

# **Facile Preparation of Biodegradable Poly( $\gamma$ -Butyrolactone) via Base Assisted Ring-Opening Polymerization**

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**Supporting Information**

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## 1 General information

All reactions were performed in flame-dried glassware using an MBraun glove box or conventional Schlenk techniques under a static pressure of argon (glove box) unless otherwise stated. Liquids and solutions were transferred with either syringes or glass pipettes. Commercially available chemicals were purchased by *Sigma-Aldrich*, *Alfa Aesar*, *ABCR*, *TCI* or *ACROS*. Incozol 2 (3-butyl-2-(1-ethylpentyl)-1,3-oxazolidine), was provided by Incorez Ltd.  $^1\text{H}$  and  $^{13}\text{C}$  spectra was recorded in  $\text{CDCl}_3$ , on a Bruker *AVANCE III* 300 or Bruker *AVANCE III* 400 spectrometers at the Organisches-Chemie Institut, Ruprecht-Karls-University Heidelberg. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ( $\text{CHCl}_3$ :  $\delta = 7.26$  ppm for  $^1\text{H}$  NMR and  $\text{CDCl}_3$ :  $\delta = 77.16$  ppm for  $^{13}\text{C}$  NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplets, m = multiplet), coupling constants (Hz), and integration. Polymer number average molecular weights ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) were measured by Size Exclusion Chromatography (SEC). The measurements were performed at 40 °C with THF as eluent and a flow rate of 1 mL.min $^{-1}$  on Agilent 1260 Infinity II GPC instrument equipped with two PLgel 3  $\mu\text{m}$  mixed-E columns. The polymer concentration in THF was 4 mg.mL $^{-1}$  and 1,2-dichlorobenzene was used as a reference. A conventional calibration with polystyrene standards was used for the molecular weight determination. The software used for the analysis was Agilent GPC/SEC software. The molecular weight ( $M_n$ ) of the homopolymer  $M_n\{\text{poly-B}\}$  or the copolymer  $M_n\{\text{poly-B-co-C}\}$  can be determined by  $^1\text{H}$ -NMR of the pure polymer by comparing the integration value of the signal from the initiator benzyl alcohol [5.12 ppm], 1,4-BDM [5.09 ppm], 1,4-BDO [3.66 ppm], 1,6-HDO [3.66 ppm], MeOH [3.47 ppm] as A, with the  $\text{CH}_2$  signal from the poly- $\gamma$ -butyrolactone at 4.12 ppm as poly-B and the 2  $\text{CH}_2$  signal from the poly- $\delta$ -valerolactone [1.67 ppm], the 2  $\text{CH}_2$  signal from the poly- $\epsilon$ -caprolactone [1.66 ppm], the  $\text{CH}_2$  signal from the poly- $\epsilon$ -decalactone [2.30 ppm] as poly-C; the protons are written  $N_A$ ,  $N_B$  and  $N_C$  corresponding to the number of proton integrated for the initiator A and the pGBL B; and  $N_{\text{OH}}$  represent the number of -OH in the initiator ( $N_{\text{OH}}(\text{monoalcohol})=1$ ,  $N_{\text{OH}}(\text{polyol})=2-4$ ).  $M_n$  was calculated the following equations:

$$(1) \quad M_n\{\text{poly} - \text{B}\} = \left[ \frac{B/N_b}{A/N_a} \times M_w(\text{B}) \right] \times N_{\text{OH}} + M_w(\text{A})$$

$$(2) \quad M_n\{\text{poly} - \text{B} - \text{co} - \text{C}\} = \left[ \left( \frac{B/N_b}{A/N_a} \times M_w(\text{B}) \right) + \left( \frac{C/N_c}{A/N_a} \times M_w(\text{C}) \right) \right] \times N_{\text{OH}} + M_w(\text{A})$$

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo STAR<sup>e</sup> DSC/TGA analyzer. Polymer samples were heated from 20 to 500 °C in  $\text{N}_2$  atmosphere at a rate of 10 °C.min $^{-1}$ . Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 200 F3 Maia apparatus under  $\text{N}_2$  atmosphere, with a flow rate of 30 mL.min $^{-1}$ . After a first scan allowing to reset thermal history, a second heating was performed from -80 to 120 °C with a heating and cooling rate of 10 °C.min $^{-1}$ . The software used for the analysis was NETZSCH Proteus-80 Analysis. MALDI-TOF were measured on a Bruker Daltonics AutoFlex Speed time-of flight (MALDI-TOF) with a 1 kHz smartbeam-II laser and HRMS

was measured on a Bruker Daltonics timsTOFleX (MALDI IM-Q-TOF) with a 10 kHz smartbeam 3D laser. Samples were prepared as followed: A spatula tip of the sample is dissolved in 25  $\mu$ L dichloromethane. 1-2  $\mu$ L of this solution were transferred to 25  $\mu$ L matrix solution ((10 mg/mL DCTB [rans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenyldene]malononitrile]) in THF. A drop of that solution is transferred to the plate to be measured. The raw data was processed in the FlexAnalysis software (Bruker Daltonics).

## 2 Optimization study of the ring-opening polymerization of GBL

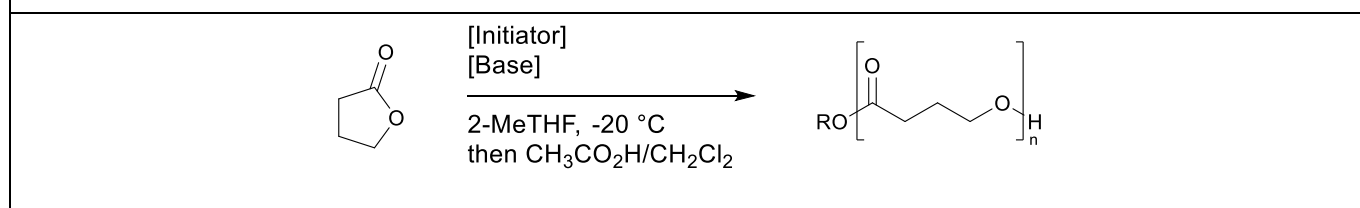
### 2.1 Screening of different bases and alcohol initiators

#### Preparation on 6.5 mmol scale (Table S1):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL vial was charged with GBL (500  $\mu$ L, 6.50 mmol, 1.0 eq) and sealed with a septum. A separate 1 mL vial was charged with a base indicated in Table S1 (0.125 mol% to 0.5 mol%) followed by 2-MeTHF (65  $\mu$ L, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), an alcohol initiator indicated in Table S1 (0.5 mol% to 1.0 mol%) and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min. If the solid constituents of the premix were not completely solubilized, the premix was used as a suspension. The vials were taken out of the glovebox. The vial containing the GBL was immersed in the cooling bath at  $-20$  °C. After 30 min equilibration at the desired temperature the ROP was initiated by dropwise addition of the premix Base/Initiator/Solvent via a gastight syringe. After 4 to 14 hours at  $-20$  °C, the polymerization was quenched by addition of 4 mL of a cold ( $-20$  °C) solution of acetic acid in  $\text{CDCl}_3$  (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

#### Preparation on 130 mmol scale (Table S1):

The ring-opening polymerization of  $\gamma$ -butyrolactone was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with GBL (10 mL, 130 mmol, 1.0 eq) and sealed with a septum. A separate 4 mL vial was charged with the base indicated in Table S1 (0.125 mol% to 0.25 mol%) followed by 2-MeTHF (1.3 mL, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), the alcohol initiator indicated in Table S1 (0.5 mol% to 1.0 mol%) and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min. If the solid constituents of the premix were not completely solubilized, the premix was used as a suspension. The reactor and the vial were taken out of the glovebox. The round bottom flask was immersed in the cooling bath at  $-20$  °C. After 40 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/Solvent via a gastight syringe. After 4 to 24 hours at  $-20$  °C, the polymerization was quenched by addition of 40 mL of a cold ( $-20$  °C) solution of acetic acid in DCM (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at  $35$  °C until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum (<0.1 mbar) for 24 hours.

**Table S1** Initial screening of various conditions including reaction time, initiator, base, or their respective ratio toward the monomer<sup>[a]</sup>

Entry	Initiator (I) /Base (B)	Mol Ratio GBL : I : B	Scale (mmol)	t (h)	Yield (%) <sup>[b]</sup>	M <sub>n</sub> exp (g/mol) <sup>[e]</sup>	M <sub>w</sub> exp (g/mol) <sup>[e]</sup>	Đ (M <sub>w</sub> /M <sub>n</sub> ) <sup>[e]</sup>
1	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	6.5	4	70	N.D.	N.D.	N.D.
2	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	6.5	14	75	N.D.	N.D.	N.D.
3	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	92 <sup>[c]</sup>	9 310	15 330	1.65
4	BnOH/ <i>t</i> -BuOK <sup>[d]</sup>	400 : 4 : 1	130	4	94 <sup>[c]</sup>	10 430	15 750	1.51
5	BnOH/ <i>t</i> -BuOK	800 : 4 : 1	130	4	52 <sup>[c]</sup>	10 230	17 990	1.76
6	BnOH/ <i>t</i> -BuOK	800 : 4 : 1	6.5	14	69	N.D.	N.D.	N.D.
7	BnOH/BnOK	400 : 4 : 1	6.5	4	64	N.D.	N.D.	N.D.
8	BnOH/ <i>t</i> -BuONa	400 : 4 : 1	130	4	61 <sup>[c]</sup>	6 510 <sup>[f]</sup>	N.D.	N.D.
9	BnOH/ <i>t</i> -BuOLi	400 : 4 : 1	130	4	12 <sup>[c]</sup>	2 910 <sup>[f]</sup>	N.D.	N.D.
10	4-Me-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	76 <sup>[c]</sup>	6 400 <sup>[f]</sup>	N.D.	N.D.
11	2,6-Cl-C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> OH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	89 <sup>[c]</sup>	8 580 <sup>[f]</sup>	N.D.	N.D.
12	2,4,6-Me-C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> OH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	83 <sup>[c]</sup>	9 080	13 640	1.50
13	MeOH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	71 <sup>[c]</sup>	11 110 <sup>[f]</sup>	N.D.	N.D.
14	1,4-BDM/ <i>t</i> -BuOK	400 : 4 : 1	6.5	4	41	N.D.	N.D.	N.D.
15	1,4-BDM/ <i>t</i> -BuOK	200 : 2 : 1	6.5	4	36	N.D.	N.D.	N.D.
16	1,4-BDM/ <i>t</i> -BuOK	400 : 2 : 1	6.5	4	27	N.D.	N.D.	N.D.
17	1,4-BDM/ <i>t</i> -BuOK	400 : 4 : 1	130	4	54 <sup>[c]</sup>	9 640	15 300	1.58
18	1,4-BDM/ <i>t</i> -BuOK	800 : 4 : 1	130	24	41 <sup>[c]</sup>	8 340	11 640	1.40
19	1,4-BDO/ <i>t</i> -BuOK	400 : 1 : 1	130	4	40 <sup>[c]</sup>	3 950	5 420	1.37
20	1,6-HDO/ <i>t</i> -BuOK	400 : 2 : 1	130	4	42 <sup>[c]</sup>	8 650	13 590	1.57
21 <sup>[g]</sup>	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	130	4	51 <sup>[c]</sup>	7 160 <sup>[f]</sup>	N.D.	N.D.
22	BnOH/ <i>t</i> -BuOK	400 : 8 : 1	6.5	4	54	4 030 <sup>[f]</sup>	N.D.	N.D.
23	BnOH/ <i>t</i> -BuOK	400 : 16 : 1	6.5	4	47	2 590 <sup>[f]</sup>	N.D.	N.D.
24	BnOH/ <i>t</i> -BuOK	400 : 24 : 1	6.5	4	29	1 560 <sup>[f]</sup>	N.D.	N.D.
25	BnOH/ <i>t</i> -BuOK	400 : 40 : 1	6.5	4	24	1 050 <sup>[f]</sup>	N.D.	N.D.

[a] **Reaction conditions:** GBL (1 eq) cooled to  $-20\text{ }^\circ\text{C}$  and then initiator, base and 2-MeTHF (100 M) mixed at rt and added dropwise to the cold GBL. Quenching using cold  $\text{CDCl}_3$  or DCM with  $\text{CH}_3\text{CO}_2\text{H}$  (0.05 eq); [b] Determined by  $^1\text{H-NMR}$  using hexamethyldisiloxane as internal standard; [c] Isolated yield; [d] Potassium *tert*-butoxide, 2 M (25% w/w)-Solution in 2-MeTHF; [e] Determined by GPC in THF; [f] M<sub>n</sub> (average mass in g/mol) was determined by  $^1\text{H-NMR}$  of the pure polymer by comparing the integration of the signal from the initiator benzyl alcohol [5.12 ppm], 1,4-BDM [5.09 ppm], 1,4-BDO [3.66 ppm], 1,6-HDO [3.66 ppm], MeOH [3.47 ppm] as A, with the CH<sub>2</sub> signal from the poly-4-hydroxybutyrate at 4.12 ppm as B. BnOH=benzyl alcohol; 1,4-BDM=1,4-benzenedimethanol; 1,4-BDO=1,4-

butanediol; 1,6-HDO=1,6-hexanediol; [g] non-inventive comparative example with the initiator, base and solvent cooled to  $-20\text{ }^{\circ}\text{C}$  and then GBL (1 eq) was added at once.

## 2.2 Screening of different solvents for the reaction mixture

### Preparation on 6.5 mmol scale (Table S2):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL vial was charged with GBL (500  $\mu$ L, 6.50 mmol, 1.0 eq) and sealed with a septum. A separate 1 mL vial was charged with the base potassium *tert*-butoxide (0.25 mol%) followed by the solvent indicated in Table S2 (65  $\mu$ L, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), the initiator indicated in Table S2 (1 mol%) and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min. The vials were taken out of the glovebox. The vial containing the GBL was immersed in the cooling bath at  $-20$  °C. After 30 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/Solvent via a gastight syringe. After 4 hours at  $-20$  °C, the polymerization was quenched by addition of 4 mL of a cold ( $-20$  °C) solution of acetic acid in  $\text{CDCl}_3$  (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

### Preparation on 130 mmol scale (Table S2):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with GBL (10 mL, 130 mmol, 1.0 eq) and sealed with a septum. A separate 4 mL vial was charged with the base potassium *tert*-butoxide (0.25 mol%) followed by the solvent indicated in Table S2 (1.3 mL, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), benzyl alcohol (1.0 mol%) and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min. The reactor and the vial were taken out of the glovebox. The round bottom flask was immersed in the cooling bath at  $-20$  °C. After 40 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/Solvent via a gastight syringe. After 4 hours at  $-20$  °C, the polymerization was quenched by addition of 40 mL of a cold ( $-20$  °C) solution of acetic acid in DCM (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at  $35$  °C until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum ( $<0.1$  mbar) for 24 hours.



**Table S2** Screening of solvents for the ROP<sup>[a]</sup>

Entry	Initiator (I) /Base (B)	Mol Ratio GBL : I : B	Solvent	Yield (%) <sup>[b]</sup>
1	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	2-MeTHF	70
2	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	DCM	50
3	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	Dioxane	54
4	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	Glyme	50
5	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	Diglyme	56
6	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	Toluene	66
7	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	DMSO	26
8	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	DMF	36
9	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	Acetonitrile	22
10	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	EtOAc	83
11	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	EtOAc	80 <sup>[c]</sup>
12	-/ <i>t</i> -BuOK	400 : 0 : 1	EtOAc	34
13	EtOH/ <i>t</i> -BuOK	400 : 4 : 1	EtOAc	40
14	BnOH/EtOAc/ <i>t</i> -BuOK	400 : 4 : 4 : 1	2-MeTHF	67
15	BnOH/ <i>t</i> -BuOK	400 : 4 : 1	none	54

[a] **Reaction conditions:** GBL (1 eq, 6.5 mmol except entry 11) cooled to -20 °C and then initiator, *t*-BuOK (0.0025 eq) and Solvent (100 M), except entry 15 were only a solution of *t*-BuOK in BnOH (1:4) was added, were mixed at rt and added dropwise to the cold GBL. Reaction time 4 hours. Quenching using cold CDCl<sub>3</sub> or DCM with CH<sub>3</sub>CO<sub>2</sub>H (0.05 eq); [b] Determined by <sup>1</sup>H-NMR using hexamethyldisiloxane as internal standard; [c] Isolated yield; 130 mmol scale.

### 2.3 Screening of different solvents for the quenching of the base

#### Preparation on 6.5 mmol scale (Table S3):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL vial was charged with GBL (500  $\mu$ L, 6.50 mmol, 1.0 eq) and sealed with a septum. A separate 1 mL vial was charged with potassium *tert*-butoxide (1.83 mg, 0.016 mmol, 0.25 mol%) followed by 2-MeTHF (65.0  $\mu$ L, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed) and benzyl alcohol (6.7  $\mu$ L, 0.065 mmol, 1 mol%), and sealed. The obtained premix Base/Initiator/2-MeTHF was homogenized for 5 min. The vials were taken out of the glovebox. The vial containing the GBL was immersed in the cooling bath at  $-20$  °C. After 30 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/2-MeTHF via a gastight syringe. After 4 hours at  $-20$  °C, the polymerization was quenched by addition of a cold ( $-20$  °C) quenching solution comprising acetic acid (acid concentration 5 mol% relative to GBL) in 4 mL of the solvent indicated in Table S3, the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. If the polymer did not redissolve at  $-20$  °C, the reaction mixture was warmed up to  $+22$  °C. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

#### Preparation on 130 mmol scale (Table S3):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with  $\gamma$ -butyrolactone (10 mL, 130 mmol, 1.0 eq) and sealed with a septum. A separate 4 mL vial was charged with potassium *tert*-butoxide (0.325 mmol, 0.25 mol%) followed by 2-MeTHF (1.3 mL, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed) and benzyl alcohol (1.3 mmol, 1.0 mol%), and sealed. The premix Base/Initiator/2-MeTHF was homogenized for 5 min. The reactor and the vial were taken out of the glovebox. The round bottom flask was immersed in the cooling bath at  $-20$  °C. After 40 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/2-MeTHF via a gastight syringe. After 4 hours at  $-20$  °C, the polymerization was quenched by addition of 40 mL of a cold ( $-20$  °C) solution of acetic acid in acetone (5  $\mu$ L/mL) and warmed to  $+22$  °C until the polymer was redissolved. The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at  $35$  °C until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum ( $<0.1$  mbar) for 24 hours.

**Table S3** Screening of the quenching solvents for the ROP<sup>[a]</sup>

Entry	Solvent for quenching	Yield <sup>[b]</sup>
1	CHCl <sub>3</sub>	70
2	1,2-DCE	68
3	1,1,2,2-TCE	69
4	Chlorobenzene	53
5	Acetophenone	18
6	Acetone	41
7	Acetone	65 <sup>[c]</sup> , M <sub>n</sub> =8 520 g/mol <sup>[d]</sup>
8	dihydrolevoglucosenon (Cyrene)	21
9	Anisole	26
10	Glyme	32
11	1,4-dioxane	31
12	(MeO) <sub>2</sub> CO	45
13	(EtO) <sub>2</sub> CO	51
14	DMSO	50
15	Acetonitrile	54

[a] **Reaction conditions:** GBL (1 eq) cooled to -20 °C and then BnOH (0.01 eq), *t*-BuOK (0.0025 eq) and 2-MeTHF (100 M) mixed at rt and added dropwise to the cold GBL. Quenching using cold solvent with CH<sub>3</sub>CO<sub>2</sub>H (0.05 eq); [b] Determined by <sup>1</sup>H-NMR using hexamethyldisiloxane as internal standard; [c] Isolated yield; [d] M<sub>n</sub> (average mass in Da) was determined by <sup>1</sup>H-NMR of the pure polymer by comparing the integration of the CH<sub>2</sub> signal from the benzyl alcohol at 5.12 ppm A, with the CH<sub>2</sub> signal from the poly-4-hydroxybutyrate at 4.12 ppm B, due to the presence of only 1 benzyl alcohol molecule per polymer chain. 1,2-DCE = 1,2-dichloroethane. 1,1,2,2-TCE = 1,1,2,2-tetrachloroethane

## 2.4 Screening of different acids for the quenching of the base

### Preparation on 6.5 mmol scale (Table S4):

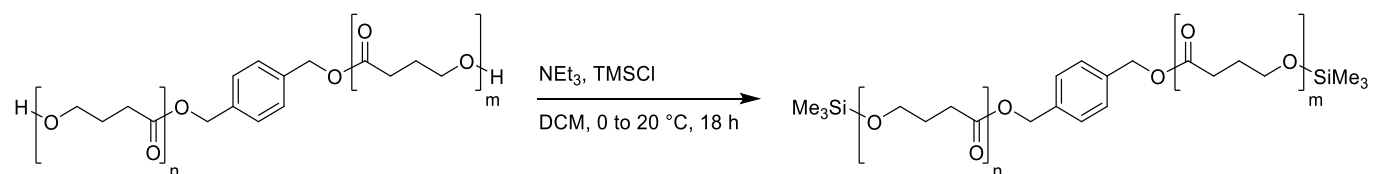
The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL-vial was charged with GBL (500  $\mu$ L, 6.50 mmol, 1.0 eq) and sealed with a septum. A separate 1 mL vial was charged with potassium *tert*-butoxide (1.83 mg, 0.016 mmol, 0.25 mol%) followed by 2-MeTHF (65.0  $\mu$ L, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed) and benzyl alcohol (6.7  $\mu$ L, 0.065 mmol, 1 mol%) and sealed. The obtained premix Base/Initiator/2-MeTHF was homogenized for 5 min. The vials were taken out of the glovebox. The vial containing the GBL was immersed in the cooling bath at  $-20$  °C. After 30 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/2-MeTHF via a gastight syringe. After 4 hours at  $-20$  °C, the polymerization was quenched by addition of 4 mL of cold ( $-20$  °C) quenching solution comprising the acid indicated in Table S4 (acid concentration 1-5 mol% relative to GBL) in 4 mL of the solvent indicated in Table S4, the precipitated polymer was gently crushed and mixed until redissolution at  $-20$  °C. If the polymer did not redissolve at  $-20$  °C, the reaction mixture was warmed up to  $+22$  °C. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

**Table S4** Screening of the different acids to quench the base

Entry	Solvent for quenching	Acid for quenching	Amount of acid relative to <i>t</i> -BuOK	pKa in H <sub>2</sub> O	Yield <sup>[a]</sup>
1	CHCl <sub>3</sub>	acetic acid	20 eq	+4.70 <sup>[1]</sup>	70
2	CDCl <sub>3</sub> /Acetone, 4 : 1	HClO <sub>4</sub> 70% (in H <sub>2</sub> O)	12 eq	-10 <sup>[2]</sup>	14
3	CDCl <sub>3</sub> /Acetone, 4 : 1	H <sub>2</sub> SO <sub>4</sub>	4 eq	-3.0 <sup>[2]</sup>	32
4	CDCl <sub>3</sub> /Acetone, 4 : 1	MeSO <sub>3</sub> H	12 eq	-0.6 <sup>[2]</sup>	29
5	CDCl <sub>3</sub>	pTSA	12 eq	-1.3 <sup>[3]</sup>	64
6	CDCl <sub>3</sub> /Acetone, 4 : 1	HCl 37% (in H <sub>2</sub> O)	12 eq	-1.1	54
7	CDCl <sub>3</sub> /Acetone, 4 : 1	HNO <sub>3</sub> 70% (in H <sub>2</sub> O)	12 eq	-1.3 <sup>[3]</sup>	66
8	CDCl <sub>3</sub> /Acetone, 1 : 1	oxalic acid 80% (in H <sub>2</sub> O)	12 eq	+1.23 <sup>[1]</sup>	56
9	CDCl <sub>3</sub> /Acetone, 1 : 1	H <sub>3</sub> PO <sub>4</sub> 85% (in H <sub>2</sub> O)	12 eq	+2.12 <sup>[3]</sup>	55
10	CDCl <sub>3</sub> /Acetone, 2 : 3	citric acid 40% (in H <sub>2</sub> O)	12 eq	+3.1 <sup>[4]</sup>	51
11	CDCl <sub>3</sub> /Acetone, 4 : 1	formic acid 85% (in H <sub>2</sub> O)	12 eq	+3.77 <sup>[1]</sup>	66
12	CDCl <sub>3</sub> /Acetone, 4 : 1	lactic acid 85% (in H <sub>2</sub> O)	12 eq	+3.87 <sup>[1]</sup>	66
13	CDCl <sub>3</sub> /Acetone, 4 : 1	acrylic Acid	12 eq	+4.69 <sup>[1]</sup>	65
14	CDCl <sub>3</sub>	propanoic acid	12 eq	+4.87 <sup>[5]</sup>	61
15	CDCl <sub>3</sub> /Acetone, 2 : 3	B(OH) <sub>3</sub> 50% (in H <sub>2</sub> O)	12 eq	+9.5 <sup>[6]</sup>	55

[a] **Reaction conditions:** GBL (1 eq) cooled to  $-20$  °C and then BnOH (0.01 eq), *t*-BuOK (0.0025 eq) and 2-MeTHF (100 M) mixed at rt and added dropwise to the cold GBL. Quenching using cold solvent with an acid; [b] Determined by  $^1\text{H-NMR}$  using hexamethyldisiloxane as internal standard.

