Supporting Information

Polycondensation of Butenediol: Synthesis of Telechelic 2-Butene-1,4-diol Oligomers

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Experimental Section

General Considerations

All materials were purchased from Aldrich and used as received unless stated otherwise. Dialysis bags were purchased from SpectraPor. The catalyst **1** was prepared as previously described.[1] The ring-opening polymerization experiments were performed in a glove box under nitrogen atmosphere. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min on a Waters chromatograph equipped with four 5 μm Waters columns (300 mm x 7.7 mm) connected in series. A Viscotek S3580 refractive index detector, Visotek VE3210 UV/vis detector and Viscotek GPCmax autosampler were employed. The system was calibrated using monodisperse polystyrene standards (Polymer Laboratories). Electrospray Ionization (ESI) Mass Spectra were collected on a ThermoFinnigan LCQ ion trap mass spectrometer operated in positive ion electrospray. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 DSC using a heating and cooling rate of 10℃/min and a nitrogen flow rate of 50 ml/min.

Allylation of CD_3OD with 2-cis-pentene-1-ol

To an NMR tube containing **1** (0.6 mg; 0.0011 mmol) was added 0.3 mL CD_3OD and 2-*cis*-pentene-1-ol (12 μL; 0.119 mmol). The tube was shaken to mix, and the reaction was monitored by ^{1}H-NMR. The B/L ratio could be measured by integration of the vinyl signal at 5.23 ppm and the methylene signal at 4.02 ppm. After 24 hours, the B/L ratio was 13/87. Conversion by ^{1}H-NMR was 53%, with a 7% NMR yield of the branched product and a 46% NMR yield of the linear product. ^{1}H-NMR and GC-MS characterization of the branched and linear products matched those reported in the literature.[4,5]

Reaction of 1 with butenediol

To an NMR tube containing **1** (1.6 mg; 0.0029 mmol) in acetone-d_6 (0.4 mL) was added 2-*cis*-butene-1,4-diol (0.2 uL, 0.0029 mmol). The tube was shaken to mix, and the reaction was monitored by ^{1}H-NMR. The identity of *cis*-3-(allyoxy)prop-2-en-1-ol was made by comparison to the literature.[3]

