

Access to high-molecular-weight poly(γ -butyrolactone) by simple commercial catalysts

Yihuan Liu^{ac}, Xin Yuan^a, Jiaqi Wu^{ac}, Xin Hu^{bc*}, Ning Zhu^{ac*}, Kai Guo^{ac}

^a College of Biotechnology and Pharmaceutical Engineering, ^b College of Materials Science and Engineering, ^c State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 211800, China * Corresponding author.

Corresponding author: xinhu@njtech.edu.cn; ningzhu@njtech.edu.cn

Experimental Section

Materials. GBL (TCI, 99%) was dried over CaH₂ overnight, vacuum-distilled and stored at room temperature. Toluene (Tol) and tetrahydrofuran (THF) (Sinopharm chemical Reagent, 99.5%) were refluxed over sodium under an argon atmosphere. Dichloromethane (DCM, Sinopharm chemical Reagent Co. 99.5%) and acetonitrile (MeCN, Sinopharm chemical Reagent Co. 99.5%) were distilled over CaH₂ under an argon atmosphere. Di-*n*-butylmagnesium (Sigma Aldrich, 1.0 M solution in heptane), *n*-butylethylmagnesium (Acros, 0.9 M solution in heptane) and *n*-butyl-sec-butylmagnesium (Sigma Aldrich, 0.7 M solution in heptane) and other reagents were purchased and used as received.

General polymerization procedures. Polymerization reactions were performed in 10 ml flame-dried ampoules interfaced to a dual-manifold Schlenk line. As an example, GBL (0.4305 g, 5.00 mmol), toluene (0.24 mL) and Ph₂CHOH (0.0184 g, 0.10 mmol) were transferred into the argon-purged ampoules and premixed for a few minutes at -50 °C. The reaction proceeded at -50 °C for 24 h after adding ⁿBu₂Mg (0.10 ml, 0.10 mmol). After a desired period of time, 0.5 mL benzoic acids/CH₂Cl₂ (10 mg/mL) was added to the reaction mixture for quenching the polymerization. The quenched mixture was dissolved in CH₂Cl₂, precipitated by cold methanol, filtered, washed with cold methanol and dried under high vacuum to a constant weight.

Characterizations. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz nuclear spectra resonance (NMR) instrument with Deuterated chloroform (CDCl₃) as solvent. Molecular weight and distribution determinations were conducted using a size exclusion chromatography (SEC) at 35 °C with tetrahydrofuran (THF) (0.7 mL/min) as the eluent. The SEC instrument consists of an Agilent HPLC system, one column (Waters Styragel HR 2.5 μ m, 300 \times 7.8 mm) and a Wyatt

Optilab Trex differential refractive index (DRI) detector. The instrument was calibrated with 10 polystyrene standards, and chromatograms were processed with Astra software (version 7.11).

Absolute molecular weight measurements: the SEC was performed using a SSI 1500 pump, coupled successively connected a Wyatt DAWN HELEOS-II multi-angle light scattering (MALS) detector (laser at $\lambda = 658$ nm) (Wyatt Technology Corporation, U.S.A.) and a DRI detector. The system was equilibrated at 35 °C in THF (flow rate of 0.7 mL/min). A series of known concentrations (sample obtained by **method c**) were injected and the change in refractive index was measured to obtain a plot of change in refractive index versus change in concentration ranging from 0.3 to 2.0 mg/mL. The slope from a linear fitting of the data was the dn/dc of the polymer. The dn/dc of polymer obtained by **method c** was determined to be 0.0789 mL/g.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) was recorded on a mass spectrometer (Ultraflextreme; Bruker Co.). Mass spectra of five hundred shots were accumulated for the spectra at a 25kV acceleration voltage. Polymers were dissolved in $CHCl_3$ at 10 mg/mL. The matrix solution (2, 5-dihydroxybenzoic acid, DHB) was prepared by dissolving 10 mg/mL in $CHCl_3$. Cationization agent (NaI, 10 mg/mL) was dissolved in a solution of isopropyl alcohol and $CHCl_3$ with a volume ratio of 60/40. Solutions were combined in a 10/5/1 volume ratio of matrix to polymer to cationization agent. Samples were prepared by mixing the matrix, cationization agent and polymer. The target was spotted with 1.0 μ L of solution and allowed to air-dry.

Thermal gravimetric analysis (TGA) was conducted on a TA TGA550 thermogravimetric analyzer. Samples were heated from 40 to 600 °C at a heating rate of 20 °C/min under a nitrogen atmosphere of 60 mL/min. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC250 instrument from -80 °C to 160 °C. The first heating rate was 10 °C/min and cooling rate was 10 °C/min while the second heating rate was 5 °C/min.

The tensile tests were performed on a SANSIZONGHENG (CMT6104) analyzer. The drawing rate was 50 mm/min for the tensile test at room temperature. The dumbbell-shaped samples with a length of 30 mm, a width of 5.0 mm and a thickness of 2 mm were prepared by hot press molding and cold press at room temperature. With the measurements repeated for 5 specimens, ultimate tensile strength and elongation at break were reported as the average values from the measured data.