## 2.5 Determination of Number of Hydroxyl end-groups



The dried polymer (50 mg) was dissolved in anhydrous DCM (5 mL). The resulting solution was cooled to 0 °C for 5 minutes and dry triethylamine (1.0 mL, 7.17 mmol) was added followed by the addition of TMS-Cl (0.5 mL, 3.94 mmol). The reaction solution was left to stir for 10 min at 0 °C, then the ice-bath was removed, and the resulting solution was left to stir at 20 °C for 18 h. After this time, the volatiles were removed under reduced pressure and the resulting solid was dried under high vacuum for 4 hours. Benzene- $d_6$  (2 mL) was added to the remaining red solid, the suspension was filtered into an NMR tube and the spectrum was recorded. From the resulting  $^1\text{H}$  NMR data, the ratio  $\text{CH}_2$  initiator : TMS end-group obtained was 4 : 17.22, translating to an average hydroxyl number of 1.91.

## 2.6 Screening of different water scavengers to set the ROP outside a glovebox

### Preparation on 130 mmol scale comprising drying of GBL by adding CaH<sub>2</sub> (Table S5, entry 1):

The ring-opening polymerization of  $\gamma$ -butyrolactone (GBL) was performed under N<sub>2</sub> atmosphere in a 50 mL Schlenk round bottom flask which was previously dried in an oven at 120 °C overnight. The flask was charged with calcium hydride (112 mg, 1 wt%) as well as GBL (10 mL, 130 mmol), flushed with N<sub>2</sub> and sealed (alternatively dry GBL can be distilled from the calcium hydride before use). The mixture in the sealed flask was then heated to 60 °C for 2 hours. After cooling to room temperature, the sealed flask was immersed in a cooling bath at -20 °C during 30 min. A separate dry vial was charged with a solution of potassium *tert*-butoxide in 2-MeTHF, 2 M, 25 wt.% (0.170 mL, 0.25 mol%), benzyl alcohol (0.135 mL, 1.30 mmol, 1 mol%), anhydrous 2-MeTHF (1.13 mL, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min and cooled to -20 °C. After 30 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/2-MeTHF via a gastight syringe. After 4 hours at -20 °C, the polymerization was quenched by addition of 40 mL of a cold (-20 °C) solution of acetic acid in DCM (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at -20 °C. The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at 35 °C until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum (<0.1 mbar) for 24 hours.

### Preparation with Incozol 2 on a 65 mmol scale (Table S5, entries 2 to 8):

The ring-opening polymerization of  $\gamma$ -butyrolactone was performed under N<sub>2</sub> atmosphere in a 50 mL Schlenk flask which was previously dried in an oven at 120 °C overnight. After performing 3 cycles of high vacuum/N<sub>2</sub> the dried flask was sealed and charged with GBL (5.0 mL, 65.05 mmol) via a gastight syringe. The water scavenger Incozol 2 (0.1 to 0.3 mol.%) was added to the GBL and the resulting mixture was stirred for 1 hour at ambient temperature. The sealed flask was then immersed in a cooling bath at -20 °C with 30 min equilibration time. A separate dry vial was charged with a solution of potassium *tert*-butoxide in 2-MeTHF, 2 M, 25 wt.% (0.35 to 0.6 mol%), the initiator indicated in Table S5 (0.25 to 1.0 mol%), 2-MeTHF (65.0  $\mu$ L, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed) and sealed. The obtained premix Base/Initiator/Solvent was homogenized for 5 min and cooled to -20 °C. After 30 min equilibration at the desired temperature the ROP of GBL was initiated by dropwise addition of the premix Base/Initiator/2-MeTHF via a gastight syringe. After 4 hours at -20 °C, the polymerization was quenched by addition of 40 mL of a cold (-20 °C) solution of acetic acid in DCM (5  $\mu$ L/mL), and the precipitated polymer was gently crushed and mixed until redissolution at -20 °C. The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at 35 °C until 20 mbar was reached). The remaining viscous liquid was

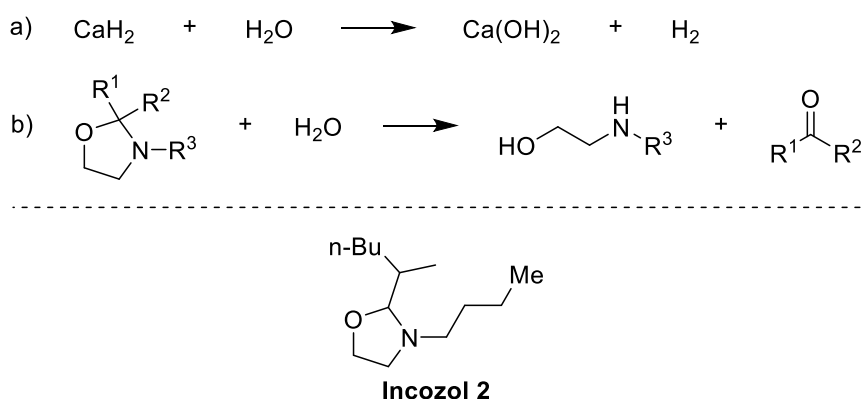
precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum (<0.1 mbar) for 24 hours.

**Table S5** Technical application of the ROP using with water scavengers<sup>[a]</sup>

Entry	Initiator (I) /Base (B)	Water scavenger (S)	Mol Ratio GBL : I : B : S	Solvent	Yield (%) <sup>[c]</sup>	M <sub>n</sub> exp (g/mol) <sup>[d]</sup>	M <sub>w</sub> exp (g/mol) <sup>[d]</sup>	Đ (M <sub>w</sub> /M <sub>n</sub> ) <sup>[d]</sup>
1	BnOH/ <i>t</i> -BuOK	CaH <sub>2</sub> <sup>[b]</sup>	400 : 4 : 1 : 14	2-MeTHF	30	7 861	13 571	1.73
2	BnOH/ <i>t</i> -BuOK	Incozol 2	500 : 5 : 3 : 1.5	2-MeTHF	53	4 259	6 657	1.56
3	BnOH/ <i>t</i> -BuOK	Incozol 2	300 : 3 : 1 : 0.3	2-MeTHF	41	8 592	13 263	1.54
4	BnOH/ <i>t</i> -BuOK	Incozol 2	200 : 2 : 1 : 0.4	Chlorobenzene	30	6 739	13 001	1.93
5	PEG <sub>400</sub> / <i>t</i> -BuOK	Incozol 2	400 : 1 : 4 : 0.8	2-MeTHF	29	8 791	15 497	1.76
6	PEG <sub>400</sub> / <i>t</i> -BuOK	Incozol 2	200 : 1 : 1 : 0.4	2-MeTHF	26	8 221	13 655	1.66
7	PEG <sub>400</sub> / <i>t</i> -BuOK	Incozol 2	200 : 2 : 1 : 0.4	2-MeTHF	31	9 083	13 017	1.43

Entry	T <sub>5%</sub> (°C) <sup>[e]</sup>	T <sub>5%</sub> (°C) <sup>[e]</sup>	T <sub>g</sub> (°C) <sup>[f]</sup>	T <sub>c</sub> (°C) <sup>[f]</sup>	T <sub>m</sub> (°C) <sup>[f]</sup>
1	225	263	-57.2	11.9	54.6
2	227	268	-46.7	17.5	58.9
3	247	285	-49.3	16.1	59.7
4	255	301	-48.0	16.1	56.3
5	235	277	-47.8	23.5	57.8
6	229	265	-46.4	26.5	59.2
7	229	265	-46.8	22.8	58.7

[a] **Reaction conditions:** GBL (1 eq) with the water scavenger cooled to -20 °C and then the initiator, *t*-BuOK 2 M (25% w/w)-solution in 2-MeTHF and 2-MeTHF were mixed at rt and added dropwise to the cold GBL. Quenching using cold solvent with CH<sub>3</sub>CO<sub>2</sub>H (0.05 eq); [b] GBL mixed with CaH<sub>2</sub> (1 wt%) and heated to 60 °C for 2 hours prior to the addition of Base /Initiator /Solvent; [c] Isolated yield; [d] Determined by GPC in THF; [e] Measured by TGA; [f] Measured by DSC.



**Scheme S1** Reaction of water with the different scavengers. (a) Calcium hydride; (b) Oxazolidine (Incozol 2).

The optimized pGBL synthesis previously developed in a glove box, failed to be replicated in more technical conditions. This was caused by the presence of residual water inhibiting the anionic ROP through deactivation of the base *t*-BuOK and formation of *tert*-butanol plus potassium hydroxide. To cope with that

issue, the use of a water scavenger was adopted to minimize water content and improve monomer conversion and yield. The water scavengers considered for this study were calcium hydride and oxazolidine derivatives (sold as Incozol 2). The results obtained for the polymerization of GBL are listed in the Table 1. An important increase in GBL conversion to 33% was observed with the addition of calcium hydride (Table S5, entry 1). By changing this water scavenger to Incozol 2, the isolated yield greatly improved up to 53% even if it remains lower than the reference reaction set in a glovebox (Table S1, entry 3 vs Table S5, entries 2–4). Utilizing the same scavenger with polyethylene glycol as initiator does not reveal a significant improvement in terms of yield while molecular weights remain in the same range (Table S5, entries 5–7). The different water scavengers react with water according to the reactions detailed in the Scheme 1. When reacting with water, oxazolidines form a ketone and an alcohol amine, which could then possibly take part in the initiation of polymerization. Moreover, it cannot be ruled out that the alcohol amine competes with BnOH, and therefore leads to lower amounts of active base needed for ROP. The calcium hydride was not soluble in the reaction media, was more difficult to eliminate during the purification process and created more undesirable solid waste, if not removed before polymerization. Therefore, the use of oxazolidine derivatives was preferred.



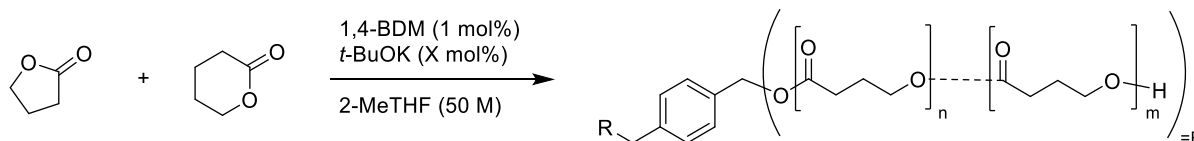
## 2.7 Comparative example

The ring-opening polymerization of  $\gamma$ -butyrolactone was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with potassium *tert*-butoxide (0.036 g, 0.325 mmol, 0.25 mol%) followed by 2-MeTHF (1.3 mL, resulting in a concentration of GBL of 100 M in the reaction mixture to be formed), benzyl alcohol (0.135 mL, 1.3 mmol, 1.0 mol%) and sealed with a septum. A separate 20 mL sealed vial was charged with GBL (10 mL, 130 mmol, 1.0 eq.). The premix Base/Initiator/Solvent was homogenized for 5 min. The reactor and the vial were taken out of the glovebox. The round bottom flask with Base/Initiator/Solvent was immersed in the cooling bath at  $-20\text{ }^{\circ}\text{C}$ . After 40 min equilibration at the desired temperature the polymerization was initiated by quick addition of the  $\gamma$ -butyrolactone via syringe. After 4 hours at  $-20\text{ }^{\circ}\text{C}$ , the polymerization was quenched by addition of 40 mL of a cold ( $-20\text{ }^{\circ}\text{C}$ ) solution of acetic acid in  $\text{CHCl}_3$  (5  $\mu\text{L}/\text{mL}$ ) until the precipitated polymer was redissolved at  $-20\text{ }^{\circ}\text{C}$ . The quenched reaction mixture was washed with distilled water (3 x 100 mL) and then the volatile constituents were evaporated using a rotative evaporator (at  $35\text{ }^{\circ}\text{C}$  until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH:H<sub>2</sub>O 9:1, filtered, washed with cold MeOH:H<sub>2</sub>O 9:1 and dried under high vacuum ( $<0.1\text{ mbar}$ ) for 24 hours, to afford the corresponding poly- $\gamma$ -butyrolactone (5.72 g, 66.4 mmol, 51% yield,  $M_n = 7\ 161\text{ g/mol}$ ).

$M_n$  (average mass in g/mol or Da) was determined by  $^1\text{H-NMR}$  of the pure polymer.

### 3 Optimization study of the ring-opening copolymerization of GBL

#### 3.1 Optimization of time, temperature, and monomer equivalents



#### Preparation on 20 mmol scale of poly(GBL-co-DVL) (Table S6):

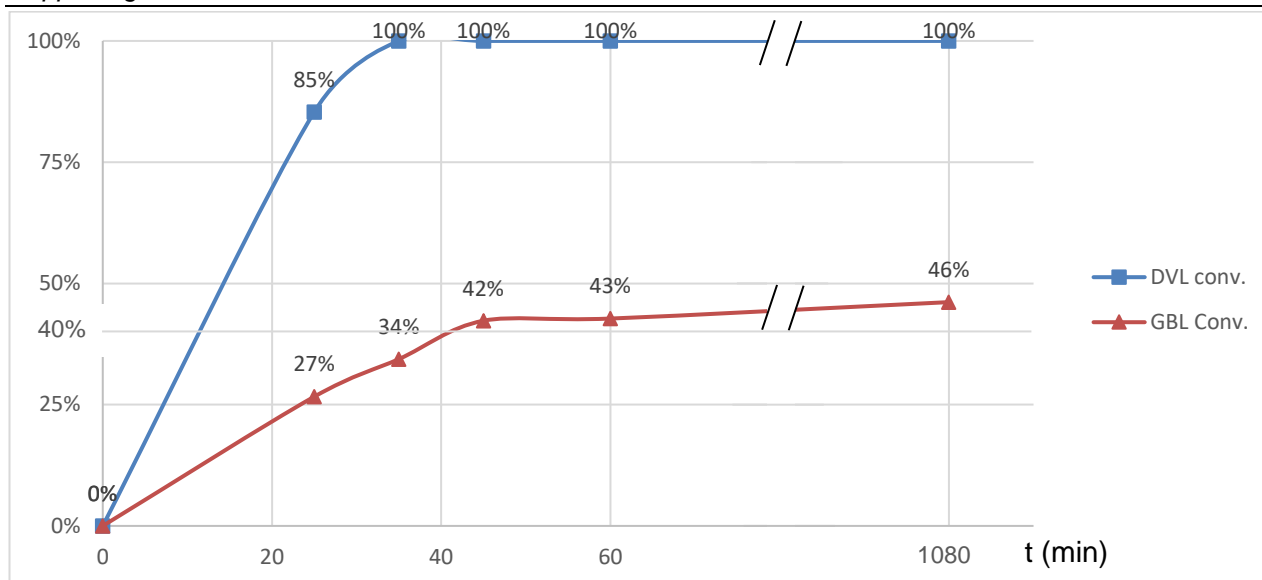
The ring-opening-copolymerization of  $\gamma$ -butyrolactone (GBL) and  $\delta$ -valerolactone (DVL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL vial was charged with both monomers, GBL (8 mmol to 13 mmol, 0.4 eq to 0.66 eq), DVL (6.5 mmol to 12 mmol, 0.33 eq to 0.6 eq) and sealed with a septum. A separate 1 mL vial was charged with the base potassium *tert*-butoxide (0.0025 eq to 0.02 eq) followed by the solvent 2-MeTHF (400  $\mu$ L, resulting in a concentration of GBL+DVL of 50 M in the reaction mixture to be formed), and the diol initiator 1,4-benzenedimethanol (0.01 eq) and sealed. The vials were taken out of the glovebox. The premix Base/Initiator/Solvent was sonicated 5 min until a homogeneous suspension was obtained. The vial containing the GBL and DVL was immersed in the cooling bath at the temperature indicated in Table S6 (from  $-21$  to  $+25$ ). After 30 min equilibration at the desired temperature the ring-opening copolymerization of GBL and DVL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After the time indicated in Table S6, the polymerization was quenched by addition of 4 mL (at the temperature indicated in Table S6) of a solution of acetic acid in  $\text{CDCl}_3$  (5  $\mu$ L/mL), and the reaction mixture immediately well homogenized with a spatula until the precipitated polymer was redissolved. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

**Table S6** Optimization of time, temperature, and monomer equivalents

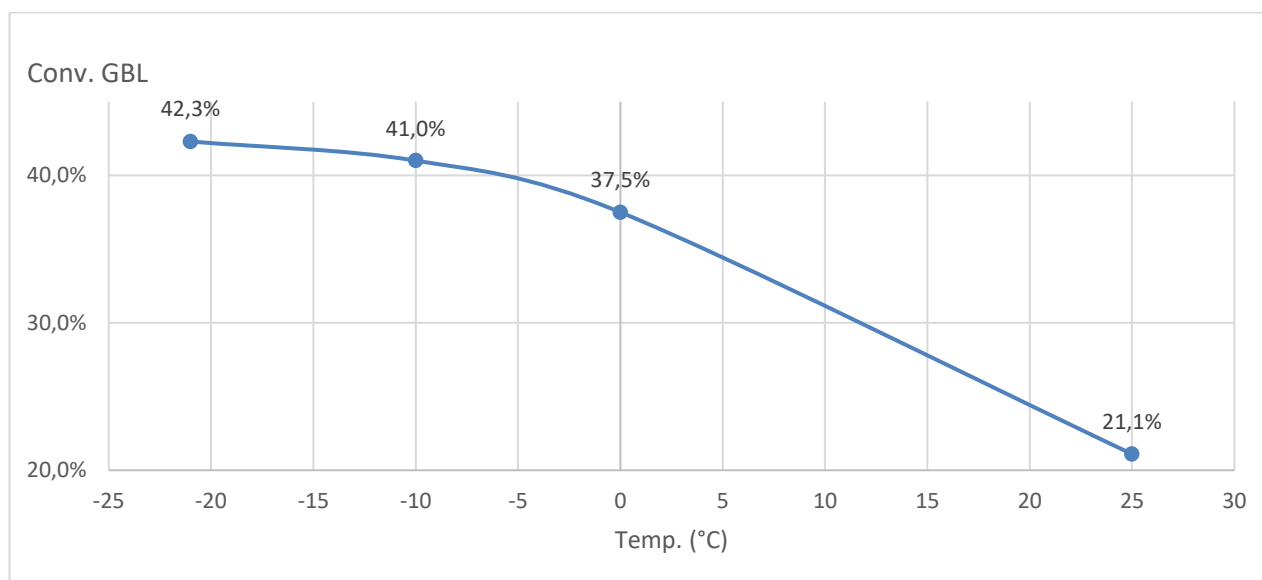
Entry	Initiator (I) /Base (B)	Mol Ratio M <sup>[a]</sup> : I : B	Ratio GBL : DVL	mmol ratio GBL : DVL	t (min)	T (°C)	Conv. DVL <sup>[b]</sup>	Conv. GBL <sup>[b]</sup>	Total conv.
1	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 2	66 : 33	13 : 6.5	240	-21	80.1%	19.9%	40.0%
2	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 1	66 : 33	13 : 6.5	240	-21	53.7%	10.4%	24.8%
3	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 1.5	66 : 33	13 : 6.5	240	-21	90.2%	19.7%	43.2%
4	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 1	66 : 33	13 : 6.5	240	-21	45.1%	12.9%	23.6%
5	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	240	-21	>99%	35.7%	57.6%
6	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.25	66 : 33	13 : 6.5	240	-21	62%	10%	27%
7	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	25	-21	85.4%	26.7%	46.2%
8	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	35	-21	>99%	34.4%	56.7%
9	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	45	-21	>99%	42.3%	63.3%
10	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	60	-21	>99%	42.8%	64.2%
11	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	18 h	-21	>99%	46.1%	66.6%
12	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	45	-10	>99%	41.0%	60.7%
13	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	45	0	>99%	37.5%	58.4%
14	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	66 : 33	13 : 6.5	45	25	>99%	21.1%	47.4%
15	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	45	25	>99%	19.5%	59.8%
16	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	45	-10	>99%	44.9%	72.4%
17	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	40 : 60	8 : 12	45	-10	>99%	34.9%	73.9%
18	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	1	-10	>99%	28.4%	65.2%
19	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	3	-10	>99%	31.0%	67.0%
20	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	5	-10	>99%	35.1%	68.1%
21	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	7	-10	>99%	37.8%	70.7%
22	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	9	-10	>99%	40.2%	71.3%
23	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	10	-10	>99%	42.1%	71.1%
24	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	20	-10	>99%	44.0%	72.0%
25	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	30	-10	>99%	44.4%	72.2%
26	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	38	-10	>99%	42.0%	71.0%
27	1,4-BDM/ <i>t</i> -BuOK	100 : 1 : 0.5	50 : 50	10 : 10	120	-10	>99%	44.3%	72.1%

[a] M=GBL+DVL

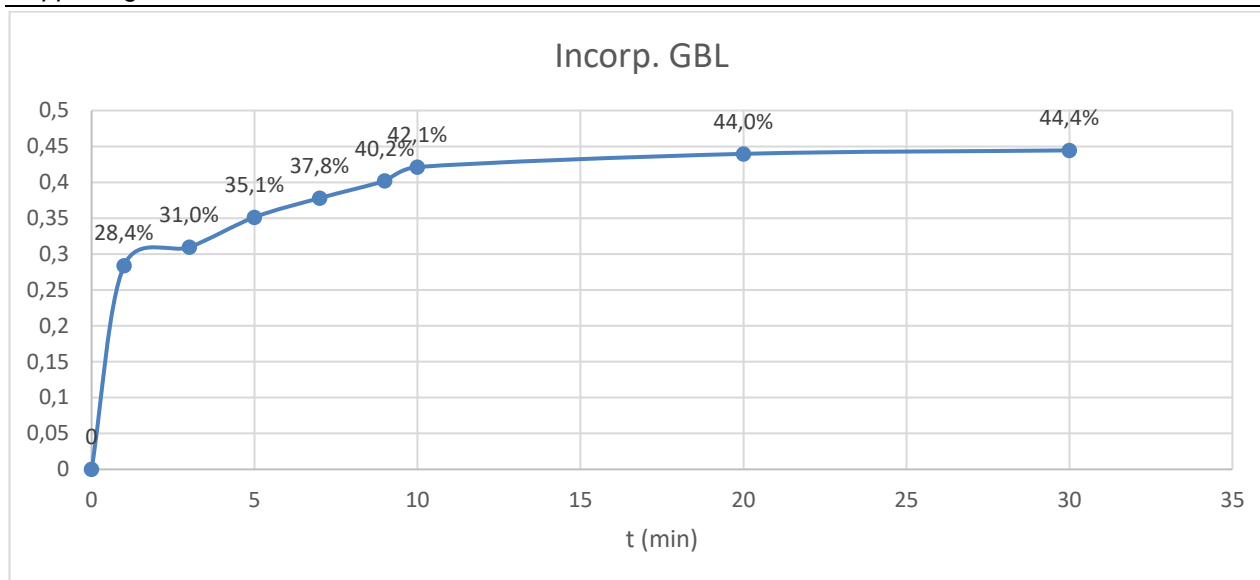
[b] Determined by <sup>1</sup>H NMR.



