Nacnac^{Bn}CuO*i*Pr: A strained geometry resulting in very high lactide polymerization activity

Todd J. J. Whitehorne,[a] Frank Schaper*,[a]

Supporting Information

Table S1. Selected bond lengths [Ǻ] and angles [°] for **2**

Cu-N1/31	1.921(3), 1.923(3)	N-Cu-N	95.2(1), 94.9(1)
Cu-N2/32	1.951(3), 1.946(3)	Cu-Cu-N1/31	129, 128
Cu-O	1.951(2), 1.979(2), 1.954(2), 1.982(2)	Cu-Cu-N2/32	136, 137
		(N,Cu)-(O,Cu)[a]	41, 43

[a] tilt angle between (N,N,Cu) and (Cu,O,O,Cu) least-square planes.

Table S2. Selected data for the polymerization of *rac*-lactide in CH_2Cl_2.

#	Catalyst/lactide	Equiv. *i*PrOH	[Cu]/(mmol·L^{-1})	*t*/s	Conversion[a] (%)	$M_{n,calc}$[c]/(g·mol^{-1})	M_n[d]/(g·mol^{-1})	M_w/M_n[d]
1	1/300	-	2.0	25	97	42005	44604	1.07
2	1/300	-	0.50	90	93	40275	37472	1.06
3	1/300	-	0.25	180	80	34654	34255	1.03
4	1/3000	-	0.25	150	95[b]	410859[b]	487976	1.48[b]
5	1/300	1	2.0	45	96	20816	27302[e]	1.04[e]
6	1/300	2	2.0	45	95	13849	19103[e]	1.04[e]
7	1/300	5	2.0	45	97	7003	8491[e]	1.07[e]
8	1/300	10	2.0	45	96	3834	5329[e]	1.11[e]
9	1/300	-	2.0	90	85	36816	45260	1.03
	1/600	-	2.0	90	91	78328	96290	1.05
	1/900	-	2.0	90	91	118111	159959	1.08

[a] Calculated from ^{1}H NMR spectra. [b] PLA precipitates at 80% conversion, final conversion estimated. [c] Calculated from ([lactide]$_0$/[*i*PrOH]$_0$+[Cu])·conversion·144 + 60. [d] Determined by size exclusion chromatography *vs.* polystyrene standards, corrected by a Mark-Houwink factor of 0.58.[1] [e] Average of multiple experiments.

Experimental

All reactions were carried out using Schlenk and glove box techniques under a nitrogen atmosphere. *Nacnac*BnH, **1**,[2] and Cu(O*i*Pr)$_2$ starting material[3] was synthesized according to literature methods. Solvents were dried by passage through activated aluminum oxide (MBraun SPS), de-oxygenated by repeated extraction with nitrogen, and stored over molecular sieves. C_6D_6 was dried over sodium and degassed by three freeze-pump-thaw cycles. $CDCl_3$ and CD_2Cl_2 were dried over 3 Å molecular sieves. *rac*-Lactide (98%) was purchased from Sigma–Aldrich, purified by 3 times recrystallization from dry ethyl acetate and kept at -30 ˚C. All other chemicals were purchased from common commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AVX 400 spectrometer. The chemical shifts were referenced to the residual signals of the deuterated solvents (C_6D_6: ^{1}H: δ 7.16 ppm, ^{13}C: δ 128.38 ppm, $CDCl_3$: ^{1}H: δ 7.26 ppm, CD_2Cl_2: ^{1}H: δ 5.32 ppm). Elemental analyses were performed by the Laboratoire d'analyse élémentaire (Université de Montréal). Molecular weight analyses were performed on a Waters 1525 gel permeation chromatograph equipped with three Phenomenex columns and a refractive index detector at 35 ˚C. THF was used as the eluent at a flow rate of 1.0 mL·min^{-1} and polystyrene standards (Sigma–Aldrich, 1.5 mg·mL^{-1}, prepared and filtered (0.2 mm) directly prior to injection) were used for calibration. Obtained molecular weights were corrected by a Mark-Houwink factor of 0.58.[1]

