Supporting Information

Integration of Upcycling and Closed-Loop Recycling through Alternative Cyclization-Depolymerization

Experimental Section

Materials

p-Toluenesulfonic acid (TsOH, A.R.), Triethylamine (Et_3N, A.R.), Pyridine (Py, A.R.), and Ethyl Acetate (EA, A.R.) were obtained from KHRON CHECALS (Chengdu, China). 1-Isopropvlimdazole (PrIm, 98+%), 4-Methylthiazole (C_4MTh, 99%), Imidazole (Im, 99%), 4-dimethylamino pyridine (DMAP, 99%) and Benzothiazole (BzTh, 99%) were obtained from Adamas-beta®. PDO was obtained from the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, China).

Methods

Thermogravimetric Analysis (TGA) was performed on a Dupont 2100 system in platinum pans under a steady nitrogen flow of 50 $ml \cdot min^{-1}$. The TGA and DTG curves were recorded at a heating rate of 10 °C $\cdot$ min^{-1}. ^1H NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at 25 °C. Matrix-Assisted Laser Desorption/Ionization Time-of-flight Mass Spectra (MALDI-TOF MS) were recorded on a Bruker Autoflex III spectrometer (reflect model), with 355 nm laser and 20 KV voltage ion source. PPDO samples were dissolved in C_2F_6CHOH/CH_2Cl_2 (5/95) at a concentration of 5 mg/mL, and then mixed with the matrix α-Cyano-4-hydroxycinnamic acid (*CHCA*). Gel Permeation Chromatography (GPC) was performed on a Waters 1515, equipped with a Waters Styragel® HT 2 THF column and a Waters Styragel® HT 4 column, with $CHCl_3$ as mobile phase (1.0 mL min^{-1}) at 35 °C. Intrinsic viscosity i.e. [η] were measured at 30 °C with concentration of about 0.1 $g \cdot dL^{-1}$ in phenol/1,1, 2,2-tetrachloroethane (1/1, volume ratio) solution using an Ubbelohde viscometer. Gas Chromatography (GC) was performed on an Agilent 7890B system equipped with HP-5 capillary column. Samples were injected (0.4 μL) in split mode (20:1), with the injector temperature at 250 °C. The column temperature was programmed in a range of 80 °C (5 min) – 20 $°C \cdot min^{-1}$ – 200 °C (5 min). The FID detector temperature was 280 °C.

Preparation of BAILs

Slowly mixing TsOH and Et_3N (molar ratio 1.00/1.00, 51.66 g/30.36 g) at 60 °C, the mixture was stirred for 4 hours until the neutralization reaction no longer exothermic. After dried the product over vacuum, [Et_3NH]TsO was prepared. Dissolving TsOH (17.22 g) with Py (7.91 g), DMAP (12.22 g), PrIm (11.02 g), C_4MTh (9.92 g), Im (6.81 g), or BzTh (13.52 g) (molar ratio 1.00/1.00) in 20-30 mL ethyl acetate (EA). After stirring for 4 h and standing in the refrigerator overnight, liquids or white powders were isolated from the EA solutions. Then, the isolated products were collected after washing with EA 3 times. Drying the products, [PrHIm]TsO, [C_4MHTh]TsO, [BzHTh]TsO, [HPy]TsO, ^{4}TsO, and [H-DMAP]TsO were prepared with yields range from 74 to 95%.

Preparation of *l*-PPDO

Typically, PDO was dried by CaH_2 overnight and distilled under reduced pressure. Loading PDO (0.5 mol, 51.05 g) firstly, 2 mol% H_2O (10 mmol, 0.18 mL) was added as initiator, and 2 mol% TsOH (10 mmol, 1.72 g) was added as catalyst. Under nitrogen atmosphere, the ring-opening polymerization of PDO was conducted at 60 °C for 8 hours. After cooling to room temperature, the reaction was terminated by adding Et_3N (20 mmol, 2.02 g) to neutralize TsOH. Then, the products were purified by precipitation from the dichloromethane/hexafluoroisopropanol ($CH_2Cl_2/C_2F_6CHOH = 95/5$) solution in methanol and dried under vacuum to a constant weight. With the control of initiator molar ratio (1, 2, 4 mol%), three *l*-PPDO samples were prepared (^{1}H NMR spectra shown in **Fig. S12-S14**). Resonances for PPDO: -C(=O)-O-CH_2- methylene hydrogen (4.32-4.35 ppm, t, 2H), -C(=O)-CH_2-O- methylene hydrogen (4.17 ppm, s, 2H), -CH_2-O- methylene hydrogen (3.78-3.80 ppm, t, 2H). Resonances for PDO: -C(=O)-O-CH_2- methylene hydrogen (4.47-4.50 ppm, t, 2H), -C(=O)-CH_2-O- methylene hydrogen (4.36-4.37 ppm, s, 2H), -CH_2-O- methylene hydrogen (3.85-3.88 ppm, t, 2H). Resonances for C_2F_6CHOH: methine hydrogen (4.21-4.27 ppm, m, 1H).

Cyclization-depolymerization of *l*-PPDO

Typically, the cyclization-depolymerization was conducted with experimental equipment shown as **Fig. S7**, a reaction flask equipped with a cooling section and a collection flask, and connecting to a vacuum line. In an experiment, [Et_3NH]TsO (e.g., 7.23 g) was added into reaction flask firstly, and dried in vacuum line for 4 h. Secondly, PPDO (e.g., 3.63 g) was loaded in nitrogen atmosphere at a concentration of 33 wt.%. Then, the cyclization-depolymerization was conducted under 100±20 Pa at 120 °C, with stirring and oil bath heating. When the distillation rate tended to zero, the reaction was terminated by cooling to room temperature and shifting vacuum to nitrogen atmosphere. After, the distilled PDO component (in cooling section and collection flask) was weighed and analysed by GC, and the undepolymerized fraction of PPDO in solution was collected after washing off [Et_3NH]TsO by methyl alcohol and vacuum drying. Under different concentrations, partially cyclized PPDO (*pc*-$PPDO_{x\ wt.\%}$) and cyclic PPDO (*c*-$PPDO_{x\ wt.\%}$) were obtained, "x wt.%" is the reactant concentration in cyclization-depolymerization.