**Figure S1** Copolymerization GBL/DVL: Kinetic at  $-20\text{ }^{\circ}\text{C}$  (Table S6, entries 7 – 11)



**Figure S2** Copolymerization GBL/DVL: Conversion of GBL in 45 min depending on temperature (Table S6, entries 9, 12 – 14)



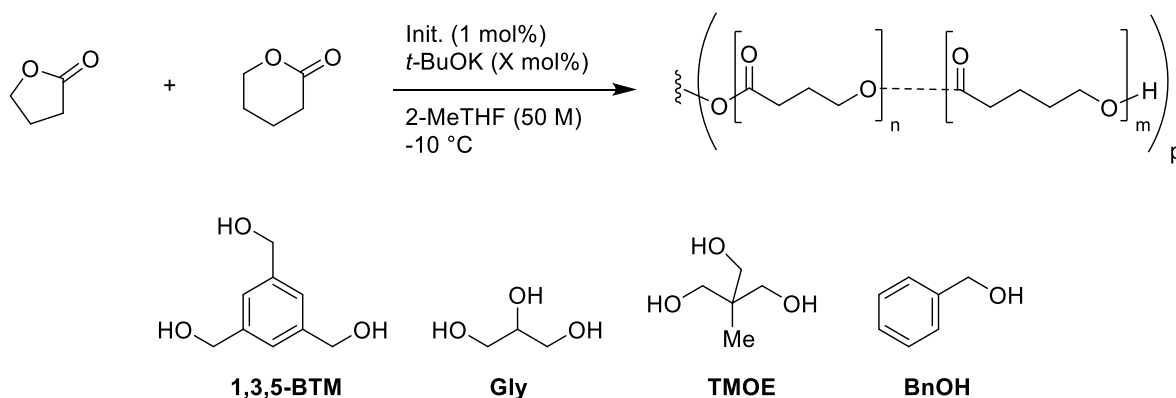
**Figure S3** Copolymerization GBL/DVL: Kinetic at  $-10\text{ }^{\circ}\text{C}$  (Table S6, entries 18 – 25)

**Large scale preparation of poly(GBL-co-DVL)**

The ring-opening copolymerization of  $\gamma$ -butyrolactone (GBL) and  $\delta$ -valerolactone (DVL) was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with GBL (10 mL, 130 mmol, 0.66 eq), DVL (6 mL, 65 mmol, 0.33 eq) and sealed with a septum. A separate 5 mL vial was charged with the base potassium *tert*-butoxide (110.5 mg, 0.985 mmol, 0.005 eq) followed by the solvent 2-MeTHF (4 mL, resulting in a concentration of GBL+DVL of 50 M in the reaction mixture to be formed), and the diol initiator 1,4-benzenedimethanol (272.2 mg, 1.97 mmol, 0.01 eq) and sealed. The reactor and the vial were taken out of the glovebox. The premix Base/Initiator/Solvent was sonicated 10 min until a homogeneous suspension was obtained. The round bottom flask was immersed in the cooling bath at  $-20$  °C. After 40 min equilibration at the desired temperature the ring-opening polymerization of GBL and DVL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 45 minutes at  $-20$  °C, the polymerization was quenched by addition of 40 mL of a cold ( $-20$  °C) solution of acetic acid in DCM (5  $\mu$ L/mL) and the reaction mixture immediately well homogenized with a spatula until the precipitated polymer was redissolved. Volatile constituents of the quenched reaction mixture were evaporated using a rotative evaporator (at 35 °C until 20 mbar was reached). The remaining viscous liquid was precipitated using cold methanol : water, 9:1, filtered, washed with cold methanol : water, 9:1 and dried under high vacuum (0.1 mbar) for 24 hours. The expected poly(GBL-co-DVL) was isolated in 65% yield with  $M_n=8\ 470$  g/mol, Conv.(DVL)>99%, Conv.(GBL)=45.6% and a composition GBL:DVL of 41:59.

$M_n$  (average mass in g/mol or Da) was determined by  $^1\text{H-NMR}$  of the pure polymer.

### 3.2 Screening of different alcohol initiators



#### Preparation on 20 mmol scale of poly(GBL-co-DVL) (Table S7):

The ring-opening-copolymerization of  $\gamma$ -butyrolactone (GBL) and  $\delta$ -valerolactone (DVL) was performed in a sealed 10 mL vial. In an Argon filled glovebox, the 10 mL vial was charged with both monomers, GBL (10 mmol, 0.5 eq), DVL (10 mmol, 0.5 eq) and sealed with a septum. A separate 1 mL vial was charged with the base potassium *tert*-butoxide (0.0025 eq to 0.01 eq) followed by the solvent 2-MeTHF (400  $\mu$ L, resulting in a concentration of GBL+DVL of 50 M in the reaction mixture to be formed) and the alcohol initiator indicated in Table S7 (0.01 eq) and sealed. The vials were taken out of the glovebox. The premix Base/Initiator/Solvent was sonicated 5 min until a homogeneous suspension was obtained. The vial containing the GBL and DVL was immersed in the cooling bath at  $-10\text{ }^\circ\text{C}$ . After 30 min equilibration the ring-opening copolymerization of GBL and DVL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 45 minutes, the polymerization was quenched by addition of 4 mL (at  $-10\text{ }^\circ\text{C}$ ) of a solution of acetic acid in  $\text{CDCl}_3$  (5  $\mu\text{L/mL}$ ), and the reaction mixture immediately well homogenized with a spatula until the precipitated polymer was redissolved. The quenched reaction mixture was analyzed by  $^1\text{H-NMR}$  to obtain the percentage of converted monomer and yield.

**Table S7** Screening of different alcohol initiators

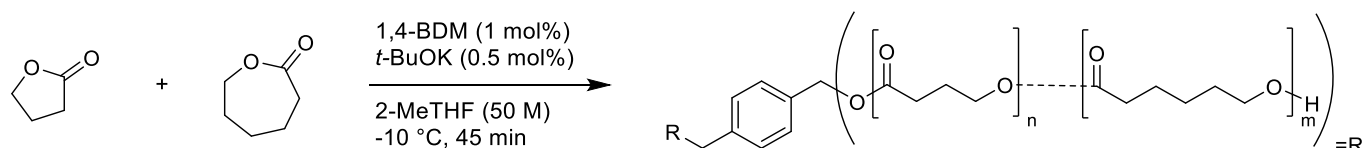
Entry	Polyol/Base	Mol Ratio	Conv.	Conv.	Total conv.
		M <sup>[a]</sup> : I : B	DVL <sup>[b]</sup>	GBL <sup>[b]</sup>	
1	1,3,5-BTM/ <i>t</i> -BuOK	100 : 1 : 0.75	94%	33%	64%
2	Gly/ <i>t</i> -BuOK	100 : 1 : 0.75	84%	26%	55%
3	TMOE/ <i>t</i> -BuOK	100 : 1 : 0.75	88%	26%	57%
4	BnOH/ <i>t</i> -BuOK	100 : 1 : 0.25	84%	22%	53%

1,3,5-BTM: 1,3,5-benzenetri-methanol; Gly: glycerol; TMOE: trimethylolethane; BnOH: benzyl alcohol.

[a] M=GBL+DVL

[b] Determined by  $^1\text{H NMR}$ .

### 3.3 Screening of different comonomers and related properties



#### Large scale preparation of poly(GBL-co-ECL)

The ring-opening copolymerization of  $\gamma$ -butyrolactone (GBL) and  $\epsilon$ -caprolactone (ECL) was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with GBL (100 mmol, 0.5 eq), ECL (100 mmol, 0.5 eq) and sealed with a septum. A separate 5 mL vial was charged with the base potassium *tert*-butoxide (1 mmol, 0.005 eq) followed by the solvent 2-MeTHF (4 mL, resulting in a concentration of GBL+ ECL of 50 M in the reaction mixture to be formed) and the diol initiator 1,4-benzenedimethanol (2 mmol, 0.01 eq) and sealed. The reactor and the vial were taken out of the glovebox. The premix Base/Initiator/Solvent was sonicated 10 min until a homogeneous suspension was obtained. The round bottom flask was immersed in the cooling bath at  $-10^\circ\text{C}$ . After 40 min equilibration at the desired temperature the ring-opening polymerization of GBL and ECL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 45 minutes at  $-10^\circ\text{C}$ , the polymerization was quenched by addition of 40 mL of a cold ( $-10^\circ\text{C}$ ) solution of acetic acid in DCM (5  $\mu\text{L/mL}$ ), and the reaction mixture immediately well homogenized with a spatula until the precipitated polymer was redissolved. Volatile constituents of the quenched reaction mixture were evaporated using a rotative evaporator (at  $35^\circ\text{C}$  until 20 mbar was reached). The remaining viscous liquid was precipitated using cold methanol : water, 9:1, filtered, washed with cold methanol : water, 9:1, and dried under high vacuum (0.1 mbar) for 24 hours. The expected poly(GBL-co-ECL) was isolated in 70% yield with  $M_n=15\ 020$  g/mol,  $\text{Conv.}(\text{ECL})>99\%$ ,  $\text{Conv.}(\text{GBL})=43\%$  and a composition GBL:ECL of 30:70.

#### Preparation on 20 mmol scale of poly(GBL-co-ECL) (Table S8)

The polymerizations were performed under  $\text{N}_2$  atmosphere in a 50 ml Schlenk tube which was previously dried in an oven at  $120^\circ\text{C}$  overnight. After performing 3 cycles of high vacuum/ $\text{N}_2$  the dried reactor was sealed and charged with GBL (13.4 mmol to 16.6 mmol, 0.67 eq to 0.83 eq) and ECL (3.4 mmol to 6.6 mmol, 0.17 eq to 0.33 eq). The water scavenger Incozol 2 (0.002 eq) was added to the GBL/ECL mixture via a gastight syringe and the resulting mixture stirred for 1 h at room temperature under  $\text{N}_2$  atmosphere. The sealed Schlenk tube was then immersed in a cooling bath at  $-10^\circ\text{C}$  during 30 min for temperature equilibration. A separate vial was dried in the oven at  $120^\circ\text{C}$  and the air was evacuated by 3 cycles of high vacuum/ $\text{N}_2$  before sealing. It was then charged with anhydrous 2-MeTHF (resulting in a concentration of GBL+ECL of 100 M in the reaction mixture to be formed), the base anhydrous solution of potassium *tert*-butoxide in 2-MeTHF (2 M, 25 wt%, 0.005 eq to 0.02 eq), and the alcohol initiator indicated in table S8 (0.01 eq) via a gastight syringe. The mixture Base/Initiator/Solvent was sonicated 10 min until a



homogeneous suspension was obtained. The ring-opening copolymerization of GBL and ECL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 4 h, the polymerization was quenched by addition of 40 mL of a cold ( $-10\text{ }^{\circ}\text{C}$ ) solution of acetic acid in DCM ( $5\text{ }\mu\text{L/mL}$ ) before gently crushing the white solid polymer formed with a spatula. The quenched mixture was allowed to warm to room temperature. It was then washed with dist. water ( $3 \times 50\text{ mL}$ ) in a separating funnel and the volatiles were evaporated using a rotative evaporator ( $40\text{ }^{\circ}\text{C}$ , until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH ( $0\text{ }^{\circ}\text{C}$ ). In the case, where the obtained precipitate was a viscous liquid, it was washed several times with MeOH by successive centrifugation/redispersions ( $4000\text{ rpm}$ ,  $2\text{ min}$ ,  $10\text{ }^{\circ}\text{C}$ ) and isolated by centrifugation before drying under reduced pressure. In the case, where the precipitate obtained was a solid, it was filtered, washed with cold MeOH and dried under vacuum using a rotative evaporator to afford the corresponding copolymer.

**Table S8** Screening of different comonomers and related properties

Entry	Ratio GBL : ECL	Mol Ratio $M^{[a]} : I : B$	Initiator (I)	Conv. GBL   ECL (%) <sup>[b]</sup>	CP GBL : ECL <sup>[b]</sup>	Isolated yield (%)
1	83 : 17	100 : 1.0 : 0.5	BnOH	47   96	69 : 31	55
2	71 : 29	100 : 1.0 : 2.0	PEG <sub>400</sub>	49   95	51 : 49	53
3	67 : 33	100 : 1.0 : 2.0	EG	51   94	47 : 53	82

Entry	$M_n$ (g/mol) <sup>[c]</sup>	$M_w$ (g/mol) <sup>[c]</sup>	$\bar{D}$ ( $M_w/M_n$ ) <sup>[c]</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>	$T_c$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>	$T_m$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>
1	9 616	21 250	2.21	-59.5	-12.0	17.2
2	12 543	17 760	1.42	-60.6	-15.6	21.3
3	8 300	12 320	1.48	-61.6	-15.0	21.3

CP = Composition of the polymer; N.D. = Not determined; EG: Ethylene Glycol.

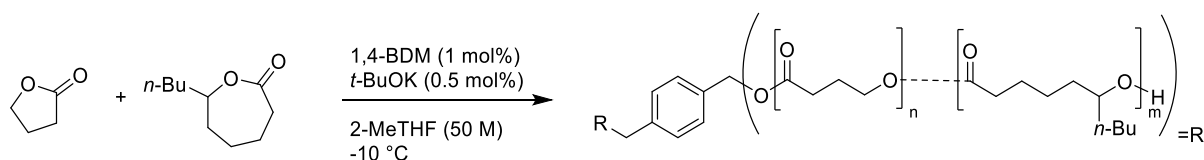
[a]  $M = \text{GBL} + \text{ECL}$

[b] Determined by  $^1\text{H-NMR}$

[c] Determined from GPC in THF

[d] Glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) were measured by DSC

### Large scale preparation of poly(GBL-co-EDL)



The ring-opening copolymerization of  $\gamma$ -butyrolactone (GBL) and  $\epsilon$ -decalactone (EDL) was performed in a flame-dried 100 mL round bottom flask. In an Argon filled glovebox, the flask was charged with GBL (100 mmol, 0.5 eq), EDL (100 mmol, 0.5 eq) and sealed with a septum. A separate 5 mL vial was charged with

the base potassium *tert*-butoxide (1 mmol, 0.005 eq) followed by the solvent 2-MeTHF (4 mL, resulting in a concentration of GBL+ EDL of 50 M in the reaction mixture to be formed) and the diol initiator 1,4-benzenedimethanol (2 mmol, 0.01 eq) and sealed. The reactor and the vial were taken out of the glovebox. The premix Base/Initiator/Solvent was sonicated 10 min until a homogeneous suspension was obtained. The round bottom flask was immersed in the cooling bath at  $-10\text{ }^{\circ}\text{C}$ . After 40 min equilibration at the desired temperature the ring-opening polymerization of GBL and EDL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 45 minutes at  $-10\text{ }^{\circ}\text{C}$ , the polymerization was quenched by addition of 40 mL of a cold ( $-10\text{ }^{\circ}\text{C}$ ) solution of acetic acid in DCM (5  $\mu\text{L}/\text{mL}$ ) and the reaction mixture immediately well homogenized with a spatula until the precipitated polymer was redissolved. The volatile constituents of the quenched reaction mixture were evaporated using a rotative evaporator (at  $35\text{ }^{\circ}\text{C}$  until 20 mbar were reached). The remaining viscous liquid was precipitated using cold methanol : water, 9:1, filtered, washed with cold methanol : water, 9:1, and dried under high vacuum (0.1 mbar) for 24 hours. The expected poly(GBL-co-EDL) was isolated in 84% yield with  $M_n=11\ 490\text{ g/mol}$ ,  $M_w=16\ 920\text{ g/mol}$ ,  $D(M_w/M_n)=1.47$ ,  $\text{Conv.}(\text{EDL})=76\%$ ,  $\text{Conv.}(\text{GBL})=92\%$  and a ratio pGBL:pEDL of 56:44.

### 3.4 Physical properties of the copolymers depending on GBL incorporation

#### Preparation on 20 mmol scale of poly(GBL-co-ECL) (Table S9, entries 3 – 5; and Table S10, entries 3 – 5)

The polymerizations were performed under N<sub>2</sub> atmosphere in a 50 ml Schlenk tube which was previously dried in an oven at 120 °C overnight. After performing 3 cycles of high vacuum/N<sub>2</sub> the dried reactor was sealed and charged with GBL (13.4 mmol to 16.6 mmol, 0.67 eq to 0.83 eq) and ECL (3.4 mmol to 6.6 mmol, 0.17 eq to 0.33 eq). The water scavenger Incozol 2 (0.002 eq) was added to the GBL/ECL mixture via a gastight syringe and stirred for 1 h at room temperature under N<sub>2</sub> atmosphere. The sealed Schlenk tube was then immersed in a cooling bath at –10 °C during 30 min for temperature equilibration. A separate vial was dried in the oven at 120 °C and the air was evacuated by 3 cycles of high vacuum/N<sub>2</sub> before sealing. It was then charged with anhydrous 2-MeTHF (resulting in a concentration of GBL+ECL of 100 M in the reaction mixture to be formed), the base anhydrous solution of potassium *tert*-butoxide in 2-MeTHF (2 M, 25 wt%, 0.005 eq to 0.02 eq), and the alcohol initiator indicated in table S9 (0.01 eq) via a gastight syringe. The mixture Base/Initiator/Solvent was sonicated 10 min until a homogeneous suspension was obtained. The ring-opening copolymerization of GBL and ECL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 4 h, the polymerization was quenched by addition of 40 mL of a cold (–10 °C) solution of acetic acid in DCM (5 µL/mL) before gently crushing the white solid polymer formed with a spatula. The quenched mixture was allowed to warm to room temperature. It was then washed with dist. water (3 x 50 mL) in a separating funnel and volatiles were evaporated using a rotative evaporator (40 °C, until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH (0 °C). In the case, where the obtained precipitate was a viscous liquid, it was washed several times with MeOH by successive centrifugation/redispersions (4000 rpm, 2 min, 10 °C) and isolated by centrifugation before drying under reduced pressure. In the case, where the precipitate obtained is a solid, it was filtered, washed with cold MeOH, and dried under vacuum using a rotative evaporator to afford the corresponding copolymer.

#### Preparation on 20 mmol scale of poly(GBL-co-DVL) (Table S9, entries 9 – 12; and Table S10, entries 9 – 12)

The polymerizations were performed under N<sub>2</sub> atmosphere in a 50 ml Schlenk tube which was previously dried in an oven at 120 °C overnight. After performing 3 cycles of high vacuum/N<sub>2</sub> the dried reactor was sealed and charged with GBL (6.6 mmol to 18.2 mmol, 0.33 eq to 0.91 eq) and DVL (1.8 mmol to 13.4 mmol, 0.09 eq to 0.67 eq). The water scavenger Incozol 2 (0.002 eq) was added to the GBL/DVL mixture via a gastight syringe and stirred for 1 h at room temperature under N<sub>2</sub> atmosphere. The sealed Schlenk tube was then immersed in a cooling bath at –10 °C during 30 min for temperature equilibration. A separate vial was dried in the oven at 120 °C and the air was evacuated by 3 cycles of high vacuum/N<sub>2</sub> before sealing. It was then charged with anhydrous 2-MeTHF (resulting in a concentration of GBL+DVL of 100 M in the reaction mixture to be formed), the base anhydrous solution of potassium *tert*-butoxide in 2-MeTHF

(2 M, 25 wt%, 0.005), and the alcohol initiator benzyl alcohol (0.01 eq) via a gastight syringe. The mixture Base/Initiator/Solvent was sonicated 10 min until a homogeneous suspension was obtained. The ring-opening copolymerization of GBL and DVL was initiated by addition of the premix Base/Initiator/Solvent via a gastight syringe at once. After 4 h, the polymerization was quenched by addition of 40 mL of a cold ( $-10\text{ }^{\circ}\text{C}$ ) solution of acetic acid in DCM ( $5\text{ }\mu\text{L/mL}$ ) before gently crushing the white solid polymer formed with a spatula. The quenched mixture was then allowed to warm to room temperature. It was then washed with dist. water ( $3 \times 50\text{ mL}$ ) in a separating funnel and then the volatiles were evaporated on rotative evaporator ( $40\text{ }^{\circ}\text{C}$ , until 20 mbar was reached). The remaining viscous liquid was precipitated using cold MeOH ( $0\text{ }^{\circ}\text{C}$ ). In the case where the obtained precipitate was a viscous liquid, it was washed several times with MeOH by successive centrifugations/redispersions (4000 rpm, 2 min,  $10\text{ }^{\circ}\text{C}$ ) and isolated by centrifugation before drying under reduced pressure. In the case, where the precipitate obtained is a solid, it was filtered, washed with cold MeOH, and dried under vacuum using a rotative evaporator to afford the corresponding copolymer.

**Table S9** Physical properties of the copolymers depending on GBL incorporation

Entry	Monomers	Initiator/Base	Ratio GBL : Co-M	Mol Ratio $M^{[a]} : I : B$	GBL conv. (%)	Co-M Conv. (%)	CP GBL : Co-M <sup>[b]</sup>
1	GBL/-	BnOH/ <i>t</i> -BuOK	100 : 0	100 : 1 : 0.25	92	-	100 : 0
2	-/ECL	-/ <i>t</i> -BuOK	0 : 100	100 : 0 : 0.5	-	79	0 : 100
3	GBL/ECL	BnOH/ <i>t</i> -BuOK	50 : 50	100 : 1 : 0.5	23	38	37 : 63
4	GBL/ECL	BnOH/ <i>t</i> -BuOK	83 : 17	100 : 1 : 0.5	47	96	69 : 31
5	GBL/ECL	BnOH/ <i>t</i> -BuOK	95 : 5	100 : 1 : 0.5	50	100	90 : 10
8	-/DVL	-/ <i>t</i> -BuOK	0 : 100	100 : 1 : 0.5	-	92	0 : 100
9	GBL/DVL	BnOH/ <i>t</i> -BuOK	33 : 67	100 : 1 : 0.5	30	66	20 : 80
10	GBL/DVL	BnOH/ <i>t</i> -BuOK	50 : 50	100 : 1 : 0.5	41	93	30 : 70
11	GBL/DVL	BnOH/ <i>t</i> -BuOK	67 : 33	100 : 1 : 0.5	49	99	49 : 51
12	GBL/DVL	BnOH/ <i>t</i> -BuOK	91 : 9	100 : 1 : 0.5	37	95	79 : 21

**Table S10** Physical properties of the copolymers depending on GBL incorporation

Entry	Monomers	CP GBL : Co-M <sup>[b]</sup>	$M_n$ (g/mol) <sup>[c]</sup>	$M_w$ (g/mol) <sup>[c]</sup>	$\bar{D}$ ( $M_w/M_n$ ) <sup>[c]</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>	$T_c$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>	$T_m$ ( $^{\circ}\text{C}$ ) <sup>[d]</sup>
1	GBL/-	100 : 0	9 310	15 330	1.65	-48.0	16.2	59.7
2	-/ECL	0 : 100	16 230	29 810	1.84	-59.4	32.5	57.6
3	GBL/ECL	37 : 63	19 770	31 820	1.61	-58	1.7	34
4	GBL/ECL	69 : 31	9 620	21 250	2.21	-59.5	-12.0	17.2
5	GBL/ECL	90 : 10	9 300	15 490	1.66	-52.2	-11.7	47.1

8	-/DVL	0 : 100	12 990	24 640	1.90	-60.7	26.3	56.2
9	GBL/DVL	20 : 80	11 830	15 790	1.33	-58.7	7.3	36.1
10	GBL/DVL	30 : 70	9 210	14 650	1.59	-56.6	-6.9	26
11	GBL/DVL	49 : 51	7 980	12 380	1.55	-59.5	-	14.6
12	GBL/DVL	79 : 21	8 700	15 000	1.72	-56.8	-	28.0

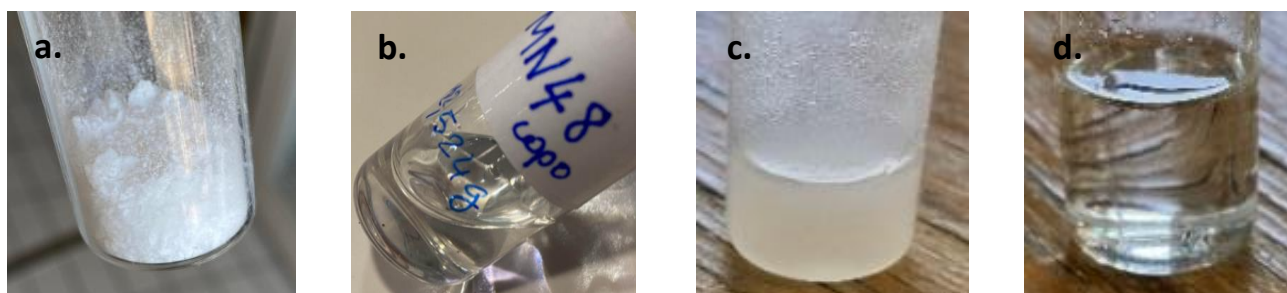
CP = Composition of the polymer

[a] M=GBL+ECL or GBL+DVL

[b] Determined by  $^1\text{H-NMR}$

[c] Determined from GPC in THF

[d] Glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting temperature ( $T_m$ ) were measured by DSC



**Figure S4** Pictures at room temperature (22 °C) of p(GBL-co-DVL) and p(GBL-co-ECL) reported in Table S9 and S10. [a] Entry 1 pGBL; [b] Entry 4 p(GBL-co-ECL), 69% of GBL; [c] Entry 10 p(GBL-co-DVL), 30% of GBL; [d] Entry 11 p(GBL-co-DVL), 49% of GBL.

### 3.5 Application of copolymer as polyol in polyurethane foam formation

A polyurethane foam was obtained by reacting the polyol obtained in table S9 entry 11 with di-isocyanate according to the following reaction equation:



Water was used as the foaming agent.

