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SUPPORTING INFORMATION

Accelerating Effect of Crown Ethers on the Lactide Polymerization catalysed by Potassium Acetate

Sébastien Moins,[a] Céline Henoumont,[b] Quentin De Roover,[a,c] Sophie Laurent,[b,d] Julien De Winter[c] and Olivier Coulembier*[a]

[a] *Center of innovation and Research in Materials and Polymers (CIRMAP), Laboratory of Polymeric and Composites Materials, University of Mons, 23 Place du Parc, B-7000, Mons, Belgium.*

[b] *General, Organic and Biomedical Chemistry; NMR and Molecular Imaging Laboratory, University of Mons, Place du Parc 20, 7000 Mons, Belgium.*

[c] *Organic Synthesis and Mass Spectrometry Laboratory (S^2MOS,) University of Mons,23 Place du Parc, B-7000, Mons, Belgium.*

[d] *Center for Microscopy and Molecular Imaging (CMMI), 8 Rue Adrienne Boland, 6041 Gosselies, Belgium.*

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Materials

L-Lactide (L-LA) (Corbionpurac) was recrystallized three times from toluene and dried under vacuum. Benzyl alcohol (BnOH) was dried over CaH_2 for 48 hours prior to its distillation under reduced pressure. Potassium acetate (≥ 99%, VWR) and caesium acetate (99.9%, VWR) were dried by heating at 100 °C under vacuum for 48 hours. 15-Crown ether-5 (15-c-5, 98%, Acros) was dried by heating at 80 °C under vacuum for 24 hours. 18-Crown ether-6 (18-c-6, 99%, Acros) was first pre-dried by heating at 80 °C under vacuum for 24 hours, then dried by three azeotropic distillations of tetrahydrofurane (THF). Compounds were all stored in a glove box ($O_2 \leq 6$ ppm, $H_2O \leq 1$ ppm). THF and toluene solvents were dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

Characterizations

^{1}H NMR-spectra were recorded using a Bruker AVANCEII 500 apparatus at r.t. in $CDCl_3$ (10mg/0.6mL) or in THF-d_8 (10mg/0.35mL). Temperature-depending experiments were performed between 25 °C and 70 °C thanks to a BVT-3200 unit, with a 5 min stabilizing time between each temperature. NMR DOSY experiments were recorded on an AVANCEII 500 spectrometer equipped with a superconducting magnet of 11.75 T (Bruker, Karlsruhe, Germany) at 27 °C. Bipolar gradient pulses with two spoil gradients were used to measure the diffusion coefficients (BPP-LED pulse sequence). The value of the gradient pulse length δ was 2 ms, while the value of the diffusion time Δ was set to 200 ms or 250 ms depending on the polymer size. The pulse gradients were incremented in 16 steps from 2% to 95% of the maximum gradient strength (53.5 G/cm) in a linear ramp and the temperature was set at 27 °C. The DOSY spectra were obtained from the TOPSPIN 2.1 software and diffusion curves were extracted on 3 different peaks of each studied structures/complexes to measure precisely their respective diffusion coefficients. In each case, the mono-exponential diffusion curves were fitted with the well-known equation 1 to extract the diffusion coefficients. The averaged diffusion coefficient was then calculated for the polymer and for TBD based on these 3 measurements.

$$I = I_o \exp[-\gamma^2 g^2 D \delta^2 (\Delta - (\delta/3) - (\tau/2))] \qquad \text{(equation 1)}$$

where I_0 is the intensity at 0% gradient, γ the gyromagnetic ratio, g the gradient strength, D the diffusion coefficient, δ the gradient pulse length, Δ the diffusion time and τ the interpulse spacing in the BPP-LED pulse sequence.

Size exclusion chromatography (SEC) was performed in THF at 35 °C using a Triple Detection Polymer Laboratories liquid chromatograph equipped with a refractive index (ERMA 7517), a UV detector (254 nm), a capillary viscometry, a light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV / RALS) and an automatic injector (Polymer Laboratories GPC-RI/UV) and four columns : a PL gel 10 µm guard column and three PL gel Mixed-B 10 µm columns (linear columns for separation of MwPS ranging from 500 to 10^6 daltons). The M_n values that were obtained by SEC are multiplied by a 0.58 correlation factor for PLA analysed with PS standards, corresponding to the Mark-Houwink equation.