Apparent kinetics of cyclization-depolymerization

Using 2 mol% H_2O initiated *l*-PPDO as reactant (3.27 g, concentration 33 wt.%), cyclization-depolymerization was conducted under 100±20 Pa at 120 °C. For every 60 minutes, the reacting solution was sampled after shifting vacuum to nitrogen atmosphere, and the ratios of undepolymerized PPDO are calculated by ^{1}H NMR ($CDCl_3$) spectral analysis (**Fig. S15**). The amount of [Et_3NH]TsO kept as a constant in cyclization-depolymerization. Therefore, [Et_3NH]TsO can be regarded as an internal standard substance in ^{1}H NMR. The integral area of 7.5-8.0 ppm (-Ph- hydrogen of [Et_3NH]TsO, $S_{7.5\text{-}8.0\ ppm}$) is used as an internal standard resonance, and the integral areas of 3.5-4.8 ppm ($S_{3.5\text{-}4.8\ ppm}$) are attributed to resonances of PPDO. Thus, the concentration of PPDO (relative to [Et_3NH]TsO) is calculated as $C^t_{PPDO} = S^t_{3.5\text{-}4.8\ ppm}/S^t_{7.5\text{-}8.0\ ppm}$ (^{t} for sampling time), and the ratio of undepolymerized PPDO (relative to the initially loaded PPDO) is calculated as C^t_{PPDO}/C^0_{PPDO}. Besides, the yield of PDO was obtained by weighting and calculation (weight of yield PDO / weight of initially loaded PPDO × 100%).

Multiple round cyclization-depolymerization experiment

Accumulation of undepolymerizable PPDO in multiple round cyclization-depolymerization experiment was operated as following: firstly, with 2 mol% H_2O initiated *l*-PPDO (5.29 g) as reactant, cyclization-depolymerization was conducted in

$[Et_3NH]TsO$ (12.22 g) without termination, under typical conditions. Secondly, a certain mass (similar to the first run) of the *l*-PPDO was reloaded into the reaction flask in nitrogen atmosphere, and the cyclization-depolymerization was again proceeded under the same conditions. Then, the repeatedly loading of the *l*-PPDO and distilling out PDO were carried out for 5 runs. Lastly, the experiment was terminated by cooling to room temperature and shifting to nitrogen atmosphere.

The production of cyclic PPDO in per liter solvent is calculated as follows: density (ρ) of $[Et_3NH]TsO$ was evaluated to be 1.13 g/mL at 60 °C. Thus, the circulative accumulation lastly generating 2.40 g *c*-PPDO in 10.81 mL (m/ρ) $[Et_3NH]TsO$ is translated to 222 g/L. The productions of referenced reports are calculated similarly. The density of the solution (PPDO/$[Et_3NH]TsO$) is treated as the same as the solvent ($[Et_3NH]TsO$). Thus, the typical mass concentration of 33 wt.% is converted to a molar concentration of 3.66 M (of repeating unit).

Repolymerization of recycled PDO

(1) With H_2O as initiator

PDO monomers yielded from cyclization-depolymerizations were collected and used without further purification. Using 2 mol% H_2O (2 mmol, 36 μL) as initiator, re-polymerization of recycled PDO (0.1 mol, 10.21 g) was conducted under the same conditions with “**Preparation of *l*-PPDO**” part.

(2) Without extra addition of initiator

PDO was dried with CaH_2 overnight, and distilled under reduced pressure. Ring-opening polymerization of PDO (0.1 mol, 10.21 g) was conducted at 80 °C in nitrogen atmosphere with 0.02 mol% stannous octoate as catalyst for 48 h. The products were purified by precipitation from the dichloromethane/hexafluoroisopropanol ($CH_2Cl_2/C_2F_6CHOH = 95/5$) solution in methanol and dried under vacuum to a constant weight.

Supplementary Data

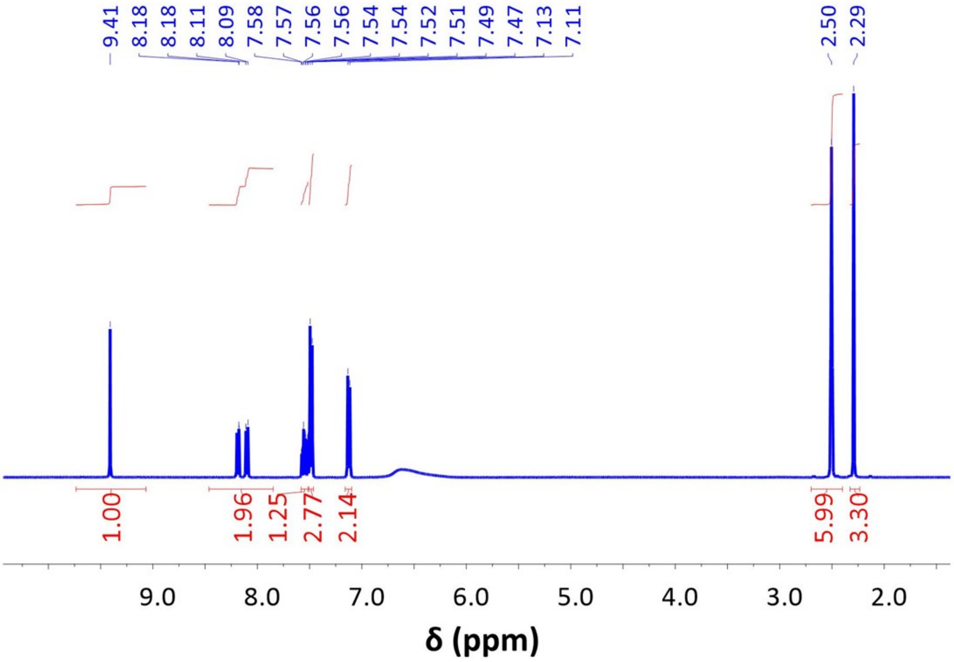

Fig. S1 ^{1}H NMR (DMSO-d6) spectrum of [PrHIm]TsO

C_2-hydrogen of [PrHIm] (9.41 ppm, s, 1H), C_4, C_5-hydrogen of [PrHIm] (8.09-8.18 ppm, dd, 2H), -CH- hydrogen of TsO (7.51-7.58 ppm, q, 1H), -Ph- hydrogen of TsO (7.11-7.49 ppm, dd, 4H), $-CH_3$ hydrogen of [PrHIm] (2.50 ppm, s, 6H), $-CH_3$ hydrogen of TsO (2.29 ppm, s, 3H). Integral ratio of the peaks follows $S_{9.41ppm}/S_{8.09\text{-}8.18ppm}/S_{7.51\text{-}7.58ppm}/S_{7.11\text{-}7.49ppm}/S_{2.50ppm}/S_{2.29ppm}$ = 1.00/1.96/1.25/4.91/5.99/3.30, suggesting [HPrIm]/TsO is about 1/1.