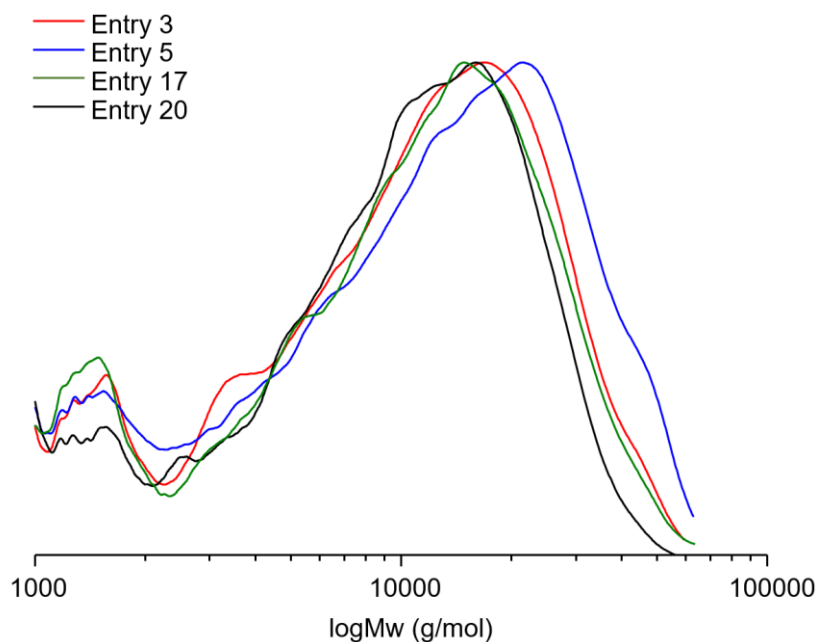
**Table S11**

Test #	H12MDI ( $\mu\text{L}$ ) [1.0 eq]	Sn(Oct) <sub>2</sub> ( $\mu\text{L}$ ) [mol%]	Polyol (mg)	H <sub>2</sub> O as foaming agent ( $\mu\text{L}$ )	Properties		
					Foaming	Bubble	Flexibility
1	100	15 [12]	500	30	Dense	Small	Soft
2	150	15 [8]	500	50	Scattered	Medium & Large	Soft+
3	250	15 [5]	500	80	Medium	Medium	Soft
4	250	30 [10]	500	-	Medium	Large	Hard
5	250	30 [10]	500	40	Scattered	Large	Soft+
6	500	30 [5]	500	100	Medium	Small	Hard+

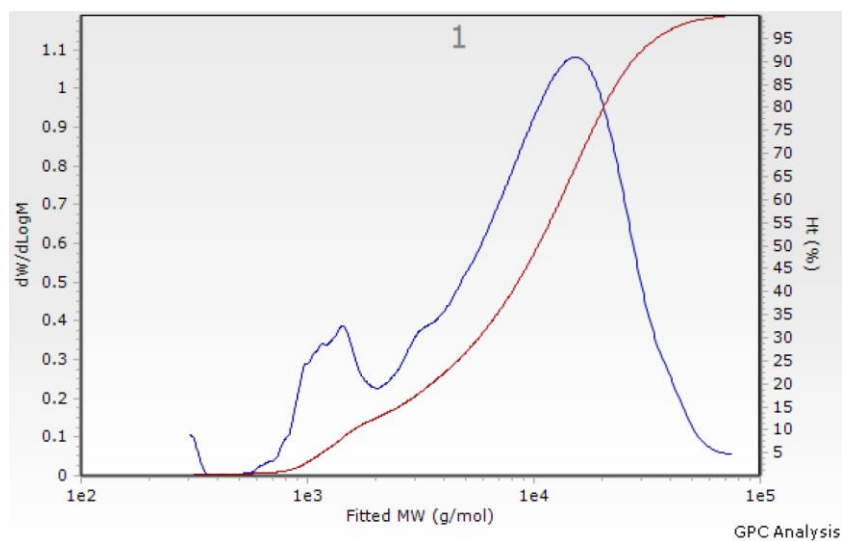
These experiments show that the poly(GBL-co-DVL) initiated with 1,4-benzenedimethanol may be used as polyol in the synthesis of polyurethane foams.

## 4 Analytical data

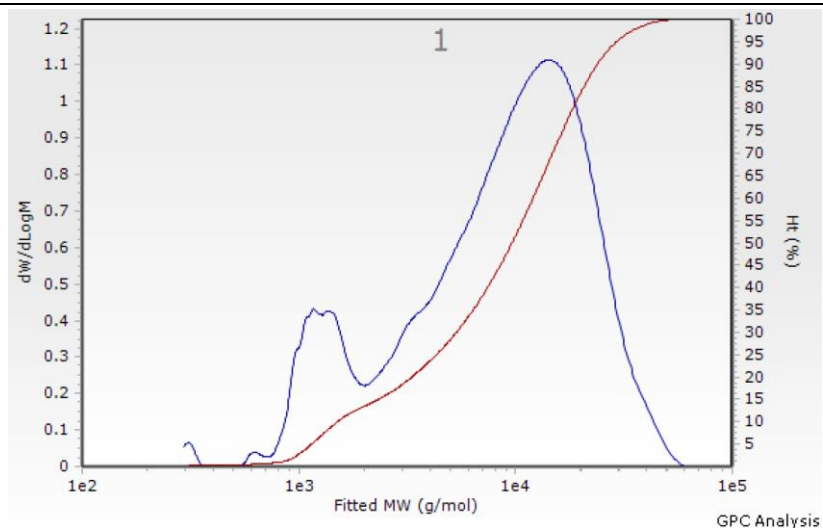
### 4.1 GPC measurement



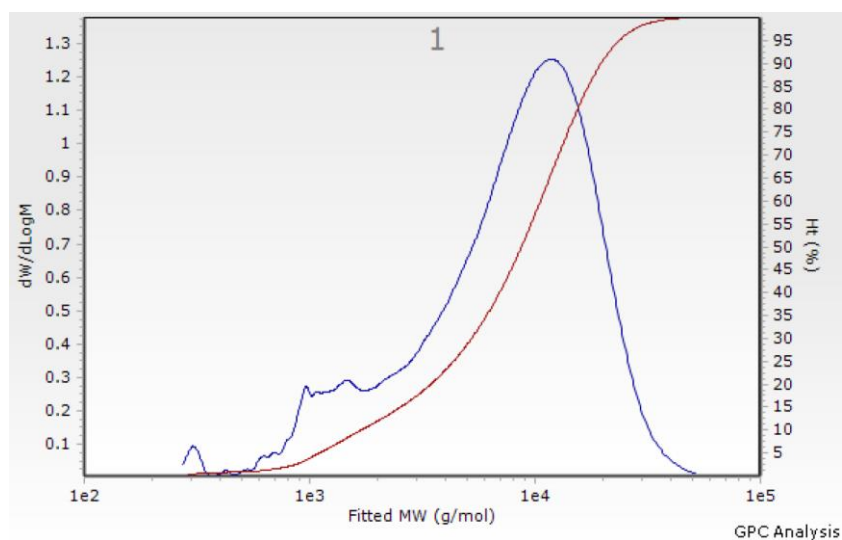
**Figure S5** GPC analysis of the polyGBL homopolymers (Table S1, entries 3, 5, 17 and 20)



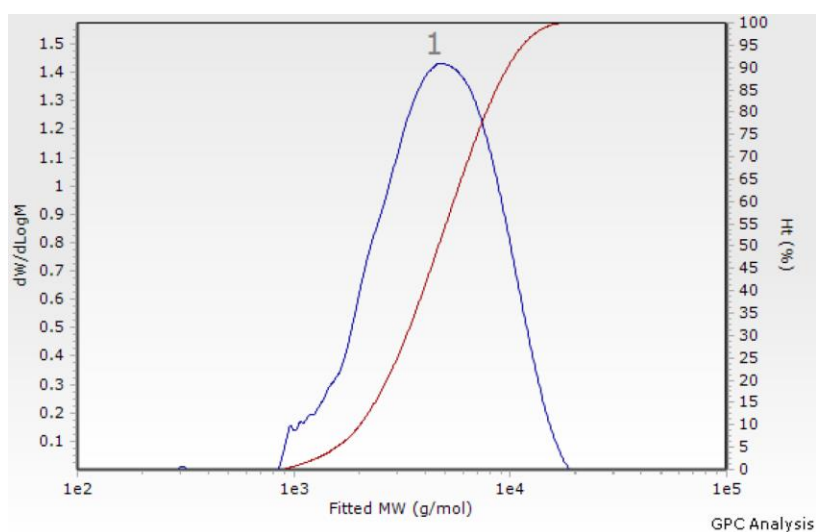
**Figure S6** GPC analysis of the polyGBL homopolymer (Table S1, entry 4)



**Figure S7** GPC analysis of the polyGBL homopolymer (Table S1, entry 12)

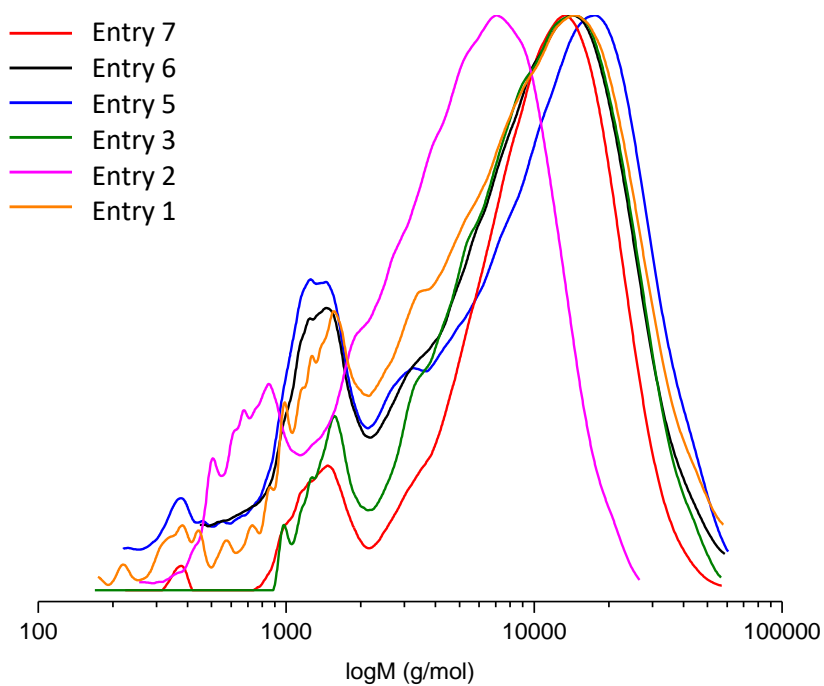


**Figure S8** GPC analysis of the polyGBL homopolymers (Table S1, entry 18)

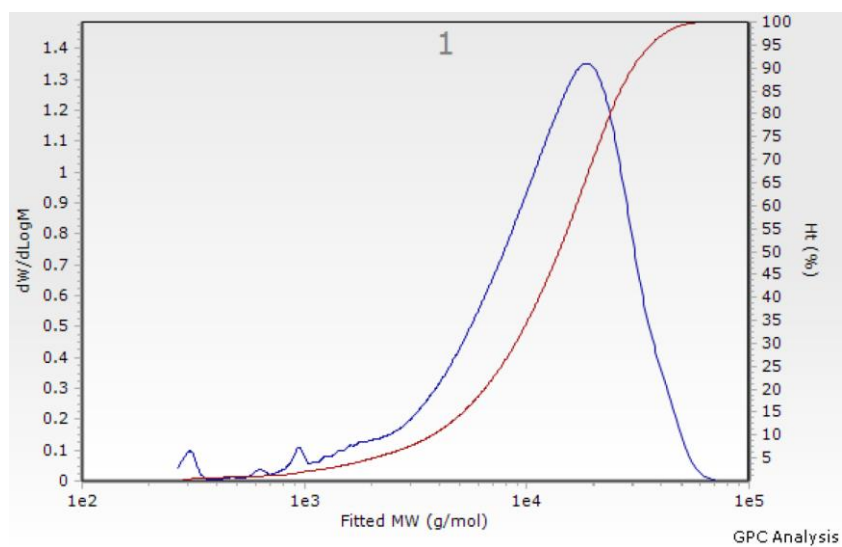


**Figure S9** GPC analysis of the polyGBL homopolymers (Table S1, entry 19)

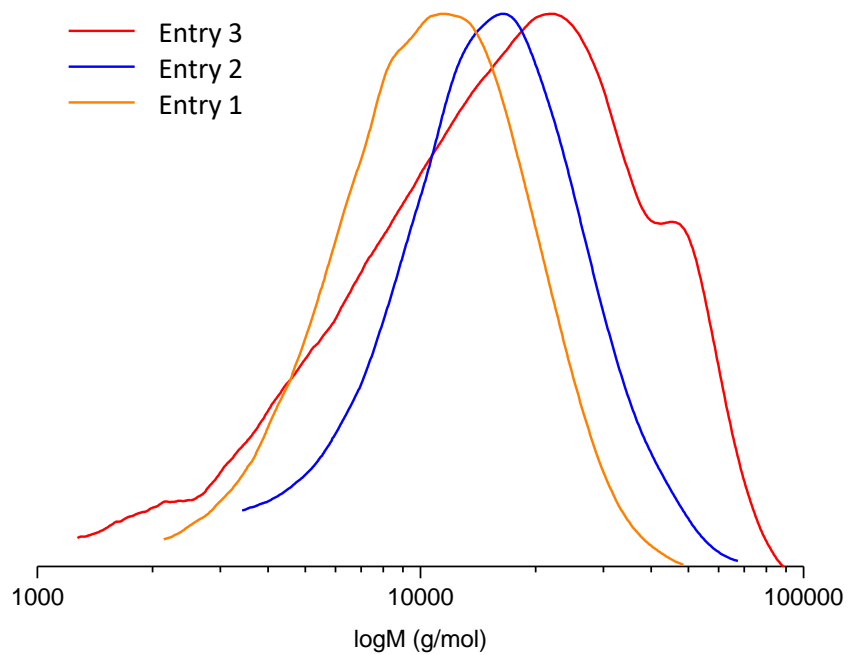




**Figure S10** GPC analysis of the polyGBL homopolymers (Table S5, entries 1 to 7)

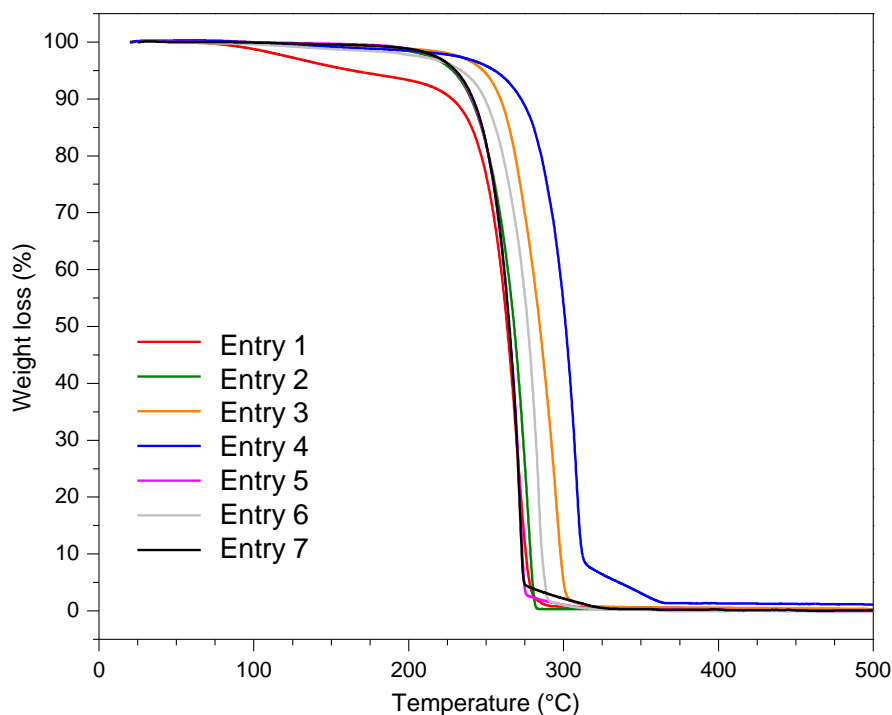


**Figure S11** GPC analysis of the large scale poly(GBL-co-EDL) copolymers (Table 3, entry 3)

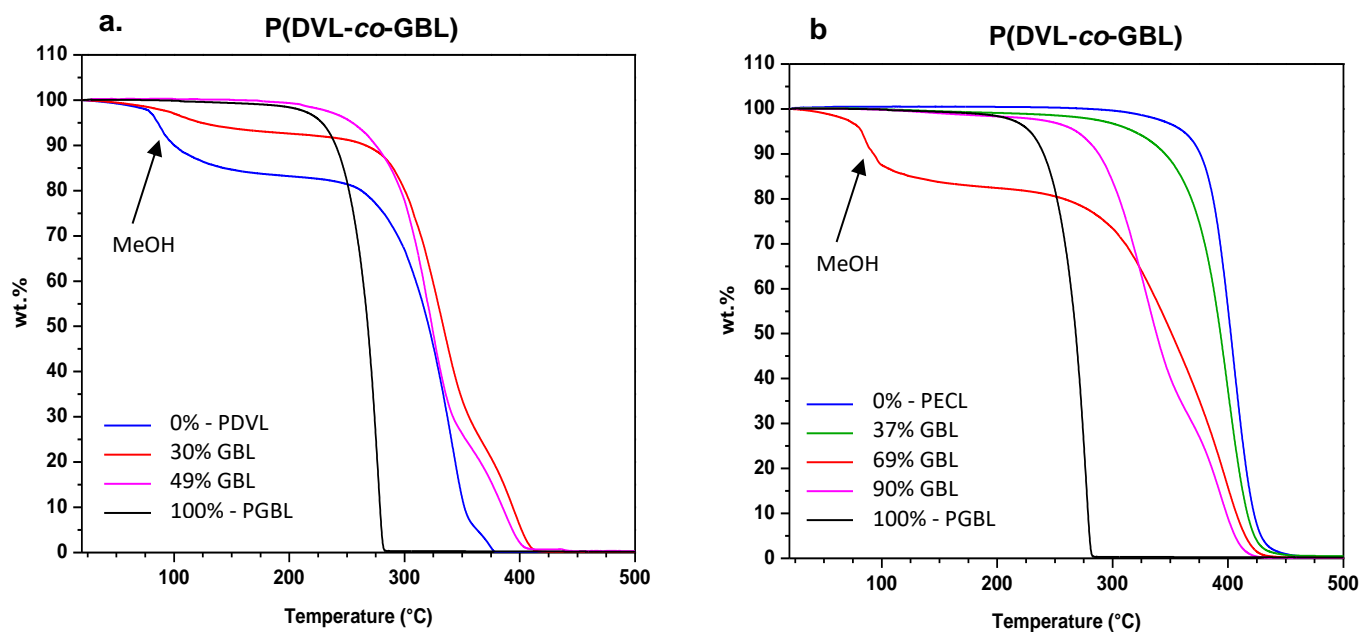


**Figure S12** GPC analysis of the large scale poly(GBL-co-ECL) copolymers (Table S8, entry 1 to 3)

## 4.2 TGA, DTG and DSC thermograms



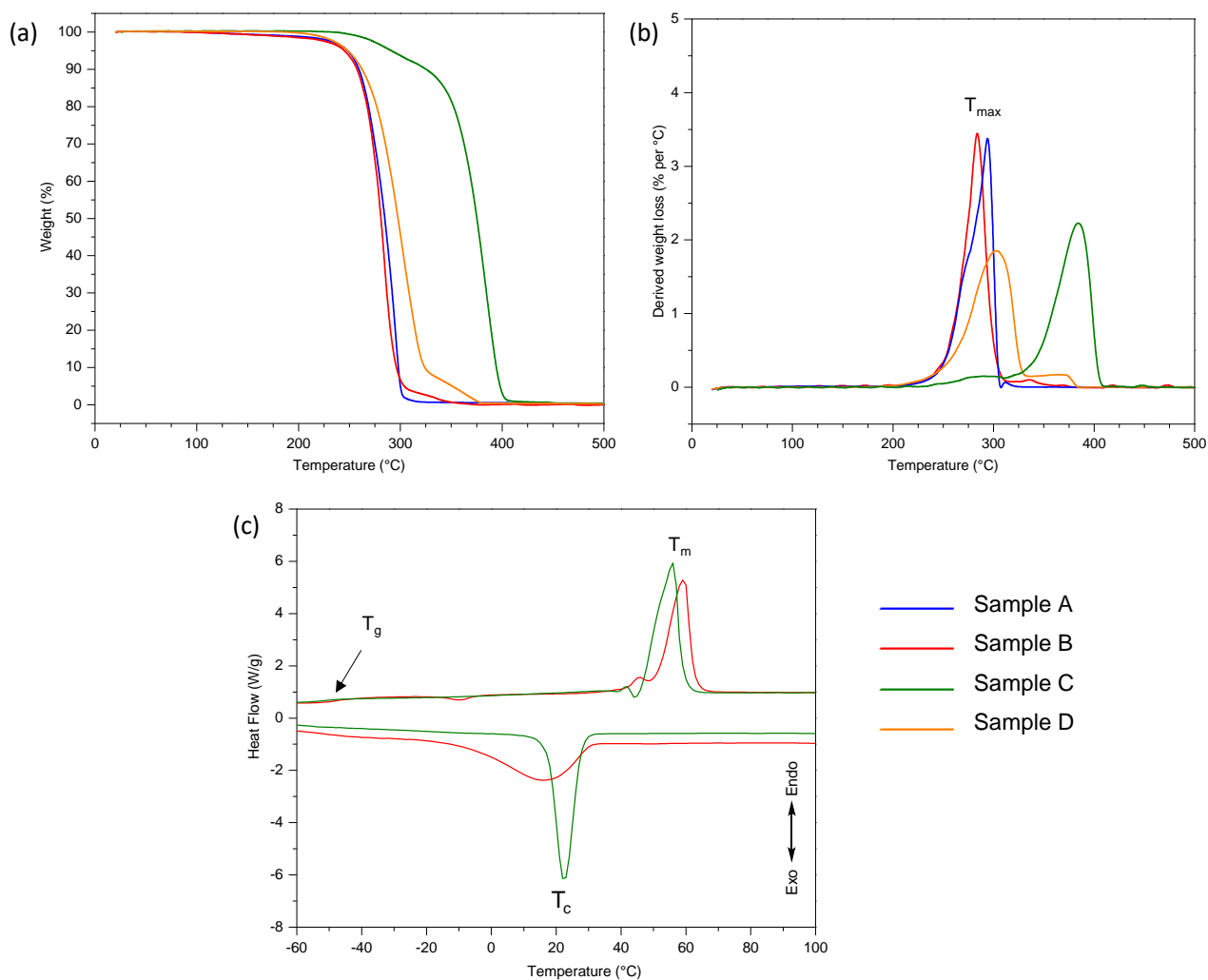
**Figure S13** TGA thermograms of the polyGBL homopolymers (Table S5, entries 1 to 7)



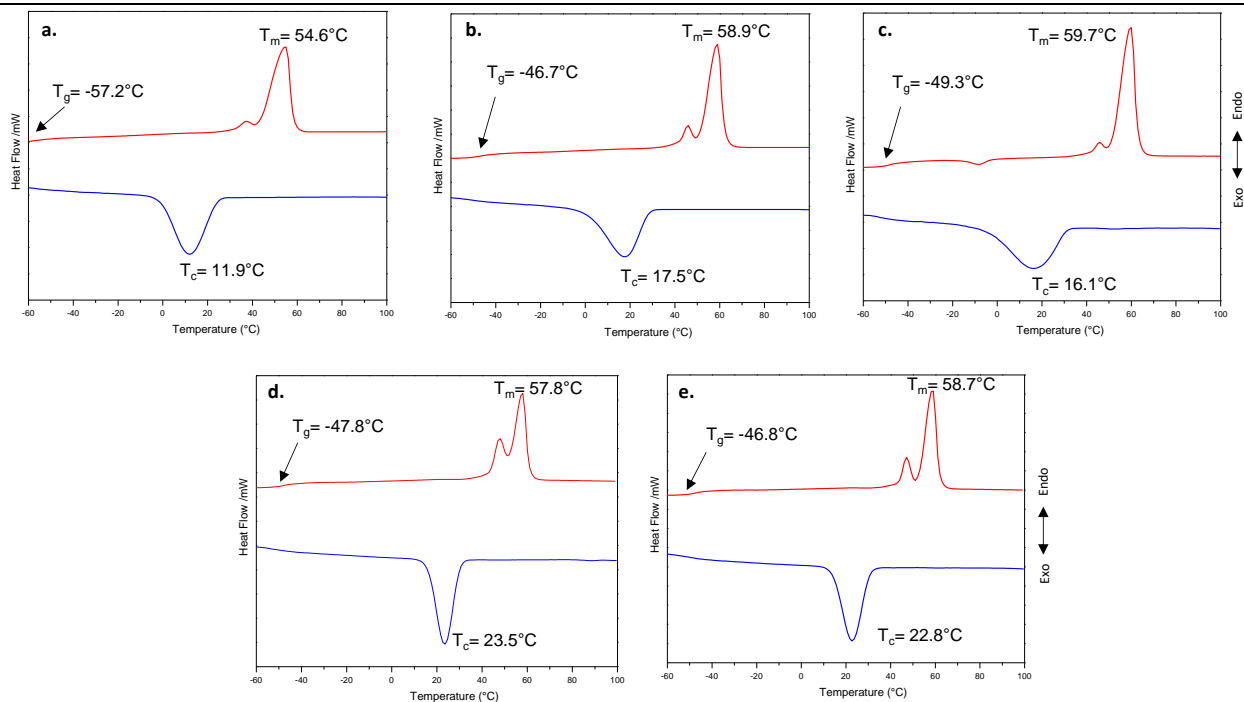
**Figure S14** TGA curves of [a] the P(GBL-co-DVL) and [b] the P(GBL-co-ECL) copolymer, both initiated with the BnOH/*t*-BuOK system. Some sample still contain some methanol, that could not be easily removed from the liquid polymers at reduced pressure (Table S9 and S10).