Supporting figures and tables

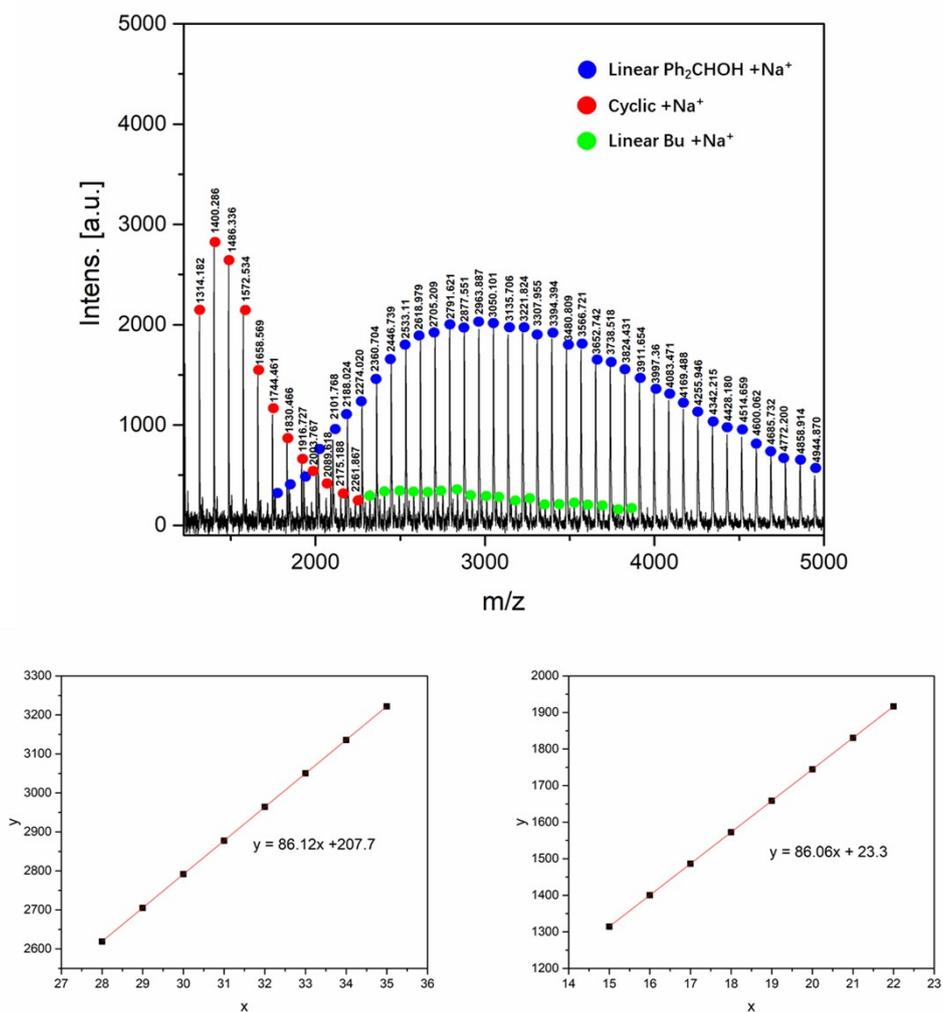


Fig. S 1 MALDI TOF spectrum of PGBL produced with [GBL]/[Ph₂CHOH]/[MgⁿBu₂] ratio of 50/1/1 and plots of m/z values (y) vs the number of γ-BL repeat units (x) for molecular ion peaks. The initiator and catalyst were mixed at -50 °C for 10 min and then monomer was added (**method a**).

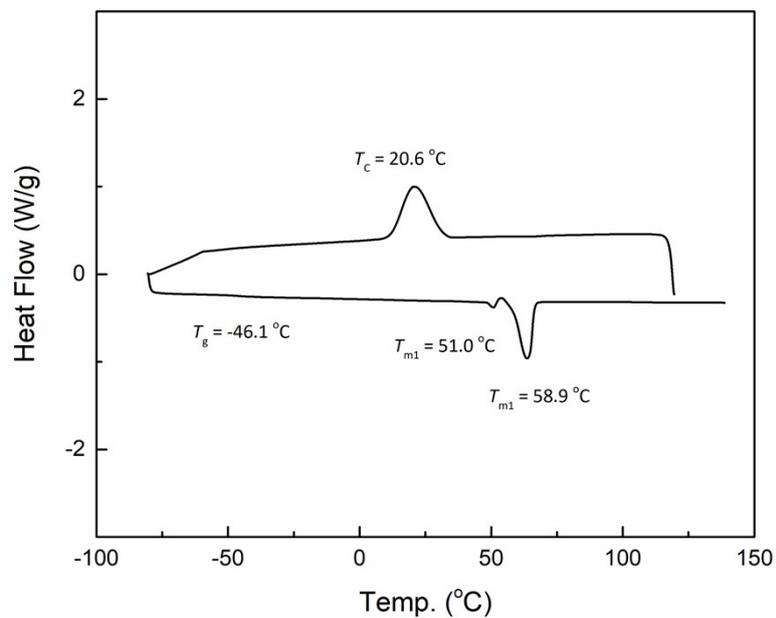


Fig. S 2 DSC curve of PGBL produced with [GBL]/[Ph₂CHOH]/[MgⁱBu₂] ratio of 50/1/1. The initiator and catalyst were mixed at -50 °C for 10 min and then monomer was added (**method a**).

