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SUPPORTING INFORMATION

Photocontrolled Lactide ROP by Light-Regulated Release of Potassium Acetate from an Azobenzene-bridged Crown Ether

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Materials

The 4-nitrobenzo-15-crown-5 (99%) was purchased from Alfa Aesar. Pd/C (10% w/w) and $KMnO_4$ (>99%) were purchased from Sigma-Aldrich. $CuSO_4$•$5H_2O$ (>99%) was purchased from Acros Organic. CH_3OH (99.9%) was purchased from Fisher Scientific. CH_2Cl_2, purchased from Brenntag, is stabilized with ethanol and distilled in the laboratory.

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) was dried by heating at 100 °C under vacuum for 48 hours. Compounds were all stored in a glove box ($O_2 \leq 6$ ppm, $H_2O \leq 1$ ppm). THF solvent was dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

Characterizations

^1H 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/0.6mL).

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 analyzed with PS standards, corresponding to the Mark-Houwink equation.

UV irradiation treatments were conducted under a compact low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (±30 nm).

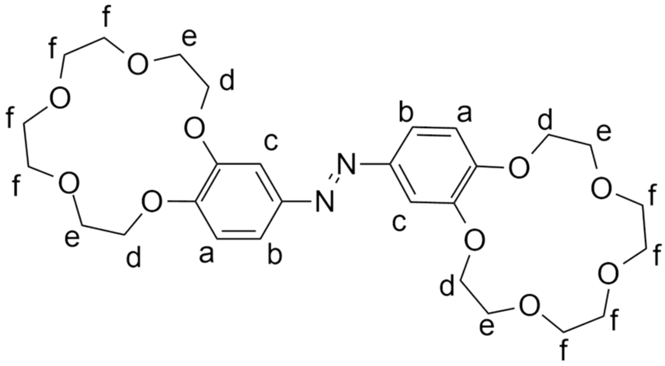
Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectra are recorded using a Waters QToF Premier mass spectrometer. A Nd-YAG laser of 355 nm with a maximum pulse energy of 65 µJ delivered to the sample at 50 Hz repeating rate is used. Time-of-flight mass analyses is performed in the reflection mode at a resolution of about 10 000. Trans-2-(3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) is used as the matrix and is prepared as a 40 mg/ml solution in chloroform. The matrix solution (1 µl) is applied to a stainless steel target and air-dried. Polymer samples are dissolved in chloroform to obtain 1 mg/mL solutions. 1 µl aliquots of these solutions are applied onto the target area (already bearing the matrix crystals) and air-dried.

Synthesis of the azobenzene-bis(15-crown-5 ether) (1)

Commercially available 4-nitrobenzo-15-crown-5 (1.00 g, 3.20 mmol) was reduced with H_2 and 10%, vs. mass of reagent, of Pd/C (10% w/w) in 20 mL of CH_3OH, under magnetic stirring, at room temperature for 48 hours to give 4-aminobenzo-15-crown-5. The reaction mixture was filtered through Celite® pad and washed with 120 mL of CH_3OH. The 4-aminobenzo-15-crown-5 is obtained by vacuum evaporation of CH_3OH as a red resin (76% yield).

The 4-aminobenzo-15-crown-5 (415 mg, 1.46 mmol) was dissolved in 20 mL of CH_2Cl_2 with $KMnO_4$ on $CuSO_4{\bullet}5H_2O$ (1.46 g). The heterogeneous mixture stirred at room temperature for 24 hours to give (**1**). Potassium permanganate supported on copper (II) sulfate pentahydrate was prepared by grinding equal amounts of $KMnO_4$ (0.73 g, 4.62 mmol, 3.16 equivalent) and $CuSO_4{\bullet}5H_2O$ (0.73 g, 2.92 mmol, 2 equivalent) in a mortar until it became homogenous. Then, the product was filtered through Celite® pad and the residue washed with 120 mL of CH_2Cl_2. (**1**) was obtained by vacuum evaporation of CH_2Cl_2 as a dark yellow powder (19% yield).