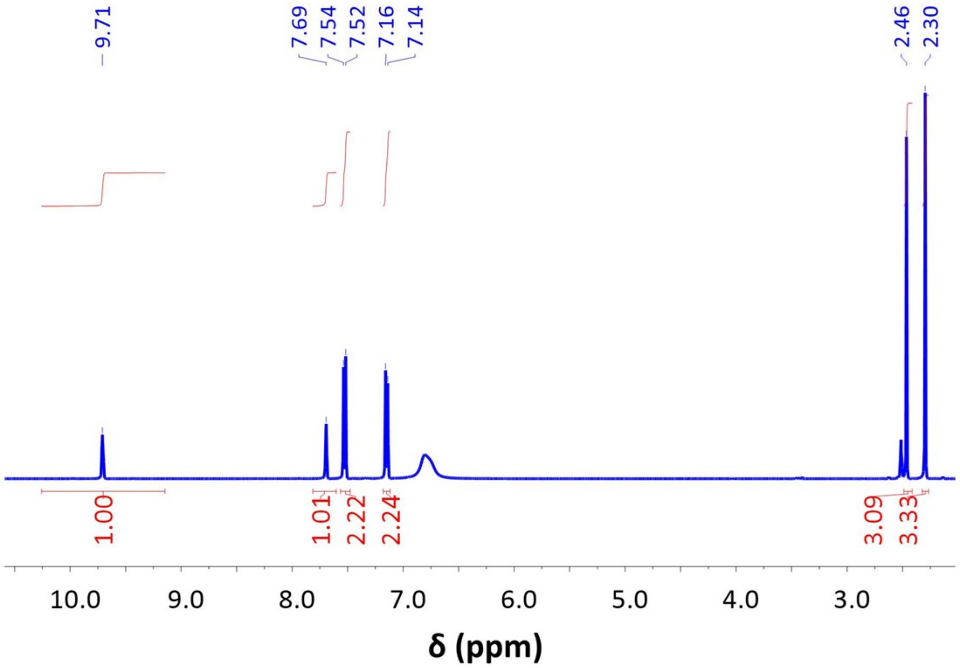

Fig. S2 ^{1}H NMR (DMSO-d6) spectrum of [C_4MHTh]TsO

C_2-hydrogen of [C_4MHTh] (9.71 ppm, s, 1H), C_5-hydrogen of [C_4MHTh] (7.69 ppm, s, 1H), -Ph- hydrogen (7.14-7.54 ppm, dd, 4H), -CH_3 hydrogen of [C_4MHTh] (2.46 ppm, s, 3H), -CH_3 hydrogen of TsO (2.30 ppm, s, 3H). Integral ratio of the peaks follows $S_{9.71ppm}/S_{7.69ppm}/S_{7.14-7.54ppm}/S_{2.46ppm}/S_{2.30ppm}$ = 1.00/1.01/4.46/3.09/3.33, suggesting [C_4MHTh]/TsO is about 1/1.

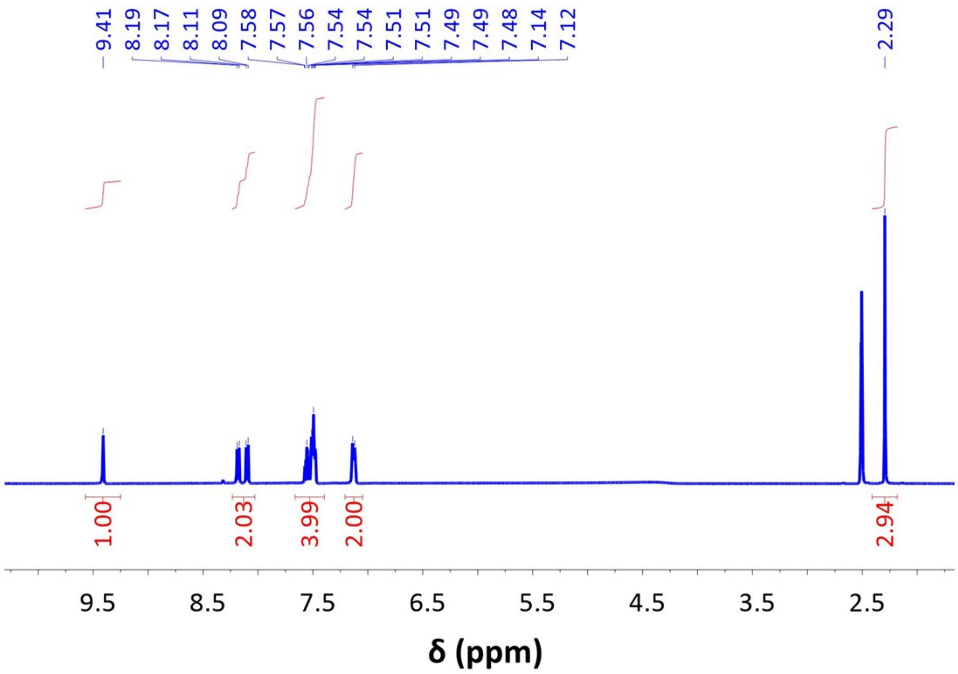

Fig. S3 ^{1}H NMR (DMSO-d6) spectrum of [BzHTh]TsO

C$_2$-hydrogen of [BzHTh] (9.41 ppm, s, 1H), C$_5$,C$_8$-hydrogen of [C$_4$MHTh] (8.09-8.19 ppm, dd, 2H), C$_6$,C$_7$-hydrogen of [C$_4$MHTh] (7.48-7.58 ppm, dt, 2H), -Ph-hydrogen of TsO (7.12-7.51 ppm, dd, 4H), -CH$_3$ hydrogen of TsO (2.29 ppm, s, 3H). Integral ratio of the peaks follows $S_{9.41ppm}/S_{8.09\text{-}8.19ppm}/S_{7.12\text{-}7.58ppm}/S_{2.29ppm}$ = 1.00/2.03/5.99/2.94, suggesting [BzHTh]/TsO is about 1/1.