***Nacnac*^{Bn}CuO*i*Pr, 2.** Cu(O*i*Pr)$_2$ (500 mg, 2.75 mmol) was suspended in hexanes or toluene (20 mL). **1** (610 mg, 2.20 mmol) was added slowly to the mixture and allowed to react at room temperature for 18 h. The reaction mixture changed colour from deep green to deep blue. Solvent and *i*PrOH was removed under reduced pressure. The blue solid was then taken up in toluene (15 mL) and filtered through a fine frit. The filtrate was placed at -25 °C, yielding X-ray quality crystals (550 mg, 63%). Anal. calcd for $C_{22}H_{28}CuN_2O_1$: C 66.1, H 7.1, N 7.0. Found: C 66.3, H 7.2, N 6.8. UV/vis (toluene): λ/nm (ε·M·cm) 357 (10000), 431 (570), 523 (560), 720 (sh, 100). UV/vis (THF): λ/nm (ε·M·cm) 421 (sh 470), 533 (400).

Lactide Polymerizations. Typical example: In a dry box, a vial was charged with a stir bar, *rac*-lactide (170 mg, 1.2 mmol) and CH_2Cl_2 (2 mL). After dissolution of lactide, a solution of **2** in CH_2Cl_2 (53 µL, 75 mM, 4 µmol) was added and a stopwatch initiated. Every 5 sec, a sample of the reaction mixture (100 µL) from the polymerization mixture was transferred to a test tube, charged with a solution of acetic acid in CH_2Cl_2 (100 µL, 4 mM, 0.4 µmol). After one minute, the remaining reaction mixture was quenched by addition of a solution of acetic acid in CH_2Cl_2 (0.8 mL, 4 mM, 3.2 µmol). Samples and polymerization mixture were then removed from the dry box and the solvent evaporated immediately under reduced pressure. If not analyzed directly, polymers were stored at –80 °C.

Microstructure analysis. P_r-values were determined from the integration of the methine region in homonuclear decoupled ^{1}H NMR spectra of PLA in $CDCl_3$ and calculated according to $P_r = 2 \cdot I_1/(I_1+I_2)$, with I_1 = 5.20 – 5.25 ppm (*rmr, mmr/rmm*), I_2 = 5.13 – 5.20

ppm (*mmr/rmm, mmm, mrm*).[4] Resonances in ^{1}H spectra were assigned according to literature.[5]

X-ray crystallography. Diffraction data were collected on a Bruker Smart 6000 with a Helios monochromator, equipped with a rotating anode source for Cu Kα radiation. Cell refinement and data reduction were done using APEX2.[6] The crystal was found to be twinned. Two twin domains were identified by CELLNOW and included with scale factors refined to 0.45, 0.45, 0.06, and 0.04. Alternative integration with 2, 3 or 5 twin domains yielded higher R_{int} values. Reported R_{int} were obtained from TWINABS[6] based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions. Absorption corrections were applied using TWINABS.[6] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on calculated positions using a riding model.

Table S3 Details of the X-ray crystal structure of **2**.

Formula	$C_{22}H_{28}N_2OCu$
Formula Mass/g·mol^{-1}	400.00
Crystal system	triclinic
a/Ă	11.3590(4)
b/Ă	12.1536(4)
c/Ă	15.8854(5)
α/°	76.981(2)
β/°	80.639(2)
γ/°	71.993(2)
Unit cell volume/Ă^3	2021.7(1)
T/K	150
Space group	P-1
No. of formula units per unit cell, Z	4
Absorption coefficient, μ/mm^{-1}	1.606
No. of reflections measured	82878
No. of independent reflections	7954
R_{int}	8.59
Final *R1* values (I > 2σ(I))	0.059
Final $wR(F^2)$ values (I > 2σ(I))	0.159
Final *R1* values (all data)	0.083
Final $wR(F^2)$ values (all data)	0.169
Goodness of fit on F^2	1.025
Residual elec. density	0.72

Polymerization kinetics

Polymerization kinetics were studied at room temperature in CH_2Cl_2 solution. For polymerizations with [**2**] = 0.125 mM or 1 mM, samples were taken in the desired intervals, quenched with AcOH and analyzed by NMR. For polymerizations with [**2**] = 2.5 mM, acquiring samples was not possible and each data point corresponds to an independent experiment, resulting in increased errors for this concentration. At least two experimental rate constants were determined for each concentration, which differed by less than 20%.