^{1}H-NMR Characterizations of (1)



(1)

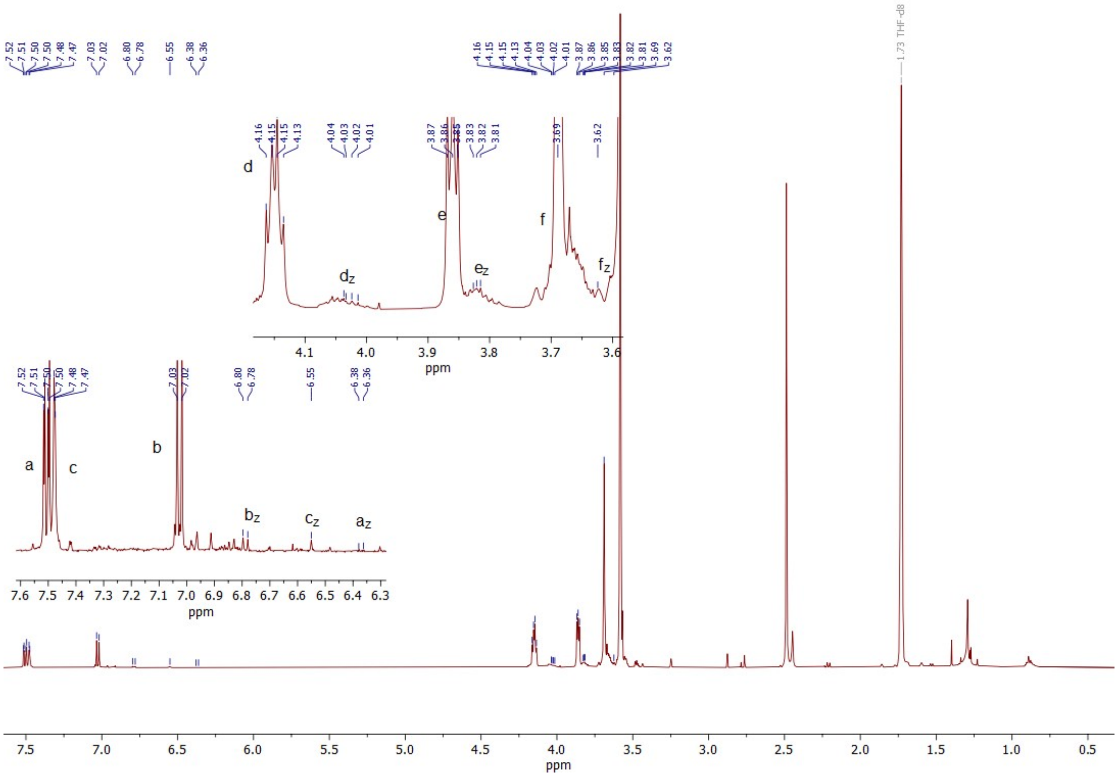


Figure S1. 500 MHz ^{1}H-NMR spectrum of **(1)** measured at 21 °C, under visible light, in THF-d_8. The ratio *E/Z* = 97/3.

^{1}H-NMR (500MHz, THF-d_8) δ = 7.51 (dd, 2H, Ha), 7.48 (br. s, 2H, Hc), 7.03 (d, 2H, Hb), 6.79 (d, Hb$_Z$), 6.55 (s, Hc$_Z$), 6.38 - 6.36 (m, Ha$_Z$), 4.15 (q, 8H, Hd), 4.04 - 4.01 (m, Hd$_Z$) 3.86 (t, 8H, He), 3.83 - 3.81 (m, He$_Z$), 3.69 (br. s, 16H, Hf), 3.62 (br. s, Hf$_Z$).

