Metal-free Synthesis of Poly(trimethylene carbonate) by Efficient Valorization of Carbon Dioxide

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1. Experimental Section

Materials and Methods

All reagents and solvents were purchased from Sigma-Aldrich, TCI, Air Liquide and used as received, unless otherwise noted. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU, 98%) and oxetane (97%) were distilled from CaH_2 and stored in a glove-box and glove-box freezer (-35 °C), respectively. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 98%) was dried by anhydrous tetrahydrofuran (THF) three times before the storage in glove-box. N50 grade CO_2 (99.999%, H_2O < 0.5 ppm) was used as received.

^{1}H-NMR spectra were measured at 298 K using a 500 MHz advance Bruker spectrometer with tetramethylsilane (TMS) as an internal standard (δ = 0.00 ppm) in chloroform-d ($CDCl_3$). 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 $mg{\cdot}ml^{-1}$ 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 $mg{\cdot}ml^{-1}$ solutions and 50 µL of 2 $mg{\cdot}ml^{-1}$ NaI solution in acetonitrile has been added to the polymer solution. 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. Size exclusion chromatography (SEC) was performed in THF at 308 K using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL min^{-1}), a triple detector: refractive index (ERMA 7517), capillary viscometry and light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC - RI/UV) and four columns: a PL gel 10 µm guard column and three PL gel Mixed - B 10 µm columns. Polystyrene (PS) standards were used for calibration.

General Procedure for Polymer Synthesis

The CO_2-based copolymers were synthesized following the general procedure. In brief, a 10 mL pressure reactor (Autoclave Suurmond BV, steel type 3/10 mL, 100 bar) with magnetic stirrer was dried in an oven at 70 °C overnight before immediately being taken into a N_2-filled glove-box. After the reactor had cooled to ambient temperature, the reagents, I_2 (50 mg, 0.197 mmol), co-catalysts (see text) and oxetane (7.88 mmol, 0.512 mL) were charged to the vessel. The vessel was sealed, removed from the glove-box and before being placed in liquid nitrogen to cool down. CO_2 was condensed into the reactor while cold *via* a Schlenk-line until the appropriate pressure was achieved. The reactor was sealed again and heated to the desired temperature. After the allotted reaction time, the reactor was again cooled by liquid nitrogen before the CO_2 gas was released slowly. Aliquots of the polymerization mixture were taken for ^{1}H NMR spectroscopic characterization to determine overall conversion and selectivity. The residue of the mixture was dissolved in a small volume of THF (5 mL) and precipitated from methanol. The resultant copolymer was dried under vacuum at 40 °C overnight (Yield = 0.58 g, 0.125 mmol, 86%). When catalyst = TBD (0.197 mmol, 0.0274 g): ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 4.29 (t, 2H, $^3J_{HH}$ = 6.0 Hz, -CH_2), 4.23 (t, 4H, $^3J_{HH}$ = 6.0 Hz, -OCH_2), 3.73 (t, 2H, $^3J_{HH}$ = 6.0 Hz, -CH_2), 3.49 (t, 4H, $^3J_{HH}$ = 6.3 Hz, -OCH_2), 2.04 (quint, 2H, $^3J_{HH}$ = 6.3 Hz, -CH_2), 1.92 (quint, 2H, $^3J_{HH}$ = 6.3 Hz, -CH_2), 1.82 (quint, 2H, $^3J_{HH}$ = 6.3 Hz, -CH_2). SEC (THF): M_n = 4630 g mol^{-1}, $Đ_M$ = 1.32

2. Supporting Tables

Table S1. Copolymerization of oxetane and CO_2 with various catalysts. [a]