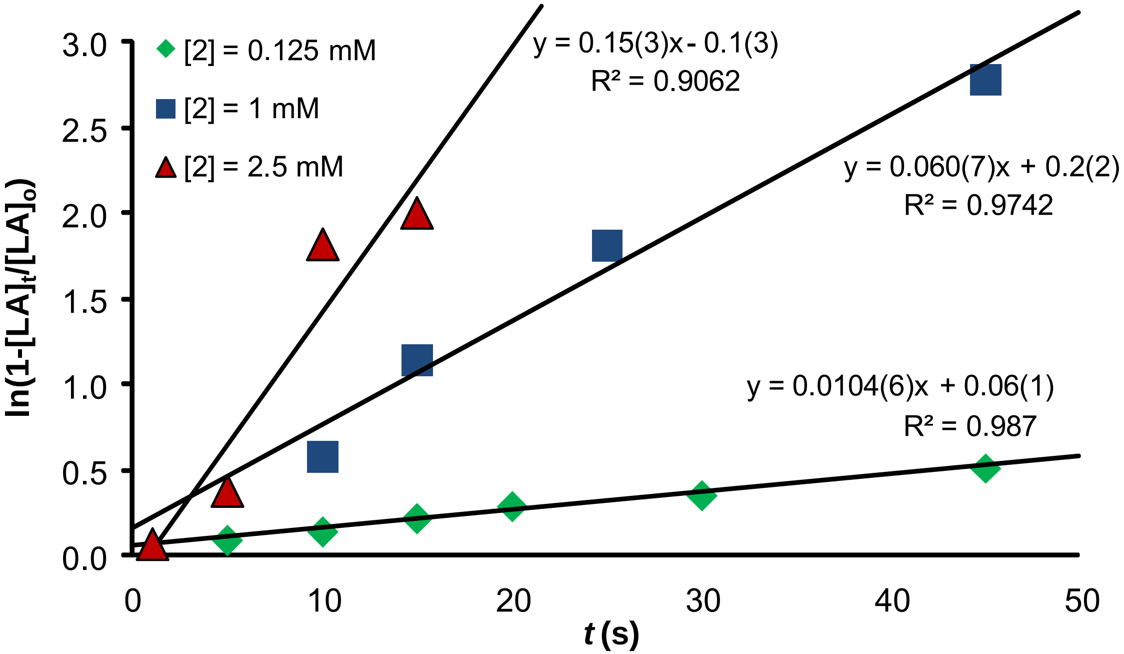

Figure S1: Selected examples of 1st order rate law determinations for varied concentrations of **2**, with [Cu]/[lactide] = 1/300.

1. M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889.
2. F. Drouin, P. O. Oguadinma, T. J. J. Whitehorne, R. E. Prud'homme and F. Schaper, *Organometallics*, 2010, **29**, 2139.
3. J. V. Singh, B. P. Baranwal and R. C. Mehrotra, *Zeitschrift für anorganische und allgemeine Chemie*, 1981, **477**, 235.
4. B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229.
5. (a) J. E. Kasperczyk, *Macromolecules*, 1995, **28**, 3937; (b) J. E. Kasperczyk, *Polymer*, 1999, **40**, 5455; (c) M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer and E. J. Munson, *Macromolecules*, 2002, **35**, 7700.
6. *APEX2*, (2006) Bruker AXS Inc., Madison, USA.
7. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.