Positive-ion MALDI-Mass Spectrometry (MALDI-MS) experiments were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65 µJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10,000. All the samples were analyzed using trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. That matrix was prepared as 40 mg.mL^{-1} solution in $CHCl_3$. The matrix solution (1 µL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in THF to obtain 1 mg.mL^{-1} solutions. Therefore, 1 µL of this solution was applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass all the ions of the distribution, and they were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

General Polymerization Procedure

In a glove box, a dried vial equipped by a stirrer is charged with KOAc (2.6 mg, 2.65 x 10^{-5} mol) and 18-c-6 (7.3 mg, 2.76 x 10^{-5} mol) in 0.4 g of dry THF. After 5 min, L-lactide (0.32 g, 2.2 x 10^{-3} mol) and 2 g of dry THF are added. Polymerization is then initiated by adding 6 µL of BnOH (5.55 x 10^{-5} mol). The sealed vial is then maintained under agitation and several withdrawals are realized to follow the kinetics by SEC.

Kinetics Results

That part gathers non colorized Excel plots with linear regression equations and associated R² values.

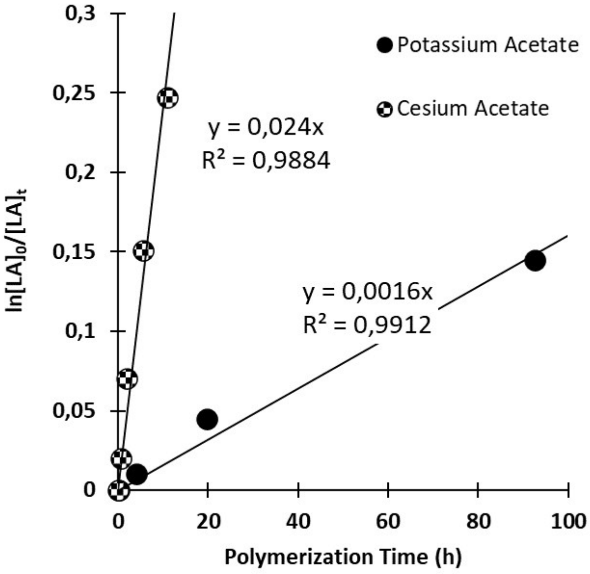

Figure S1 [article Fig.2]. Semilogarithmic plots of L-LA polymerizations initiated with BnOH and catalysed with KOAc and CsOAc. Conditions of polymerizations: $[\text{L-LA}]_0/[\text{BnOH}]_0/[\text{cat.}]_0$ = 40/1/0.5, $[\text{L-LA}]_0$ = 1M, THF solvent, 21 °C.

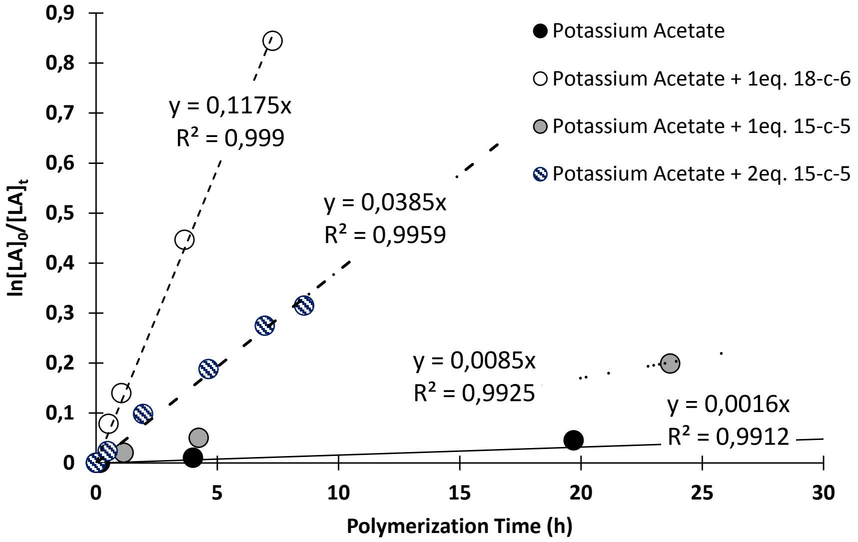

Figure S2 [article Fig.3]. Semilogarithmic plots of L-LA polymerizations initiated with BnOH and catalysed with KOAc, $[KOAc]_0/[18\text{-}c\text{-}6]_0$ = 1 and $[KOAc]_0/[15\text{-}c\text{-}5]_0$ = 1 and 0.5. Conditions of polymerizations: $[L\text{-}LA]_0/[BnOH]_0/[cat.]_0$ = 40/1/0.5, $[L\text{-}LA]_0$ = 1M, THF solvent, 21 °C.

