Electronic Supplementary Material (ESI) for Green Chemistry.

Bio-based polycarbonate from limonene oxide and CO_2 with high molecular weight, excellent thermal resistance, hardness and transparency

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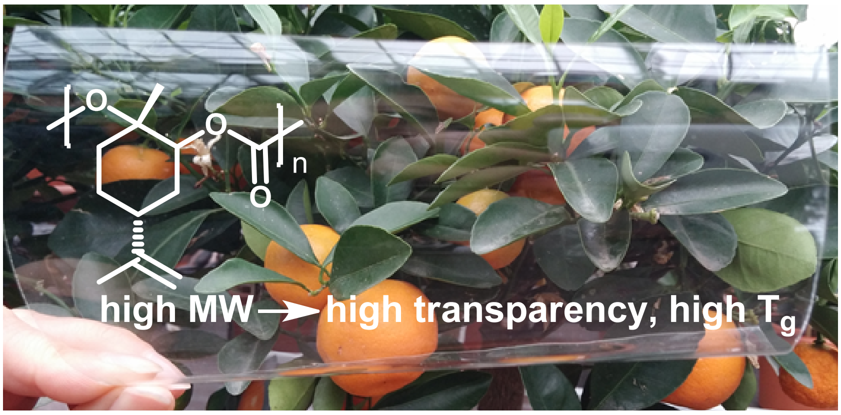
Supporting Information



Completely bio-based high molecular weight aliphatic poly(limonene carbonate) with excellent transparency, superior hardness compared to BPA-PC and a high T_g of 130 °C.

NMR Analysis of PLimC from copolymerisation of *trans*-LO and CO_2 with (bdi)ZnOAc.

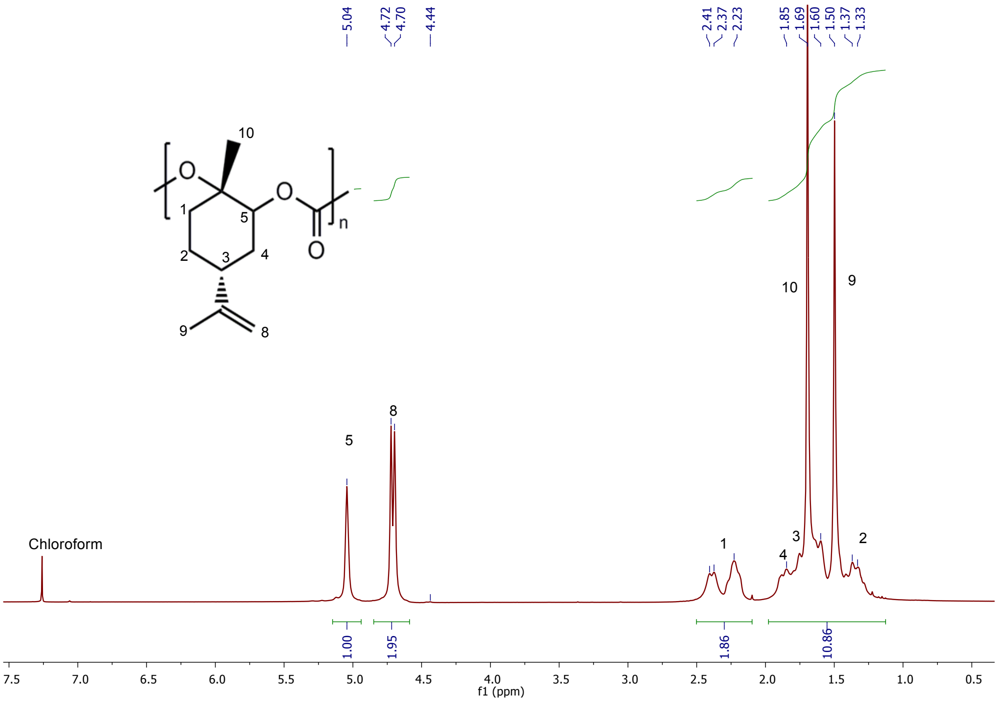


Fig. S1: ^1H NMR spectrum of PLimC (entry 5, table 1) recorded at 300 MHz in $CDCl_3$.

^1H NMR (300 MHz, $CDCl_3$): δ 5.04 (1H, s, C(5)H), 4.71 (2H, m, C(8)H_2), 2.42-2.20 (2H, m, C(1)H_2), 1.85 (2H, m, C(4)H_2), 1.71 (1H, m, C(3)H), 1.69 (3H, s, C(10)H_3), 1.50 (3H, s, C(9)H_3), 1.33 (2H, m, C(2)H_2) ppm