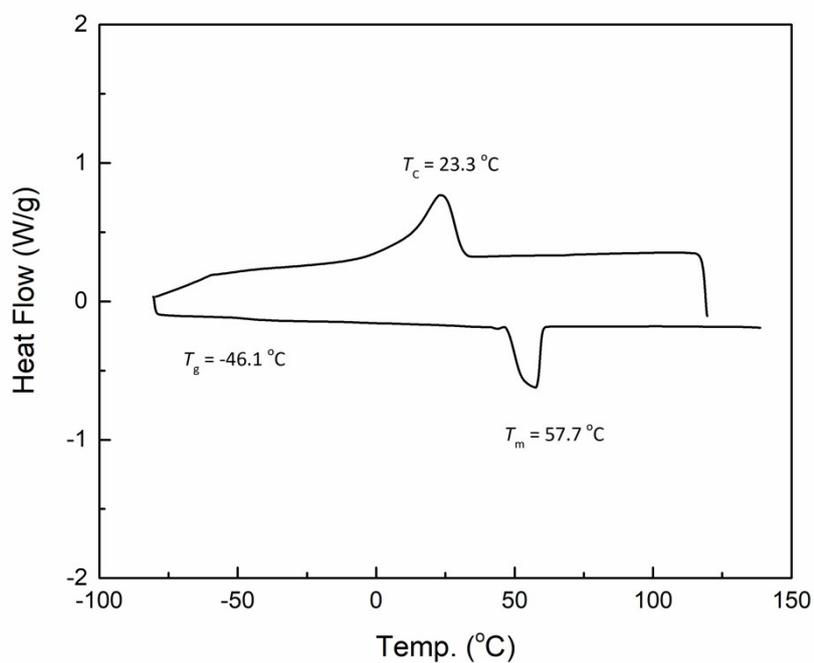


Fig. S 3 DSC curve of PGBL produced with [GBL]/[Ph₂CHOH]/[MgⁱBu^sBu] ratio of 50/1/1. The initiator and monomer were mixed at -50 °C for 10 min and then catalyst was added (**method b**).

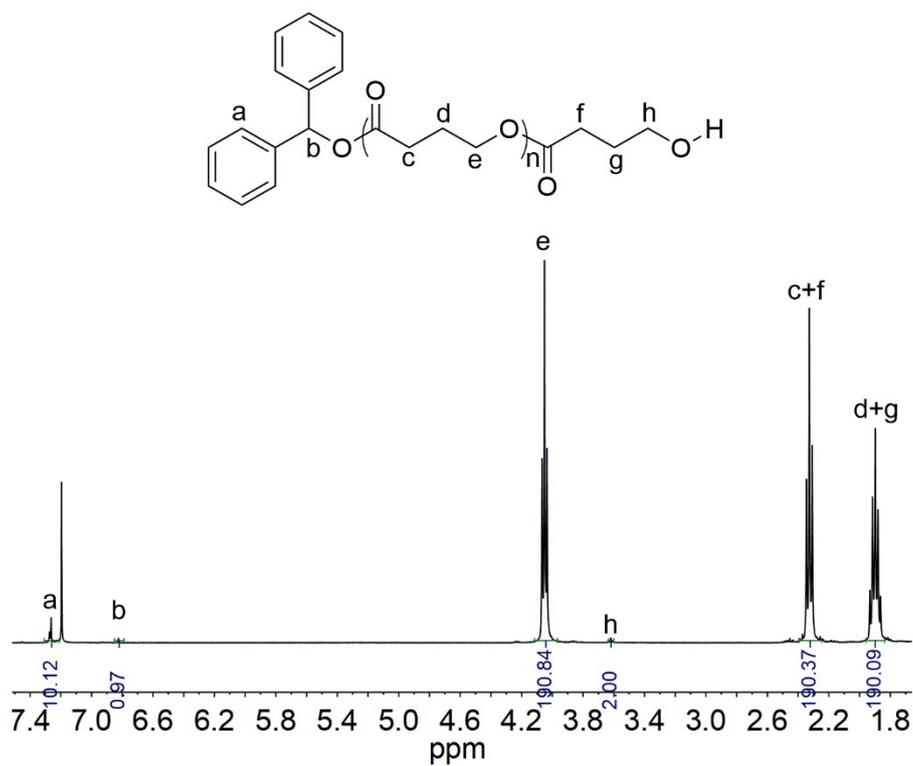


Fig. S 4 ^1H NMR of PGBL (CDCl_3) produced with $[\text{GBL}]/[\text{Ph}_2\text{CHOH}]/[\text{Mg}^n\text{Bu}^s\text{Bu}]$ ratio of 50/1/1. The initiator and monomer were mixed at $-50\text{ }^\circ\text{C}$ for 10 min and then catalyst was added (**method b**).