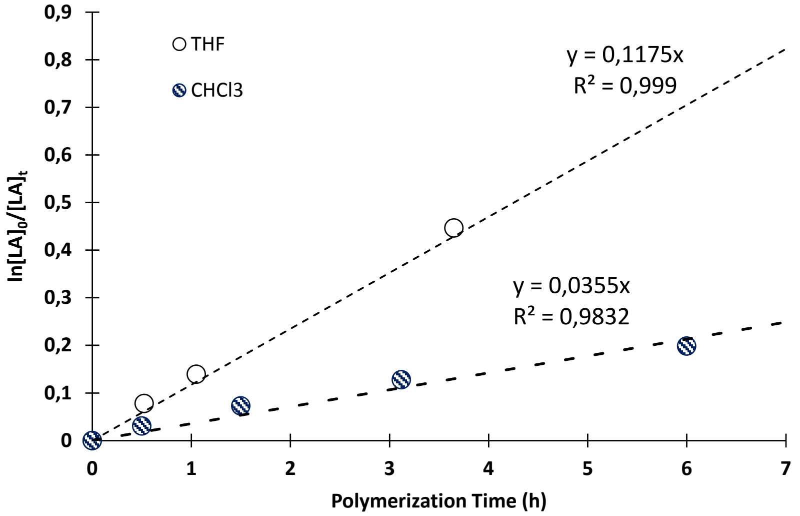

Figure S3 [article Fig.5 left]. Semilogarithmic plots of L-LA polymerizations initiated with BnOH and catalysed with $[KOAc]_0/[18\text{-}c\text{-}6]_0$ = 1 in THF and $CHCl_3$. Conditions of polymerizations: $[L\text{-}LA]_0/[BnOH]_0/[KOAc]_0/[18\text{-}c\text{-}6]_0$ = 40/1/0.5/0.5, $[L\text{-}LA]_0$ = 1M, 21 °C.