Entry	Catalyst	Time (h)	Pressure (MPa)	Oxetane Conversion (%)[b]	Selectivity (%)[b]			TON	TOF (h^{-1})	M_n (SEC)[c] g mol^{-1}	$Đ_M$[c]
					TMC	Carbonate Linkages	Ether Linkages				
1	DBU	24	1	82	8	72	20	32.8	1.37	1,360	1.71
2	MTBD	24	1	46	11	71	18	18.4	0.77	5,240	1.35
3	MTBD	44	1	80	9	73	18	29.2	0.73	6,000	1.45
4	TBD	24	1	88	<1	88	12	38.75	1.61	4,630	1.32
5	P_4-*tert*-Bu	24	1	15	>99	0	0	6	0.25	NA	NA
6	P_4-*tert*-Bu	168	1	83	71	19	10	33.2	0.20	320	1.42
7[d]	1.3-bis-HFAB	24	10	39	2	98	<1	13	0.54	1,000	1.15
8[d]	1.3-bis-HFAB	24	10	92	2	98	<1	30.6	1.27	2,000	1.30
9[d]	1.3-bis-HFAB	24	5	72	5	95	<1	23.9	0.99	1,500	1.33
10[d]	1.3-bis-HFAB	24	2	25	4	96	<1	8.32	0.35	<1,000	N.A

[a] Copolymerization conditions: 7.88 mmol oxetane, 2.5 mol% I_2 and base cocatalyst, 1 MPa CO_2, 105 °C. [b] Oxetane conversion and selectivity were determined from ^1H NMR spectroscopy of crude mixture; [c] Determined by SEC in tetrahydrofuran (THF) with polystyrene standard.[d] The results are based on the literature.[1]

Table S2. Coupling of CO_2 and oxetane using I_2/P_4-tert-Bu with various reaction time [a].

Entry	Reaction time / days	Selec. %			Con. % [b]
		TMC	Carbonate Linkages	Ether Linkages	
1	1	>99	0	0	15
2	3	>99	0	0	20
3	5	>99	0	0	30
4	7	71	19	10	83

[a] Coupling conditions: 7.88 mmol of oxetane, $[M]_0/[I_2]_0/[P_4\text{-}tert\text{-}Bu] = 40/1/1$, 3 MPa of CO_2, at 105 °C. [b] Conversion and selectivity were determined from ^1H NMR spectroscopy of the product mixture.

Table S3. Optimization of coupling of CO_2 and oxetane using I_2/TBD under different catalysts ratio [a].

Entry	TBD loading mol%	Catalyst ratio/ I_2:TBD	Selec. %			Con. % [b]	$M_{\mathrm{n\,SEC}}$[c] g·mol^{-1}	$Đ_{\mathrm{M\,SEC}}$ [c]
			TMC	Carbonate Linkages	Ether Linkages			
1	1.25	2:1	2	71	27	77	4,150	1.42
2	2.5	1:2	<1	85	15	31	5,000	1.34
3 [d]	2.5	1:2	2	94	4	51	4,280	1.47
4	5	1:1	<1	57	43	97	4,970	1.32
5	2.5	0:1	0	0	0	0	0	0
6 [e]	0	1:0	3	27	70	44	1,600	1.53

[a] Copolymerization conditions: 7.88 mmol of oxetane, 1 MPa of CO_2, at 105 °C for 24 h. [b] Conversion and selectivity were determined from ^{1}H NMR spectroscopy of product mixture. [c] Determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) with polystyrene standard. [d] CO_2 pressure is 3 MPa with 3 days. [e] The yield of oligomer is extremely low (3%).

Table S4. Copolymerization of CO_2 and oxetane using I_2/TBD with initiators [a].

Entry	Initiator	Selec. %			Con. % [b]	$M_{\mathrm{n\,SEC}}$[c] g·mol^{-1}	$Đ_{\mathrm{M\,SEC}}$ [c]
		TMC	Carbonate Linkages	Ether Linkages			
1	BnOH	<1	78	22	72	3,100	1.56
2	BuOH	3	82	15	55	4,250	1.33
3 [d]	BnOH	2	80	18	94	3,830	1.70
4 [e]	H_2O	7	49	44	65	1,000	1.79