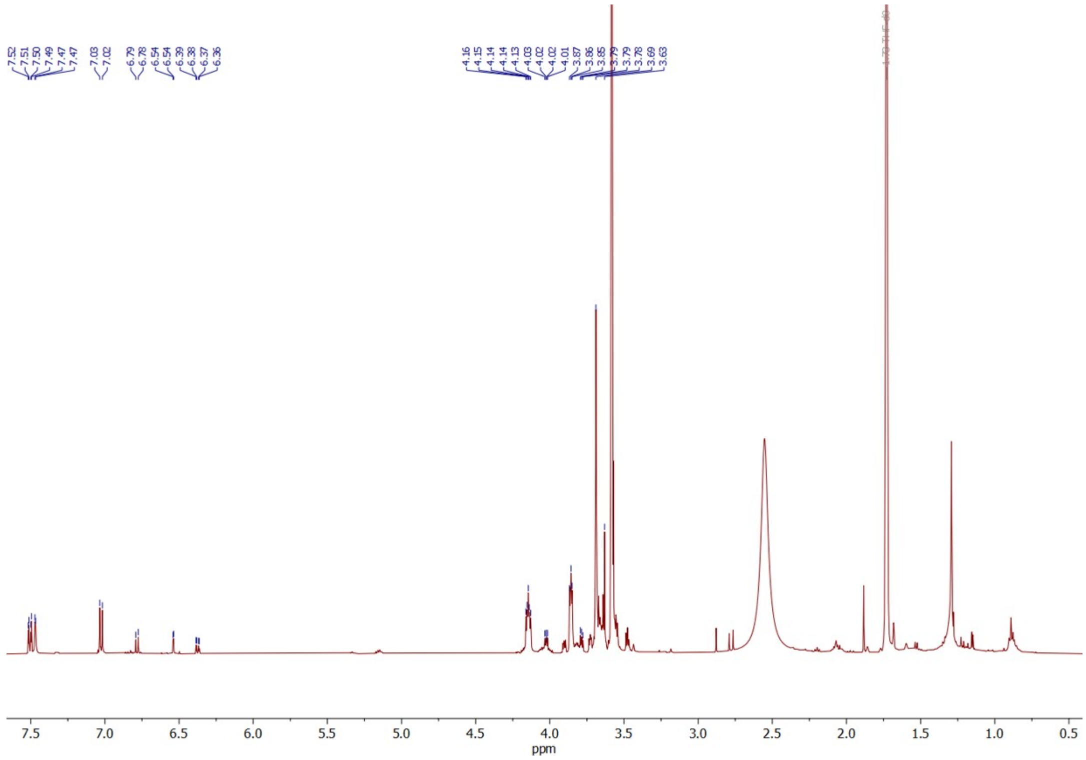


Figure S2. 500 MHz ^{1}H-NMR spectrum of **(1)** with 1 equivalent of potassium acetate measured at 21 °C, under visible light, in THF-d_8. The ratio *E/Z* = 81/19.