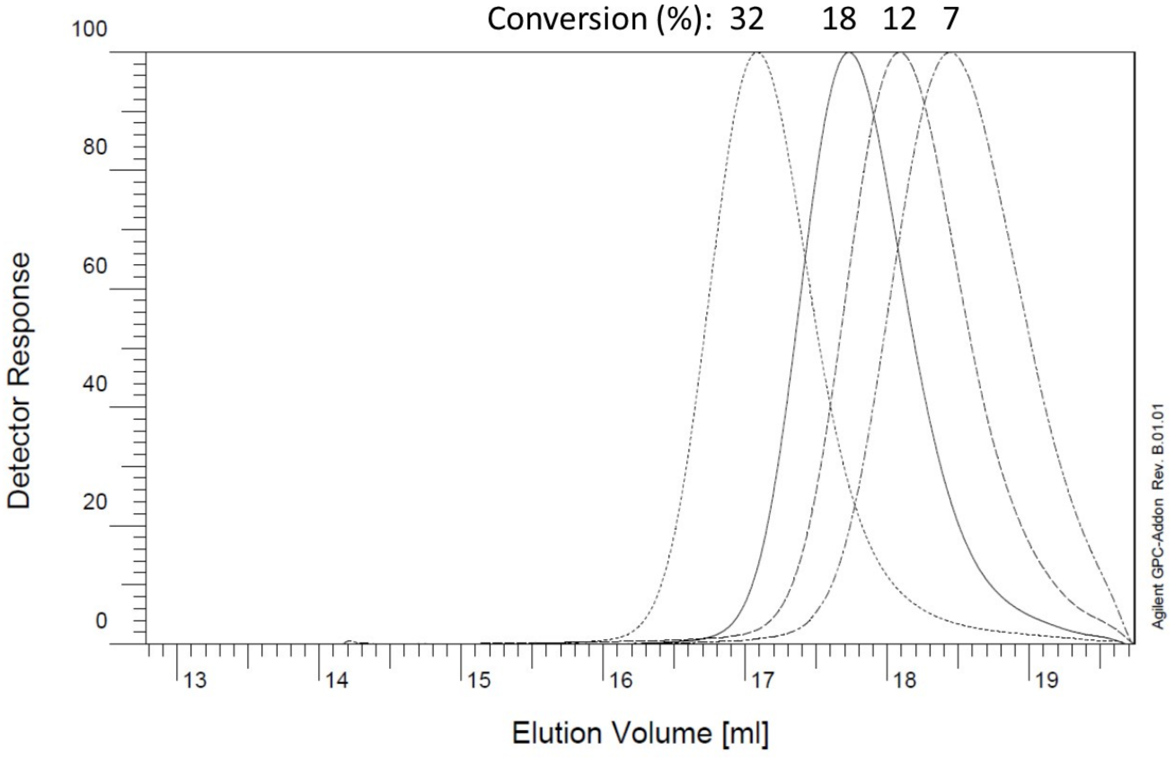

Figure S4. SEC traces recorded during the KOAc/18-c-6 complex-catalysed ROP of L-LA in $CHCl_3$. Conditions of polymerizations: $[L\text{-}LA]_0/[BnOH]_0/[KOAc]_0/[18\text{-}c\text{-}6]_0 = 40/1/0.5/0.5$, $[L\text{-}LA]_0 = 1M$, 21 °C.

MALDI Results

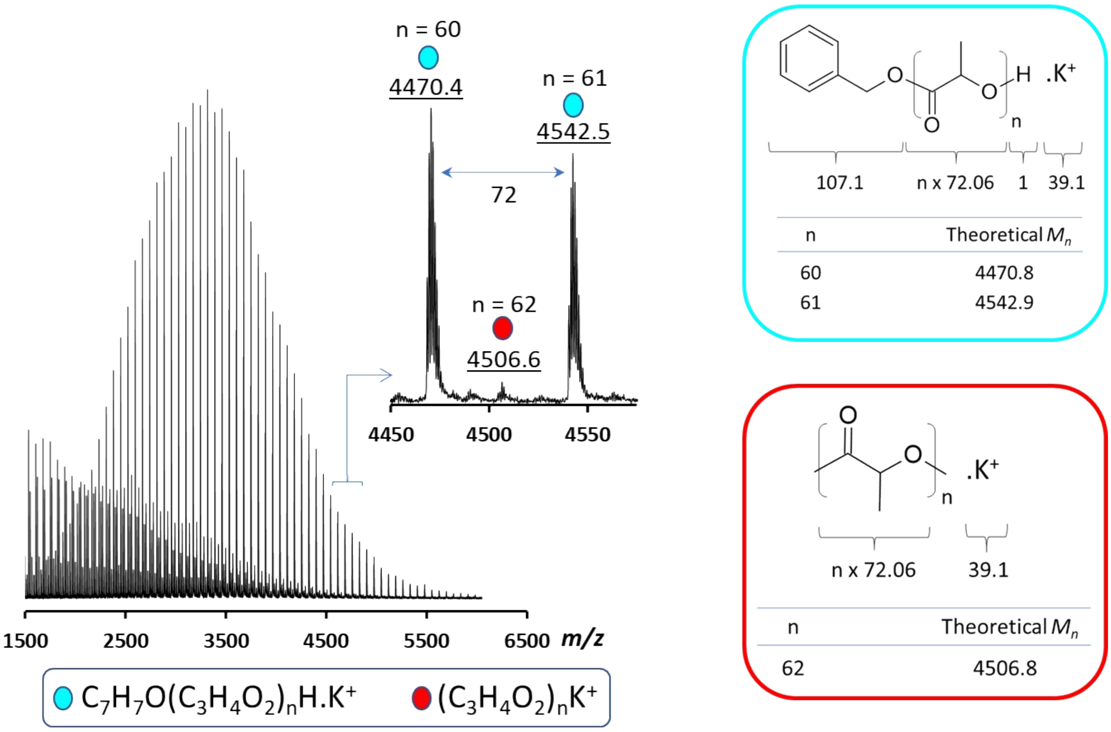

Figure S5 [article Fig.6]. Comparison of theoretical and experimental PLA molar masses determined by MALDI-ToF analysis.