The TGA analysis curves in (Figure S14) show a decrease in the thermal stability of the copolymers with the incorporation of GBL in the polyester chain; with the latest thermal degradation being recorded for pDVL, followed by pECL and the earliest for pGBL homopolymers. The

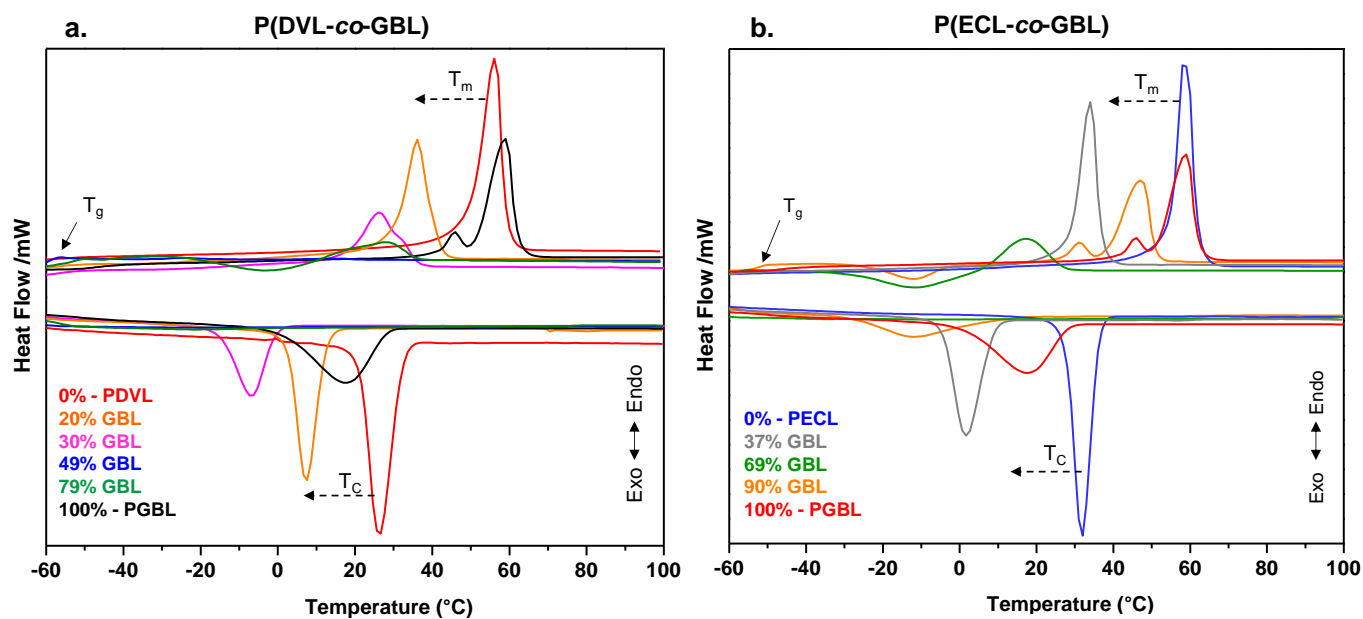
intermediate degradation curves were measured for the corresponding copolyesters, indicating the evolution of the thermal properties of the materials along with the evolution of the GBL content.



**Figure S15** Overlay of TGA (a), DTG (b) and DSC (c) thermograms of predominantly linear and cyclic pGBL homopolymers synthesized with a BnOH/*t*-BuOK initiator/base system (Table 2).



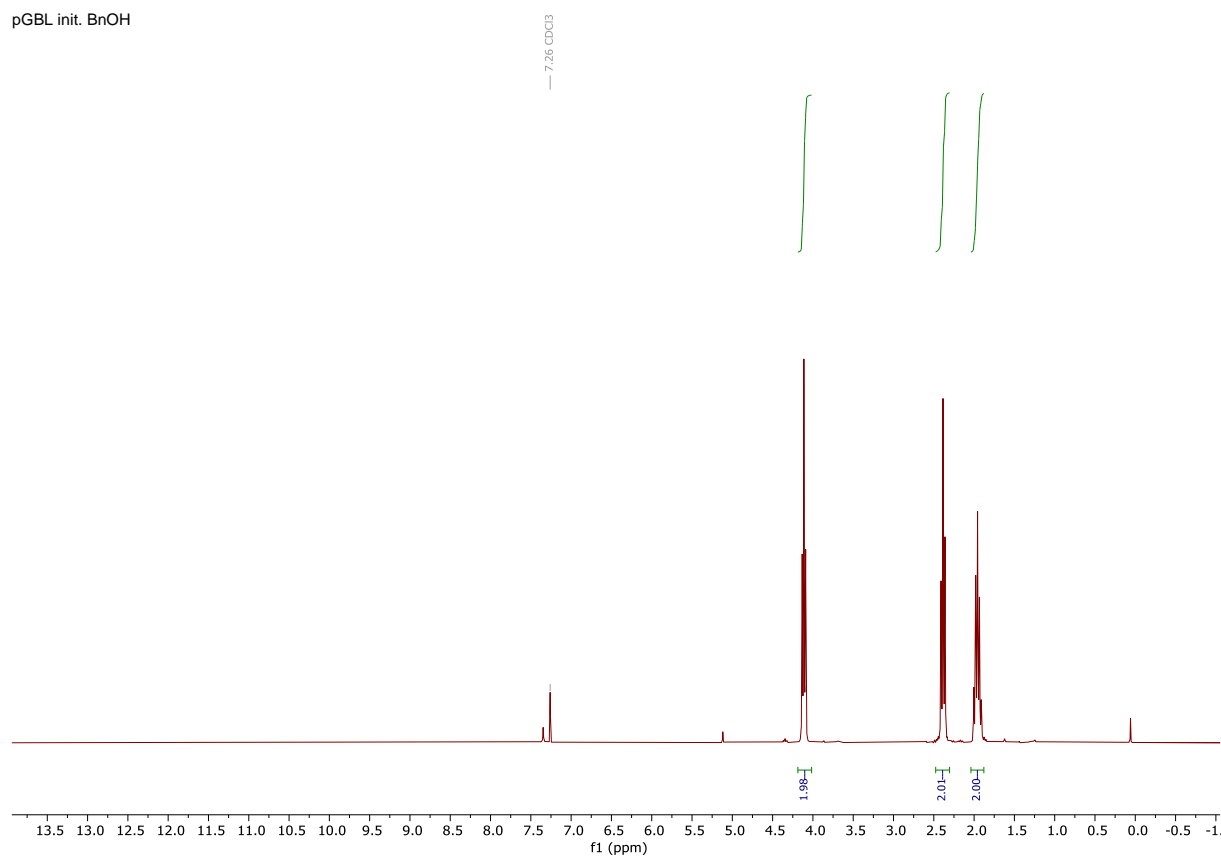
**Figure S16** DSC thermograms of the pGBL homopolymers (Table S5, a. entry 1; b. entry 2; c. entry 3; d. entry 5; e. entry 7)



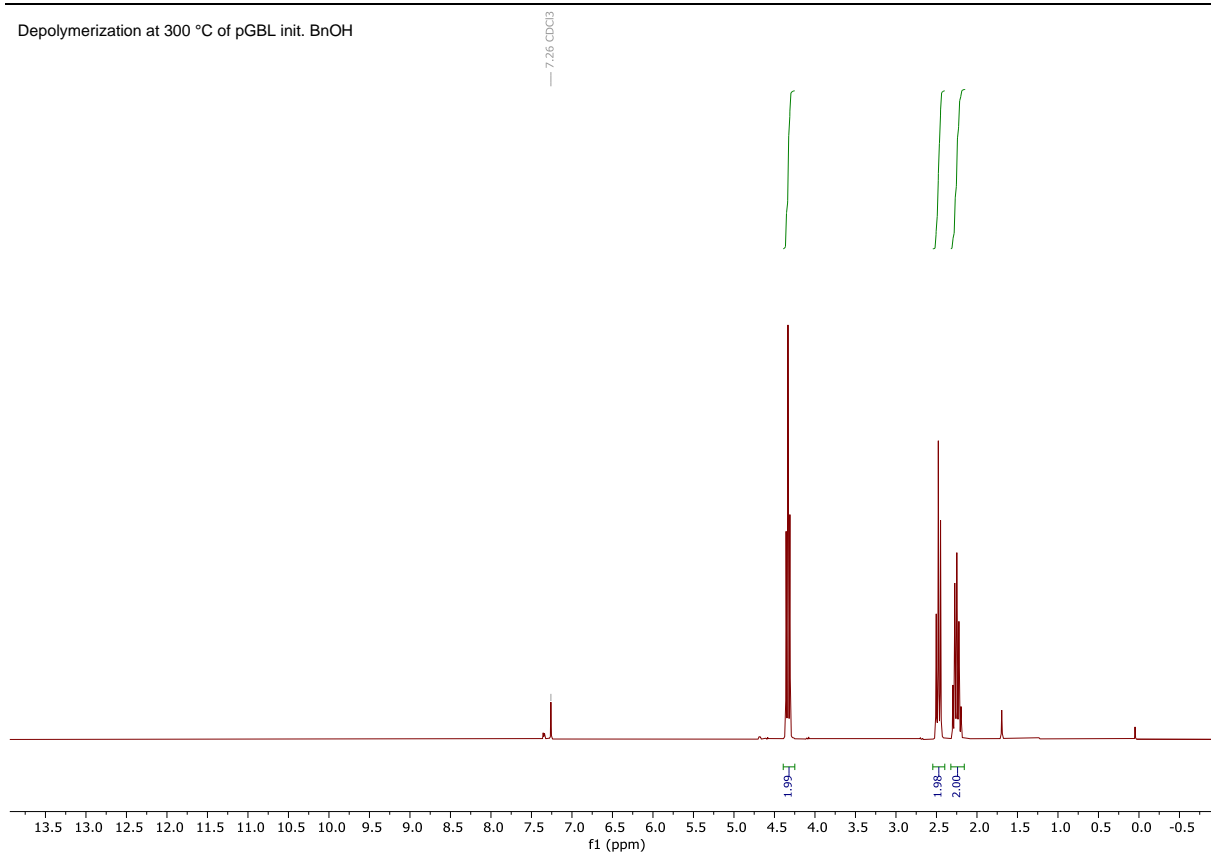
**Figure S17** DSC thermograms of the p(GBL-co-DVL) (a) and the p(GBL-co-ECL) (b) copolymer, both initiated with the BnOH/*t*-BuOK system; with the copolymer compositions in % of GBL

### 4.3 Recycling of GBL from homopolymer and copolymer

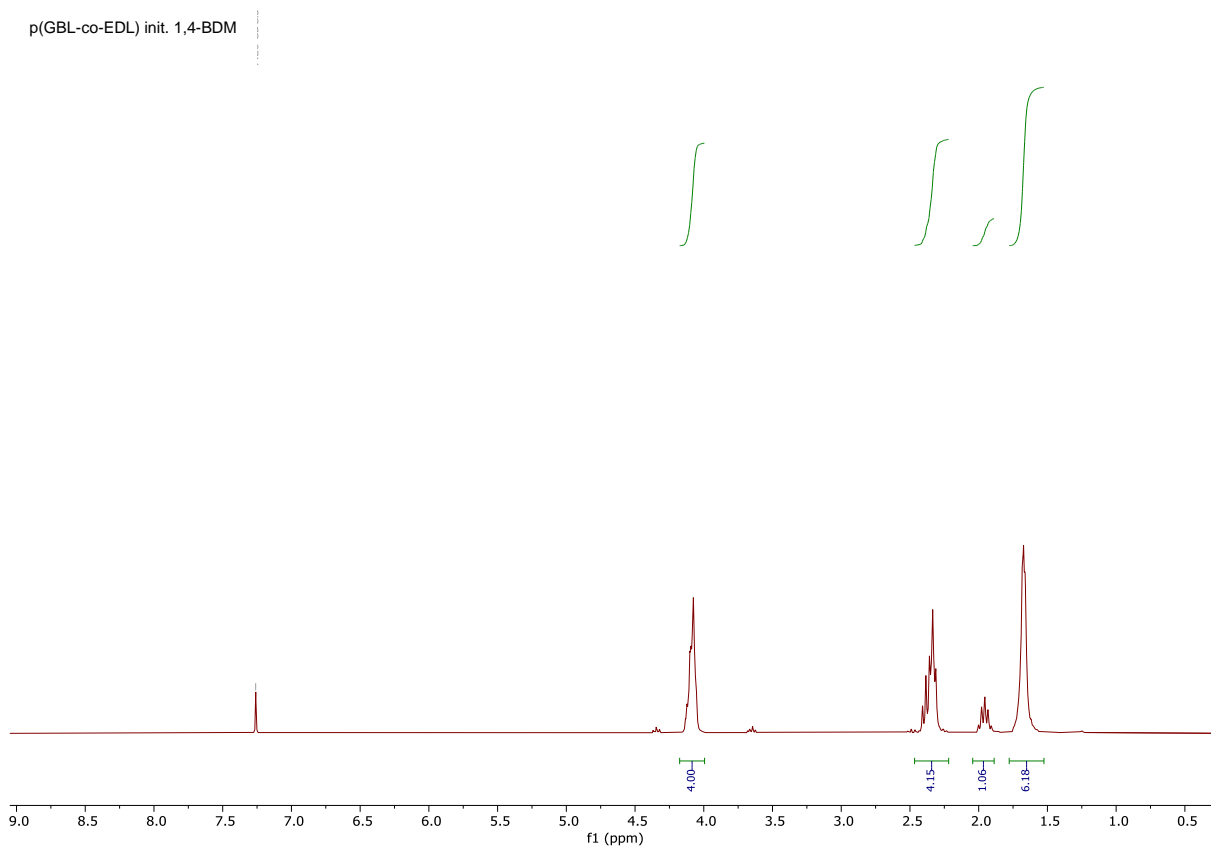
The recycling of  $\gamma$ -butyrolactone (GBL) was performed in a sealed 38 mL ACE-Tube. The tube was charged with pGBL initiated with BnOH (300 mg) or p(GBL-co-DVL) initiated with 1,4-BDM (300 mg) and sealed. The reactor was heated without further additive at 300 °C for 3 hours. After cooling down to +22 °C, the resulting solution was diluted in dichloromethane (4 mL) and the volatile evaporated. 97% of GBL was recovered from pGBL and 95% was recovered from p(GBL-co-EDL).



**Figure S18** Pure pGBL initiated with BnOH before heating at 300 °C

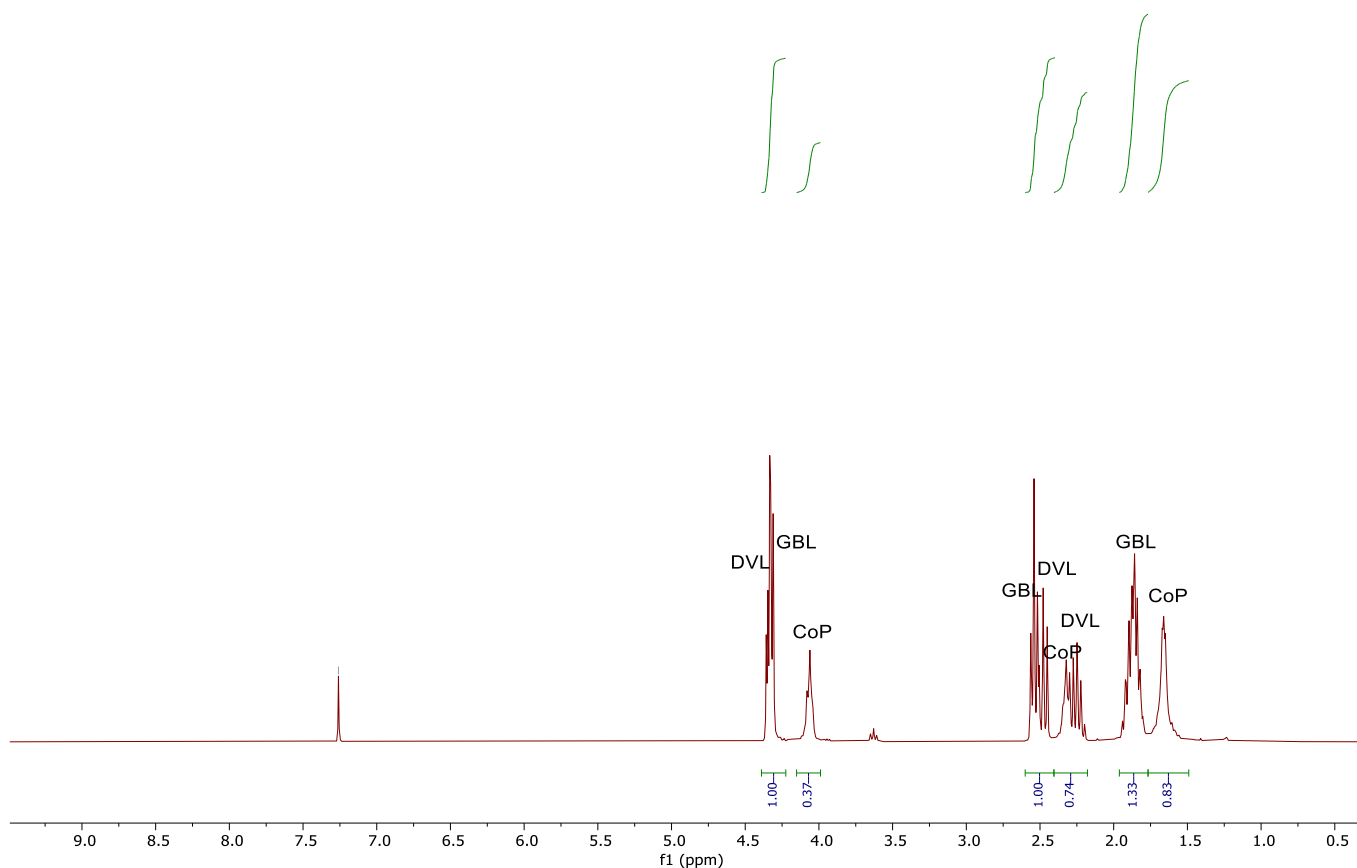


**Figure S19** Pure pGBL initiated with BnOH after heating at 300 °C



**Figure S20** Pure p(GBL-co-DVL) initiated with 1,4-BDM before heating at 300 °C

Depolymerization at 300 °C of p(GBL-co-EDL) init. 1,4-BDM



**Figure S21** Pure p(GBL-co-DVL) initiated with 1,4-BDM after heating at 300 °C

Besides the thermal depolymerisation, two other systems were tried, but no depolymerization was observed under these conditions.

Conditions A: 400 mg of pGBL (made according to entry 2 in table 1) was stirred together with BnOH and *t*-BuOK (ratio pGBL:BnOH:*t*-BuOK = 400:4:1) in 1 mL 2-MeTHF in a closed ACE-tube at 120°C for 15 h. No depolymerization could be observed by NMR analysis of the mixture.

Conditions B: 100 mg of pGBL (made according to entry 2 in table 1) was stirred with 2 mol% ZnCl<sub>2</sub> in 1 mL toluene in a closed ACE tube at 120°C for 6 h. No depolymerization could be observed by NMR analysis of the mixture.



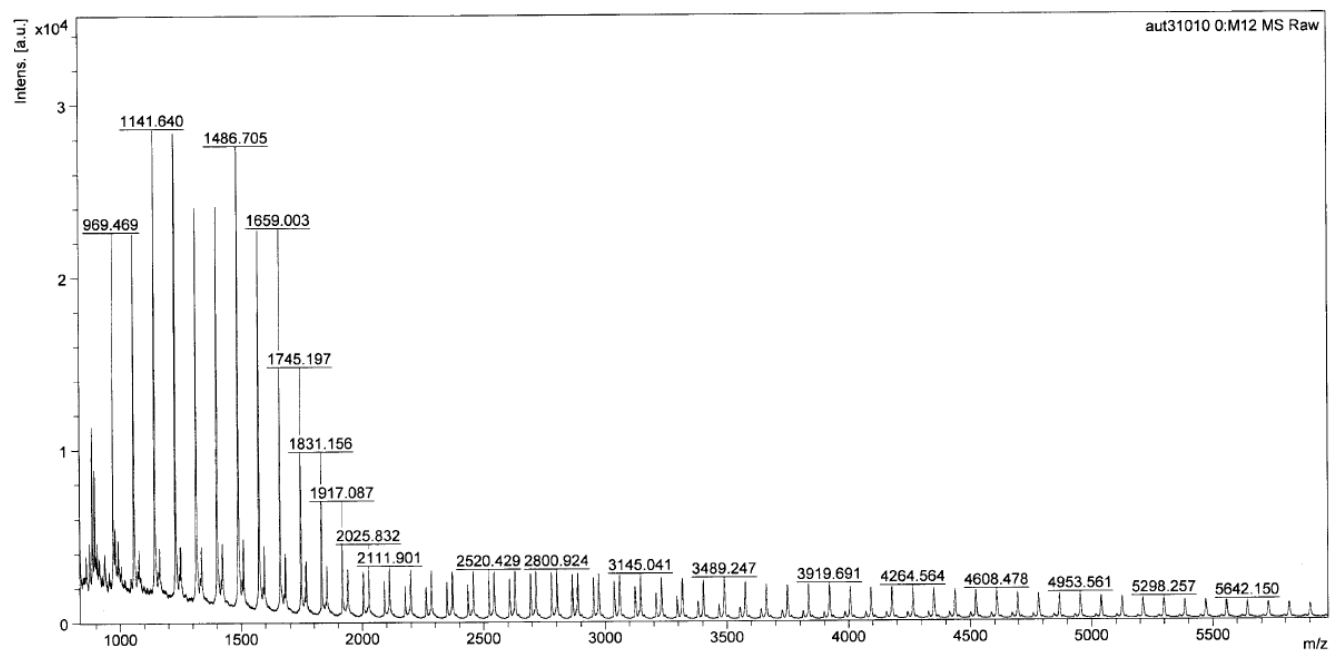
## 4.4 MALDI-TOF-MS Spectra

### 4.4.1 BnOH initiated polyGBL (entry 3 of Table 1 and entry 4 of Table S1)

The  $m/z$  of the cyclic signals C are corresponding to  $[\text{GBL}]_n + \text{Na}^+$  and the linear signals L to  $\text{BnO}-[\text{GBL}]_n + \text{Na}^+$ . The distance between the corresponding peaks linear as well as cyclic is 86, the mass of the repeating unit GBL. At lower molecular weights the signals for the cyclic polymers are dominant but then at higher molecular weights, the linear peaks are dominant (see also the GPC measurements). One must keep in mind, that the MALDI is not quantitative and in the GPC as major fraction are the higher molecular linear polymers are detected. For the linear polymer, incorporation of the initiator BnOH is detected, therefore one end group of the linear polymer chain is considered to be OH.