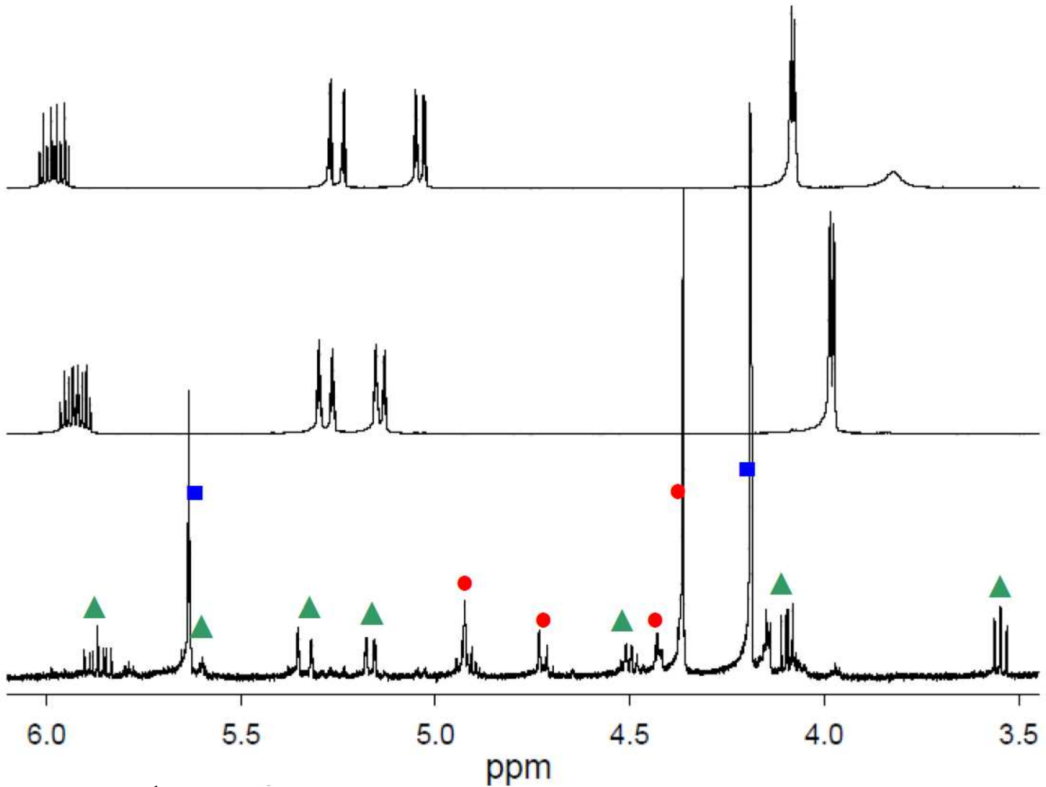

Figure S1. (upper) ^{1}H-NMR (500 MHz, acetone-d$_6$) spectrum of allyl alcohol (Aldrich). (middle) ^{1}H-NMR (500 MHz, acetone-d$_6$) spectrum of allyl ether (Aldrich). (bottom) ^{1}H-NMR (500 MHz, acetone-d$_6$) spectrum of a solution containing **1** (●) and *cis*-2-buten-1,4-diol (■) partially converted to the ether reaction product (▲).

General polymerization experiment

Catalyst **1** (16.3 mg, 0.029 mmol) was weighed directly into a glass vial with a tightly fitting cap. To the vial was added reagent grade acetone (2 mL) and a stir bar, and the mixture was stirred until homogeneous. In a single aliquot, 2-*cis*-butene-1,4-diol was added (2 mL, 24.4 mmol), and the vial was tightly capped and left stirring for 48 hours. Acetonitrile was added (1 mL) to quench the reaction, and volatiles removed under high vacuum. The crude polymer was taken up in reagent grade dichloromethane (~2 mL), and the addition of hexanes (~5 mL) precipitates the oligomer **2** as a viscous oil, which was isolated from the turbid supernatant by pipette. Crude **2**: ESI: $HO(C_4H_6O)_nH$, n=3-20; for n=7 + Na^+, m/z =531.44 vs 531.28 g/mol (see Figure S2). GPC: M_n=415 g/mol; M_w/M_n =2.21, linear to branched enchainment L/B = 92/8. Yield: 1.715 g, 80%. The oligomer **2** was loaded into a dialysis bag (1,000 g/mol molecular weight cut off) with approximately 10x volume of CH_2Cl_2. The bag was closed and submerged in a stirred vessel of methanol. The methanol was changed once after 5 h and the contents of the bag were dried under vacuum for 19 h to afford poly(2-butene-1,4-diol) **2**: ^{1}H-NMR (500 MHz, acetone-d$_6$) δ 5.80 (d, 1H); 5.70 (s, 32H); 5.31 (m, 2H); 4.08 (s, 64H); 4.00 (m, 1H); 3.46 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.9; 133.0; 129.6; 128.2; 118.8; 79.8; 73.3; 70.5; 66.2; 65.8; 65.7; 64.6; 58.8 (see Figure S5). GPC: M_n=4,987 g/mol; M_w/M_n = 1.303. Yield: 21 mg, 4%, linear to branched enchainment L/B = 94/6.

The supernatant from the hexanes precipitation (cyclic oligomer fraction) was removed of volatiles and analyzed: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.80 (d, 1H); 5.70 (s, 32H); 5.31 (m, 2H); 4.08 (s, 64H); 4.00 (m, 1H); 3.46 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 129.6; 66.2. ESI: $(C_4H_6O)_n$, n=3-10; for n=3+ H^+, m/z =210.87 vs 211.12 g/mol (see Figure S4). Yield: 26 mg; 5%.