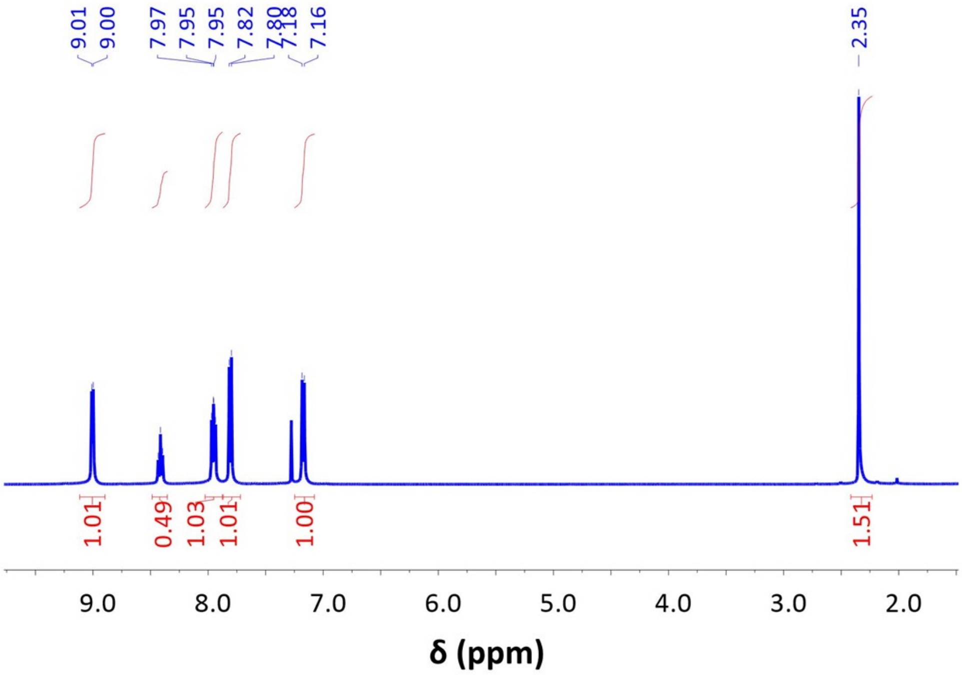

Fig. S4 ^{1}H NMR ($CDCl_3$) spectrum of [HPy]TsO

Hydrogens of pyridine ring [HPy] (7.95-9.01 ppm, m, 5H), -Ph- hydrogen of TsO (7.16-7.82 ppm, dd, 4H), $-CH_3$ hydrogen of TsO (2.35 ppm, s, 3H). Integral ratio of the peaks follows $S_{7.95\text{-}9.01ppm}/S_{7.16\text{-}7.82ppm}/S_{2.35ppm} = 2.53/2.01/1.51$, suggesting [HPy]/TsO is about 1/1.

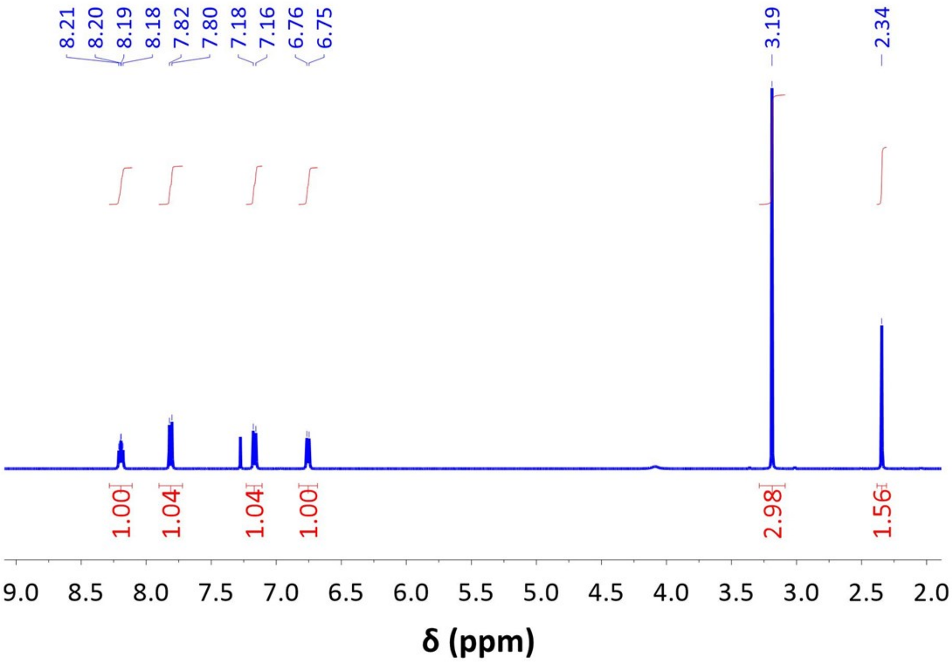

Fig. S5 ^{1}H NMR ($CDCl_3$) spectrum of [H-DMAP]TsO

Hydrogens of pyridine ring [H-DMAP] (7.80-8.21 ppm, dd, 4H), -Ph- hydrogen of TsO (6.75-7.18 ppm, dd, 4H), $-CH_3$ hydrogen of [H-DMAP] (3.19 ppm, s, 6H), $-CH_3$ hydrogen of TsO (2.34 ppm, s, 3H). Integral ratio of the peaks follows $S_{7.80\text{-}8.21ppm}/S_{6.75\text{-}7.18ppm}/S_{3.19ppm}/S_{2.34ppm}$ = 2.04/2.04/2.98/1.56, suggesting [H-DMAP]/TsO is about 1/1.