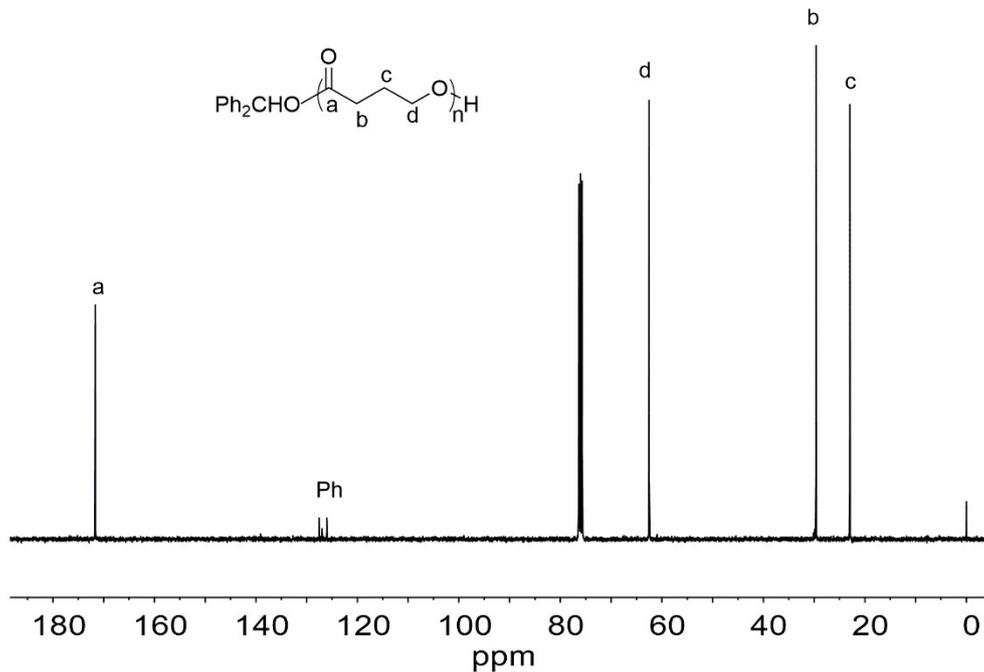


Fig. S 5 ^{13}C NMR of PGBL (CDCl_3) produced with $[\text{GBL}]/[\text{Ph}_2\text{CHOH}]/[\text{Mg}^n\text{Bu}^s\text{Bu}]$ ratio of 50/1/1. The initiator and monomer were mixed at $-50\text{ }^\circ\text{C}$ for 10 min and then catalyst was added (**method b**).

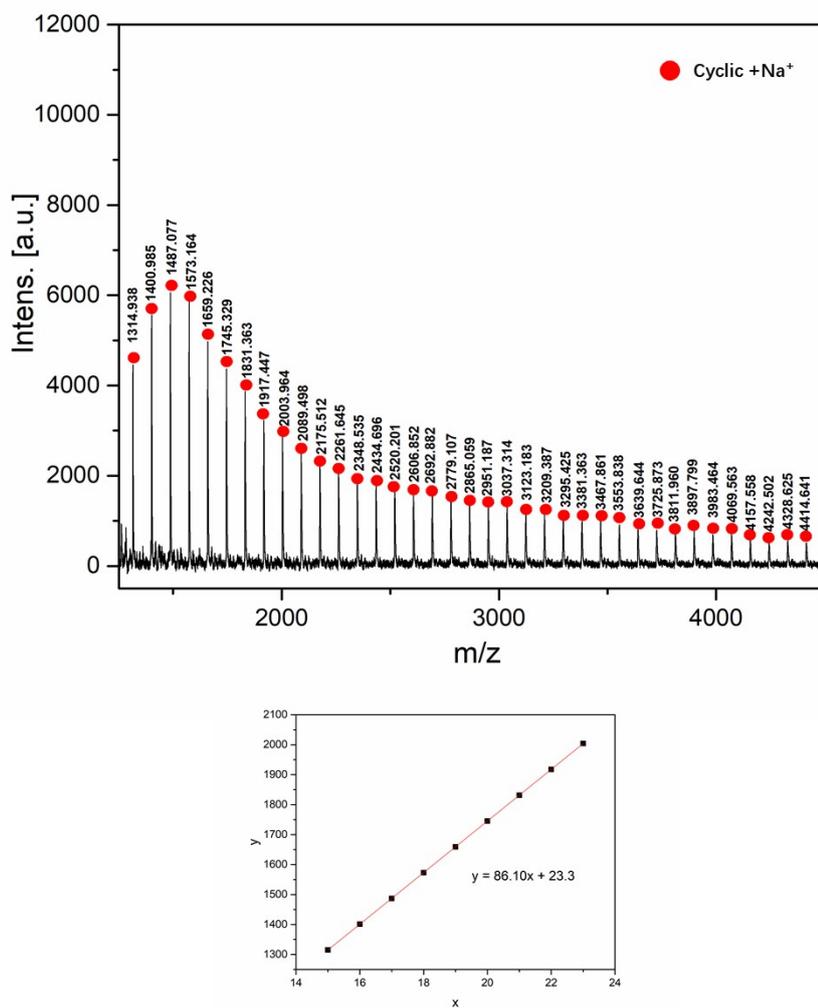


Fig. S 6 MALDI TOF spectrum of PGBL produced with [GBL]/[MgⁿBu₂] ratio of 50/1 and plots of m/z values (y) vs the number of γ -BL repeat units (x) for molecular ion peaks. The monomer was precooled at -50 °C for 10 min and then catalyst was added (**method c**).

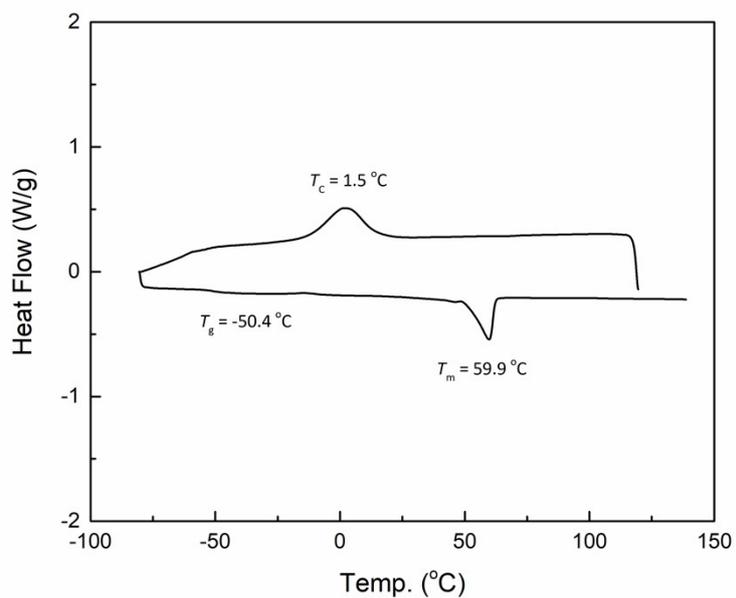


Fig. S 7 DSC curve of PGBL produced with $[\text{GBL}]/[\text{Mg}^n\text{Bu}_2]$ ratio of 50/1. The monomer was precooled at -50°C for 10 min and then catalyst was added (**method c**).