[a] Copolymerization conditions: 7.88 mmol of oxetane, $[M]/[I_2]_0/[TBD]_0/[Initiator]_0$ = 100/2.5/2.5/1, 1 MPa of CO_2, at 105 °C for 24 h. [b] Conversion and selectivity were determined from ^{1}HNMR spectroscopy of product mixture. [c] Determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) with polystyrene standard. [d] 1 equivalent P_4-*tert*-Bu is used to deprotonate BnOH in first to obtain alkoxide ion. [e] $[M]/[I_2]_0/[TBD]_0/[H_2O]_0$ = 100/2.5/2.5/1.25

Table S5. Polymerization of TMC initiated by the adduct of I_2/oxetane. [a]

Entry	$[TMC]_0/[I_2\text{-oxetane}]_0$	Con.[b] %		Selec. % [b]			$M_{\mathrm{n\,SEC}}$[c] g·mol^{-1}	$Đ_{\mathrm{M\,SEC}}$ [c]
		TMC	EP	TMC	Carbonate linkages	Ether linkages		
1	40	>99	50	<1	94	6	5,870	1.67
2	80	>99	80	<1	98	2	10,000	1.84
3[d]	40	>99	83	<1	>99	<1	4,300	1.53

[a] Copolymerization conditions: 197 μmol of I_2/oxetane adduct (2.5mol%), [M]/[C] = 40/1, 1 MPa of N_2, at 105°C for 24 h. [b] Conversion and selectivity were determined from ^{1}HNMR spectroscopy of product mixture. [c] Determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) with polystyrene standard. [d] Experiment was carried out at 1MPa of CO_2 at 105°C for 24 h.

