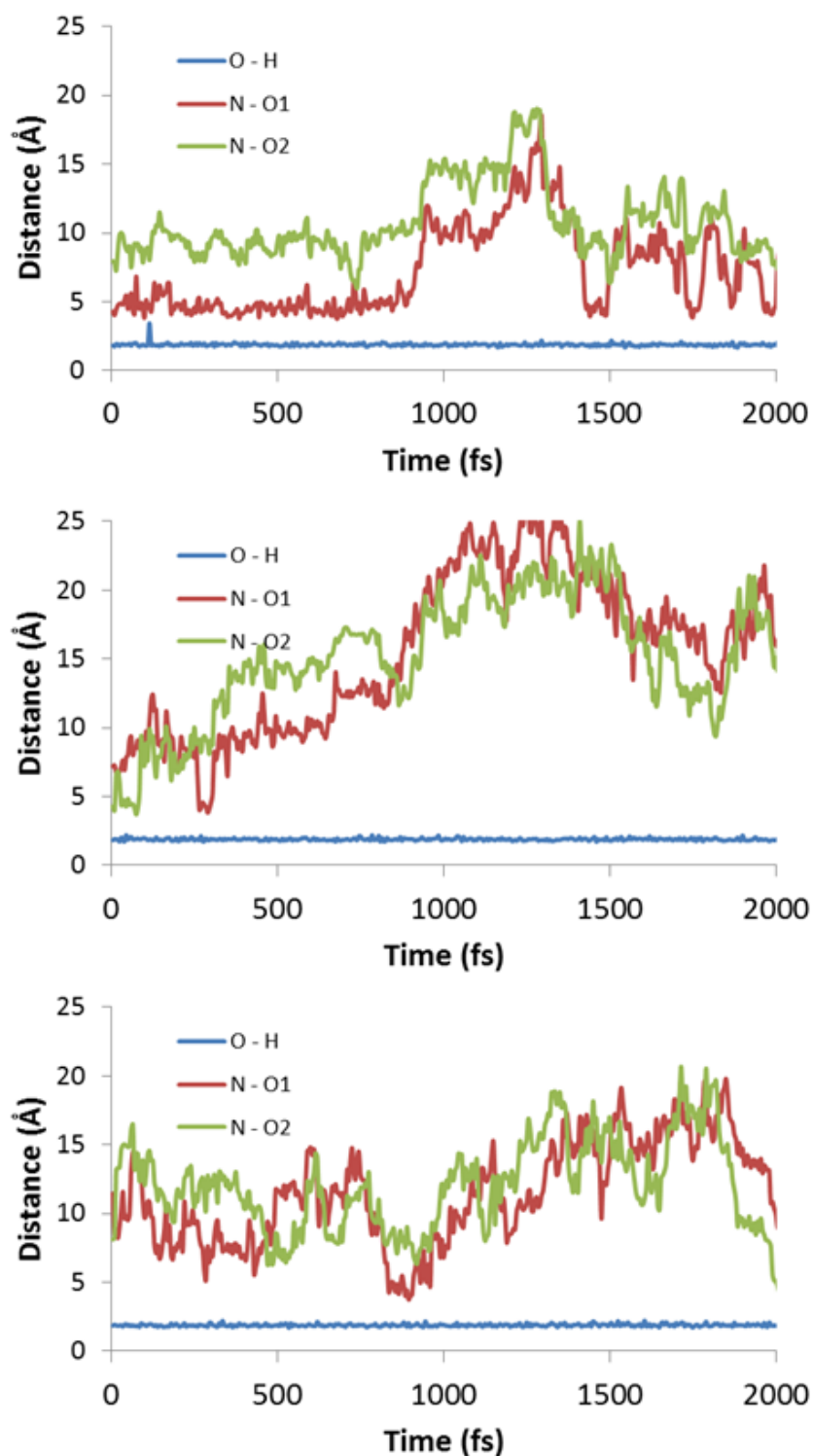
Figure SI6. Evolution of the distances between the oxygen atom of the betaine molecule and the hydrogen atom of the alcohol group of methanol (blue lines) and between the nitrogen atom of the betaine and the two oxygen atoms of the carbonyl groups of L-LA (red and blue lines) along the snapshots recorded every 5 ps during the first 2 ns of a 5 ns-long NVT (T= RT) molecular dynamics performed on a 30 Å x 30 Å x 30 Å unit cell containing m-BE, methanol, L-LA and chloroform molecules.
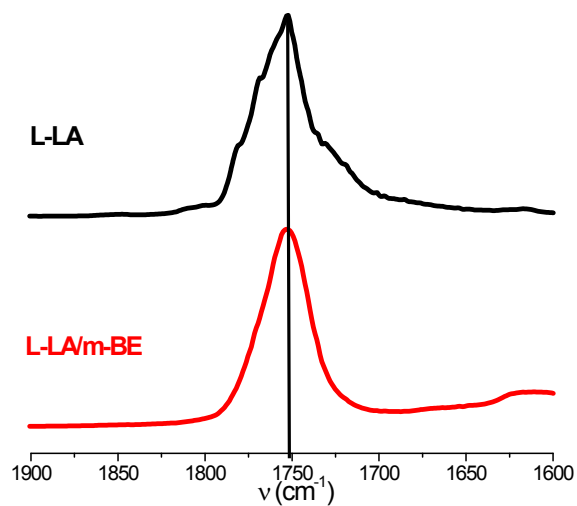
Figure SI7. Zoom of FT-IR spectra of L-LA and mixture of L-LA and m-BE.
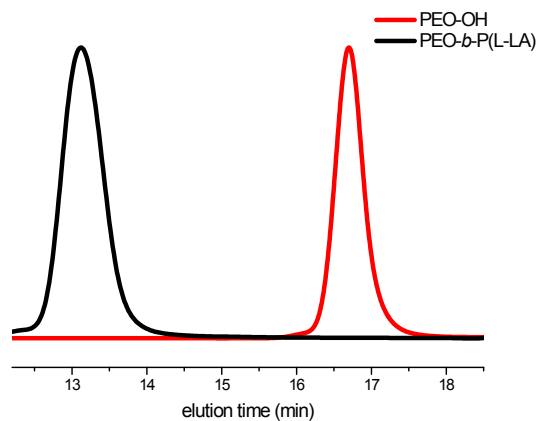