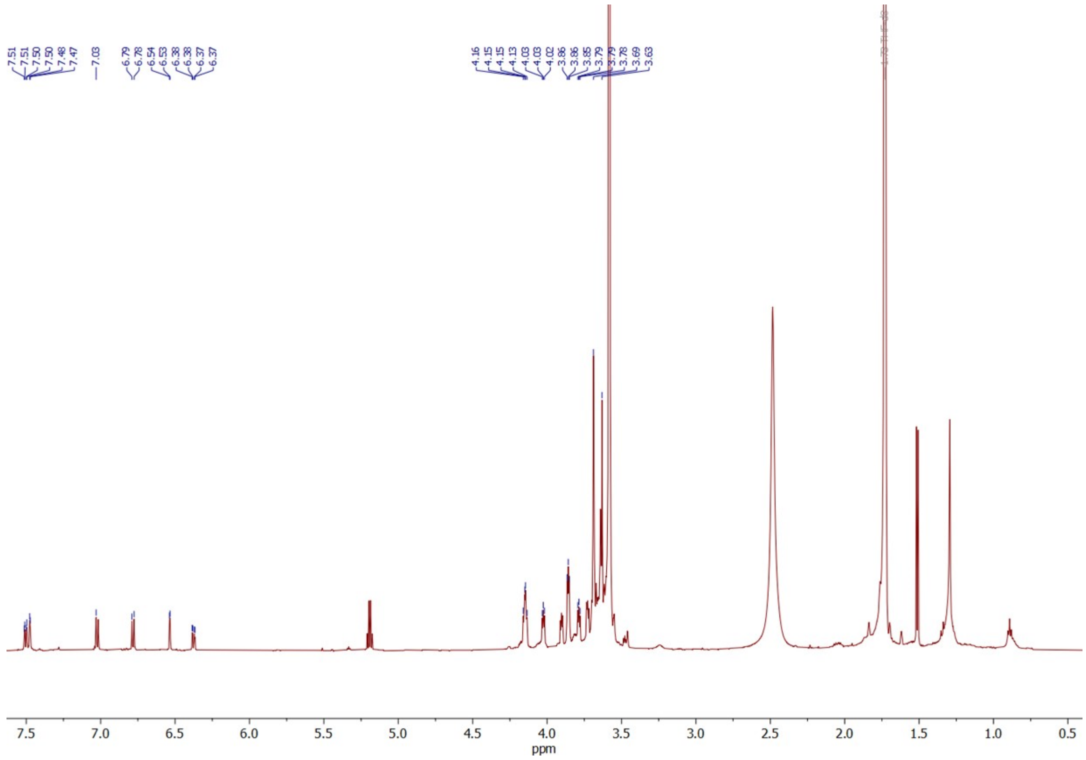


Figure S3. 500 MHz ^{1}H-NMR spectrum of **(1)** with 1 equivalent of potassium acetate measured at 21 °C, after 2 hours UV light irradiation, in THF-d_8. The ratio *E/Z* = 53/47.

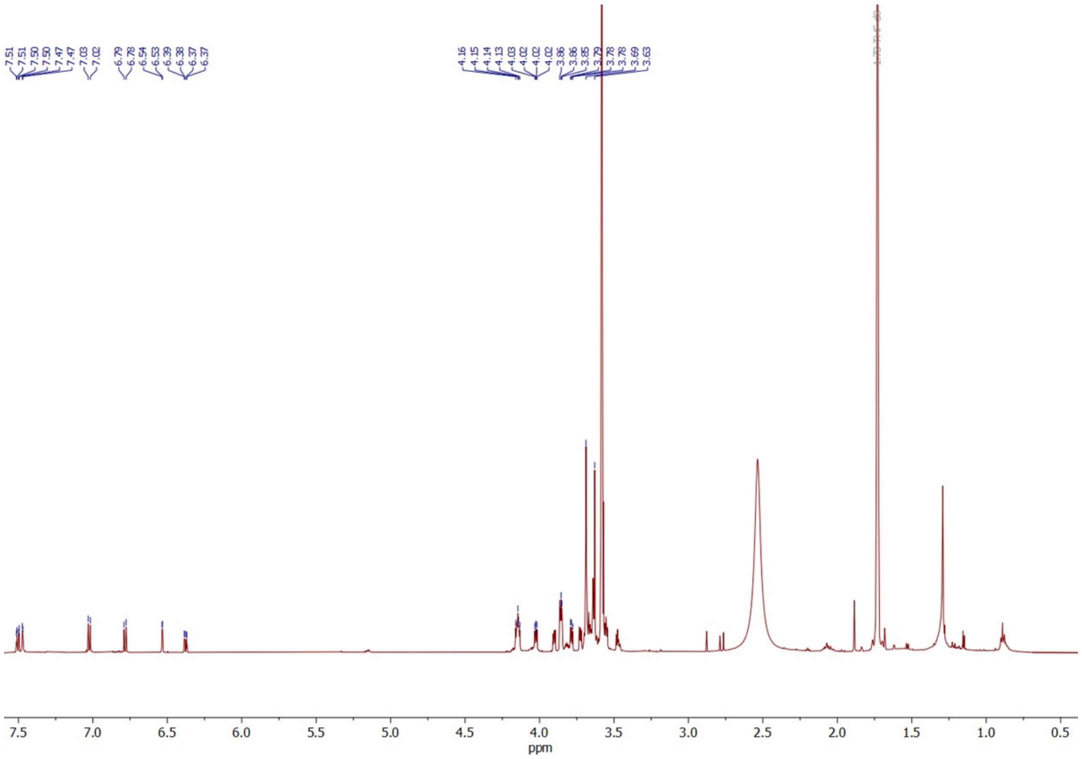


Figure S4. 500 MHz ^{1}H-NMR spectrum of **(1)** with 1 equivalent of potassium acetate measured at 21 °C, after 17 hours UV light irradiation, in THF-d_8. The ratio E/Z = 60/40.