3. Supporting ^{1}H NMR Spectra

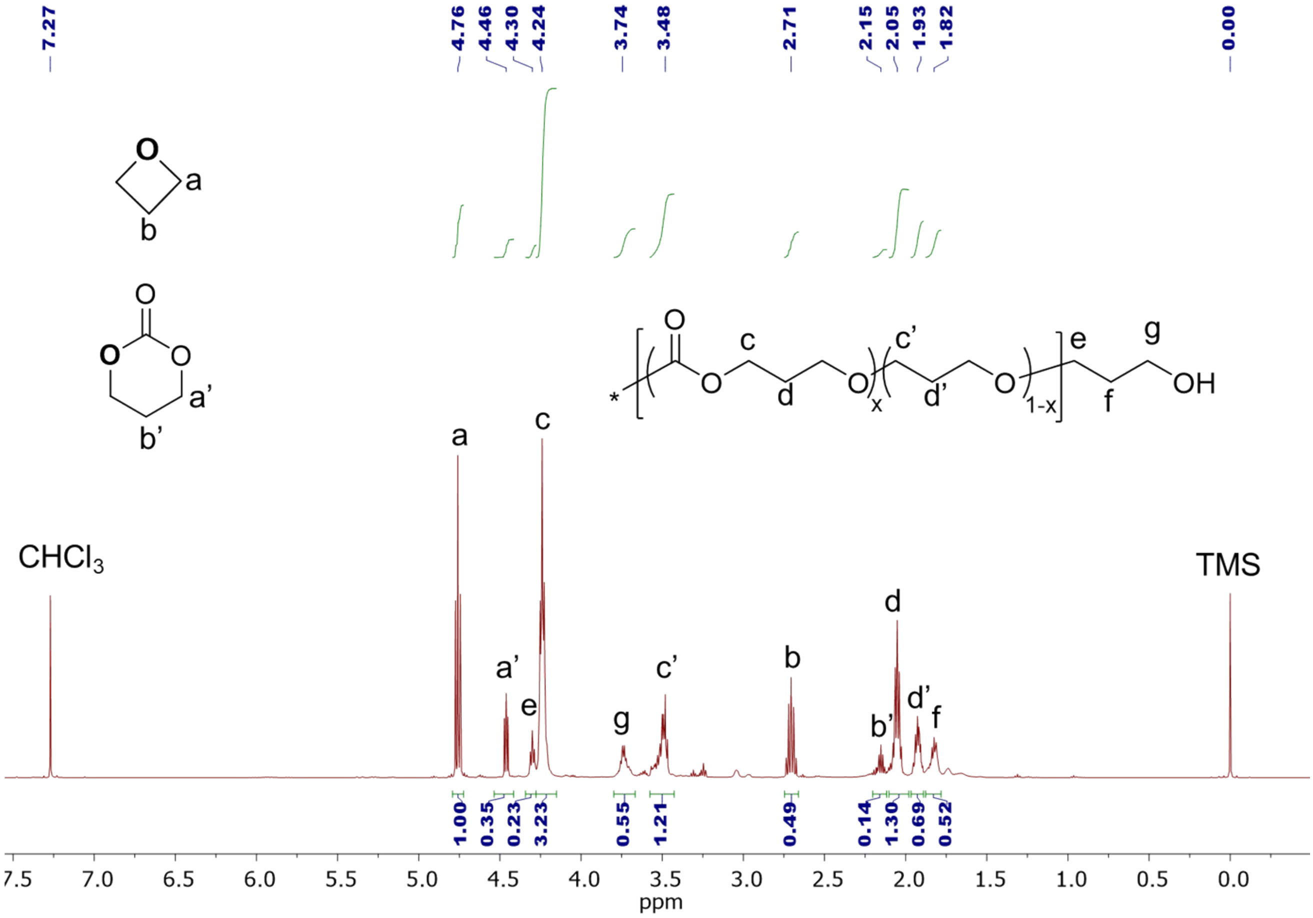

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the resultant mixture of polymerization (Table 1, entry 1). Conditions: 7.88 mmol oxetane, $[I_2]_0/[DBU]_0/[EP]_0 = 1/1/40$, 1 MPa CO_2, 105 °C, 24h.