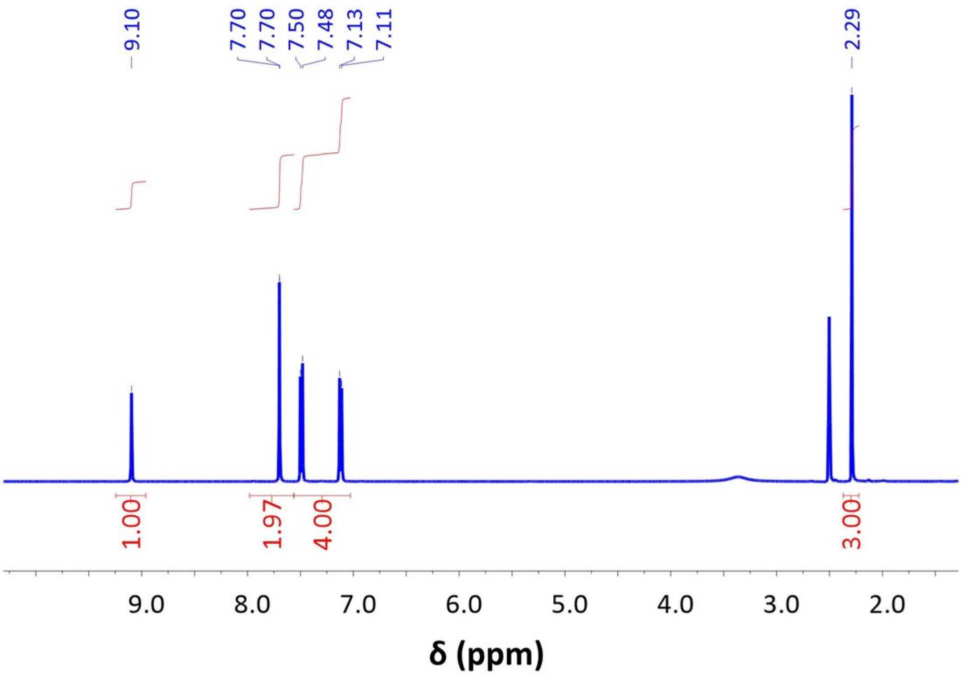

Fig. S6 ^{1}H NMR (DMSO-d6) spectrum of [HIm]TsO

C_2-H of [HIm] (9.10 ppm, s, 1H), C_4, C_5-H of [HIm] (7.70 ppm, d, 2H), -Ph- hydrogen of TsO (7.11-7.50 ppm, dd, 4H), -CH_3 hydrogen of TsO (2.29 ppm, s, 3H). Integral ratio of the peaks follows $S_{9.10ppm}/S_{7.70ppm}/S_{7.11\text{-}7.50ppm}/S_{2.29ppm}$ = 1.00/1.96/4.00/3.00, suggesting [HIm]/TsO = 1/1.

^{1}H NMR (DMSO-d6) spectrum of [Et_3NH]TsO: -Ph- hydrogen (7.12-7.51 ppm, dd, 4H), -CH_2- hydrogen (3.05-3.12 ppm, m, 6H), -CH_3 hydrogen of TsO (2.29 ppm, s, 3H), -CH_3 hydrogen of [Et_3NH] (1.14-1.18 ppm, t, 9H). Integral ratio of the peaks follows $S_{7.12\text{-}7.51ppm}/S_{3.05\text{-}3.12ppm}/S_{2.29ppm}/S_{1.14\text{-}1.18ppm}$ = 0.66/1.00/0.50/1.50, suggesting [Et_3NH]/TsO = 1/1.

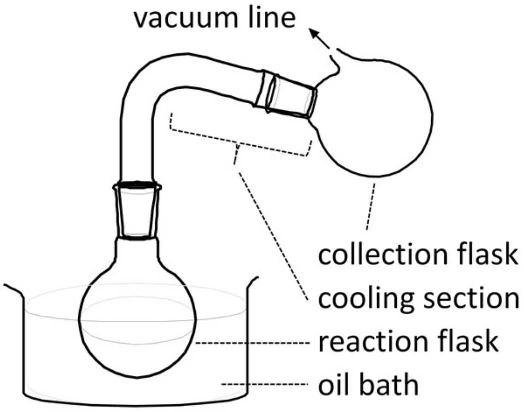

Fig. S7 Schematic diagram of experimental equipment

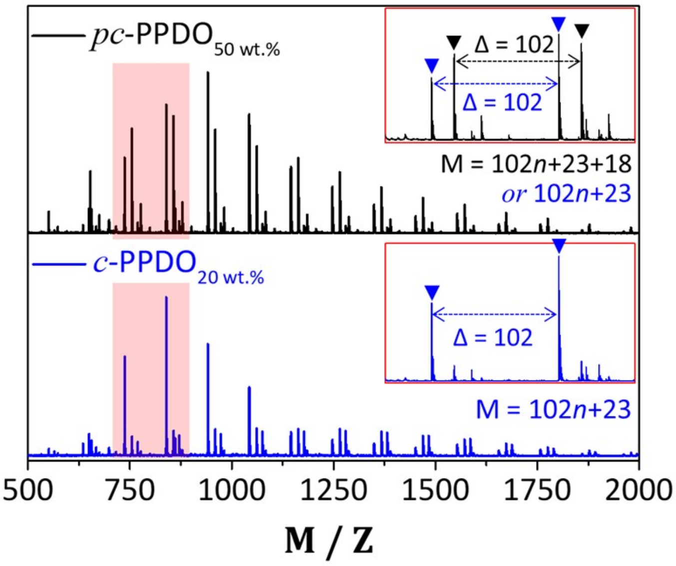

Fig. S8 MALDI-TOF MS spectra of *pc*-PPDO$_{50\text{ wt.\%}}$ and *c*-PPDO$_{20\text{ wt.\%}}$

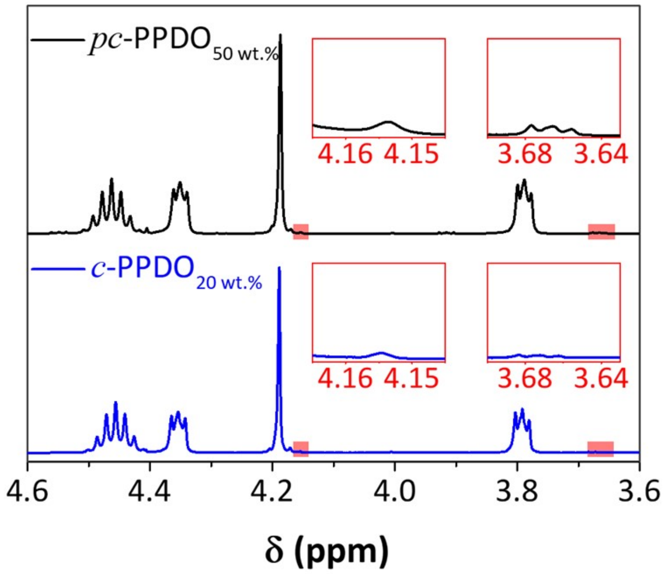

Fig. S9 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectra and the partially enlarged views of *pc*-PPDO$_{50\ wt.\%}$ and *c*-PPDO$_{20\ wt.\%}$

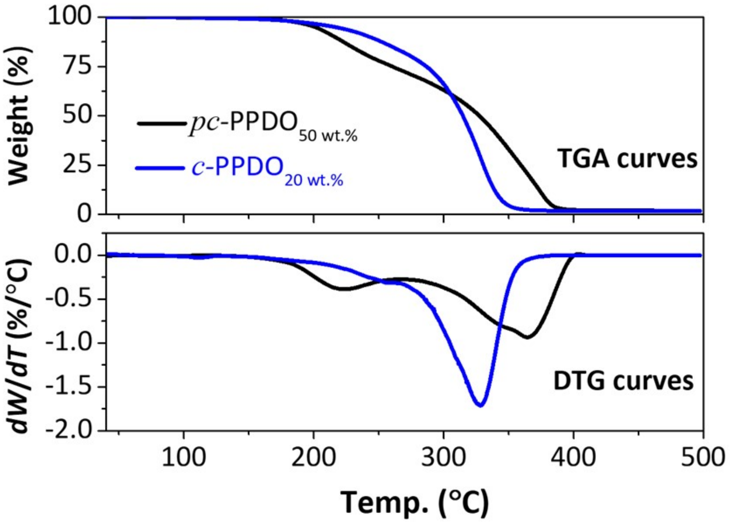

Fig. S10 TGA and DTG curves of *pc*-PPDO$_{50\ wt.\%}$ and *c*-PPDO$_{20\ wt.\%}$