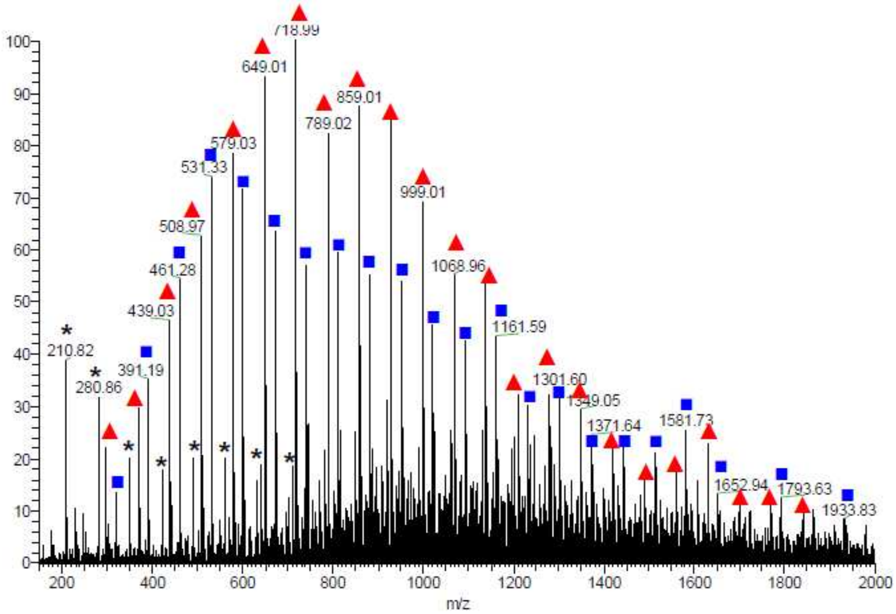

Figure S2. ESI-MS of the crude polymerization material (Table 1, entry 1). The signals marked with the ▲ are due to linear, telechelic oligomers + H^+; the ■ to linear, telechelic oligomers + Na^+; and * to cyclic oligomers + H^+.

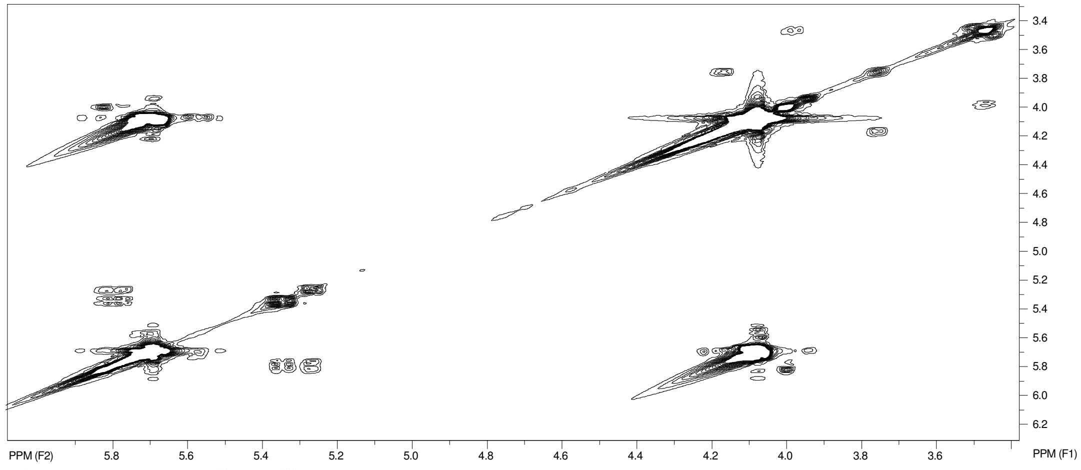

Figure S3. ^{1}H-^{1}H COSY (500 MHz, acetone-d_6) of poly(2-butene-1,4-diol) **2**.