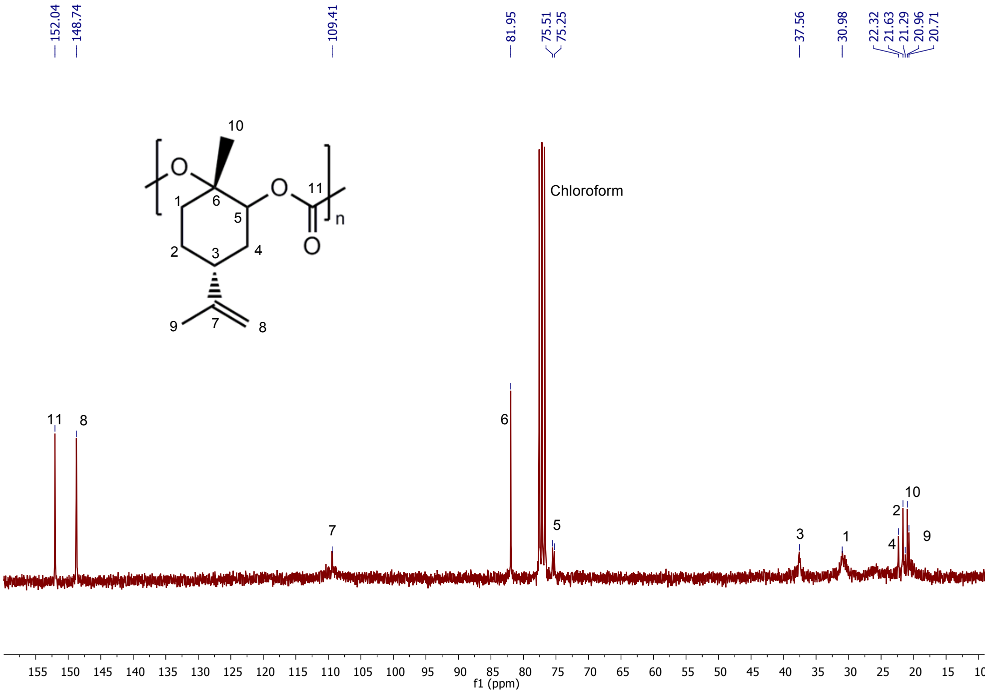


Fig. S2: ^{13}C NMR spectrum of PLimC (entry 5, table 1) recorded at 300 MHz in $CDCl_3$.

^{13}C NMR (300 MHz, $CDCl_3$): δ 152.0 (C11), 148.7 (C8), 109.4 (C7), 82.0 (C6), 75.4 (C5), 37.6 (C3), 31.0 (C1), 22.3 (C4), 21.6 (C2), 21.0 (C10), 20.7 (C9) ppm

DSC Analysis of PLimC

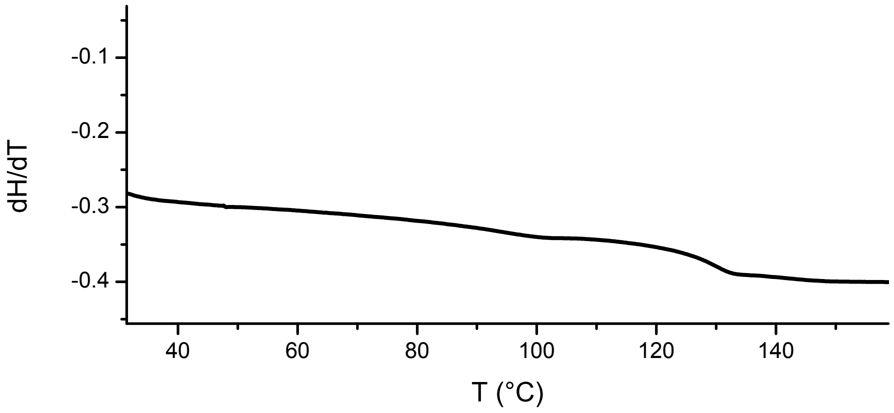


Fig. S3: DSC thermogram of PLimC (entry 5, table 1) with second heating curve measured at 10 K min^{-1}.

Characterisation of EDTA immobilised on silica

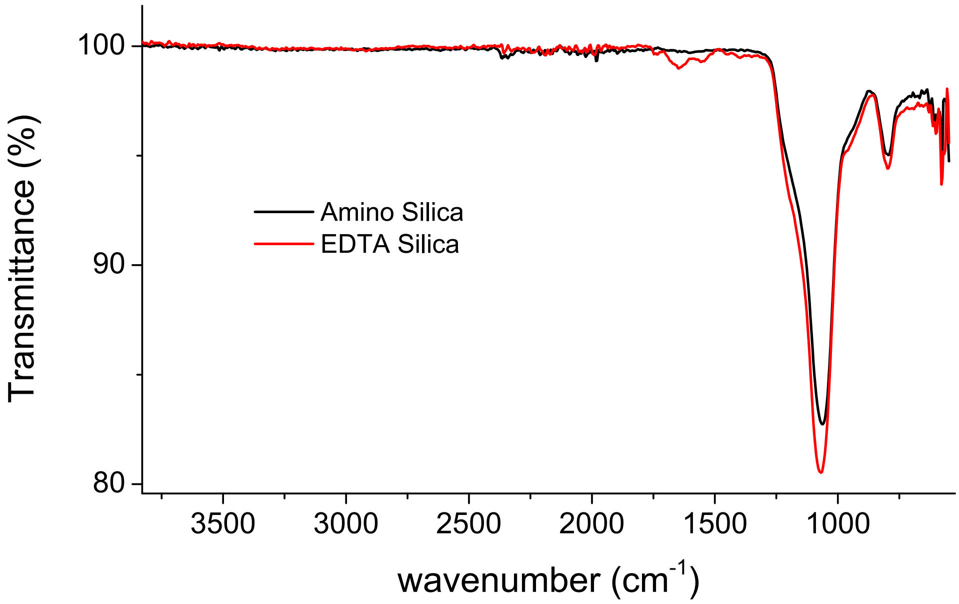


Fig. S4: ATR-FTIR spectra of amino-functionalised silica (straight) and EDTA functionalised silica (dotted).

