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Bulky *ortho*-disubstituted phenolates of magnesium, calcium and zinc: structural features and comparison of catalytic properties in polymerization of ε-caprolactone and *rac*-lactide

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S1. General experimental remarks

All synthetic manipulations were performed under inert atmosphere using argon glove box and argon-vacuum line. Toluene, diethyl ether, and THF were refluxed with Na/benzophenone/dibenzo-18-crown-6, and distilled prior to use. Pentane and hexanes were refluxed over Na/K alloy for 12 hours, and then distilled. CH_2Cl_2 was washed with aqueous Na_2CO_3, stirred with $CaCl_2$ powder, refluxed over CaH_2 for 8 h, and distilled. $CDCl_3$ was distilled over P_2O_5 and stored over 4 Å molecular sieves. Metallocene synthesis was performed using standard Schlenk technique. Et_2Zn (1.1 M solution in toluene) and Bu_2Mg (1 M solution in heptane) were used as purchased (Aldrich). Racemic 3,6-dimethyl-1,4-dioxane-2,5-dione (LA) (Sigma-Aldrich, 99 %) was purified prior to use by sublimation and subsequent recrystallizations from dry toluene followed by drying *in vacuo*. ε-Caprolactone (ε-CL) (Sigma-Aldrich, 97 %) was distilled over CaH_2 prior to use. Benzyl alcohol (Acros, 99 %) was distilled over BaO and stored under argon. 4-*tert*-butyl-2,6-bis(diphenylmethyl)phenol (BDPMP)[1] and $CaI_2(THF)_4$[2] were synthesized using previously described methods.

$CDCl_3$ (Cambridge Isotope Laboratories, Inc., D 99.8 %) was used as purchased. THF-d_8 (Aldrich, ≥99.5 atom % ^2H) and benzene-d_6 (Aldrich, ≥99.6 atom % ^2H) were stored over sodium/benzophenone and condensed into NMR tubes using the Schlenk technique. NMR spectra were recorded on an Avance Bruker spectrophotometer (400 MHz) in $CDCl_3$, in THF-d_8 or in benzene-d_6. The chemical shifts are reported in ppm relative to the solvent residual peaks.

Size exclusion chromatography (SEC) was performed on an Agilent PL-GPC 220 chromatograph equipped with a PLgel column, and THF was used as the eluent (1 ml/min). The measurements were recorded with universal calibration according to a polystyrene standard at 40 °C. The molecular weights of all PLAs were corrected by a factor of 0.58 and all PCLs by a factor

of 0.56. Elemental analysis (C, H) was performed on a Perkin Elmer Series II CHNS/O Analyser 2400.[3]

S2. Preparation of BDPMP complexes

[Zn(Et)(μ-BDPMP)]2. Toluene solution of Et_2Zn (1.1 M, 3.0 ml, 3.3 mmol) was added to the stirred mixture of BDPMP-H (1.448 g, 3.00 mmol) and toluene (20 ml). After 30 seconds the solution became clear, and stirring was stopped. Next day, colorless precipitate was formed. Several crystals were taken out for X-ray studies, the precipitate was filtered off, washed with hexane (2×10 ml), and dried under dynamic vacuum. The yield of **1** was 1.569 g (1.36 mmol, 90.8%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.31-7.24 (m, 8H, H_{Ph}); 7.23-7.17 (m, 8H, H_{Ph}); 7.12-7.06 (m, 4H, H_{Ph}); 6.93 (s, 2H, -OC_6H_2); 6.20 (s, 2H, -C$H$$Ph_2$); 1.01 (s, 9H, -C($CH_3$)$_3$); 0.76 (t, $^3J_{HH}$ = 8.1 Hz, 3H, -CH_2CH_3,); -0.39 (quartet, 2H, -CH_2CH_3). For $C_{76}H_{76}O_2Zn_2$, 1152.20 Calc.: C 79.23% H 6.65% O 2.78%; Found: C 79.11% H 6.44% O 2.85%.

Mg(BDPMP)2(THF)2. Heptane solution of Bu_2Mg (1.0 M, 3.3 ml, 3.3 mmol) was added dropwise to stirred solution of BDPMP-H (2.888 g, 6.0 mmol) in a mixture of toluene (10 ml) and THF (4 ml). After 3 min of stirring the mixture was stored at room temperature. After 6 h, the solution was decanted form the microcrystalline precipitate. The solid was washed with hexane (2×10 ml), and dried under dynamic vacuum. The yield of **2** was 2.701 g (2.39 mmol, 79.5%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (d, 16H, o-H_{Ph}), 7.14-7.03 (m, 20H, m-H_{Ph} and OC_6H_2), 6.98 (t, 8H, p-H_{Ph}), 6.54 (s, 4H, -C$H$$Ph_2$), 2.85-2.70 (m, 8H, O$CH_2$), 1.21 (s, 18H, -C($CH_3$)$_3$), 0.99-0.87 (m, 8H, CH_2). To obtain crystals suitable for X-ray studies, 250 mg of the product was dissolved in minimal amount of a THF/toluene mixture (1:4 *v/v*), a large excess of hexane was layered on top. Crystals were formed after 4 days. For $C_{80}H_{82}MgO_4$, 1131.83 Calc.: C 84.90% H 7.30% O 5.65%; Found: C 84.44% H 7.35% O 5.77%.

