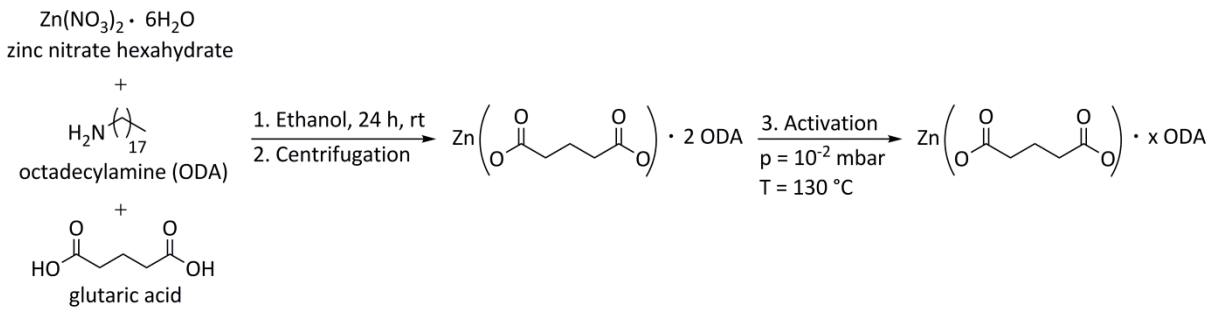
Supplementary Information

Synthesis of ZnGA

Active ZnGA was synthesized as previously reported (see Scheme S1).[1] 0.80 kg (2.7 mol) zinc nitrate hexahydrate and 0.34 kg (2.6 mol) GA were dissolved in 40.1 L ethanol and stirred for 15 minutes. Subsequently, 3.00 kg (11.1 mol) ODA were added and the reaction mixture was stirred vigorously for 24 hours at room temperature. The suspension was transferred into 500 mL tubes and centrifuged at 3000 rpm (1500 g) for 5 min. The colorless supernatant was discarded and the residue was collected and washed with 14 L ethanol. The washing procedure was repeated two times. After removing the residual solvent *in vacuo* at 50 °C 1.81 kg (97 %) of the ZnGA-ODA-adduct were obtained. Elem. anal. found (calcd. for ZnGA · 2 ODA): C, 67.0 (67.0); H, 11.4 (11.5); N, 3.81 (3.74); O, 8.75 (8.71).

The adduct was pestled and ODA was removed in a conical 10 L reactor (Juchheim Laborgeräte GmbH) at reduced pressure (10^{-2} mbar) and 135 °C for 6.5 d. The resulting light-brownish solid was ball-milled at 300 rpm for 1.5 h using 20 mm stainless steel balls under inert atmosphere. Subsequently, the solid was transferred into the 10 L reactor. Residual ODA was removed at reduced pressure (10^{-2} mbar) and 135 °C for 3.5 d yielding 487 g ZnGA. Elem. anal. found (calcd. for ZnGA·0.34 ODA): C, 42.9 (46.5); H, 5.89 (6.76); N, 1.67 (1.66); O, 24.9 (22.3)



Scheme S1: **Synthesis of the catalytic precursor ZnGA · 2 ODA and subsequent activation to nanoscopic ZnGA.**

Figure S1 displays the SEM image of nanoscopic ZnGA. The particle size is in accordance with the literature.[1]

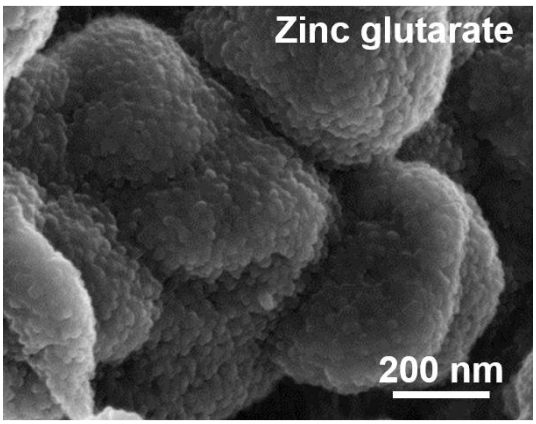


Figure S1: SEM image of nanoscopic ZnGA.

The PXRD of nanoscopic ZnGA and standard ZnGA prepared as previously reported[2] is displayed in Figure S2.

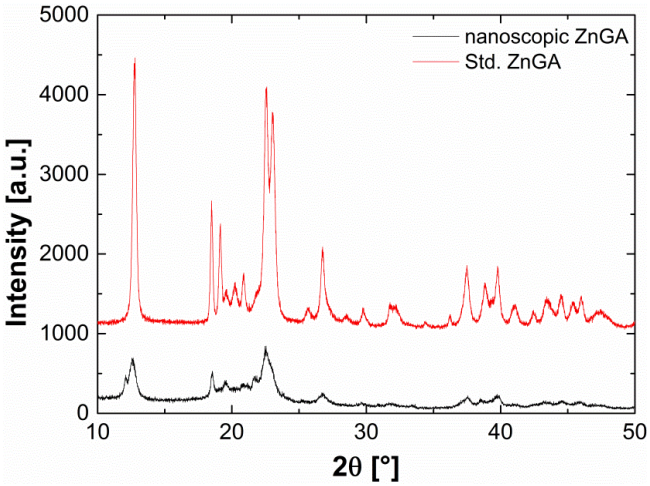


Figure S2. PXRD of nanoscopic ZnGA in comparison to standard ZnGA.