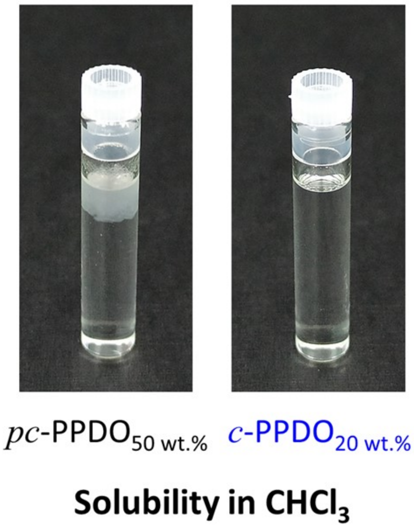

Fig. S11 Digital photographs of *pc*-PPDO$_{50\ \text{wt.\%}}$ and *c*-PPDO$_{20\ \text{wt.\%}}$ chloroform solutions (1 wt.%)

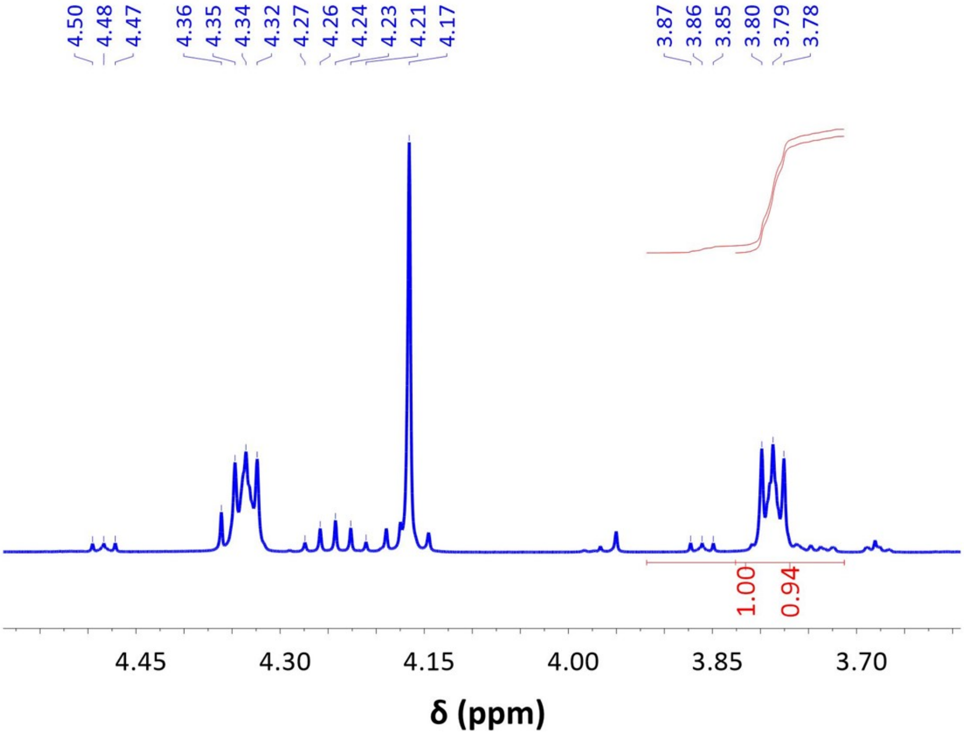

Fig. S12 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectrum of the polymerized mixture initiated by 4 mol% H_2O and catalysed by TsOH

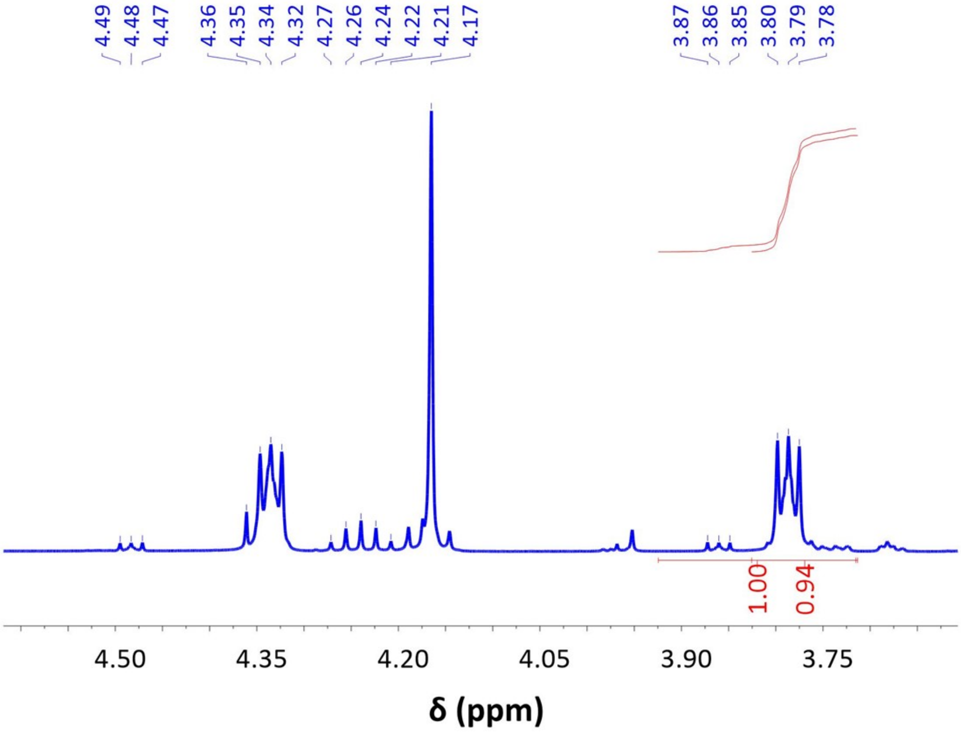

Fig. S13 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectrum of the polymerized mixture initiated by 2 mol% H_2O and catalysed by TsOH