The resonances of functionalisation on silica particles are rather low (Figure S4), i.e. amine vibrations are not observable at all and EDTA carbonyl vibrations are weak. Hence thermogravimetric analysis was employed to quantify the degree of functionalisation (Figure S5).

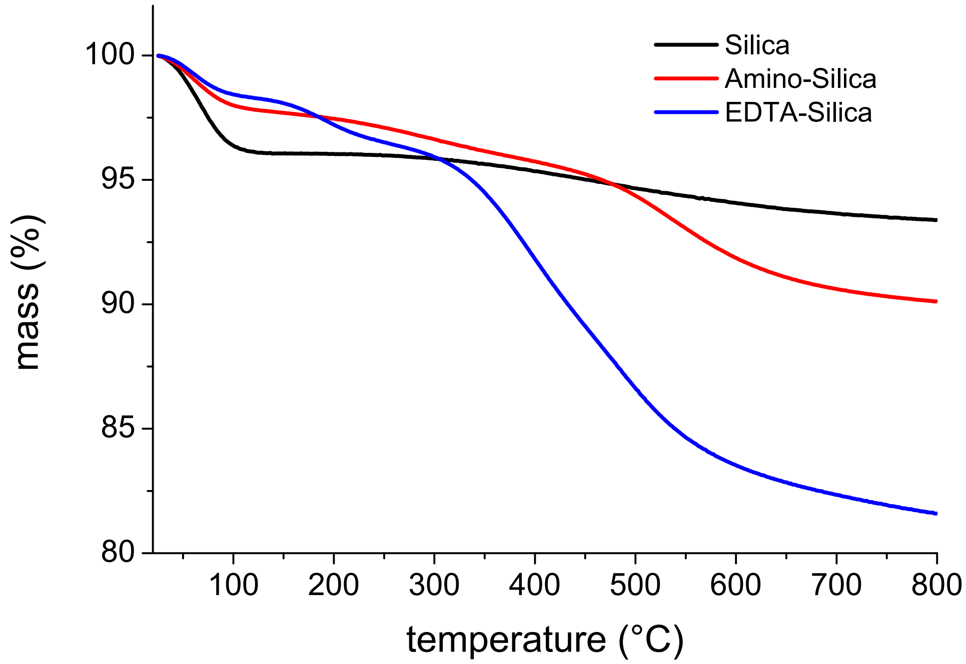


Fig. S5: Thermogravimetric analysis of Silica, amino-functionalised silica and EDTA-functionalised silica.