D:\Data\CaRLa\aut31010\0\_M12\1\1SLin

Comment 1	Vollgraff, CaRLa	Method	D:\Methods\flexControl\Methods\L_P_600-6000_Da_PVP.par				
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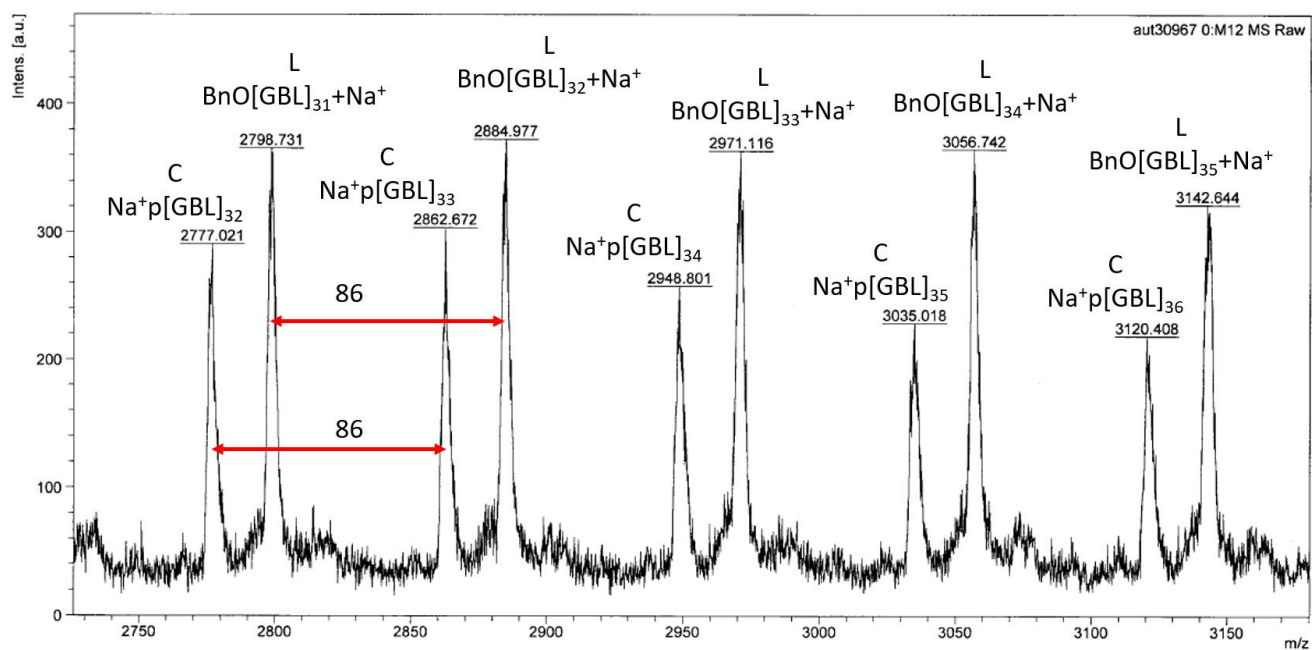
Bruker FlexAnalysis V. 3.4.79.0

MALDI Mass Spectrum

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D:\Data\CaRLa\aut30967\0\_M12\1\1SLin

Comment 1	Vollgraff, CaRLa	Method	D:\Methods\flexControl\Methods\LP_500-5000_Da_PVP.par				
Comment 2	AF02-203 in DCTB	Laser: Power	57	No. Shots	2500	Focus	37



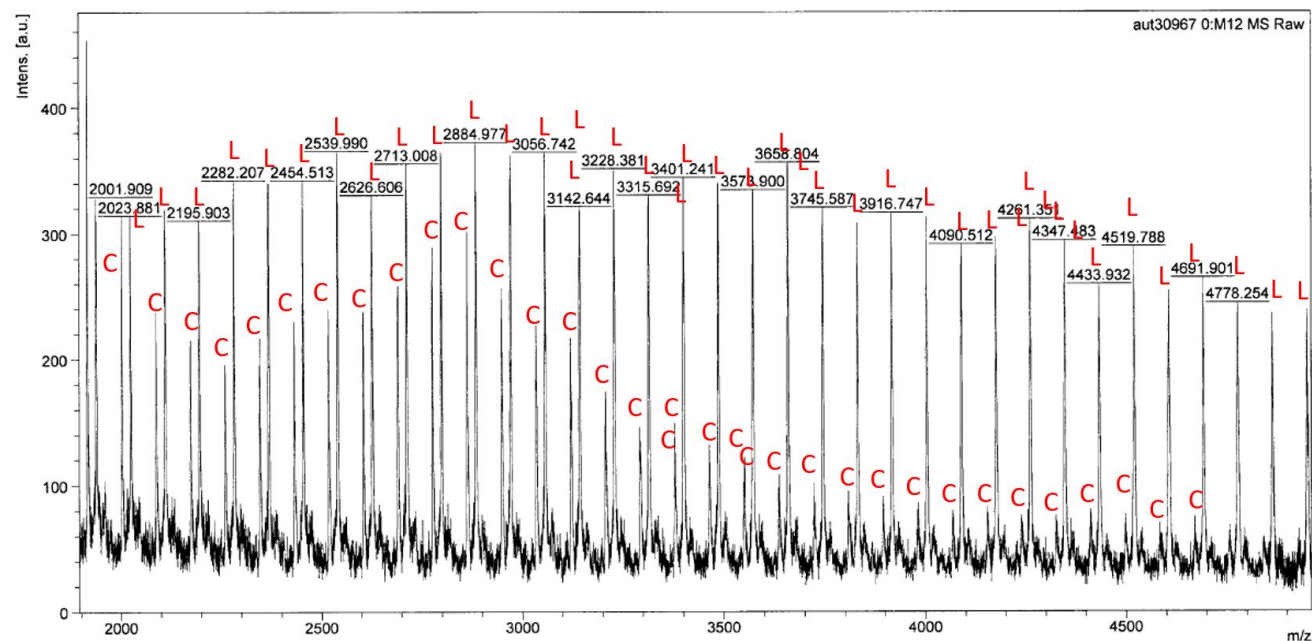
Bruker FlexAnalysis V. 3.4.79.0

MALDI Mass Spectrum

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D:\Data\CaRLa\aut30967\0\_M12\1\1SLin

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Comment 2	AF02-203 in DCTB	Laser: Power	57	No. Shots	2500	Focus	37



Bruker FlexAnalysis V. 3.4.79.0

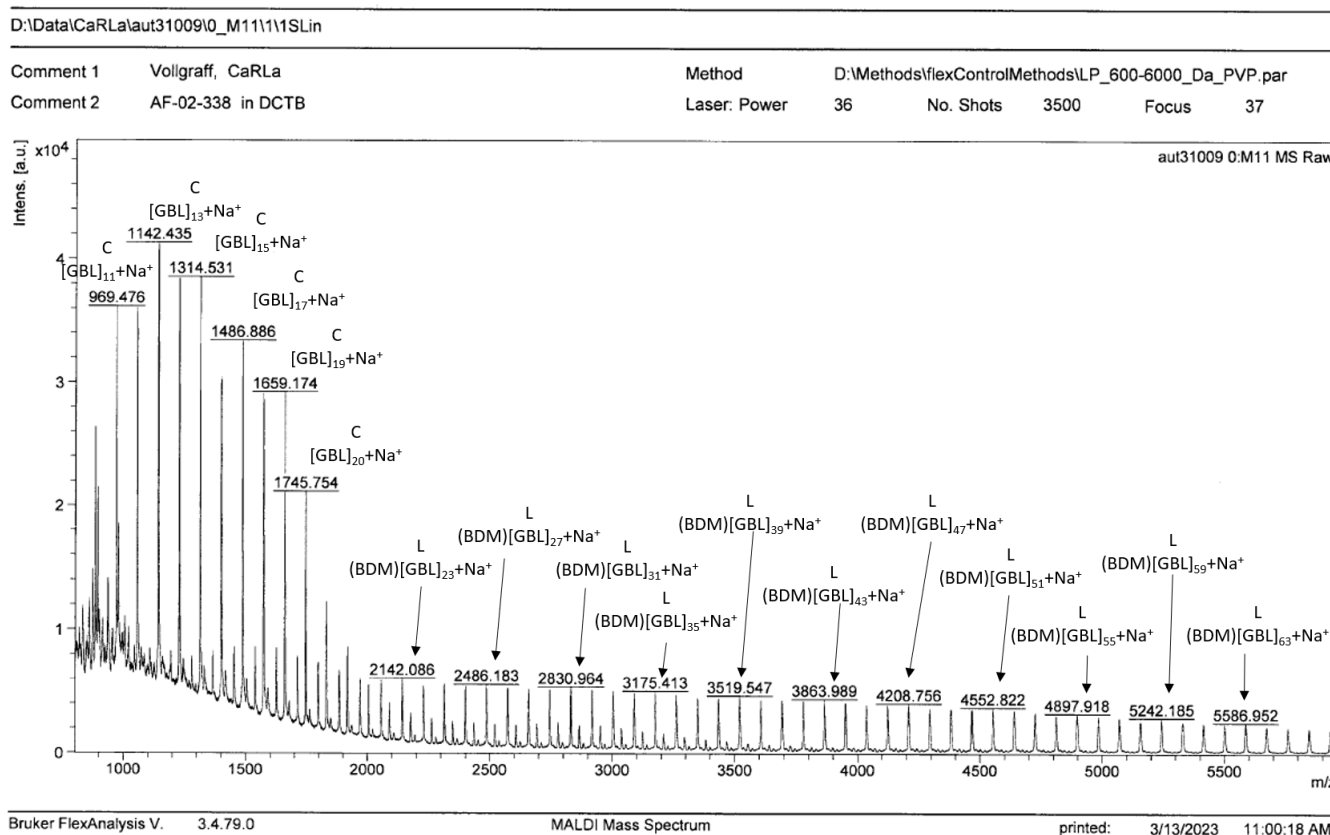
MALDI Mass Spectrum

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**Figure S22** MALDI-TOF mass spectra of the pure pGBL produced with BnOH/*t*-BuOK (4:1) (entry 3 of Table 1 and entry 4 of Table S1) and *m/z* values. C = cyclic polymer, L = linear polymer. Note: The first of the three shown spectra is measured at a lower laser power.

#### 4.4.2 1,4-BDM initiated polyGBL (entry 11 of Table 1 and entry 17 of Table S1)

The  $m/z$  of the cyclic signals C are corresponding to  $[\text{GBL}]_n+\text{Na}^+$  and the linear signals L to  $(\text{BDM})\text{-}[\text{GBL}]_n+\text{Na}^+$ . The distance between the corresponding peaks linear as well as cyclic is 86, the mass of the repeating unit GBL. At lower molecular weights the signals for the cyclic polymers are dominant but then at higher molecular weights, the linear peaks are dominant (see also the GPC measurements). One must keep in mind, that the MALDI is not quantitative and in the GPC as major fraction are the higher molecular linear polymers are detected. For the linear polymer, incorporation of the difunctional initiator 1,4-BDM is detected, therefore both end groups of the linear polymer chains are considered to be OH.

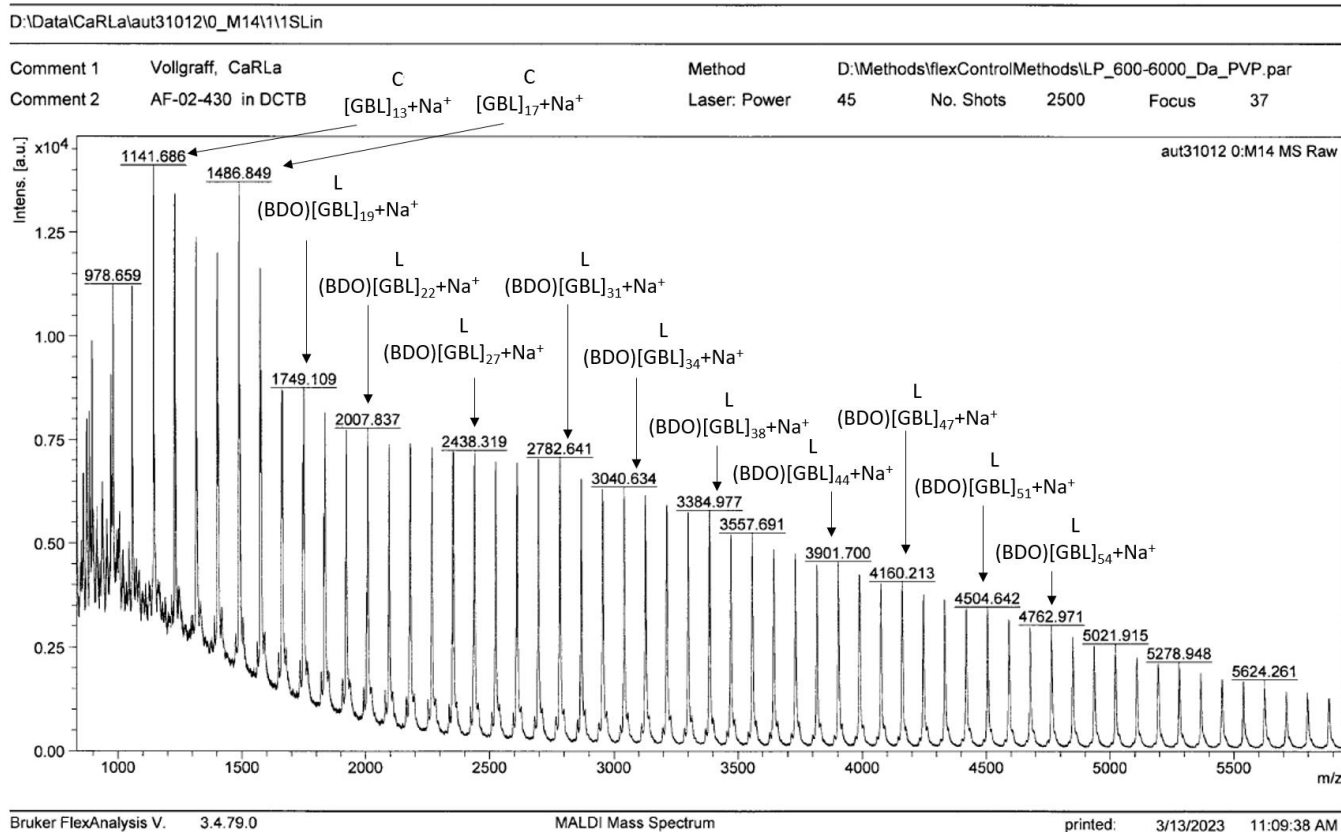


**Figure S23** MALDI-TOF mass spectra of the pure pGBL produced with 1,4-BDM/*t*-BuOK (4:1) (entry 11 of Table 1 and entry 17 of Table S1) and  $m/z$  values. C = cyclic polymer, L = linear polymer.

#### 4.4.3 1,4-BDO initiated polyGBL (entry 12 of Table 1 and entry 19 of Table S1)

The  $m/z$  of the cyclic signals C are corresponding to  $[\text{GBL}]_n+\text{Na}^+$  and the linear signals L to  $(\text{BDO})\text{-}[\text{GBL}]_n+\text{Na}^+$ . The distance between the corresponding peaks linear as well as cyclic is 86, the mass of the

repeating unit GBL. At lower molecular weights the signals for the cyclic polymers are dominant but then at higher molecular weights, the linear peaks are dominant (see also the GPC measurements) and hardly any signals for cyclic polymers can be detected at  $m/z$  above 1500. One must keep in mind, that the MALDI is not quantitative and in the GPC as major fraction are the higher molecular linear polymers are detected. For the linear polymer, incorporation of the difunctional initiator 1,4-BDO is detected, therefore both end groups of the linear polymer chains are considered to be OH.



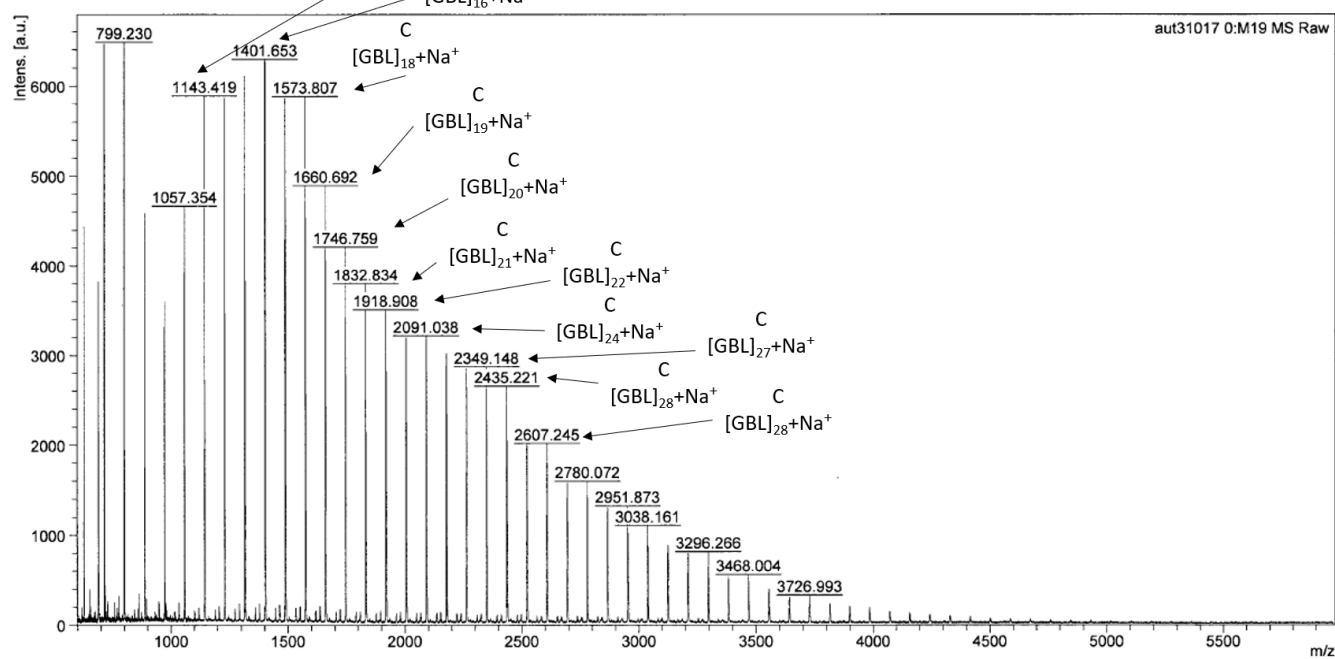
**Figure S24** MALDI-TOF mass spectra of the pure pGBL produced with 1,4-BDO/*t*-BuOK (4:1) (entry 12 of Table 1 and entry 17 of Table S1) and  $m/z$  values. C = cyclic polymer, L = linear polymer.

#### 4.4.4 BnO initiated polyGBL in EtOAc (entry C of Table 2 and entry 11 of Table S2)

The  $m/z$  of the cyclic signals C are corresponding to  $[\text{GBL}]_n+\text{Na}^+$ . Signals for linear polymers could not be detected in this case. According the MALDI, this sample consists only of cyclic poly-GBL. The distance between the corresponding peaks is 86, the mass of the repeating unit GBL.

D:\Data\CaRLa\aut31017\0\_M19\11\SLin

Comment 1	Vollgraff, CaRLa	Method	D:\Methods\flexControlMethods\LP_600-6000_Da_PVP.par				
Comment 2	Table2SC in DCTB	Laser: Power	86	No. Shots	2500	Focus	37



Bruker FlexAnalysis V. 3.4.79.0

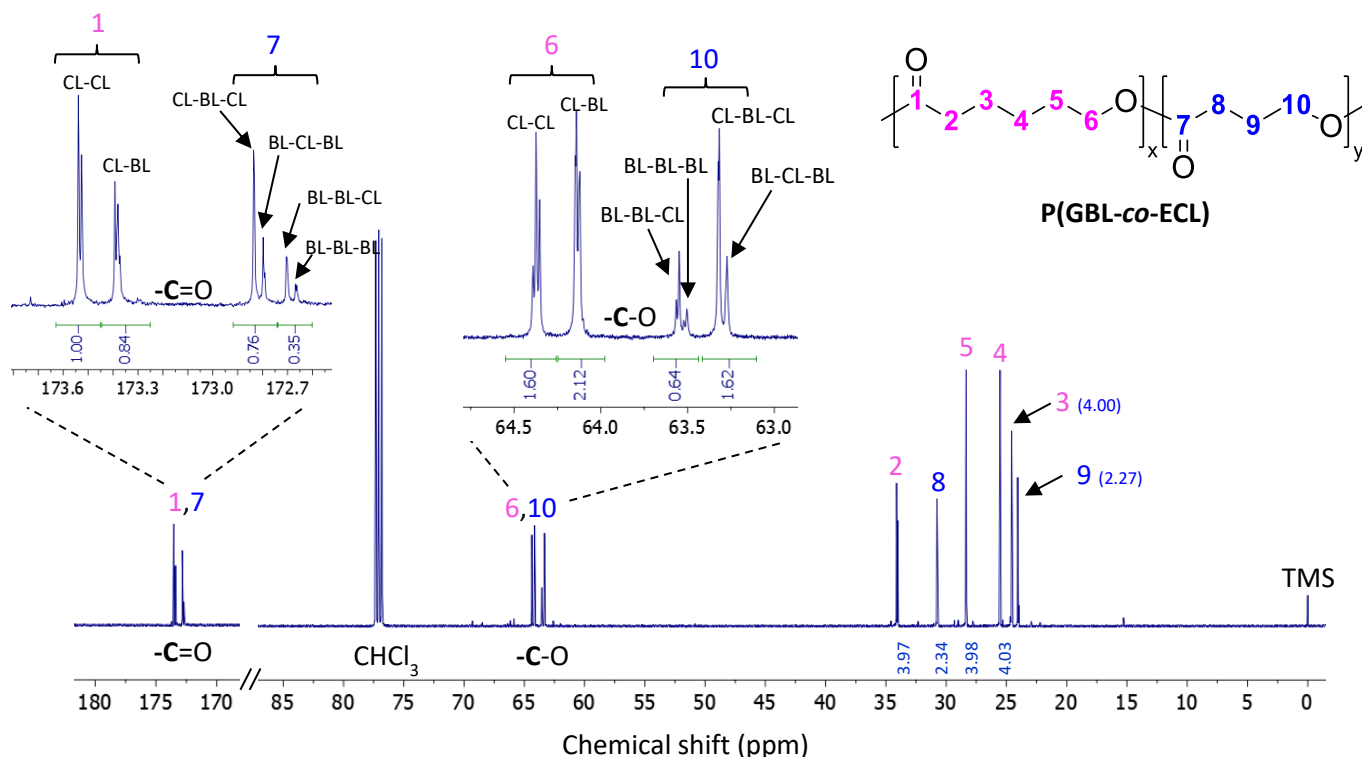
MALDI Mass Spectrum

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**Figure S25** MALDI-TOF mass spectra of the pure pGBL produced with BnOH/*t*-BuOK (4:1) in EtOAc (entry C of Table 2 and entry 11 of Table S2) and *m/z* values. C = cyclic polymer.

## 4.5 NMR Spectra

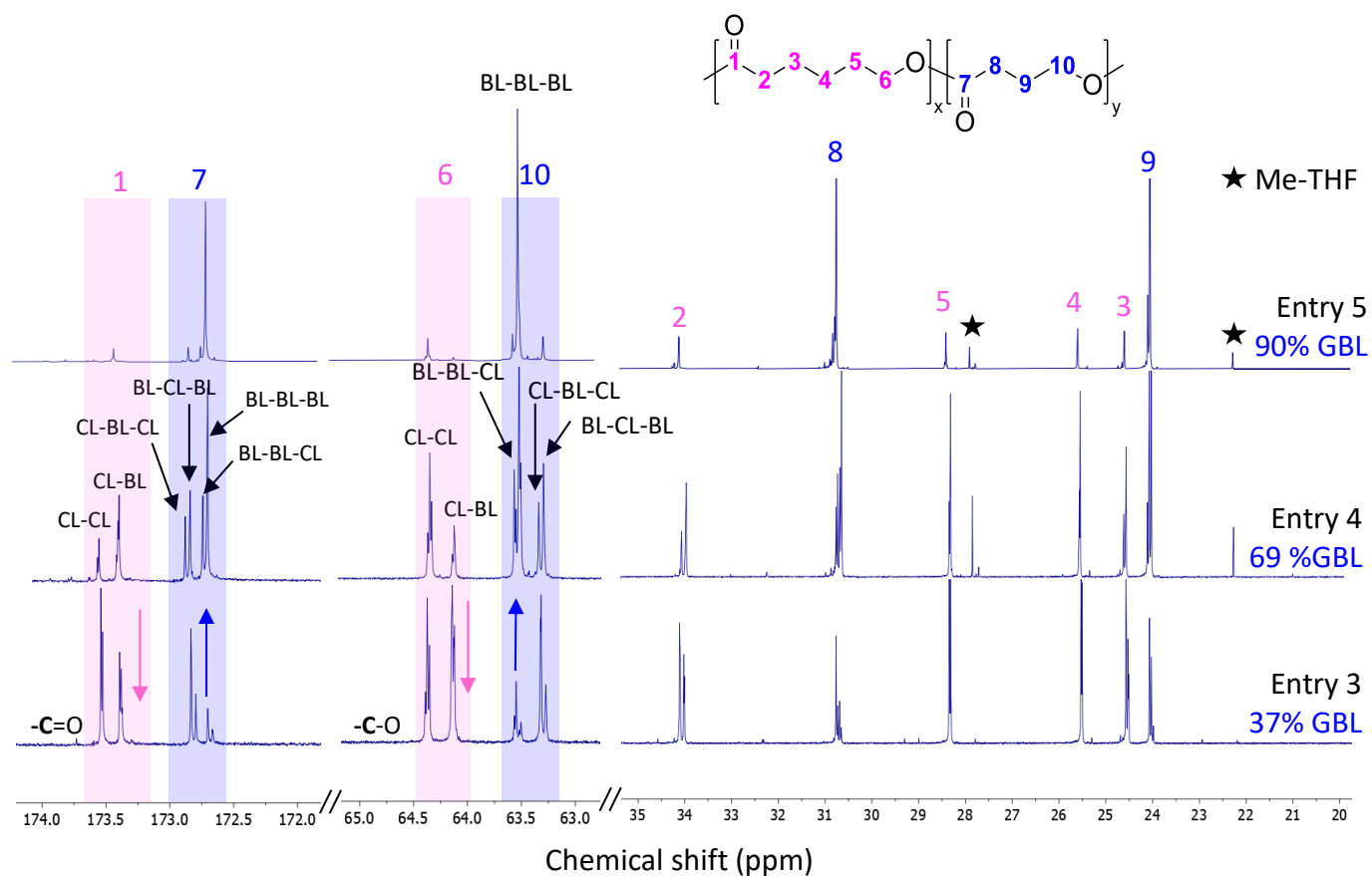
In the case of poly(GBL-co-ECL) copolymers, a study of the sequence was also performed by  $^{13}\text{C}$  NMR. The spectra presented in (figure S12) shows that the signals of the  $-\text{C}=\text{O}$  bond is split into two different groups, which are attributed to ECL (C1, 173.3 to 173.6 ppm) and GBL (C7, 172.0 to 173.0 ppm) units. Furthermore, each one also split into several signals, which are characteristic of a certain sequence. For instance, the  $-\text{C}=\text{O}$  peaks at 173.4 and 173.5 ppm (C1, ECL) can be attributed respectively to ECL-GBL alternating sequences and ECL-ECL continuous sequences (here simplified CL-BL and CL-CL). This observation can also be made with the GBL quartet (C7) with CL-BL-CL alternating sequences or BL-BL-BL continuous sequences. In addition, the same structures are detected for the adjacent  $-\text{C}-\text{O}$  signals (C6 and C10). The number of continuous sequences is lower than the alternated ones, thereby revealing the randomness of the copolymer microstructure.