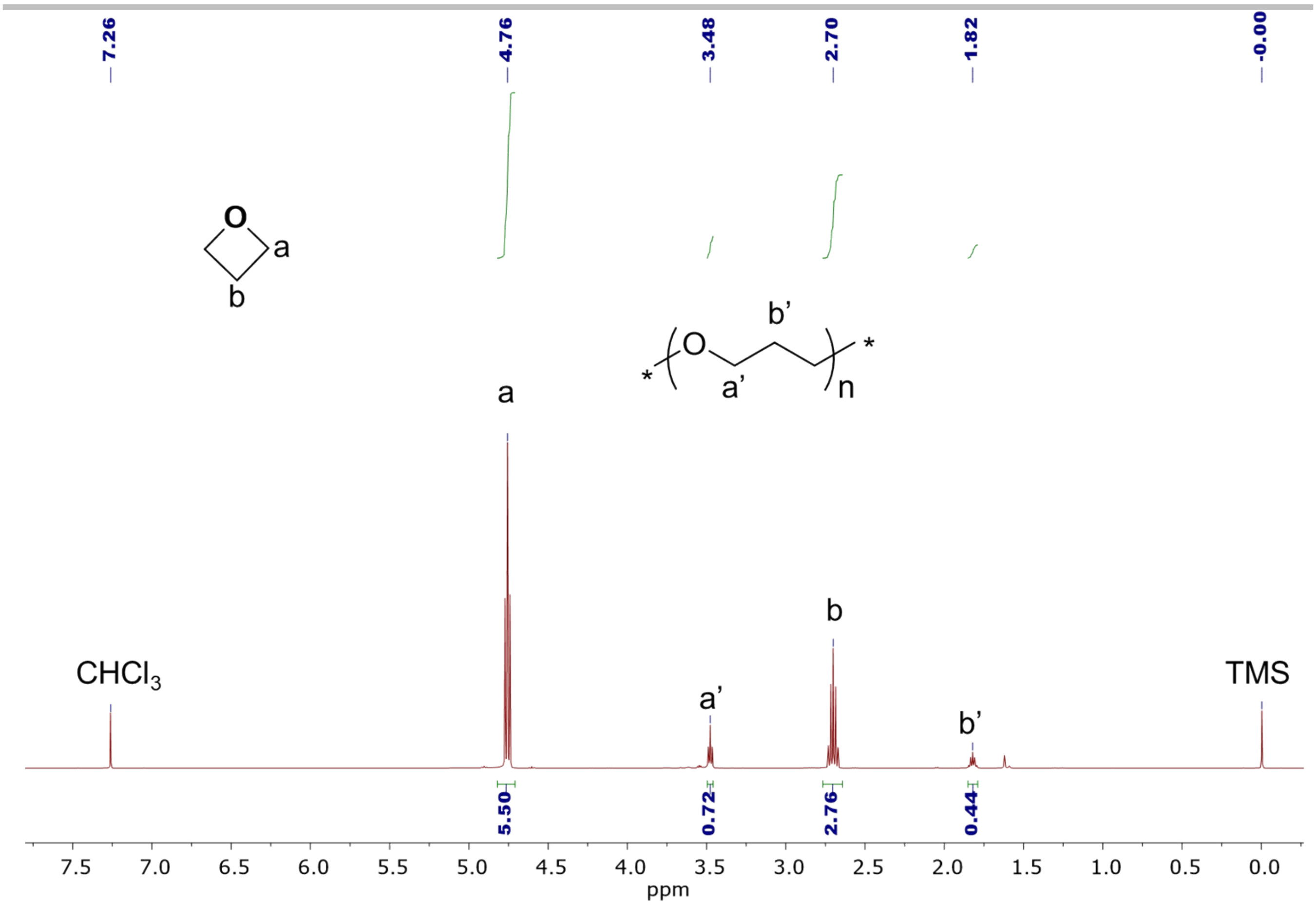

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the resultant mixture of oligomerization. Conditions: 7.88 mmol oxetane, $[I_2]_0//[EP]_0 = 1/40$, 0.1 MPa N_2, 105 °C, 8 mintues.