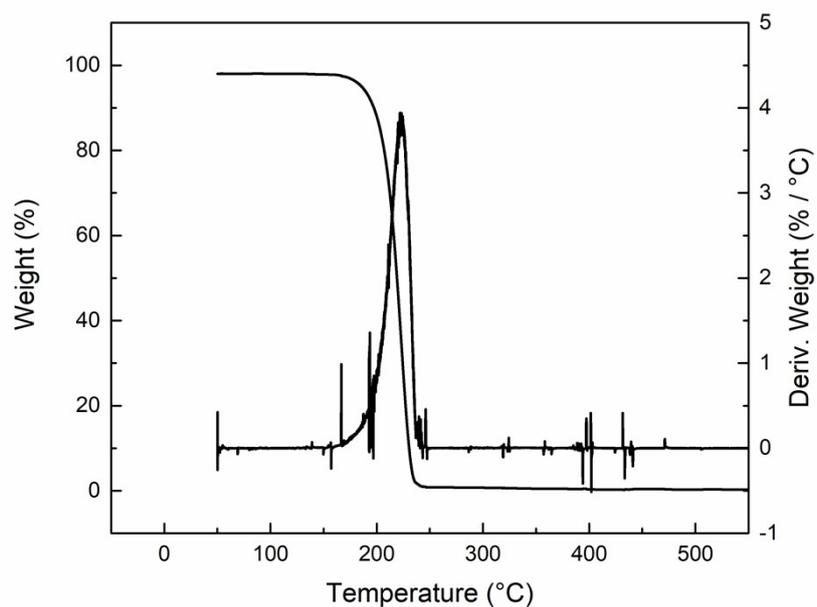


Fig. S 8 TGA and DTG curves of PGBL produced with $[\text{GBL}]/[\text{Mg}^n\text{Bu}_2]$ ratio of 50/1. The monomer was precooled at -50°C for 10 min and then catalyst was added (**method c**).

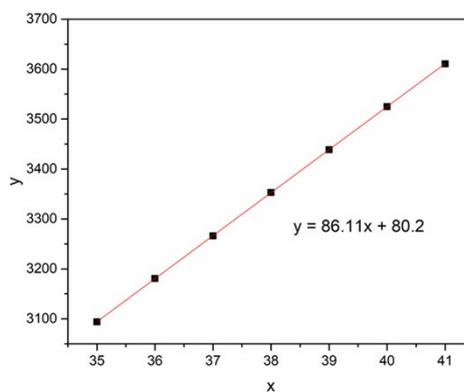
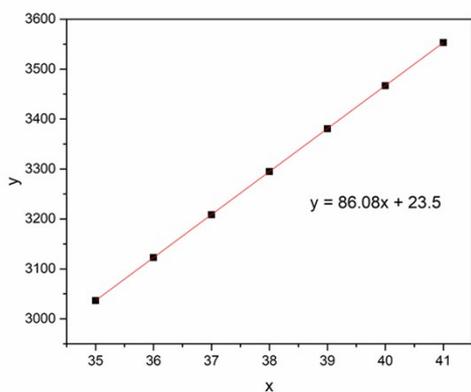
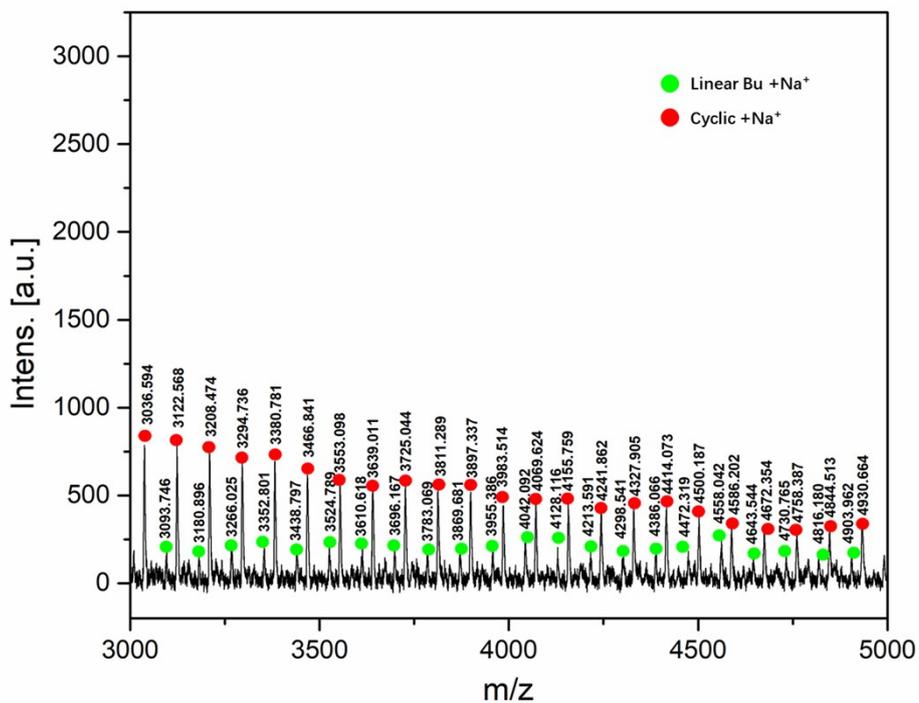


Fig. S 9 MALDI TOF spectrum of PGBL produced with [GBL]/[MgⁿBu₂] ratio of 10/1 (-50 °C, 1h) and plots of m/z values (y) vs the number of γ -BL repeat units (x) for molecular ion peaks. The monomer was precooled at -50 °C for 10 min and then catalyst was added (**method c**).