The mole fractions of CO_2 in PO in dependence of the pressure are displayed in Figure S3 for different temperatures. The values for 90 °C were extrapolated using the PENG-ROBINSON equation of state.

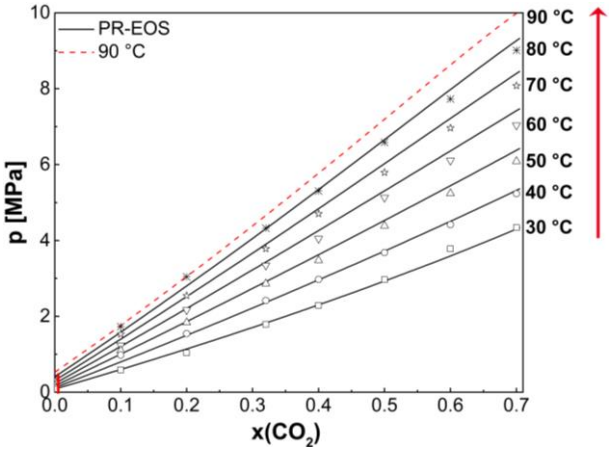


Figure S3: CO_2-solubility data in PO at temperatures between 30 and 80 °C.[3] The red dots display the vapor pressure of neat PO, *i.e.* the pressure at $x(CO_2) = 0$.[4] The mole fraction of CO_2 under the specific reaction conditions was obtained solving the PENG-ROBINSON equation of state. The dotted red line displays the extrapolated x(CO2) at 90 °C.

The pseudo-living behavior of the copolymerization was also observed at other pressures (Figure S4).

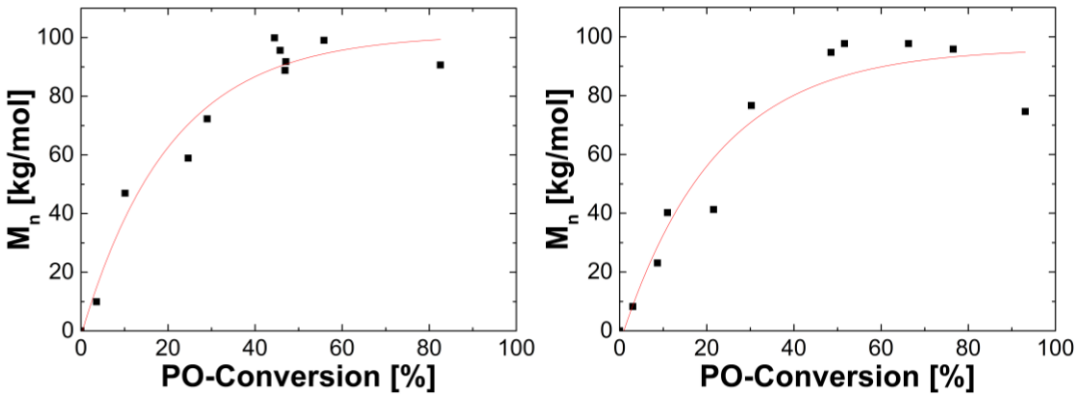


Figure S4: Conversion dependence of the number average molecular weight for the PO/CO_2 polymerization at 60 °C and 2.35 MPa (left) and 4.1 MPa (right).

Table S1 displays the additional experimental results for the verification of the prediction accuracy.

Table S1: Experimental data for the validation of the found empirical models. Reaction conditions: V_{PO} = 50 mL, t = 4 h.

T [°C]	p [MPa]	m(Kat) [mg]	TOF[a] [h^{-1}]	F_{Carb}[b] [mol.-%]	M_n[c] [kg/mol]	M_w[c] [kg/mol]
60	0.6	25	103	75.5	38.4	157
30	2.35	25	7	79.8	1.3	3.3
90	2.35	25	160	78.8	40.3	71
60	4.1	25	165	91.8	40.2	331
30	0.6	137.5	31	86.5	22.7	151
90	0.6	137.5	47	37.9	21.0	86
30	4.1	137.5	13	75.6	13.4	102
90	4.1	137.5	179	82.7	64.5	113
60	0.6	250	59	70.3	60.1	265
30	2.35	250	35	82.5	26.9	306
90	2.35	250	104	70.3	38.3	65
60	4.1	250	122	91.1	95.8	394

[a] [$g_{Polymer}/g_{Zn}$ h], [b] determined by ^{1}H-NMR spectroscopy, [c] determined by SEC in THF against PS standards

References

1 Verfahren zur Herstellung von Zinkdicarboxylaten, WO 2013/034489, 2013.

2 S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott and B. Rieger, *J. Am. Chem. Soc.*, 2011, **133**, 13151–13161.

3 J.-J. Wang, J.-T. Duan, L. Wang, X.-P. Gu and L.-F. Feng, *J. Chem. Eng. Data*, 2010, **55**, 3379–3382.

4 T. R. Bott and H. N. Sadler, *J. Chem. Eng. Data*, 1966, **11**, 25–25.