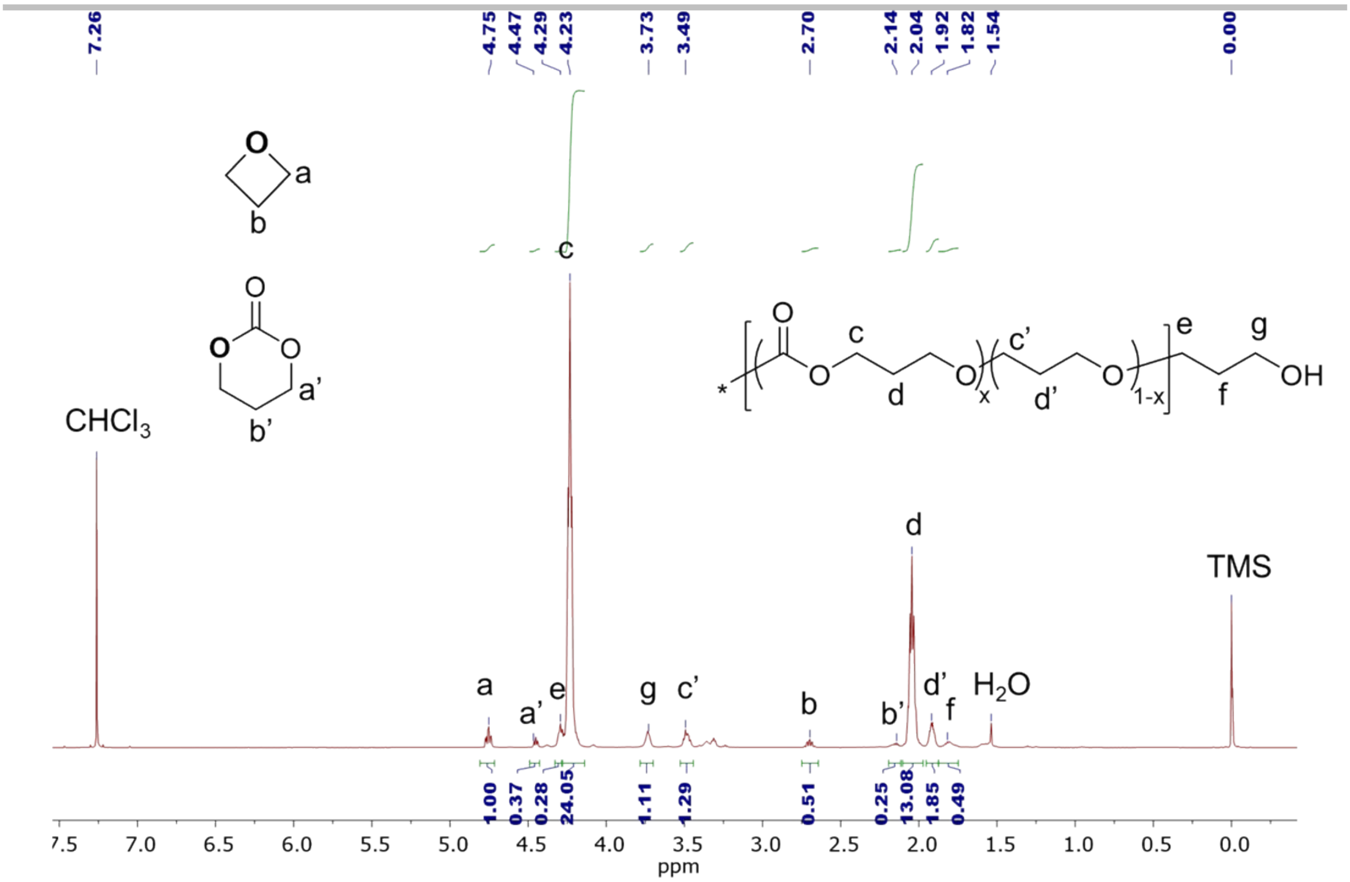

Figure S3. ^{1}H NMR spectrum (CDCl$_3$, 500 MHz) of the resultant mixture of polymerization (Table 2, entry 3) Conditions: 7.88 mmol oxetane, $[I_2]_0/[TBD]_0/[EP]$ = 1/1/40, 3 MPa CO_2, 105 °C, 7 days.