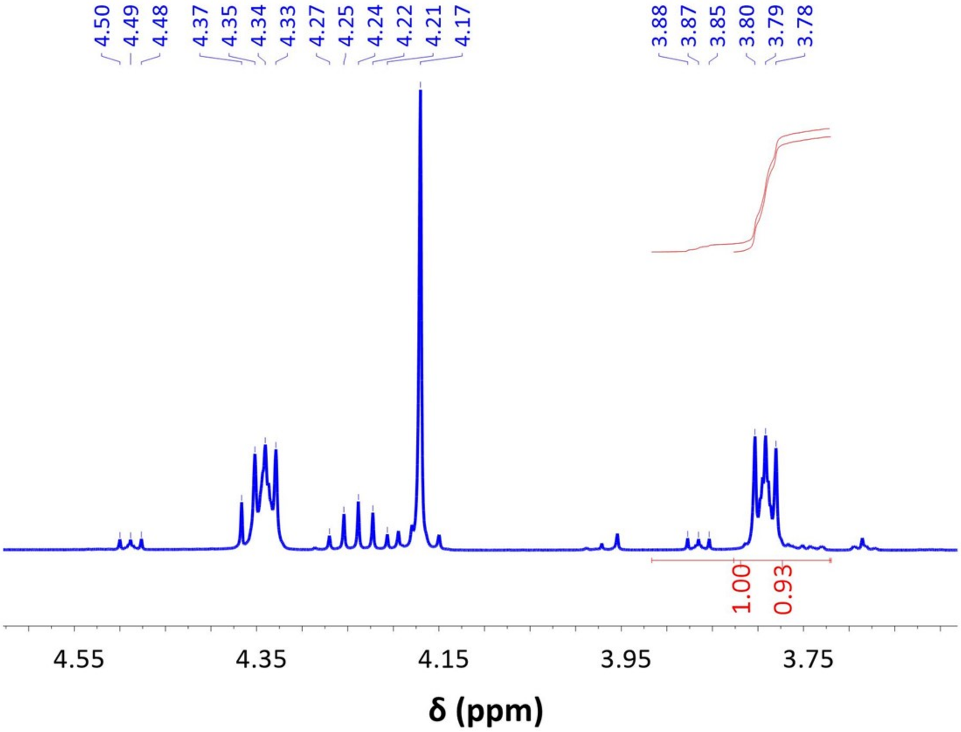

Fig. S14 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectrum of the polymerized mixture initiated by 1 mol% H_2O and catalysed by TsOH

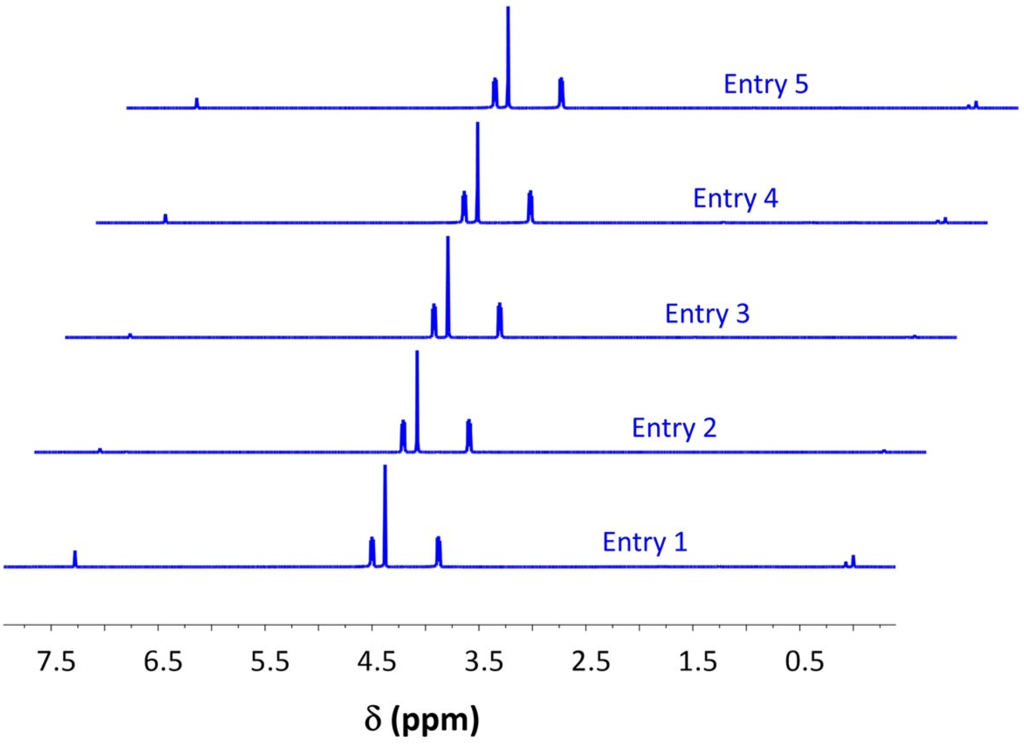

Fig. S15 ^{1}H NMR ($CDCl_3$) spectra of the distillates in cyclization-depolymerization experiments (**Table 1**)

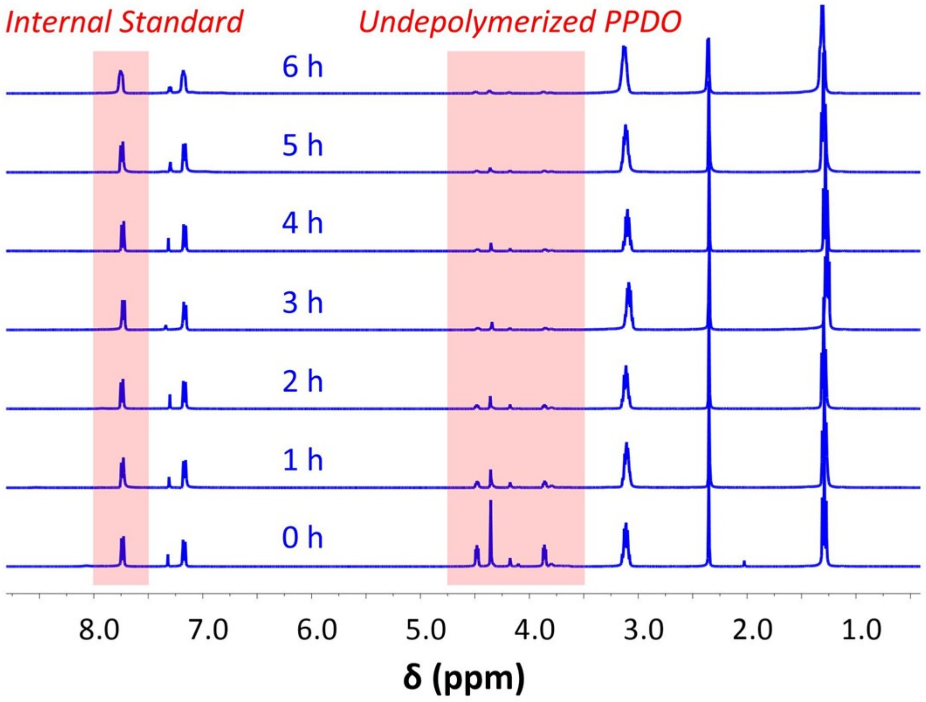

Fig. S16 ^{1}H NMR (DMSO-d6) spectra of sampled reacting solutions in kinetics experiment