Kinetic investigation of copolymerisation of LO and CO_2

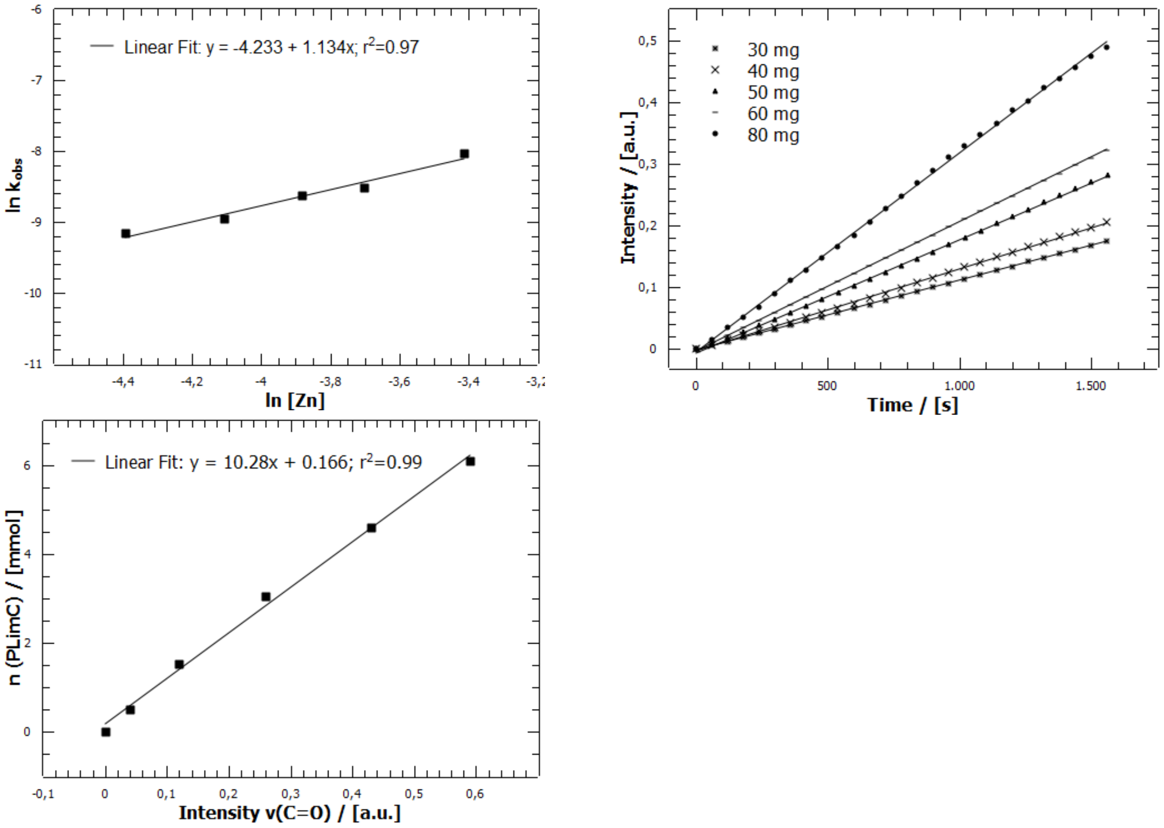


Fig. S6: Left: Determination of catalyst order in copolymerisation of CO_2/LO. Right: Determination of the copolymerisation rate k_{obs} as a change of absorbance at 1749 cm^{-1} with time at different loadings of (bdi)Zn(OAc) (Reaction conditions: 5 mL limonene oxide, 11 bar CO_2, 20 °C, catalyst concentration: 12.3 - 32.9 mM, without solvent, measured in reactor 1 of the ATR IR Mettler Toledo). Bottom: Calibration curve (neat LO), n(PLimC) against the intensity of the carbonyl stretching bond of PLimC, pressurised with 11 bar CO_2 at 20 °C in reactor 1.

Table S1. Summary of the IR experiments (catalyst concentration 12.3-32.9 mM, 11 bar CO_2, 5 mL LO, 20 °C).

V (LO) / [mL]	n (LO) / [mmol]	Total volume / [mL]	n (Zn) / [mmol]	[Zn] / [M]	ln c(Zn)	k_{obs} / [a.u.·s^{-1}]^a	ln k_{obs}	TOF / [h^{-1}]^b
5.00	30.5	5.00	0.061	0.0123	-4.40	0.000110	-9.12	70
5.00	30.5	5.00	0.082	0.0165	-4.10	0.000129	-8.96	60
5.00	30.5	5.00	0.103	0.0206	-3.88	0.000180	-8.62	66
5.00	30.5	5.00	0.123	0.0247	-3.70	0.000201	-8.51	62
5.00	30.5	5.00	0.165	0.0329	-3.41	0.000325	-8.03	74

[a] k_{obs} is defined as biggest slope of a respective curve in a.u.·s^{-1}. [b] TOF (turnover frequency) = mol(PLimC)·mol(Zn)$^{-1}$·h^{-1} (calibration curve S6, bottom).

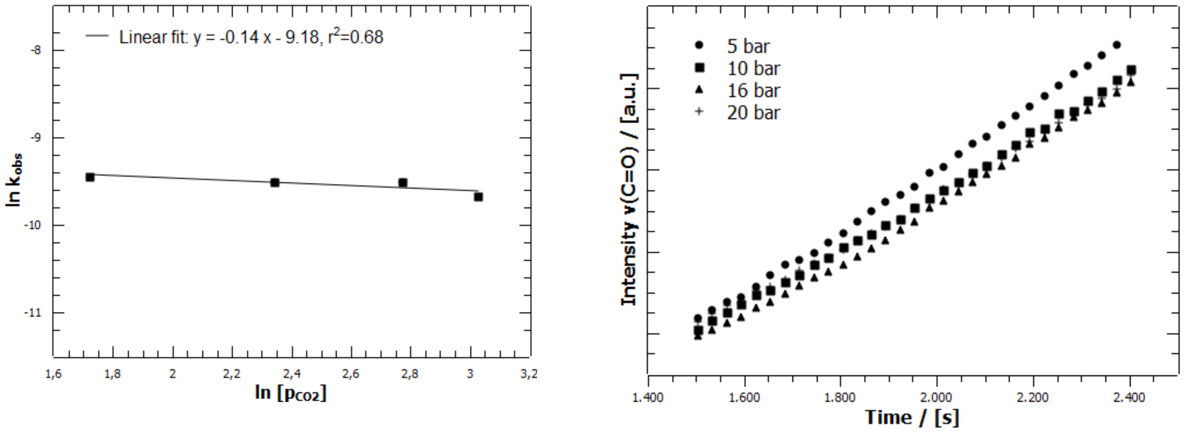


Fig. S7: Left: Determination of carbon dioxide order in copolymerisation of CO_2/LO. Right: Determination of the copolymerisation rate k_{obs} as a change of absorbance at 1749 cm^{-1} with time at different CO_2 pressures (Reaction conditions: 5 mL limonene oxide, catalyst loading 0.4 %, 20 °C, CO_2 pressure 5-20 bar, measured in reactor 2 of the ATR IR Mettler Toledo).

