

**Living Ring-Opening Polymerization of β -Butyrolactone Initiated by
Mononuclear Zirconium Compounds Containing Sterically Hindered
N,O-Chelate and Anionic Dimethylamide Ligands**

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Supporting Information

Experimental section

Materials and method

Beta-butyrolactone (BBL) was purchased from Sigma-Aldrich, and purified by drying using CaH_2 (4 wt%) at 35 °C for 3 days followed by distillation (40-50 °C, 30 mbar). Bis(dimethylamido)bis[1-((dimethylamino)methyl)cyclohexanolate]zirconium (initiator) was facile synthesized according to our previously reported procedure. ^1H and ^{13}C NMR spectra were recorded in deuterated chloroform (CDCl_3) using a Bruker instrument (600 or 300 MHz). The molecular weight and polydispersity index (M_w/M_n , PDI) of products were determined by gel permeation chromatography (GPC) using a Waters 2410 refractive index detector (Milford, MA, USA) with a Waters 515 HPLC pump. The GPC column was eluted with THF at a flow rate of 1.0 mL/min. GPC curves were calibrated using a polystyrene standard with molecular weights ranging from 162 to 6,570,000 g/mol^{-1} .

BBL Polymerization procedure

In a glove box, Zr initiator (10.0 mg), BBL (350 mg), and toluene- d_8 (1.546 g) were added into a vial of 4 mL, and the reaction was run under room temperature at a stirring rate of 600 rpm. ^1H NMR sample was taken from the solution at different polymerization time. The conversion was calculated based on the integration area of methine for PHB and methyl for BBL.

GPC sample was prepared as follows. After measuring ^1H NMR of these samples, they were quenched by adding two drops of acetic acid. The resulting solution was filtered over celite, and the filtrate was vacuumed under 40 °C for several hours. The residue compound was diluted with THF (approximately 1.0 mg/mL), which was used for GPC measurement after the filtration using PTFE filter (0.2 μm).

Synthesis of the isopropoxide Zr compound with N,O-chelate ligand

In a glove box, bis(dimethylamido)bis[1-((dimethylamino)methyl)cyclohexanolate]zirconium (200 mg) was dissolved in toluene (5 mL). Then, the mixed solution of 2-propanol (62 μ L, 1 equivalent to dimethylamide Zr compound) and toluene (5 mL) was added dropwise to the prepared solution and stirred at room temperature. After 6 h, the product was obtained with a stoichiometric yield. The ^1H NMR spectrum was provided in the Fig. S4-B).

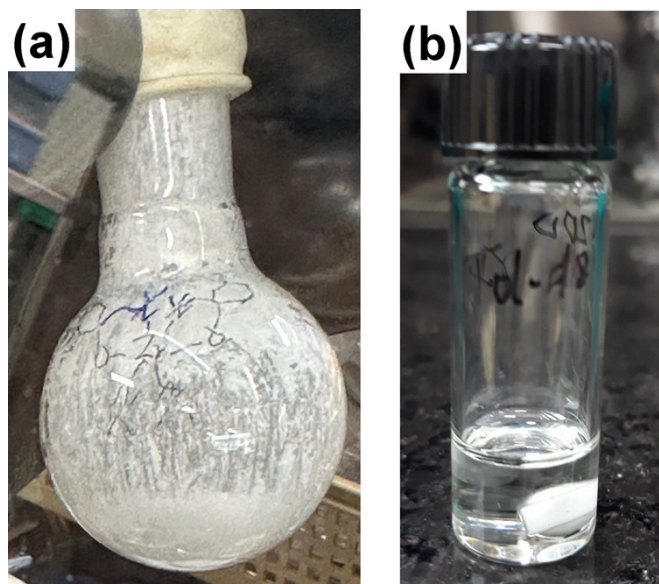


Fig. S1 Photographs of the Zr-initiator (a) and the polymerization solution at room temperature for 24 h (b).