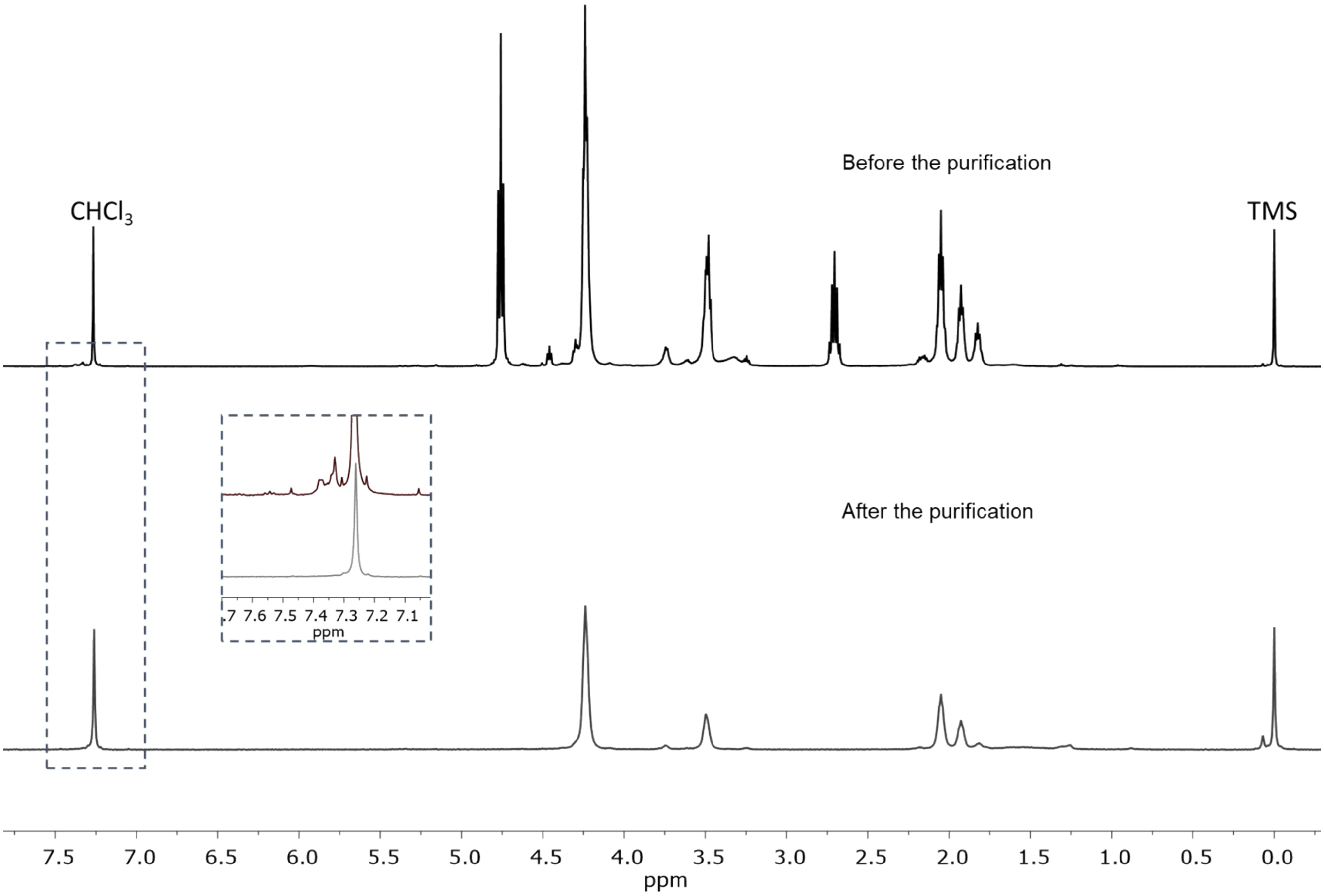

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of copolymer before and after the precipitation from methanol (Table S3, entry 1). Conditions: 7.88 mmol of oxetane, $[M]/[I_2]_0/[TBD]_0/[BnOH]_0$ = 100/2.5/2.5/1, 1 MPa of CO_2, at 105 °C for 24 h.