Table S2. Summary of the IR experiments (CO_2 pressure 5-20 bar, 0.061 mmol catalyst, 5 mL LO).

V (LO) / [mL]	n (LO) / [mmol]	Total volume / [mL]	n (Zn) / [mmol]	CO_2 pressure	ln (CO_2 pressure)	k_{obs} / [a.u.·s^{-1}]^a	ln k_{obs}
5.00	30.5	5.00	0.061	5.6	1.72	0.000078	-9.45
5.00	30.5	5.00	0.061	10.4	2.34	0.000074	-9.51
5.00	30.5	5.00	0.061	16.0	2.77	0.000074	-9.51
5.00	30.5	5.00	0.061	20.6	3.03	0.000063	-9.68

[a] k_{obs} is defined as biggest slope of a respective curve in a.u.·s^{-1}.

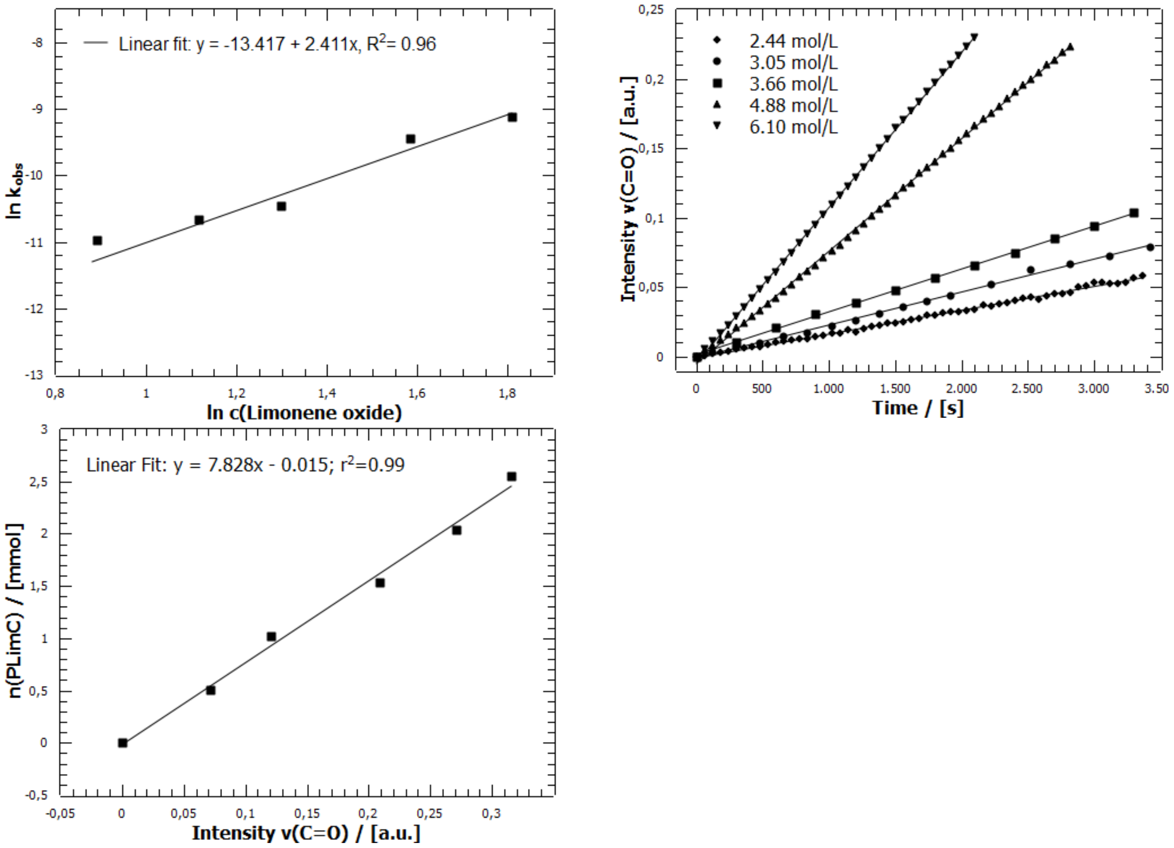


Fig. S8: Left: Determination of limonene oxide order in copolymerisation of CO_2/LO. Right: Determination of the copolymerisation rate k_{obs} as a change of absorbance at 1749 cm^{-1} with time at different LO concentrations (Reaction conditions: n(catalyst) = 0.061 mmol, 20 °C, 11 bar CO_2, concentration LO: 2.4 - 6.1 mol/L, measured in reactor 1 of the ATR IR Mettler Toledo). Bottom: calibration curve (2.5 mL toluene), n(PLimC) against the intensity of the carbonyl stretching bond of PLimC, pressurised with 11 bar CO_2 at 20 °C in reactor 1.

Table S3. Summary of the IR experiments (concentration (LO) 2.4-6.1 M, 11 bar CO_2, 0.061 mmol catalyst).