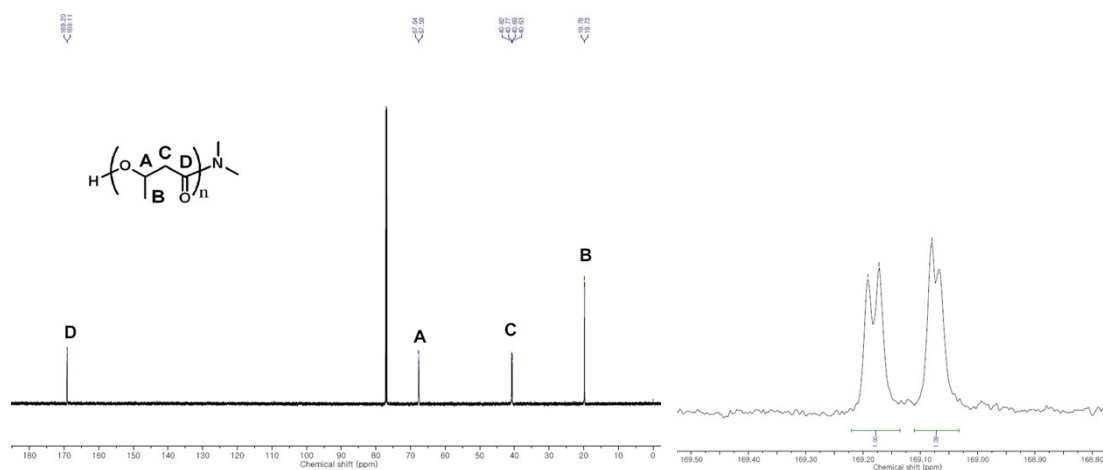


Fig. S2 ^{13}C NMR spectra of the purified PHB using 1 wt% HCl in CH_3OH . Left, whole ^{13}C NMR spectrum; Right, carbonyl region of the ^{13}C NMR spectrum of PHB (CDCl_3 , 600 MHz).

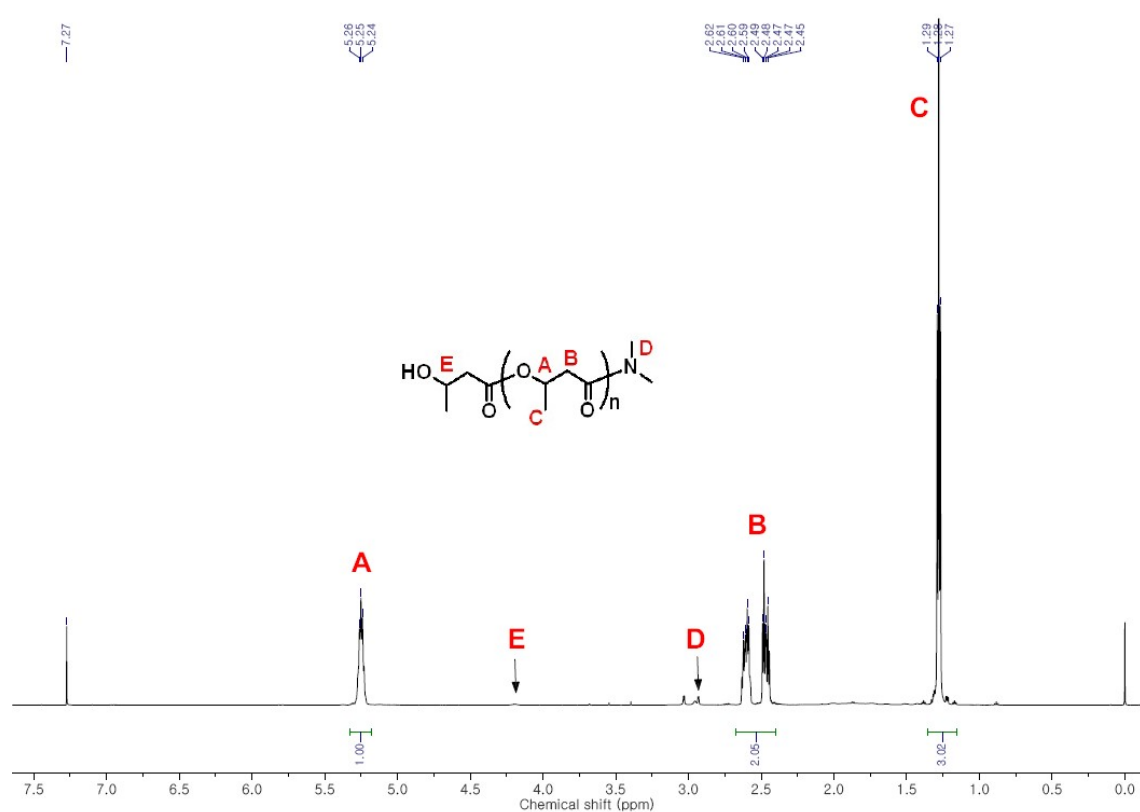


Fig. S3 ^1H NMR spectrum of the purified PHB using 1 wt% HCl in CH_3OH . (CDCl_3 , 600 M NMR).