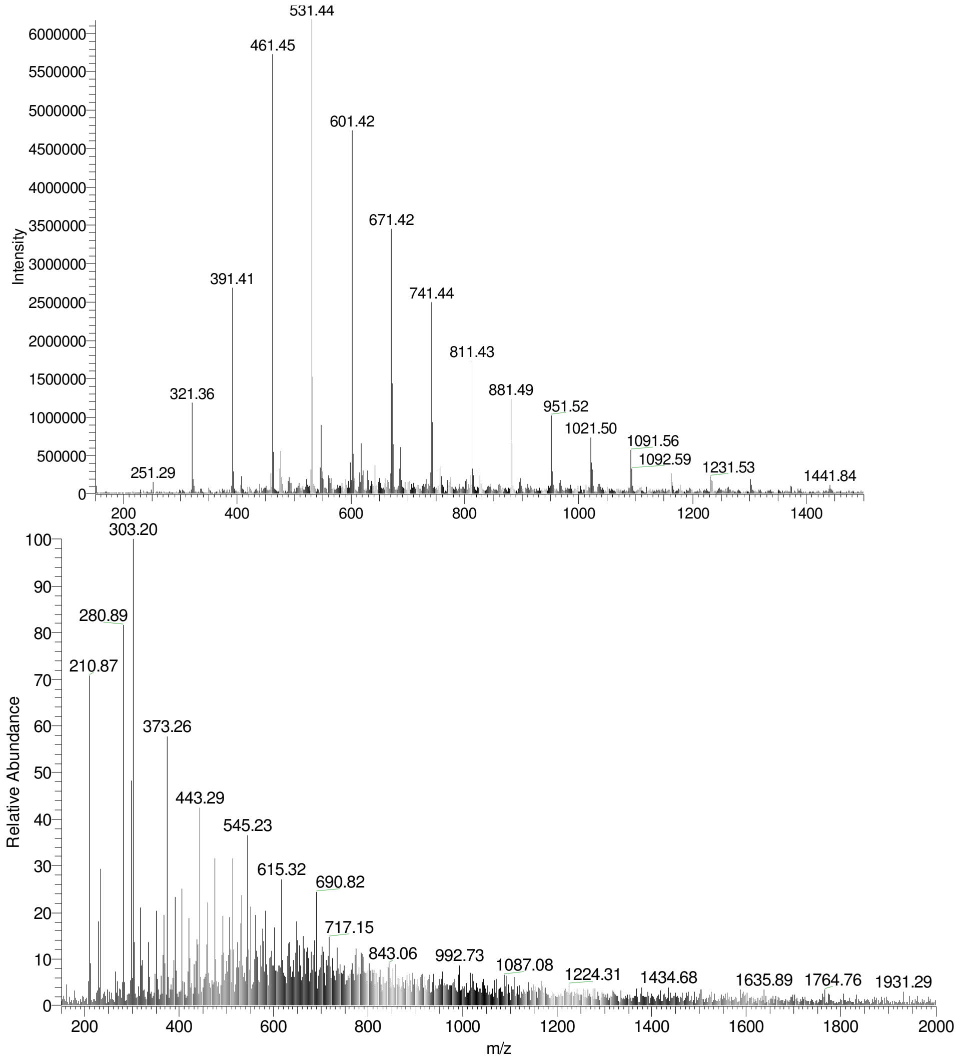

Figure S4. (upper) ESI of poly(2-butene-1,4-diol) **2** after precipitation from $CH_2Cl_2$with hexanes: $HO(C_4H_6O)_nH$, n=3-20; for n=7 + Na^+, m/z =531.44 vs 531.28 g/mol (lower) ESI of the hexanes-soluble cyclic oligomer fraction from the polymerization reaction. $(C_4H_6O)_n$, n=3-10; for n=3+ H^+, m/z =210.87 vs 211.12 g/mol, the Na^+ adducts are visible at +23 m/z.

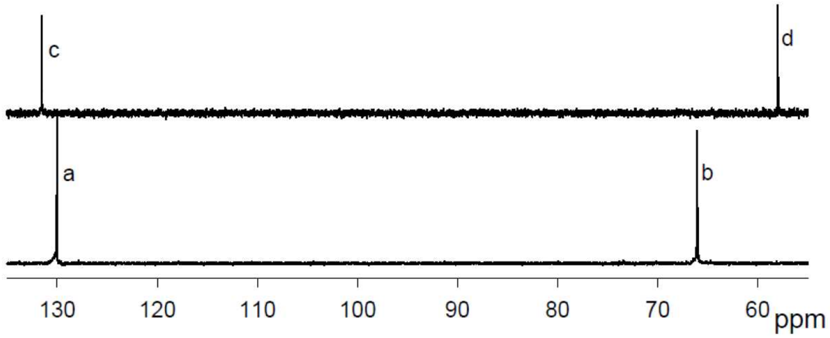

Figure S5. ^{13}C-NMR (D_2O, acetone internal standard) spectrum of poly(butenediol), **2**; (lower, a=CH; b=CH_2) and 2-*cis*-butene-1,4-diol (upper, c=CH; b=CH_2).