DOSY Results

Diffusion coefficients of pristine reagents and various mixtures are gathered in the following table:

	Diffusion coefficient (10^{-9} m²/s) of			
Reagent	**L-LA**	**BnOH**	**KOAc**	**18-c-6**
L-LA	1.79			
BnOH		2.23		
KOAc			3.96	
18-c-6				1.52
BnOH + KOAc		2.26	3.47	
BnOH + KOAc + 18-c-6		1.24	1.32	0.96
KOAc + 18-c-6			0.83	0.81
L-LA + 18-c-6	1.66			1.22
L-LA + KOAc + 18-c-6	1.29		2.04	1.01

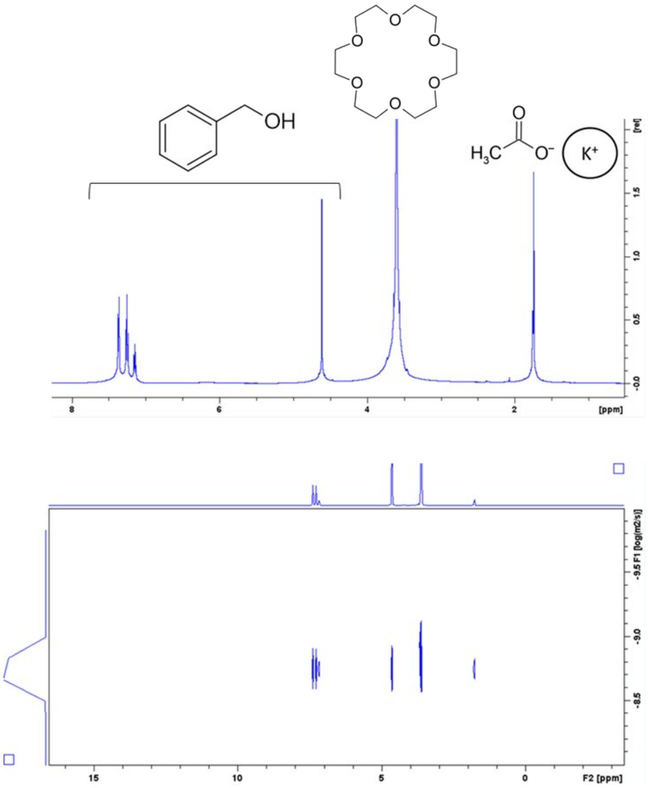

Figure S6. DOSY spectrum of a mixture of benzyl alcohol, 18-c-6 and potassium acetate. Solvent: THF-d_8, temperature: 27 °C.

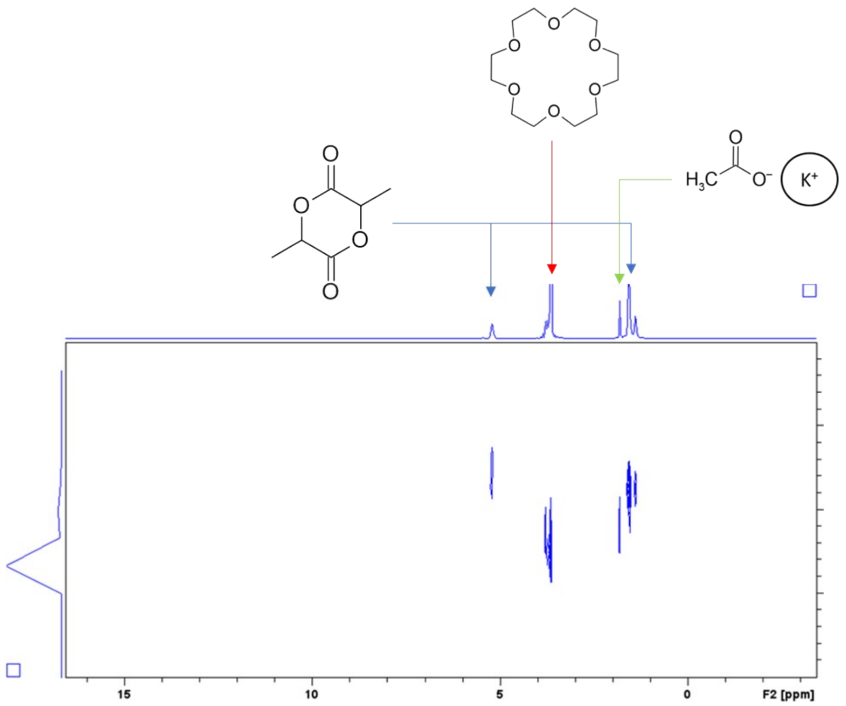

Figure S7. DOSY spectrum of a mixture of lactide, 18-c-6 and potassium acetate. Solvent: THF-d_8, temperature: 27 °C.