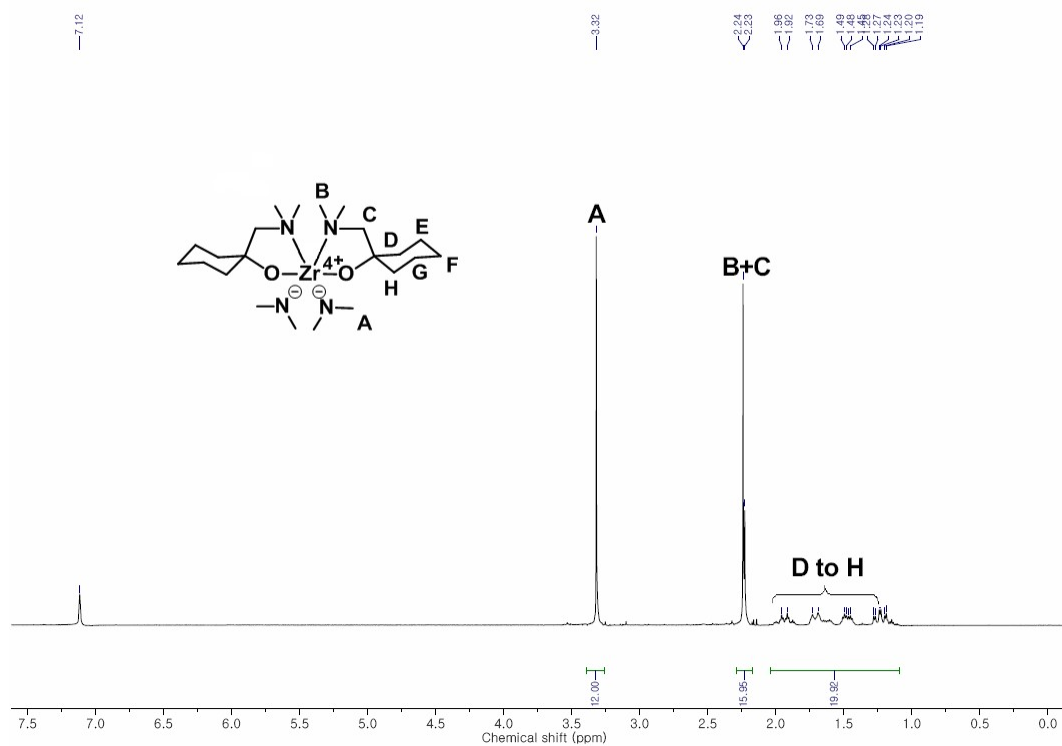


Fig. S4-A ^1H NMR spectrum of the dimethylamide Zr compound (C_6D_6 , 600MHz).