**Figure S26**  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  of the p(GBL-co-ECL) copolymer reported in entry 3 of Table S9 and S10 (GBL : ECL = 37 : 63)

Figure S13 presents three compositions of p(GBL-co-ECL) copolymers with increasing GBL incorporation from bottom to top. First, we can clearly see the increase in the intensity of the aliphatic GBL peaks (C8 and C9) with the increase in GBL mol% in the copolymers. Additionally, this is also accompanied by an increase in the BL continued sequences such as BL-BL-BL at 63.5 ppm or at 172.7 ppm. This phenomenon was expected because, as the copolymer chains get richer in GBL, the number of GBL-to-GBL continuous sequences is increasing as well. In parallel, the decrease in the intensity of ECL peaks is clearly visible in the aliphatic region, as well as for

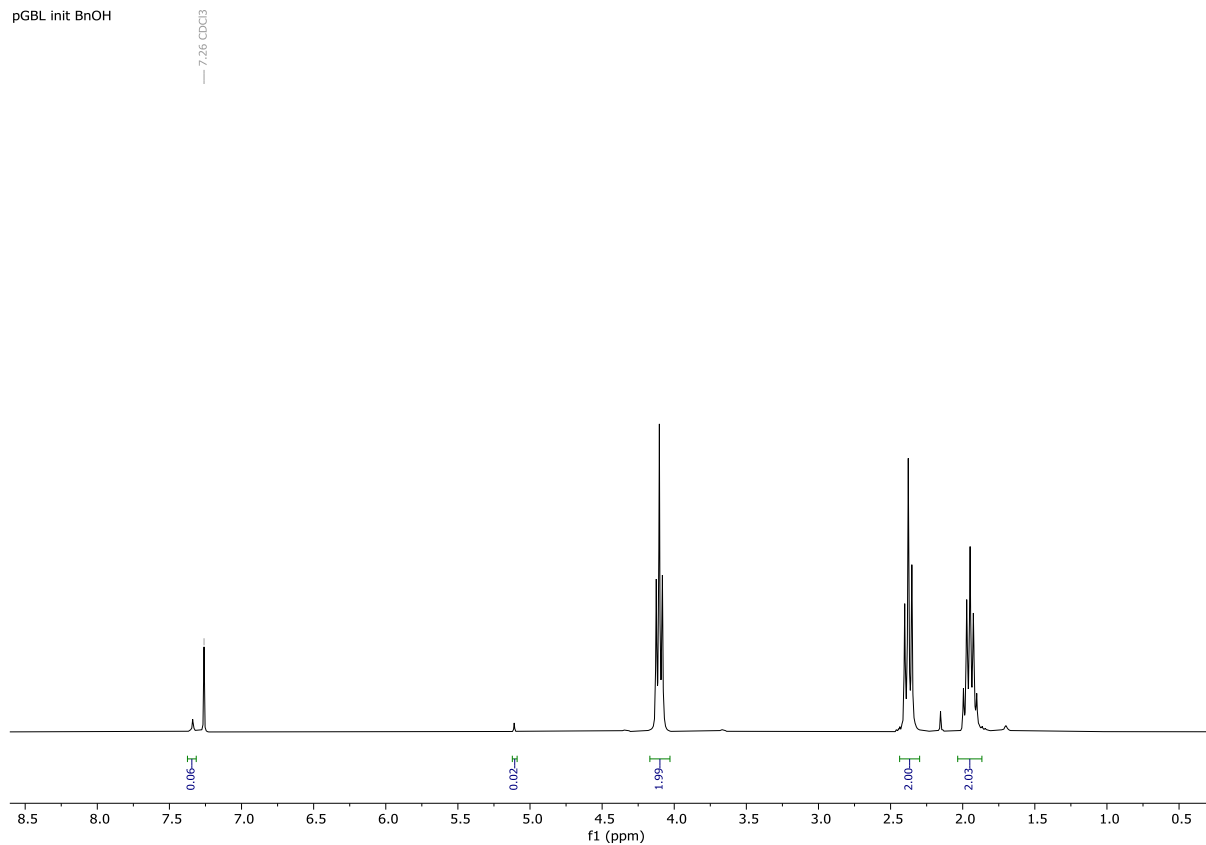
the peaks related to ECL-to-GBL alternative sequences such as CL-BL-CL at 172.8 ppm or BL-CL-BL at 63.3 ppm.



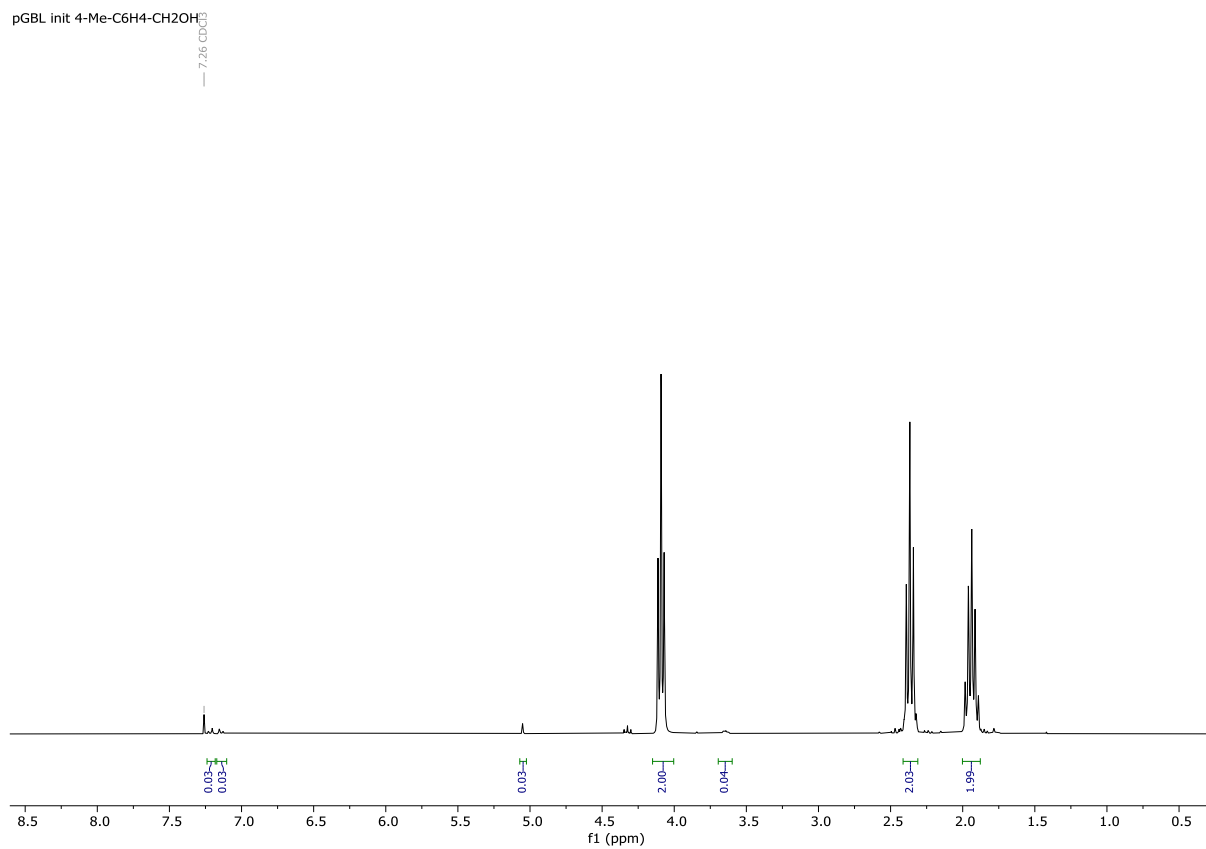
**Figure S27** <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> of the p(GBL-co-ECL) copolymer reported in Table S9 and S10 entries 3 – 5. Entry 3 (GBL : ECL = 37 : 63) ; entry 4 (GBL : ECL = 69 : 31) and entry 5 (GBL : ECL = 90 : 10)

**Poly- $\gamma$ -butyrolactone initiated with benzyl alcohol.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL init BnOH

**Poly- $\gamma$ -butyrolactone initiated with 4-Me- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ .  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

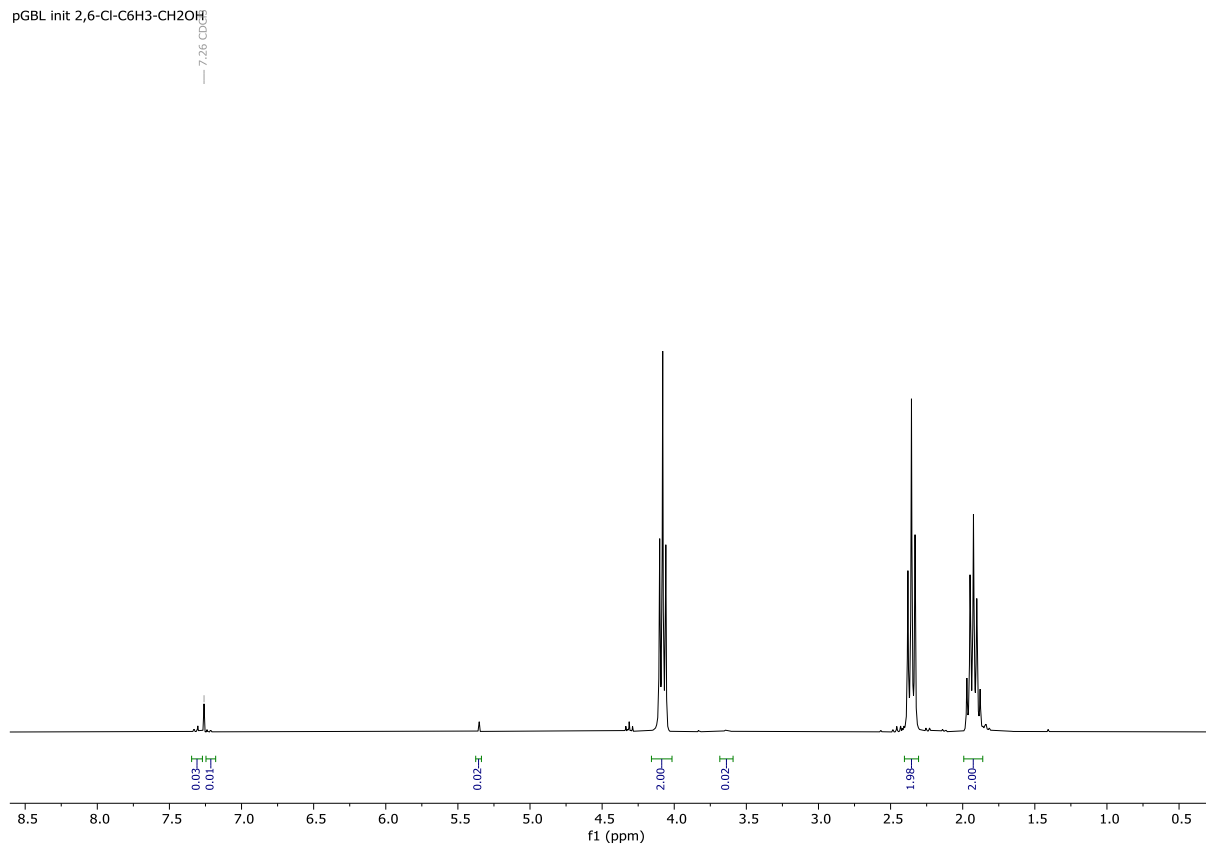
pGBL init 4-Me-C6H4-CH2OH



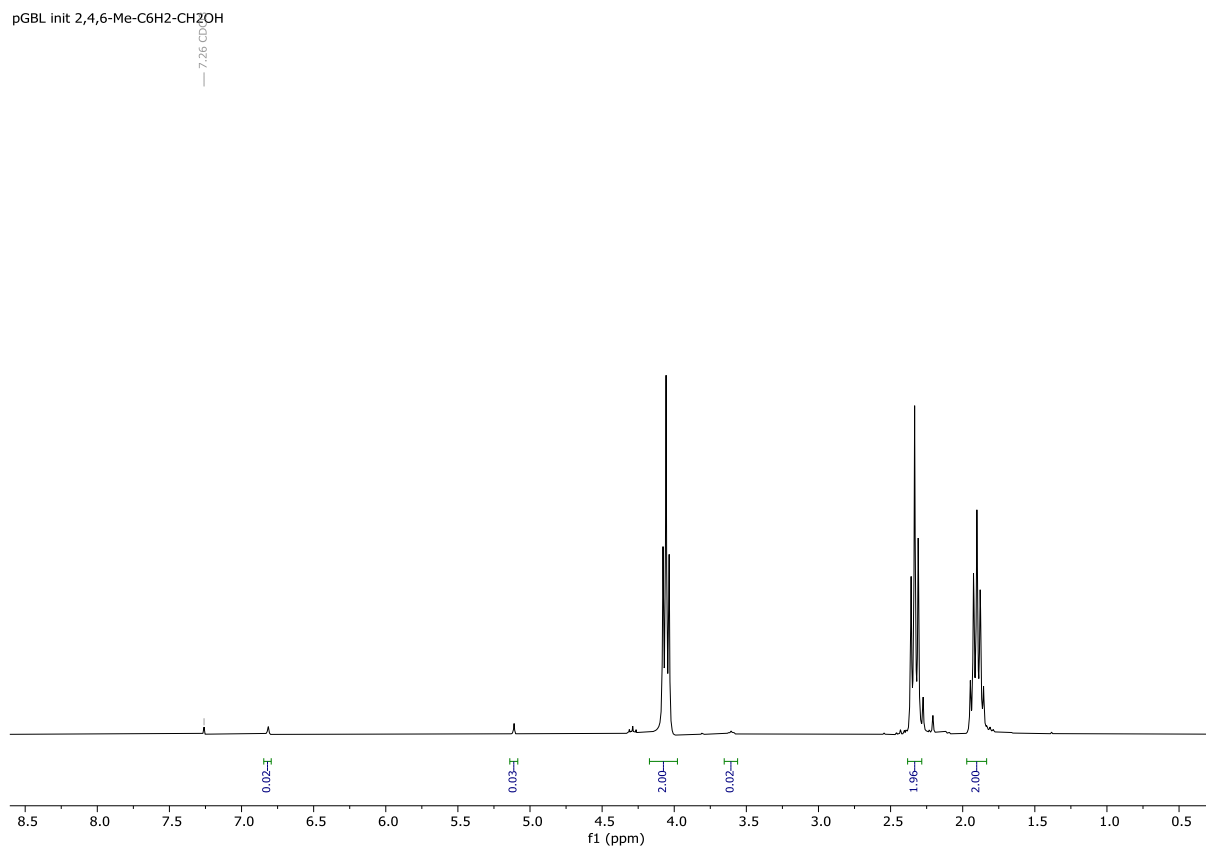


**Poly- $\gamma$ -butyrolactone initiated with 2,6-Cl-C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>OH. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K)**

pGBL init 2,6-Cl-C6H3-CH2OH

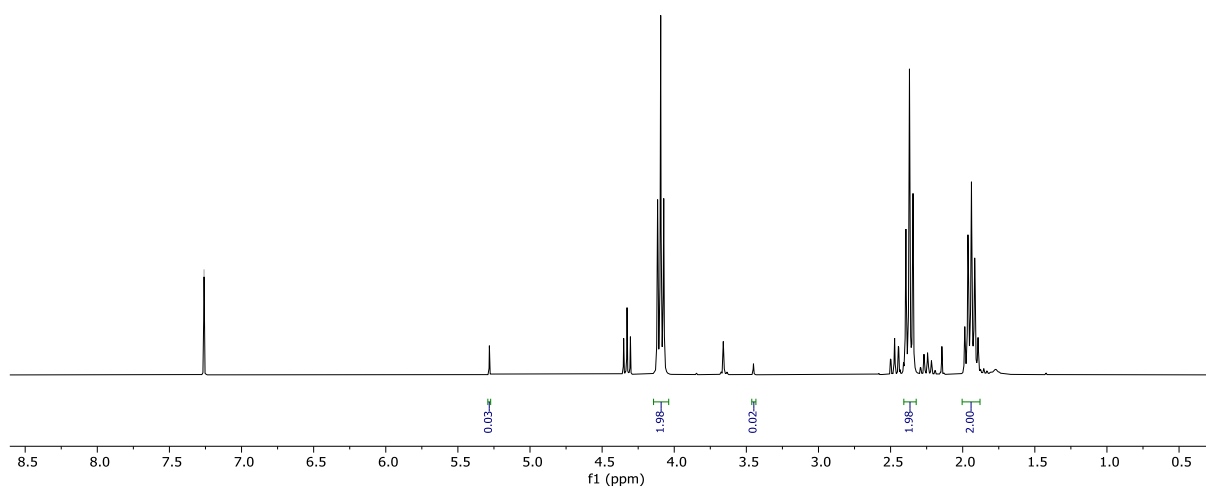
**Poly- $\gamma$ -butyrolactone initiated with 2,4,6-Me-C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>OH. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K)**

pGBL init 2,4,6-Me-C6H2-CH2OH

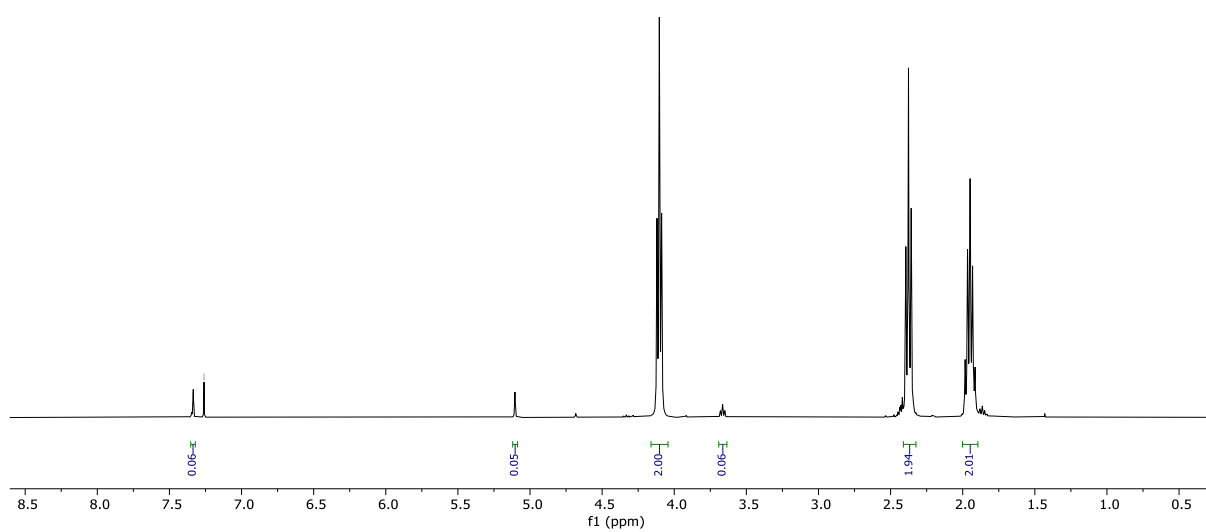


**Poly- $\gamma$ -butyrolactone initiated with MeOH.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL init MeOH

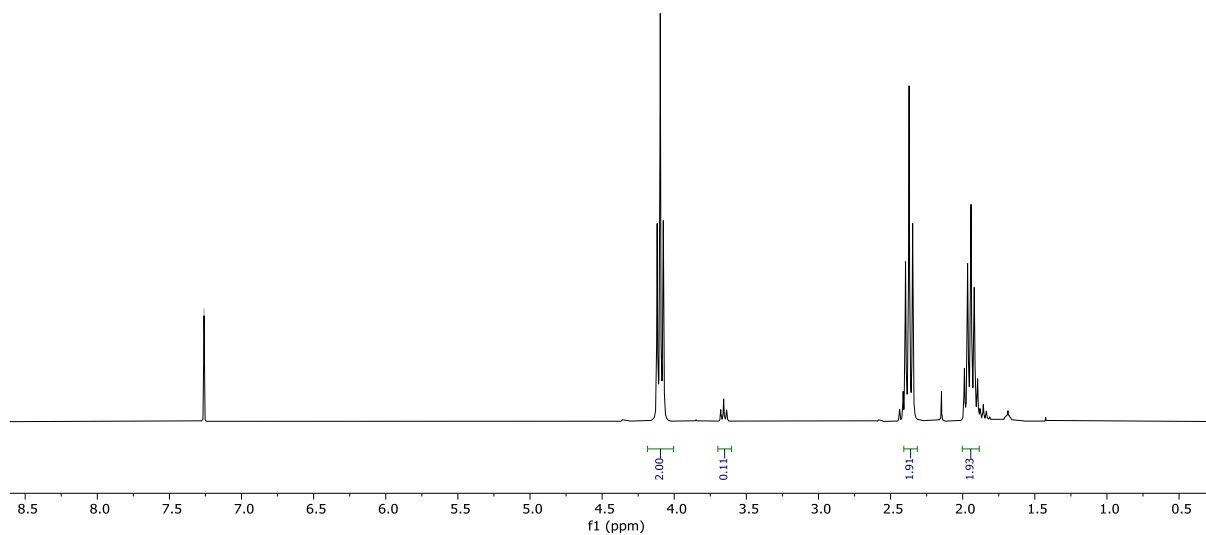
— 7.26  $\text{CDCl}_3$ **Poly- $\gamma$ -butyrolactone initiated with 1,4-BDM.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL init 1,4-BDM

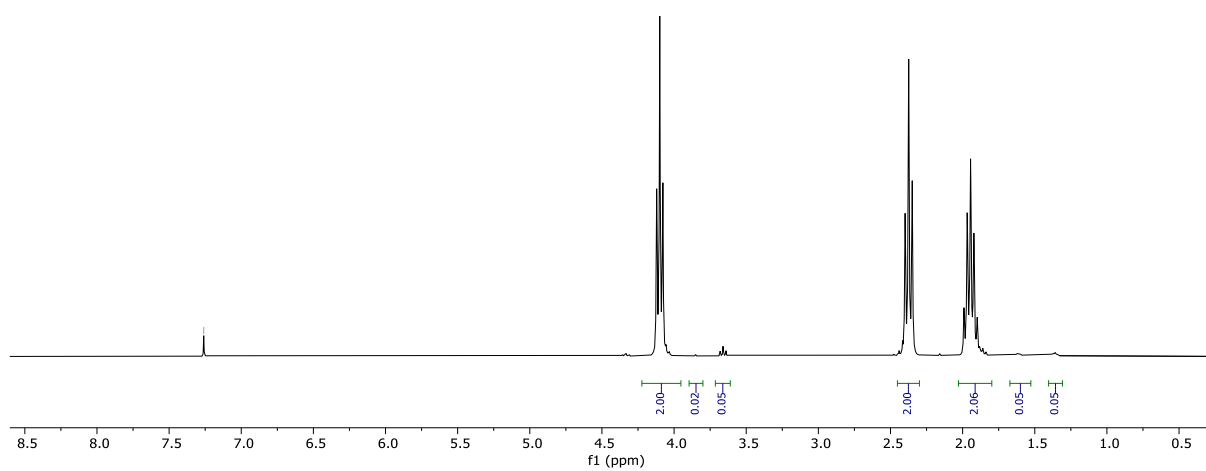
— 7.26  $\text{CDCl}_3$ 

**Poly- $\gamma$ -butyrolactone initiated with 1,4-BDO.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL init 1,4-BDO