General Polymerization Procedure

In a glove box, a dried vial equipped with a stirrer is charged with KOAc (2.45 mg, 2.50×10^{-5} mol) and **1** (14 mg, 2.50×10^{-5} mol) in 0.5 g of dry THF. After 5 min, L-lactide (0.29 g, 1.99×10^{-3} mol) and 1 g of dry THF are added. Polymerization is then initiated by adding 5.2 μL of BnOH (5.19×10^{-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.

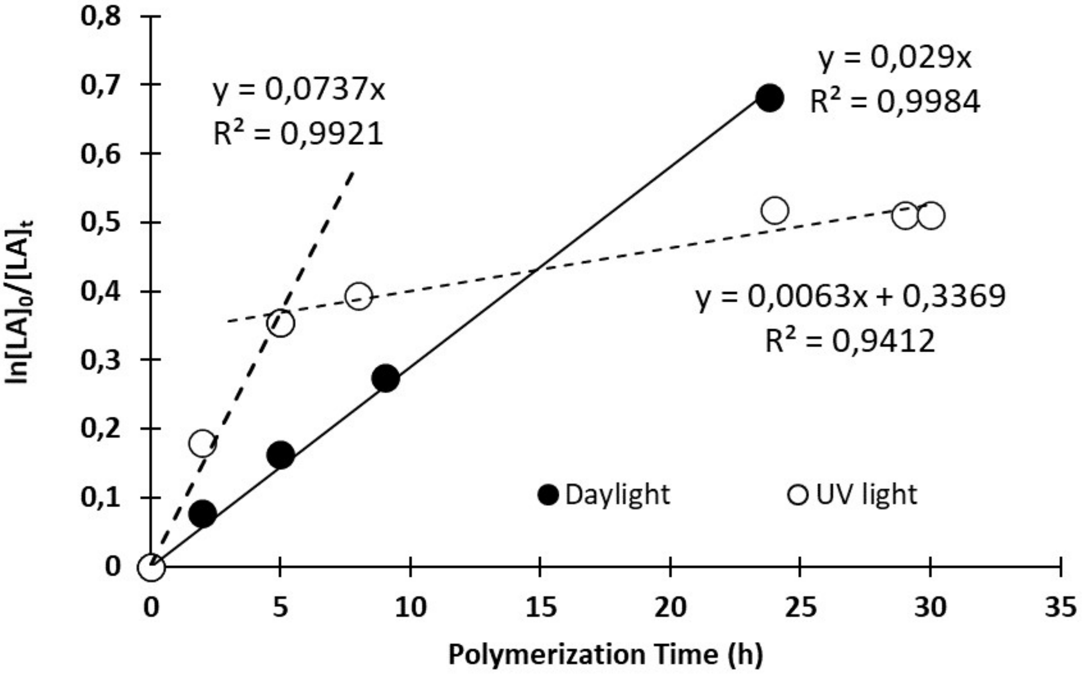


Figure S5 [article Fig.3]. Semilogarithmic plots of L-LA polymerizations initiated with BnOH and catalysed with KOAc/**1** under daylight (●) and UV light (○). Conditions of polymerizations: $[\text{L-LA}]_0/[\text{BnOH}]_0/[\text{KOAc}]_0/[\mathbf{1}]_0$ = 40/1/0.5/0.5, $[\text{L-LA}]_0$ = 1M, THF solvent, 21 °C.