Figure SI8. SEC profiles of PEO-*b*-P(L-LA) (black line, on the left) diblock copolymer and PEO-OH (red line, on the right) (SEC in $CHCl_3$, PS standards, 1 ml.min^{-1}, T = 30°C).
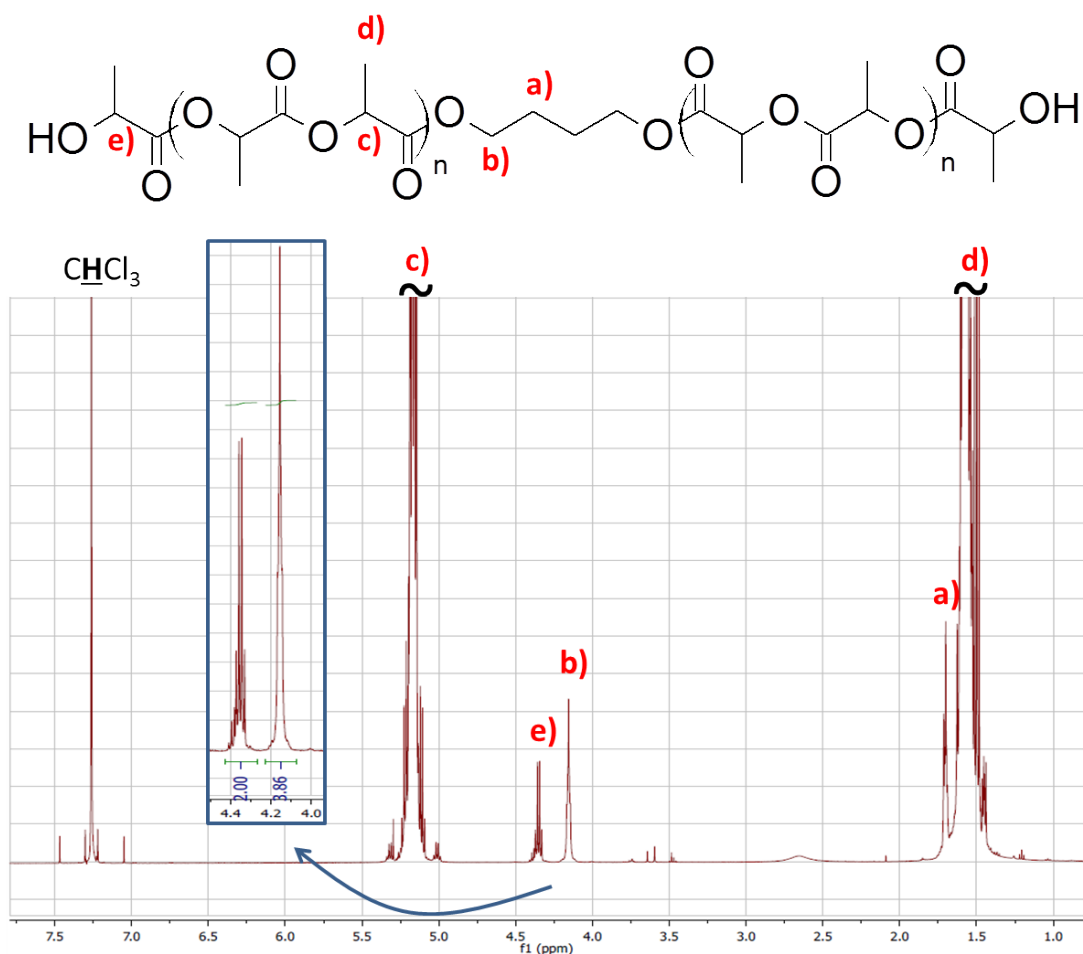
Figure SI9. ^{1}H NMR spectrum (CDCl$_3$, 21°C, 500 MHz) of a P(L-LA) obtained from L-LA ROP initiated from 1,4-butanediol (Table 1, entry 10)

C – References

(1)   Coulembier, O.; Moins, S. b.; Dubois, P. *Macromolecules* 2011, *44*, 7493.

(2)   Tsutsumi, Y.; Yamakawa, K.; Yoshida, M.; Ema, T.; Sakai, T. *Organic Letters* 2010, *12*, 5728.

(3)   *Materials Studio Modelling v6.0.0 Accelrys Software Inc, San Diego, CA* 2011.

(4)   Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *The Journal of Physical Chemistry* 1990, *94*, 8897.

(5)   Pan, P.; Kai, W.; Zhu, B.; Dong, T.; Inoue, Y. *Macromolecules* **2007**, *40*, 6898-6905.