Ca(BDPMP)2(THF)3. A $PhCH_2K$ (0.260 g, 2.00 mmol) solution in THF (5 ml) was added dropwise to a stirred solution of BDPMP-H (0.92 g, 1.90 mmol) in THF (5 ml). The resulting solution was added to a stirred suspension of $CaI_2(THF)_4$ (0.530 g, 0.910 mmol) in THF (5 ml). The reaction mixture was stirred for 30 min, and centrifuged. The resulting solution was concentrated under vacuum to c.a. 7 ml, and hexane (15 ml) was layered on top. After 3 days, single crystals of **3a** formed. Some crystals (52 mg, 0.01 mmol, 4.0%) were taken out for the single crystal X-ray studies. The remaining solution was decanted from the crystals, which were then washed with hexane (3×10 ml), and dried under dynamic vacuum to give 0.671 g (0.519 mmol, 57.1%) of **3b**. ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (d, 16H, o-H_{Ph}), 7.14-7.07 (m, 20H, m-H_{Ph} and OC_6H_2), 6.99 (t, 8H, p-H_{Ph}), 6.31 (s, 4H, -C$H$$Ph_2$), 3.27-3.18 (m, 16H, O$CH_2$), 1.27-1.15 (m, 34H, -C(CH_3)$_3$ and CH_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.13 (m, 16H, H_{Ph}), 7.13-7.04 (m, 24H, H_{Ph}), 6.55 (s, 4H,

OC_6H_2), 6.00 (s, 4H, C*H*Ph_2), 3.36-3.27 (m, 16H, OCH_2, 1.66-1.58 (m, 16H, CH_2), 0.98 (s, 18H, C(CH_3)$_3$). For $C_{184}H_{212}Ca_2O_{14}$ (**3a**), 2727.86 Calc.: C 81.02% H 7.83% O 8.21%; Found: C 81.15% H 7.75% O 8.08%.

S3. Polymerization experiments

ε-Caprolactone polymerization. A preheated 10 ml glass ampoule was equipped with a magnetic stir bar and filled with dry argon. ε-CL (0.77 ml, 6.9 mmol) was transferred into the ampoule, and benzyl alcohol (7.2 μl, 69 μmol) was added. Then, THF was added to achieve an overall volume of 6.7 ml. The mixture was thermostated using external glycol bath. THF solution (0.2 ml of a 0.34 M) of catalyst (68 μmol) was injected into the stirred monomer solution. The monomer conversion was determined using ^{1}H NMR spectroscopy by integration of the monomer $CH_2OC=O$ (δ=4.14 ppm) and polymer $CH_2OC=O$ (δ=3.98 ppm) resonance signals. A 5-fold excess of acetic acid was injected into the ampoule to neutralize the catalyst and stop the process. The polymer was precipitated from the resulting solution with a 10-fold volume excess of diethyl ether. The polymer was filtered, washed with diethyl ether and dried under vacuum.

rac-Lactide polymerization. A preheated glass ampoule was equipped with a magnetic stir bar and a septum and then filled with dry argon. After cooling to room temperature, *rac*-lactide (1.00 g, 6.9 mmol) was placed into the ampule. Benzyl alcohol (7.2 μl, 69 μmol) was injected through the septum. Then, THF was added to achieve the required concentration. THF solution (0.2 ml of a 0.345 M) of catalyst (68 μmol) was injected into the stirred monomer solution at the required temperature. The monomer conversion was determined using ^{1}H NMR spectroscopy by integration of the monomer C*H*(CH_3)OC=O (δ=5.12 ppm) and polymer C*H*(CH_3)OC=O (δ=4.96–5.08 ppm) resonance signals. After a certain time period, a 5-fold excess of acetic acid was injected into the ampoule to neutralize the catalyst and stop the process. The resulting solution was poured into a 10-fold volume excess of diethyl ether. The precipitated polymer was filtered, washed with diethyl ether, and dried under vacuum. The microstructure of the resulting polymer was determined by analysis of the homonuclear decoupled ^{1}H NMR spectra.[4]

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