V (LO) / [mL]	n (LO) / [mmol]	Total volume / [mL]	n (Zn) / [mmol]	[LO] / [M]	ln c(LO)	k_{obs} / [$a.u.\cdot s^{-1}$][a]	ln k_{obs}	TOF [h^{-1}][b]
2.00	12.2	5.00	0.061	2.44	0.892	0.000017	-11.0	n.d.
2.50	15.3	5.00	0.061	3.05	1.115	0.000024	-10.7	11
3.00	18.3	5.00	0.061	3.66	1.297	0.000029	-10.5	n.d.
4.00	24.4	5.00	0.061	4.88	1.585	0.000079	-9.44	n.d.
5.00	30.5	5.00	0.061	6.10	1.808	0.000110	-9.12	70

[a] k_{obs} is defined as biggest slope of a respective curve in $a.u.\cdot s^{-1}$. [b] TOF (turnover frequency) = mol(PLimC)·mol(Zn)$^{-1}$·h^{-1} (Calibration curve S8 (2.5mL toluene) and S6 (no toluene) bottom).

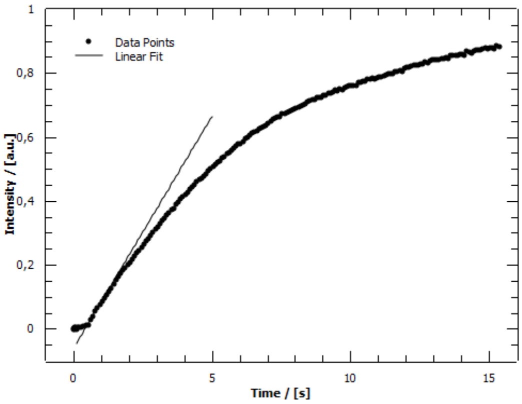


Fig. S9: Intensity of the carbonyl stretching bond of PLimC against time with an induction period of about one hour. (Reaction conditions: concentration limonene oxide: 3.66 mol/L, 11 bar CO_2, room temperature, catalyst concentration: 0.4 %, volume (toluene): 2.0 mL.).

Table S4: Determination of the calibration curve by varying concentrations of PLimC and LO.

Mass of Poly(limonene carbonate) [g]	Volume of toluene [mL]	Volume of limonene oxide [mL]	Concentration of limonene oxide [M]	Conversion [a.u.]	Intensity of ν(C=O) [a.u.]
0.00	2.50	2.50	3.05	0	0
0.10	2.50	2.40	2.93	0.04	0.072
0.20	2.50	2.30	2.81	0.08	0.121
0.30	2.50	2.20	2.68	0.12	0.209
0.40	2.50	2.10	2.56	0.16	0.271
0.50	2.50	2.00	2.44	0.20	0.316
0.75	2.50	1.75	2.13	0.30	0.431
1.00	2.50	1.50	1.83	0.40	0.598
1.50	2.50	1.00	1.22	0.60	0.800
2.00	2.50	0.50	0.61	0.80	1.000

Determination of the calibration curve. A defined amount of poly(limonene carbonate), toluene and limonene oxide were transferred into the IR-autoclave. After pressurizing the autoclave with 11 bar CO_2 at room temperature the system needs about two hours to completely solve the polymer to get a stable value for the intensity of the carbonyl stretching bond (measured in reactor 2 of the ATR IR Mettler Toledo).