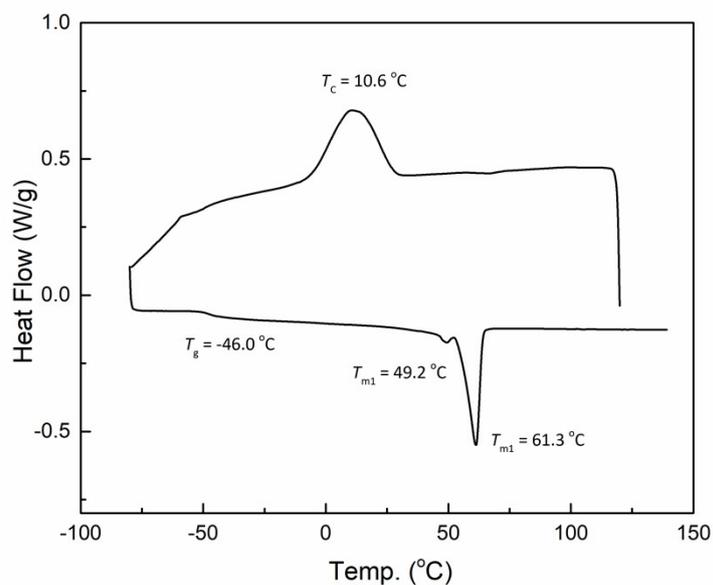


Fig. S 10 DSC curve of PGBL produced with [GBL]/[MgⁿBu₂] ratio of 10/1 (-50 °C, 1h). The monomer was precooled at -50 °C for 10 min and then catalyst was added (**method c**).

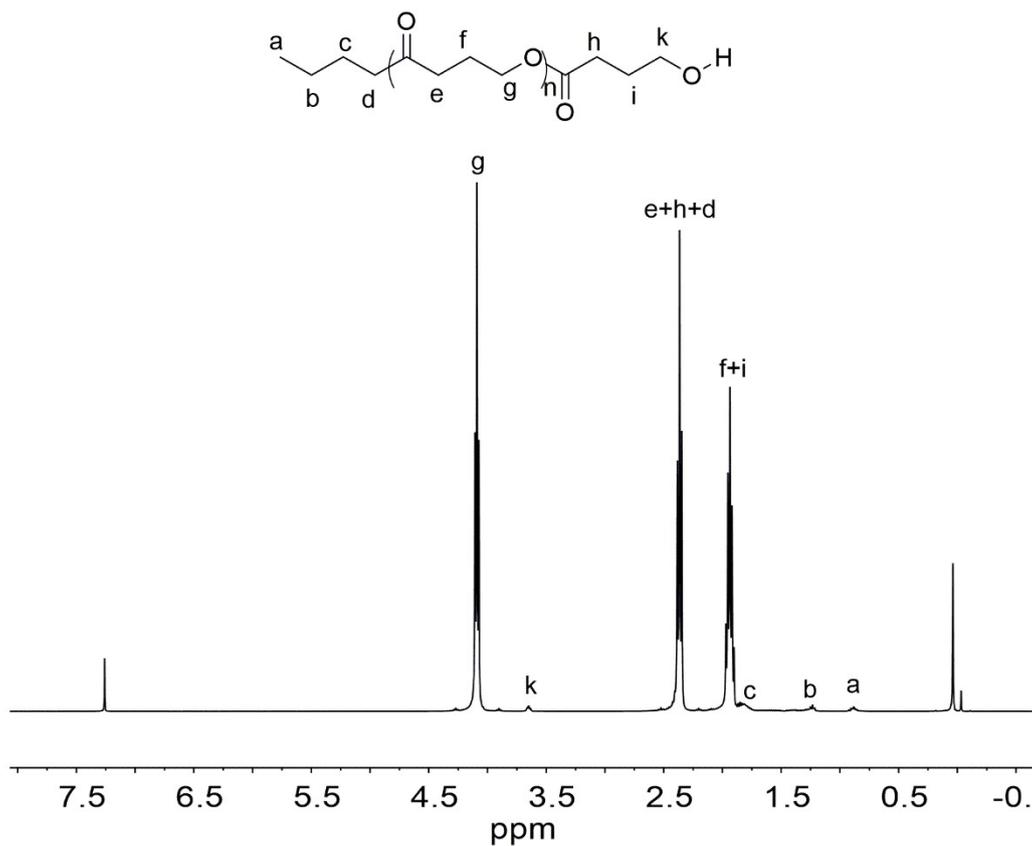


Fig. S 11 ¹H NMR of PGBL produced with [GBL]/[MgⁿBu₂] ratio of 10/1 (-50 °C, 1h). The monomer was precooled at -50 °C for 10 min and then catalyst was added (**method c**).