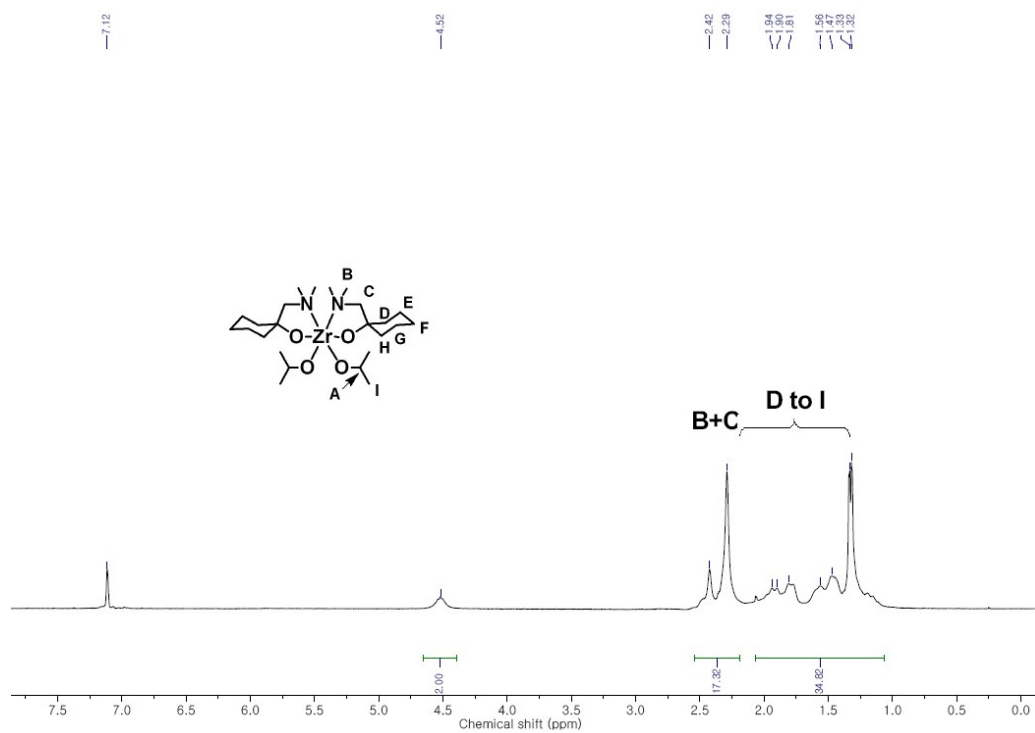


Fig. S4-B ^1H NMR spectrum of the ispropoxide Zr compound (C_6D_6 , 600MHz).

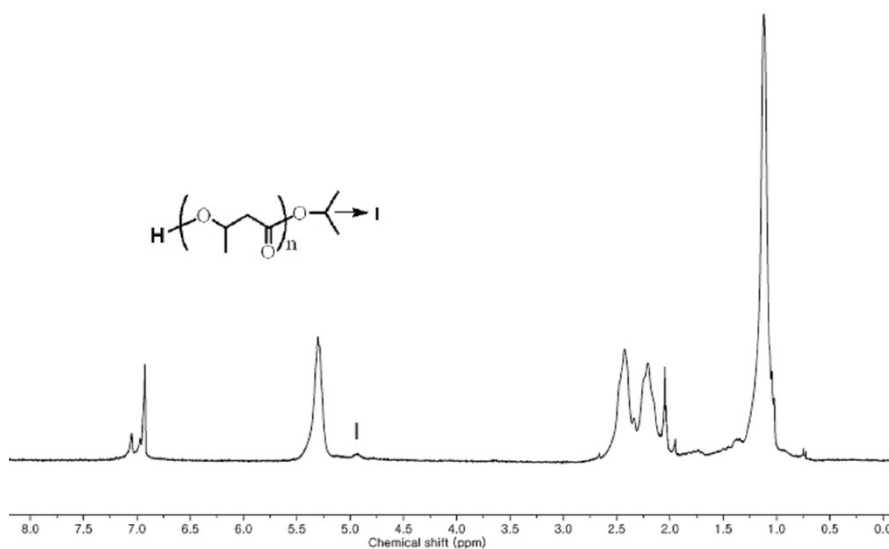


Fig. S5 ¹H NMR spectrum of PHB synthesized from isopropoxide Zr with N,O-chelate ligand (CDCl₃, 300 MHz).

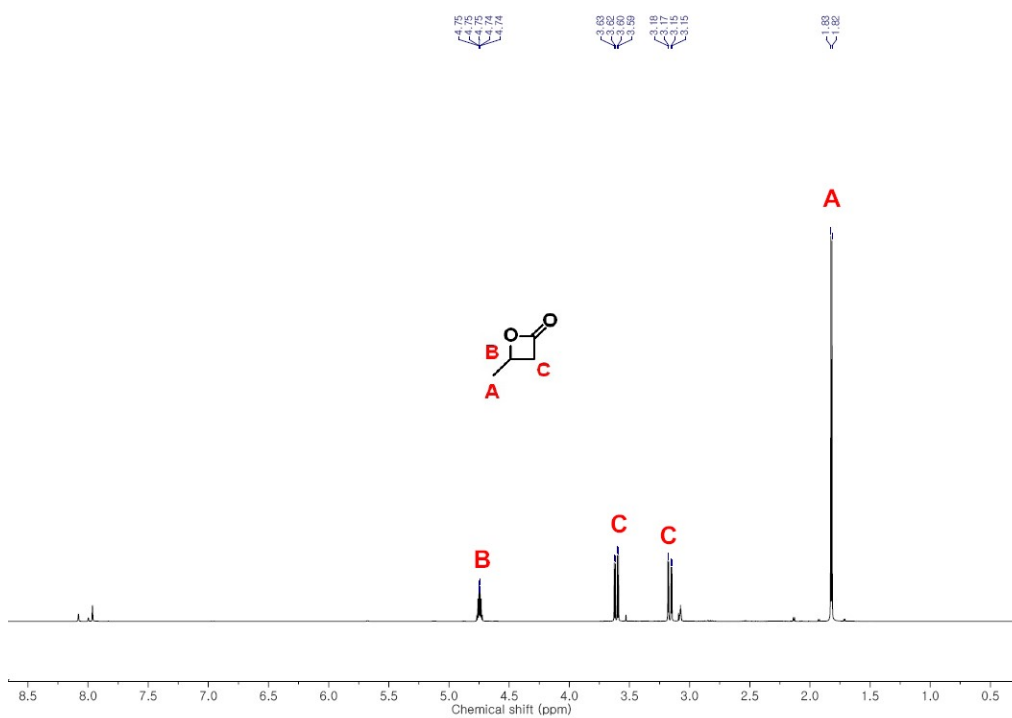


Fig. S6 ¹H NMR spectrum of the product synthesized from TDMAZ initiated BBL polymerization at room temperature for 24 h in toluene-*d*₈ (BBL/TDMAZ = 200/1, 2.5 M).