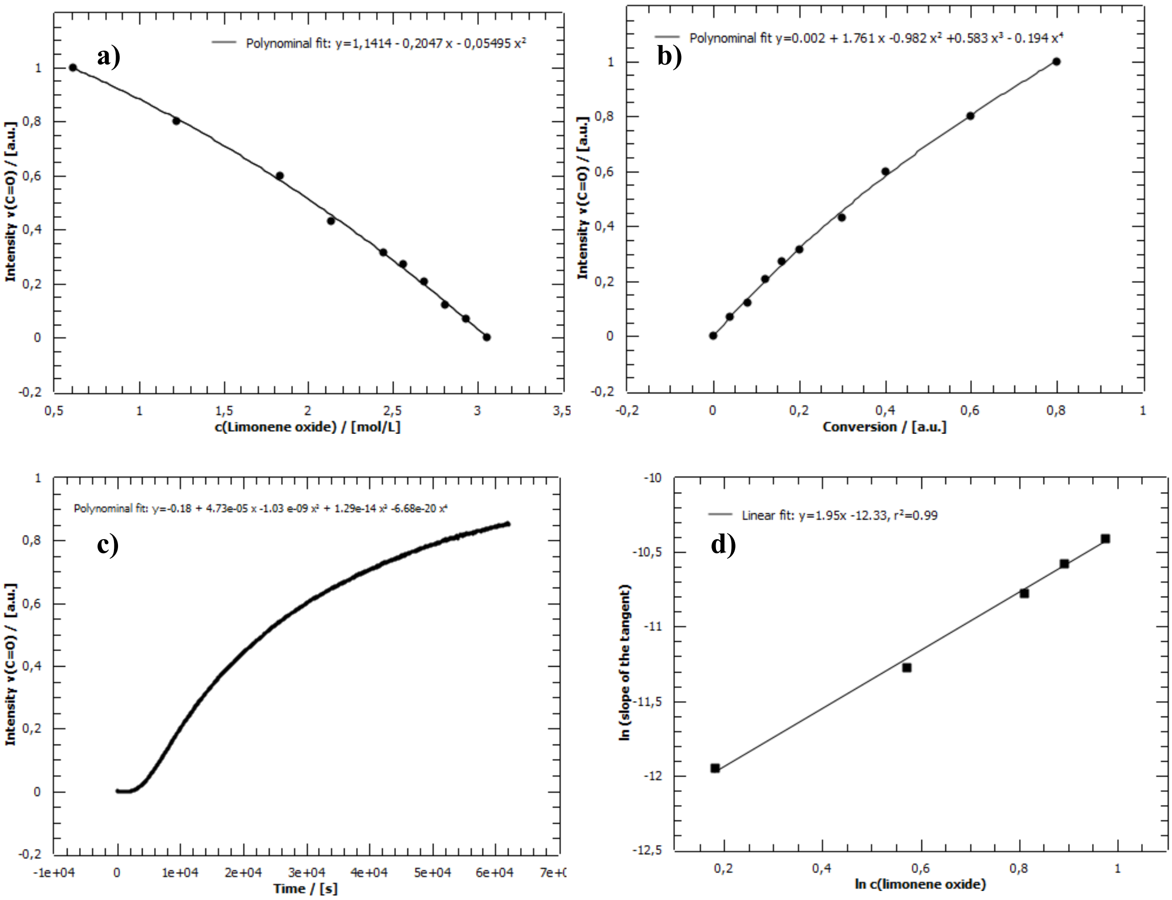


Fig. S10: a) Intensity of the carbonyl stretching bond of PLimC against the concentration of LO measured in the in situ ATR-IR. b) Intensity of the carbonyl stretching bond of PLimC against conversion. c) Intensity of the carbonyl stretching bond of PLimC against time (Reaction conditions 2.5 mL LO, 2.5 mL toluene, 11 bar CO_2, room temperature, catalyst loading 0.4 %), d) Determination of the order in limonene oxide by double logarithmic plot of the slope of the tangent against the concentration of LO.

Derivation of the polynominal fit:

(1) $f(x) = -0.18 + 4.73e\text{-}05\ x - 1.03\ e\text{-}09\ x^2 + 1.29e\text{-}14\ x^3 - 6.68e\text{-}20\ x^4$

(2) $f'(x) = 4.73e\text{-}05 - 2.06e\text{-}09\ x + 3.87e\text{-}14\ x^2 - 2{,}67e\text{-}19\ x^3$

Table S5: Overview about the correlation of the conversion and the corresponding concentration of limonene oxide with the intensity of the carbonyl stretching bond and the slope of the tangent. (Reaction conditions: 2.5 mL toluene, 2.5 mL limonene oxide, catalyst loading 0.4 %, 11 bar CO_2, room temperature).

Conversion [a.u.]	Intensity v[C=O]	Slope of tangents (f´(x))	ln f´(x)	c (limonene oxide) / [M]	ln c(limonene oxide)
0.2	0.316	3.01e-05	-10.41	2.44	0.97
0.3	0.431	2.56e-05	-10.57	2.13	0.89
0.4	0.598	2.10e-05	-10.77	1.83	0.81
0.6	0.800	1.27e-05	-11.27	1.22	0.57
0.8	1.000	6.47e-06	-11.95	0.61	0.18