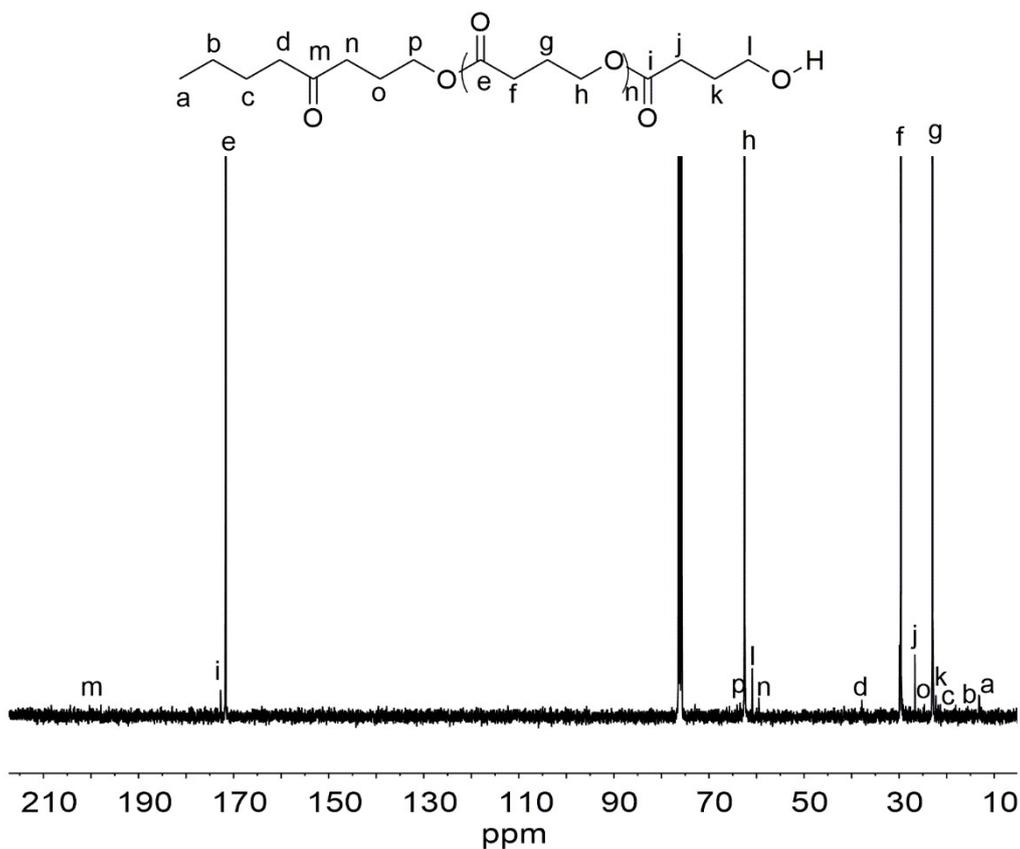


Fig. S 12 ¹³C NMR of PGBL produced with [GBL]/[MgⁿBu₂] ratio of 10/1 (-50 °C, 1h). The monomer was precooled at -50 °C for 10 min and then catalyst was added (**method c**).

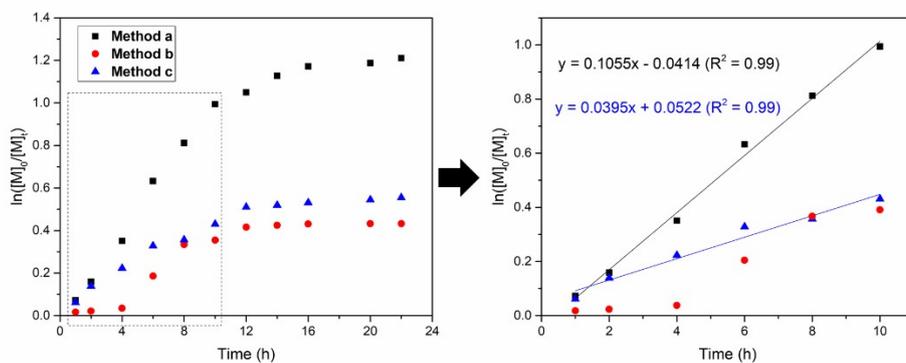


Fig. S 13 Semilogarithmic kinetic plots for MgⁿBu₂ catalyzed ROP of GBL by three methods.