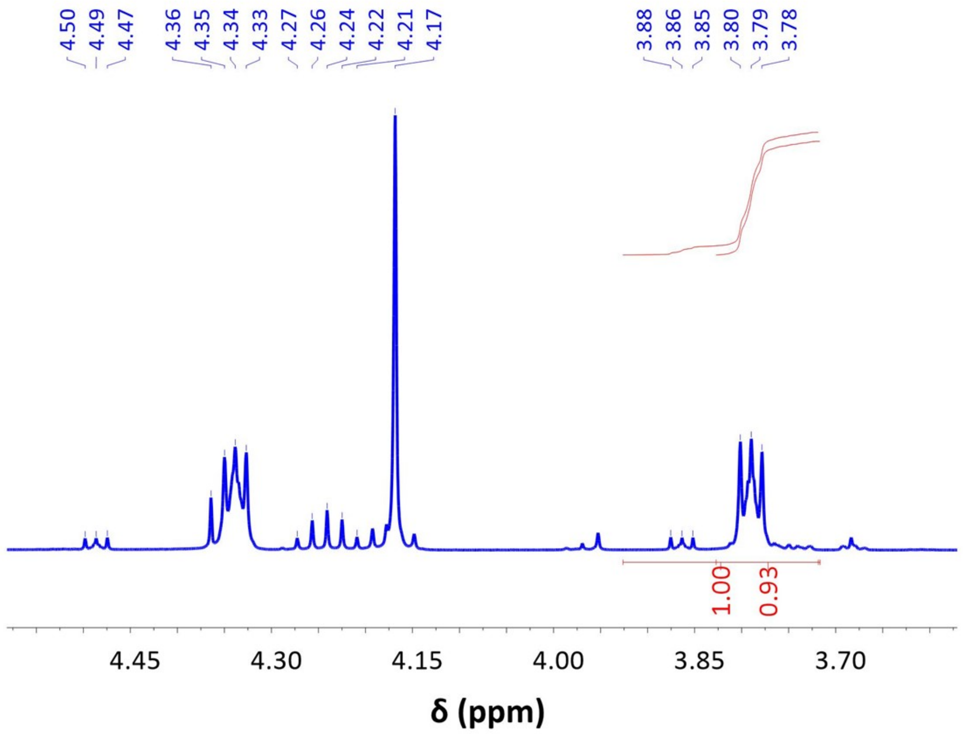

Fig. S17 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectrum of the repolymerized mixture initiated by 2 mol% H_2O and catalysed by TsOH

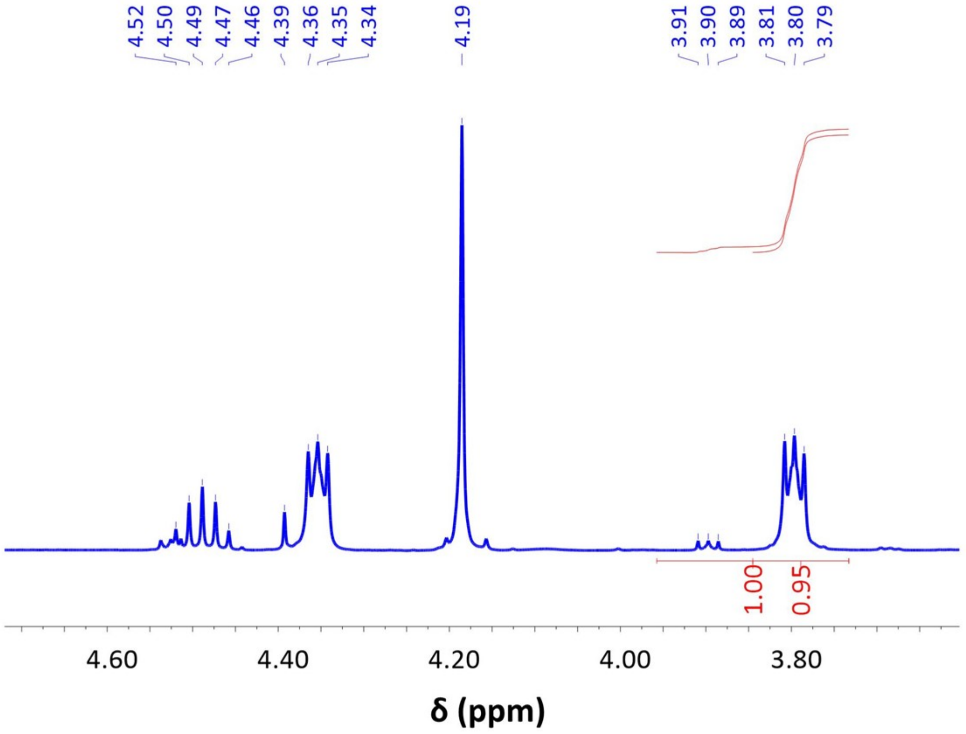

Fig. S18 ^{1}H NMR (98% $CDCl_3$ + 2% C_2F_6CHOH) spectrum of the repolymerized mixture catalysed by $Sn(Oct)_2$

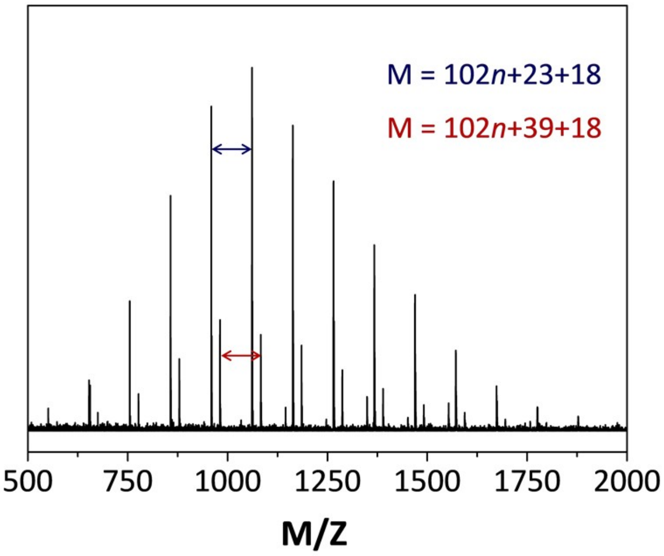

Fig. S19 MALDI-TOF MS spectrum of hydrolysed *c*-PPDO