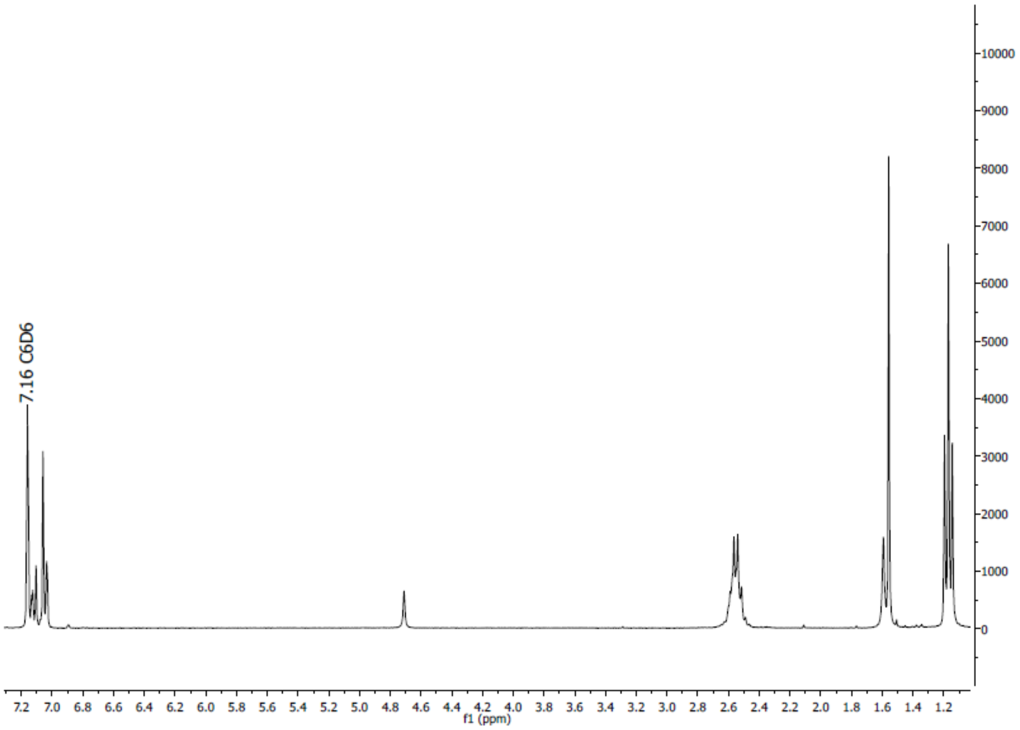


Fig. S11: ^{1}H NMR spectrum of the catalyst (bdi)ZnOAc recorded in C_6D_6.

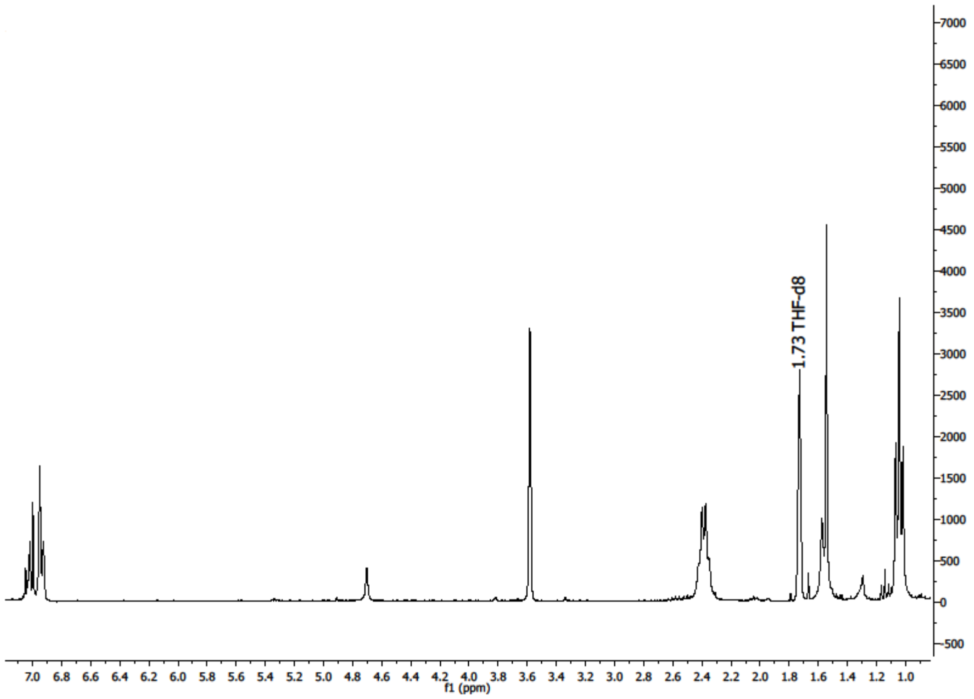


Fig. S12: ^{1}H NMR spectrum of catalyst (bdi)Zn(OAc) recorded in THF-d_8.

Stress Strain Curves of PLimC

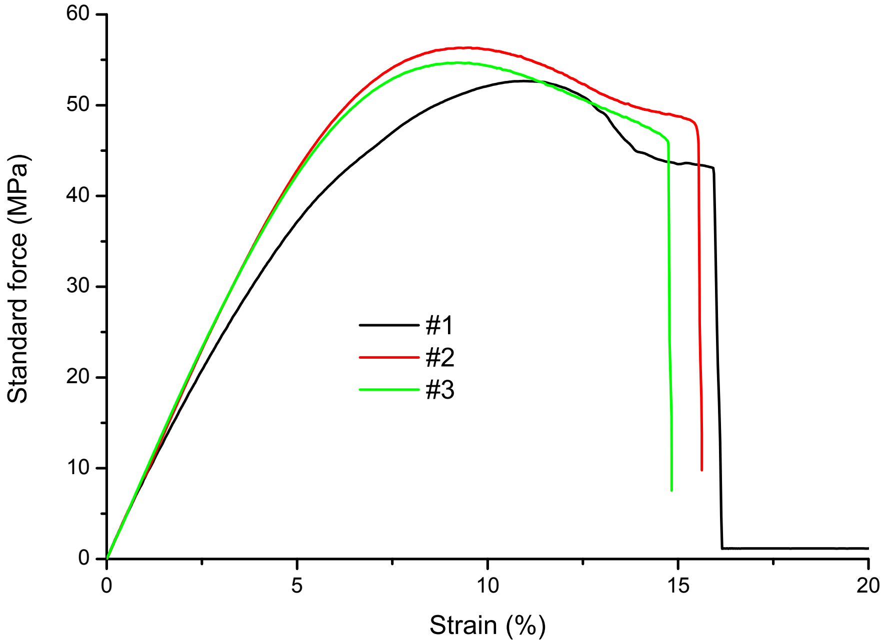


Figure S13: Stress strain curves of PLimC with M_n = 54 kDa, measured at a strain rate of 5 mm/min.