MALDI MS Characterization of PLA sample

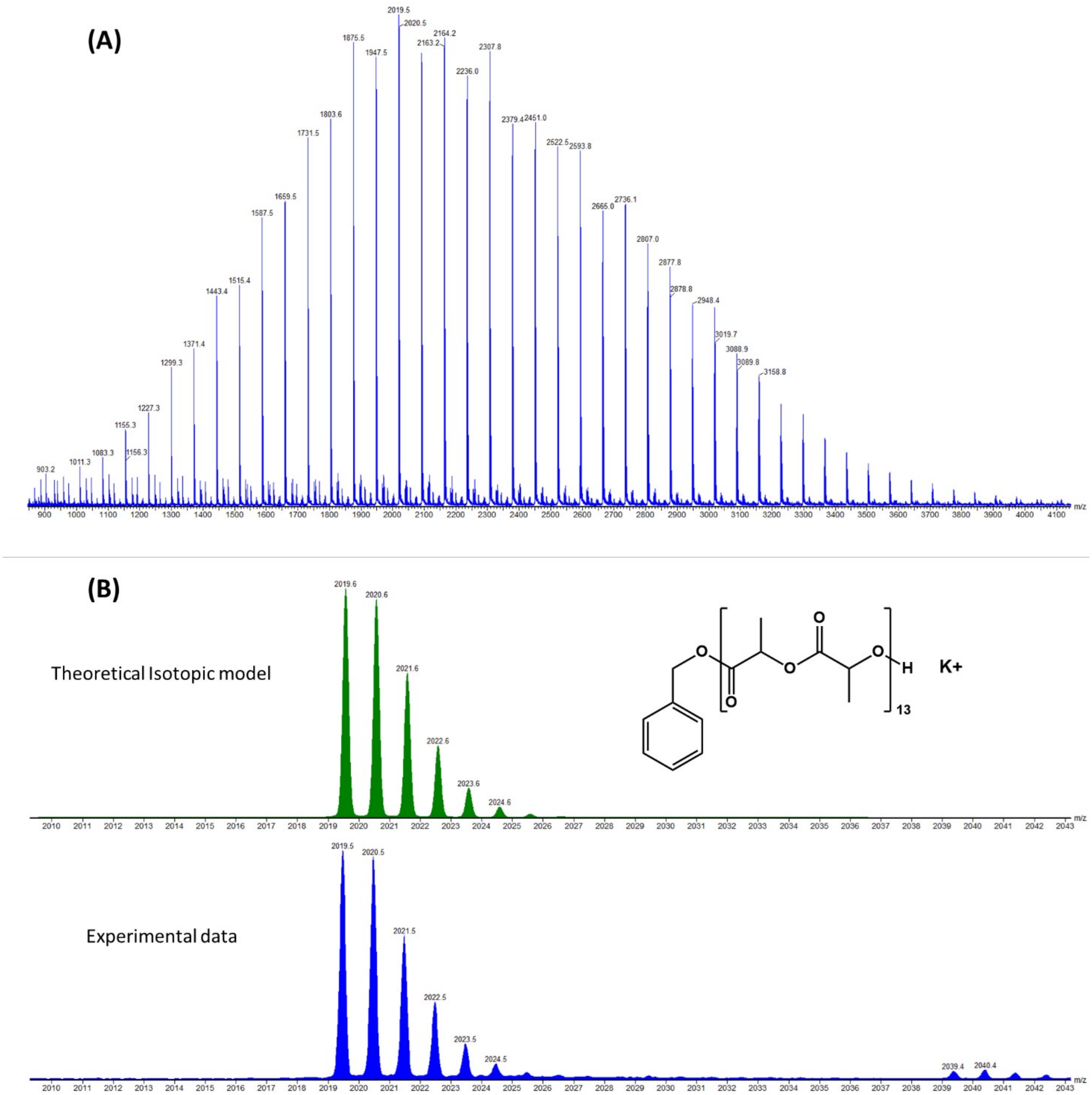


Figure S6. **(A)** MALDI-ToF MS of PLA obtained by L-LA ROP initiated with BnOH and catalysed with [KOAc]$_0$/[**1**]$_0$ = 1 in THF under daylight. Conditions of polymerizations: [L-LA]$_0$/[BnOH]$_0$/[KOAc]$_0$/[**1**]$_0$ = 40/1/0.5/0.5, [L-LA]$_0$ = 1M, 21 °C, polym. time = 23.9 hours (see Fig.3); **(B)** Expansion of region from *m/z* 2010 to 2043 and a simulated mass distribution.