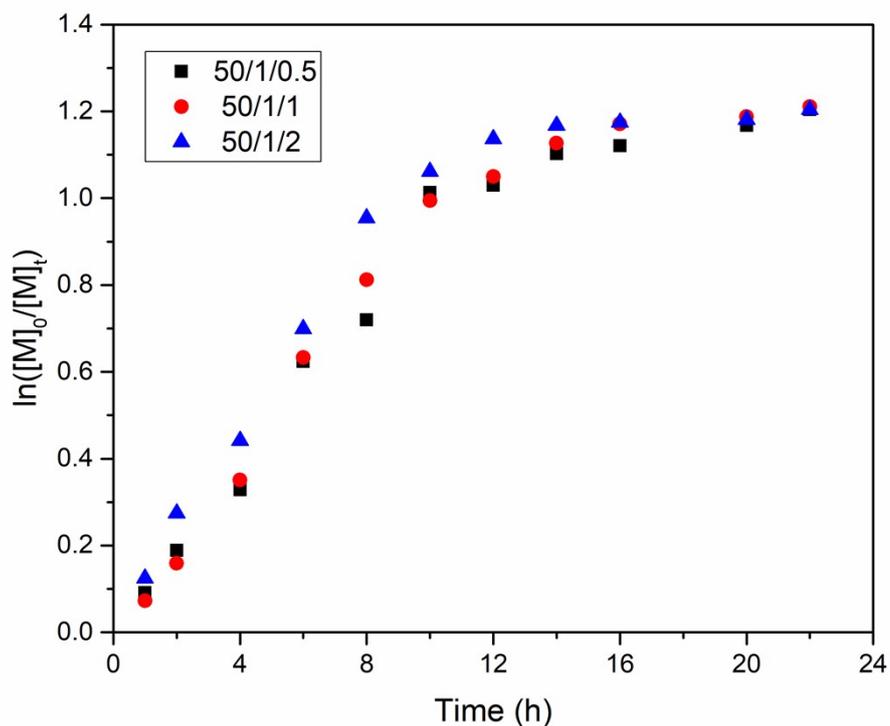


Fig. S 14 Semilogarithmic kinetic plots for Mg^nBu_2 catalyzed ROP by **method a** with feed ratio of 50/1/0.5, 50/1/1 and 50/1/2.

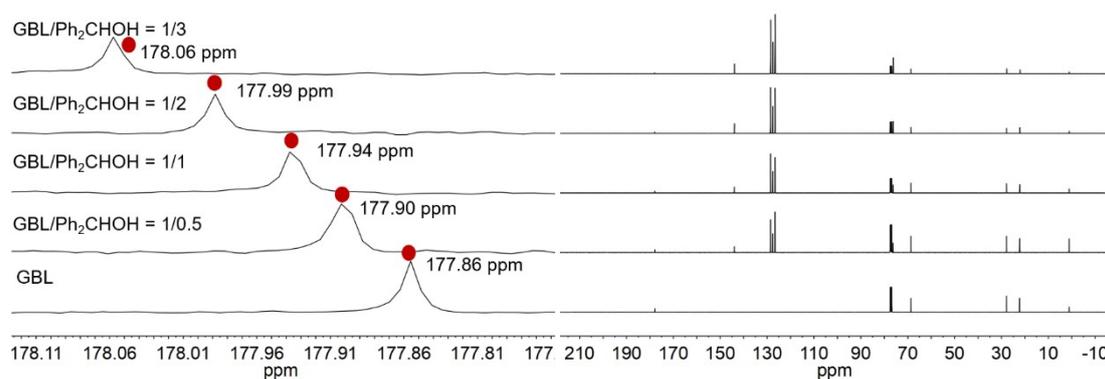


Fig. S 15 The chemical shifts of the carbonyl carbon of GBL in the ^{13}C NMR spectrum observed in the presence of Ph_2CHOH ($CDCl_3$).

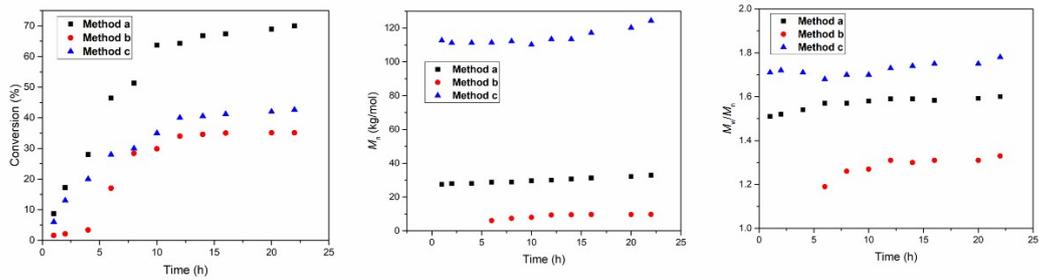


Fig. S 16 The dependence of monomer conversion, molecular weight (M_n) and polydispersity (M_w/M_n) on the reaction time.

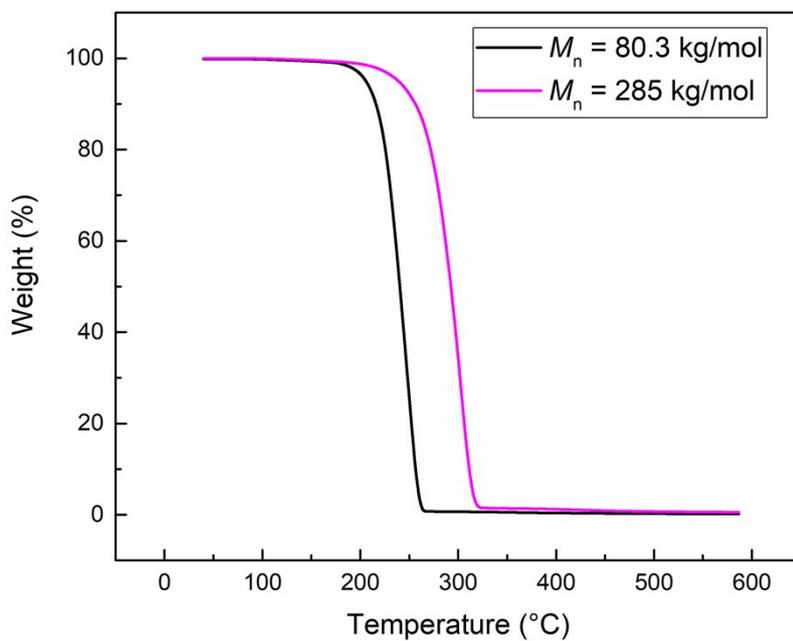


Fig. S 17 TGA curves of PGBL with various molecular weights.