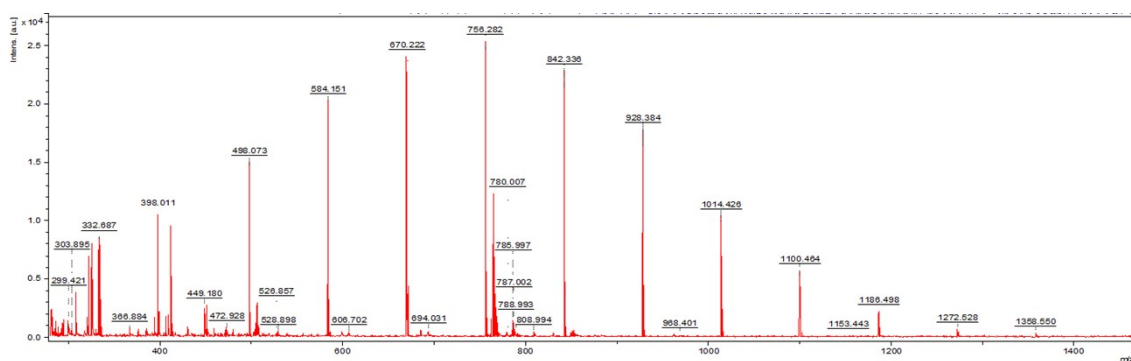


Fig. S7 MALDI-TOF spectrum of oligomer PHB isolated from polymerization of BBL at room temperature for 8 h (BBL/initiator = 200/1).

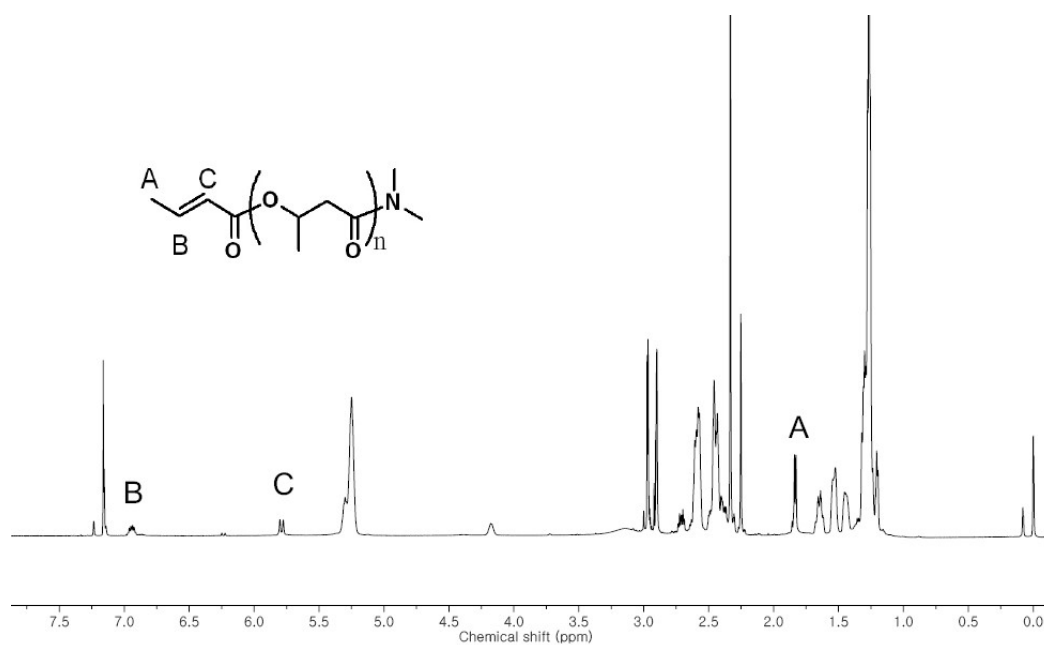


Fig. S8 ¹H NMR spectrum of oligomerization product (CDCl₃, 600 MHz).