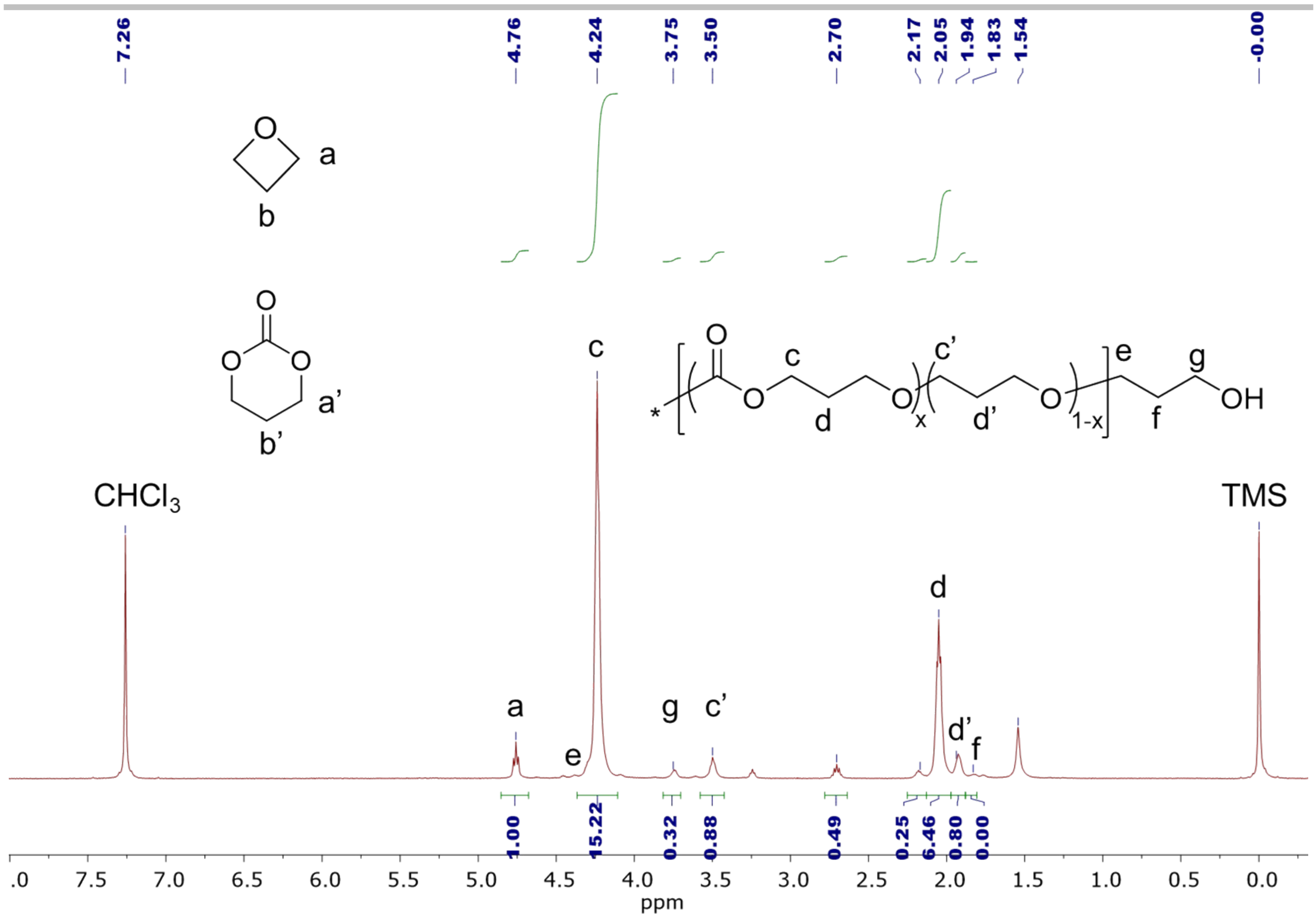

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the resultant mixture of polymerization (Table S4, entry 1). Copolymerization conditions: 197 μmol of I_2/oxetane adduct (2.5mol%), $[TMC]_0/[Initiator]$ = 40/1, 1 MPa of N_2, at 105°C for 24 h.

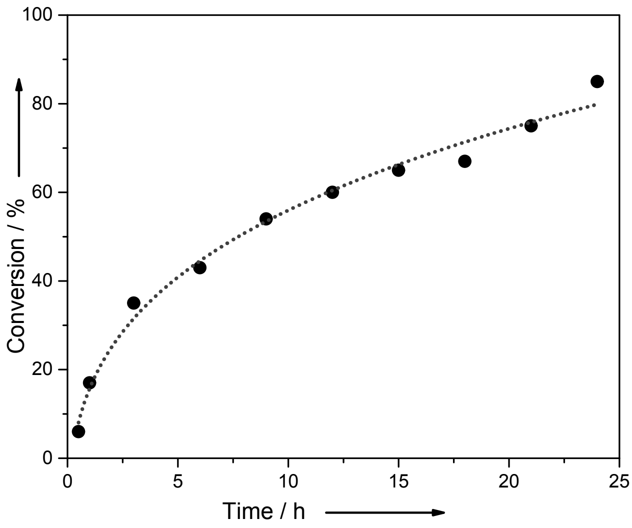

Figure S6. Chart of conversion of oxetane against time. Conditions of reaction: Copolymerization conditions: 197 μmol of I_2 (2.5 mol%), 7.88 mmol of oxetane, $[M]/[I_2]_0/[TBD]_0$ = 40/1/1, 1 MPa of CO_2, at 105 °C.

4. Reference

[1] M. Alves, B. Grignard, A. Boyaval, R. Méreau, J. De Winter, P. Gerbaux, C. Detrembleur, T. Tassaing, C. Jérôme, *ChemSusChem* **2017**, *10*, 1128-1138.