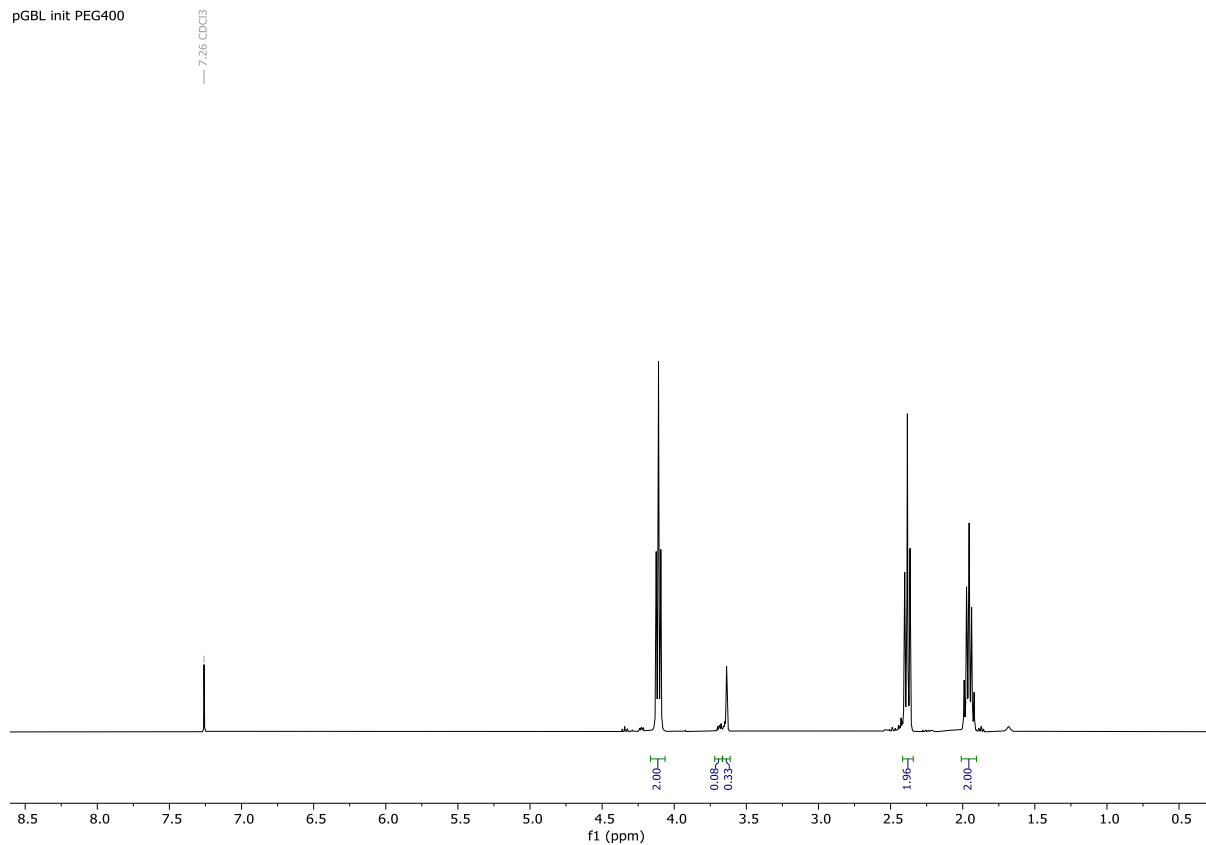
— 7.26  $\text{CDCl}_3$ **Poly- $\gamma$ -butyrolactone initiated with 1,6-HDO.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL init 1,6-HDO

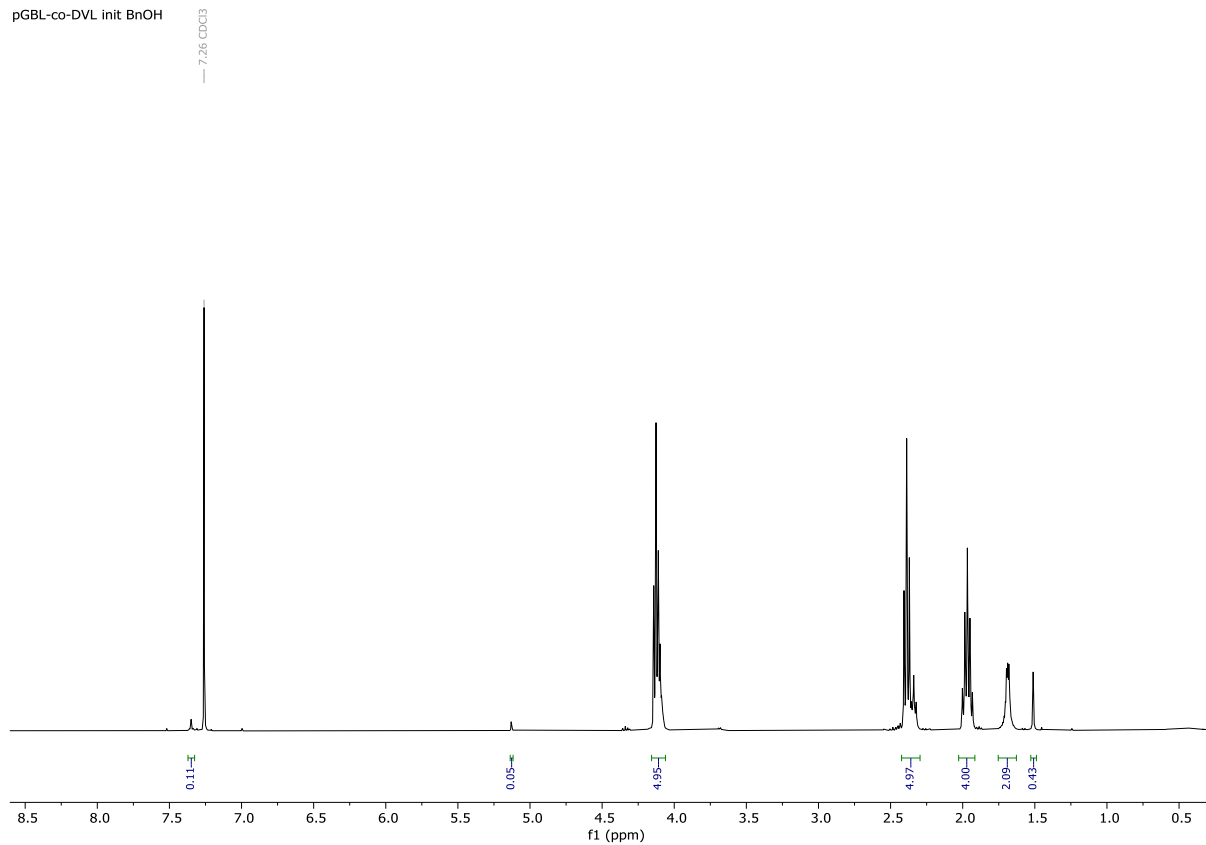
— 7.26  $\text{CDCl}_3$ 

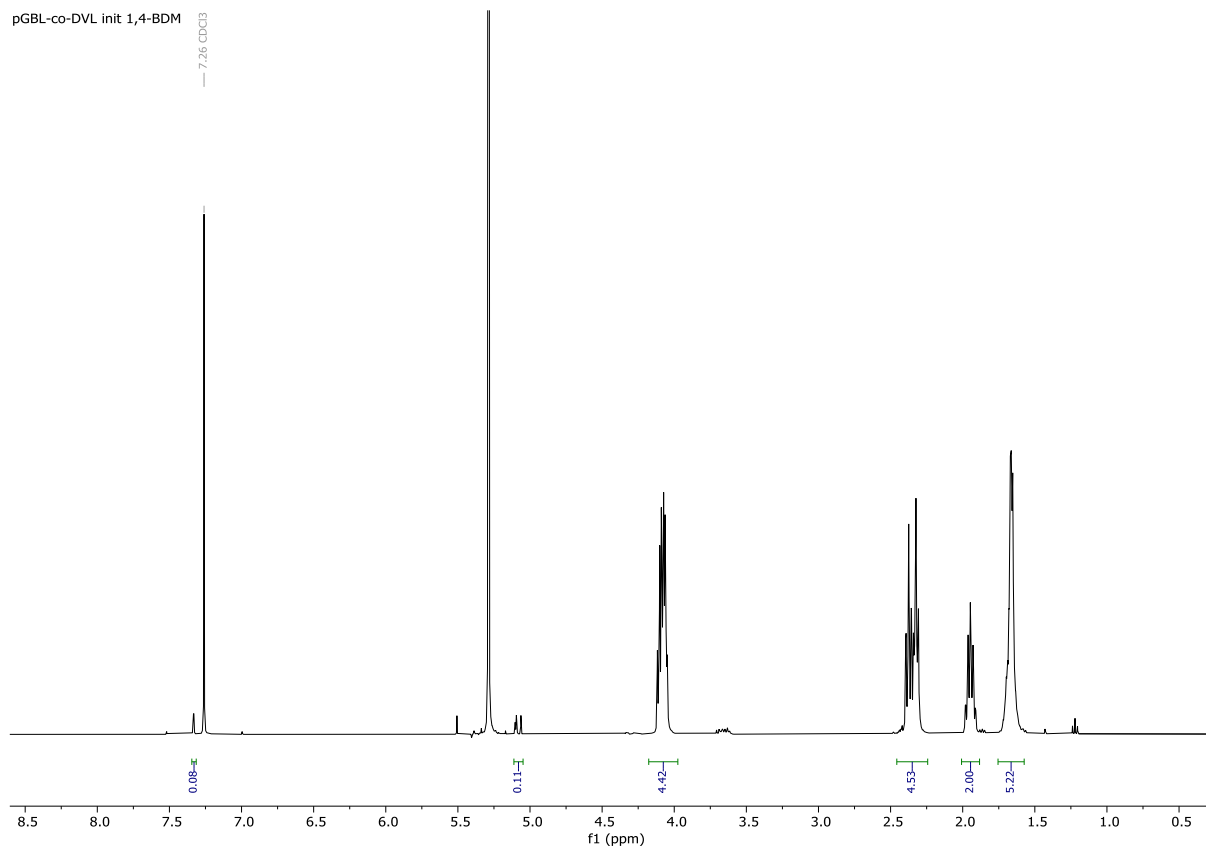
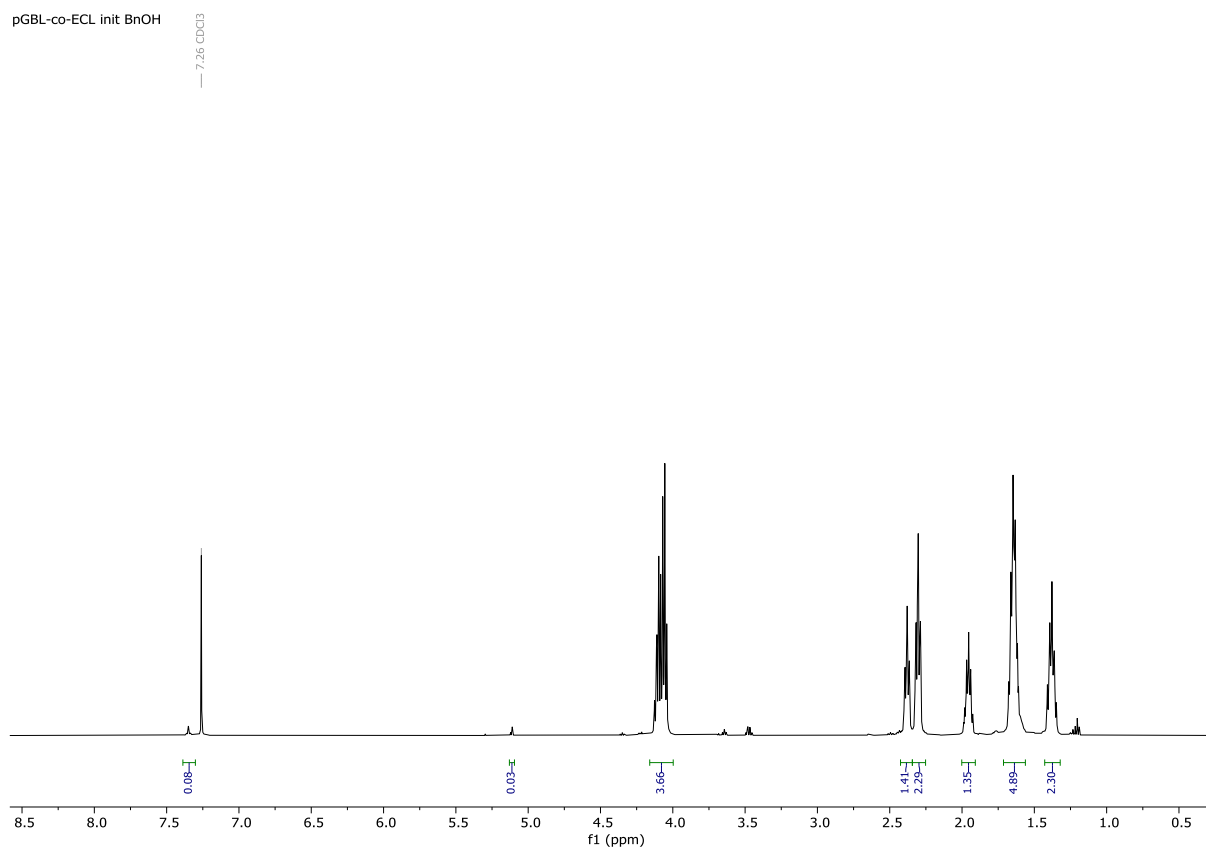
**Poly- $\gamma$ -butyrolactone initiated with PEG<sub>400</sub>. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K)**

pGBL init PEG400

**Poly-( $\gamma$ -butyrolactone-co- $\delta$ -valerolactone) initiated with benzyl alcohol. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K)**

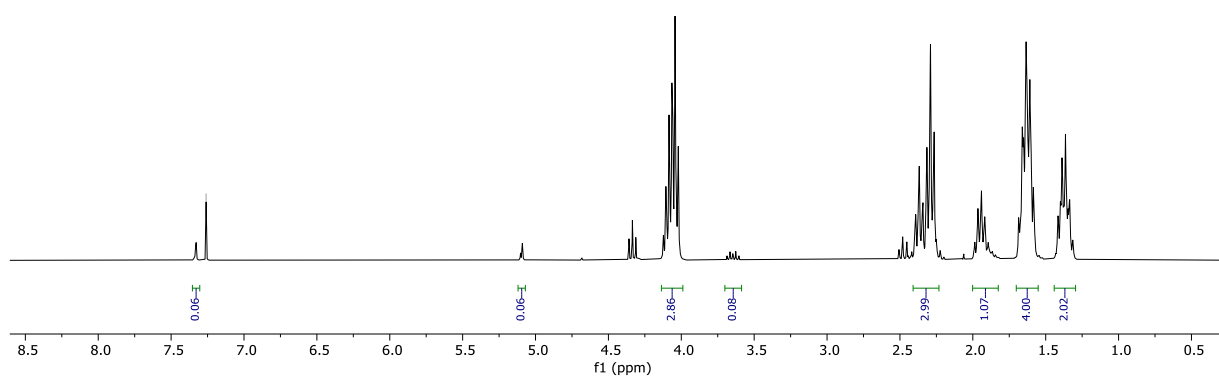
pGBL-co-DVL init BnOH



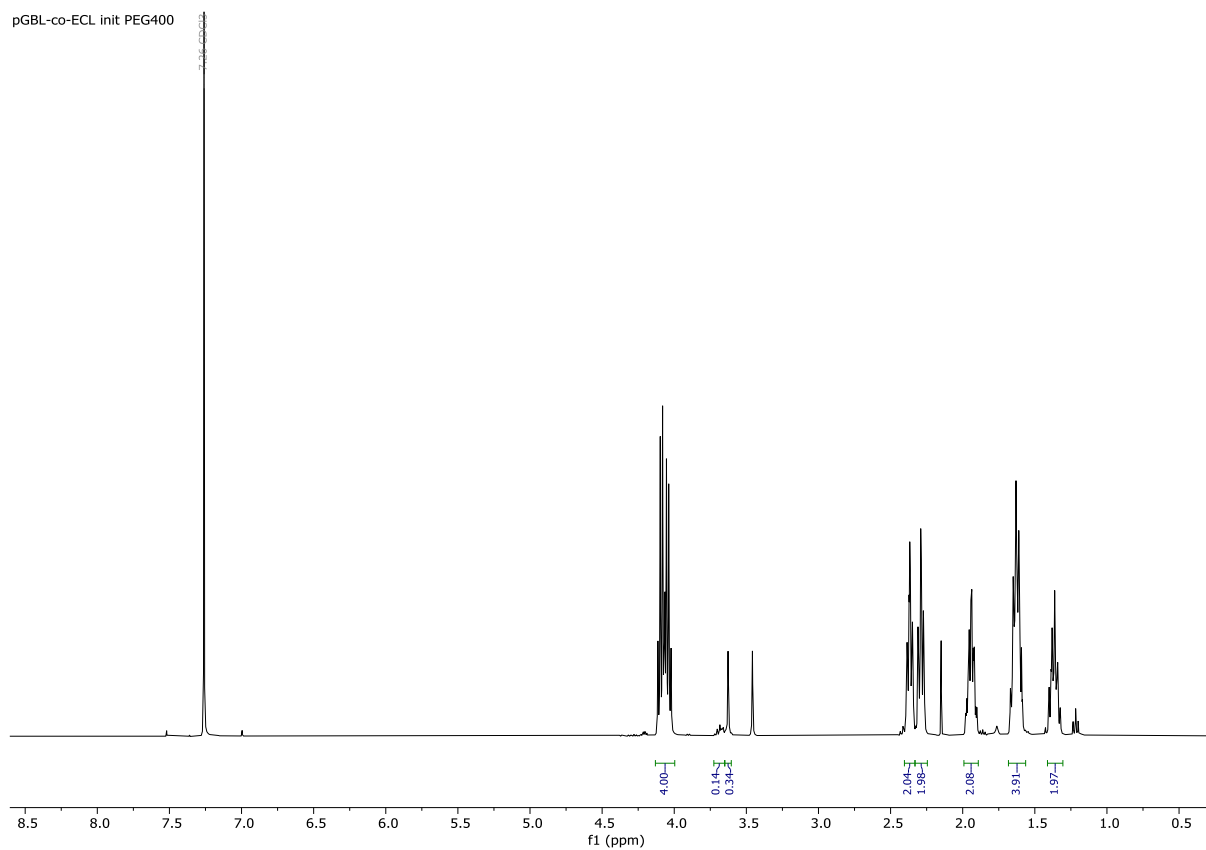
**Poly( $\gamma$ -butyrolactone-co- $\delta$ -valerolactone) initiated with 1,4-BDM.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)****Poly( $\gamma$ -butyrolactone-co- $\epsilon$ -caprolactone) initiated with benzyl alcohol.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

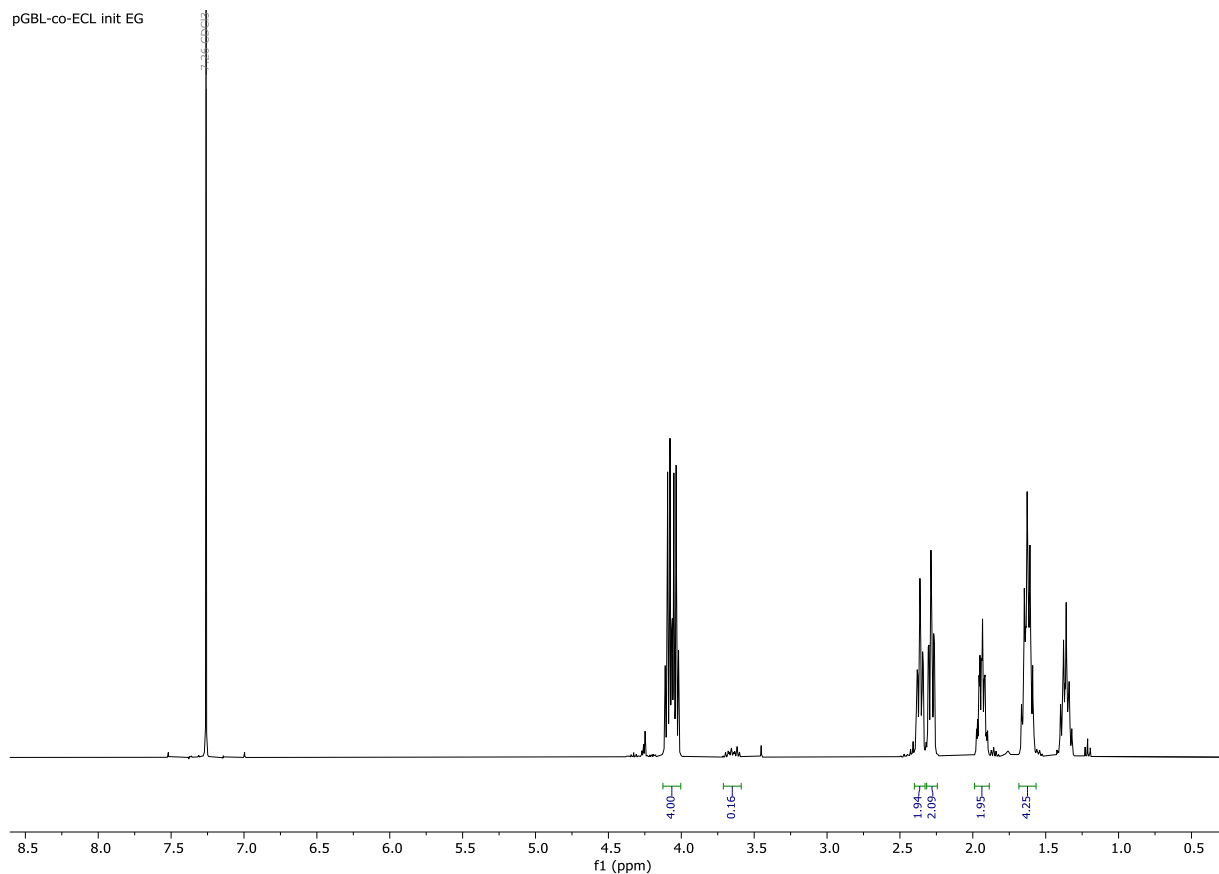
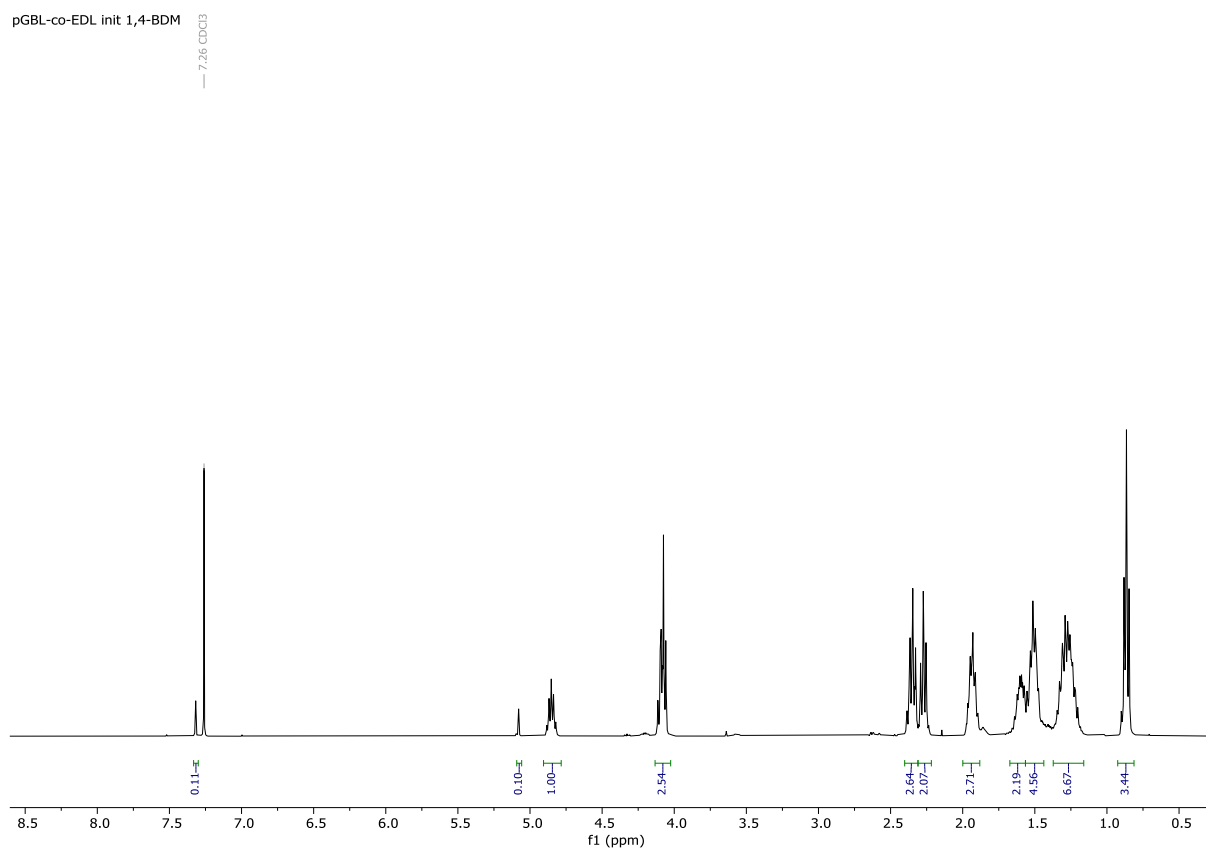
**Poly-( $\gamma$ -butyrolactone-co- $\epsilon$ -caprolactone) initiated with 1,4-BDM.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL-co-ECL init 1,4-BDM

7.26  $\text{CDCl}_3$ **Poly-( $\gamma$ -butyrolactone-co- $\epsilon$ -caprolactone) initiated with PEG<sub>400</sub>.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

pGBL-co-ECL init PEG400



**Poly( $\gamma$ -butyrolactone-co- $\epsilon$ -caprolactone) initiated with ethylene glycol.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)****Poly( $\gamma$ -butyrolactone-co- $\epsilon$ -decalactone) initiated with 1,4-BDM.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K)**

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