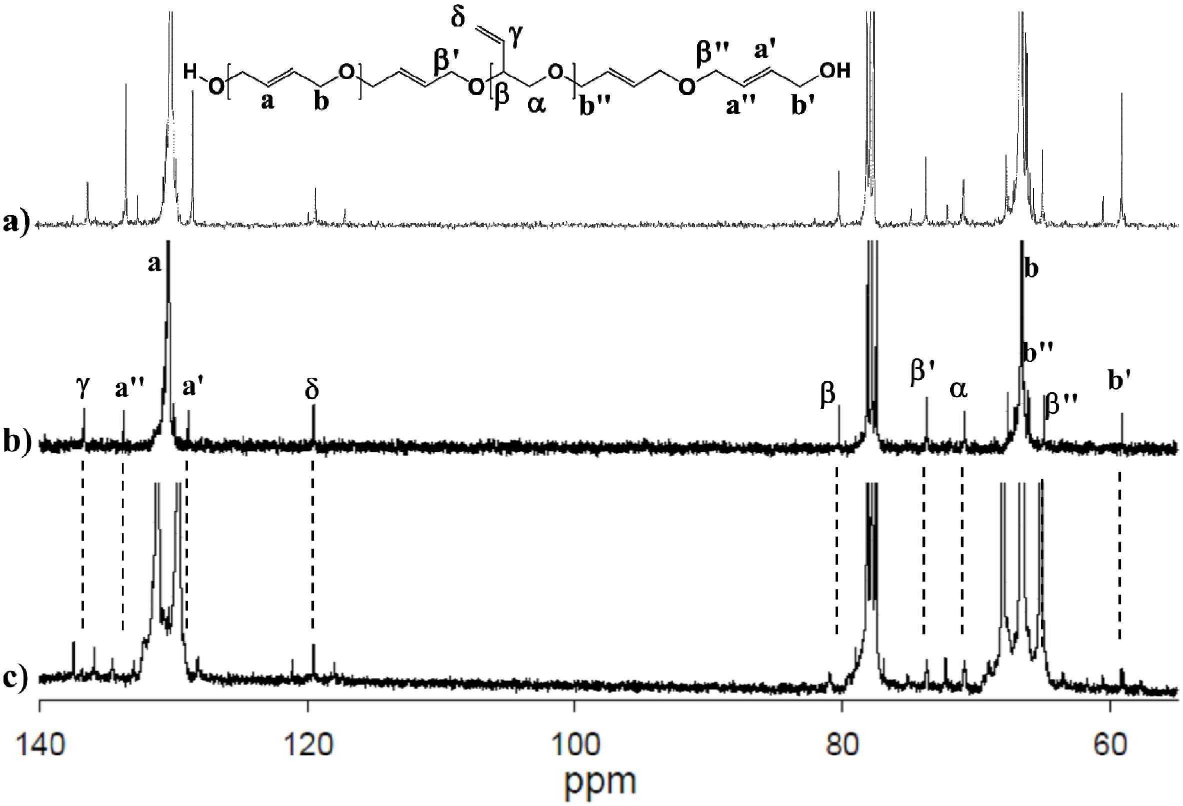

Figure S6. ^{13}C-NMR ($CDCl_3$) spectrum of **2** (a) (M_n= 1950) acquired with power-gated decoupling (125 MHz); (b) (M_n=5000) acquired with power-gated decoupling (100 MHz) . (c) (M_n=5000) acquired with gated decoupling (100 MHz).

2-*trans*-1,4-butenediol

Complex **1** (1 mg, 0.0018 mmol) was weighed directly into an NMR tube to which was added D_2O (0.5 mL) and 3 drops of acetone-d_6 (reference) and 2-*cis*-1,4-butenediol (0.1 mL, 1.2 mmol). The tube was shaken to mix, and the isomerization occurred over several hours yielding 2-*trans*-1,4-butenediol[2] ^{1}H-NMR (400 MHz, D_2O) δ 5.74 (t, 2H); 4.21 (d, 4H). ^{13}C-NMR (100 MHz, D_2O) δ 131.59; 58.37.

2-cis-butene-1,4-diol Polymerization Experiment with Drying

A 50 ml Schlenk flask loaded with a stir bar, Ru(IV) complex **1** (14.8 mg; 0.025 mmol), 2-*cis*-1,4-butene-1,4-diol (3.9 mL; 0.047 mol), 3.8 mL $CH_2Cl_2$and 1.9 mL ethyl ether was equipped with a reflux condenser packed with 4Å molecular sieves. The solution was stirred at 50 °C for 48 h, and a small aliquot for ^{1}H-NMR and GPC was taken. ^{1}H-NMR (400 MHz, $CDCl_3$) 5.80 (d, 1H); 5.70 (s, 14H); 5.31 (m, 2H); 4.08 (s, 28H); 4.00 (m, 1H); 3.46 (m, 2H). GPC: M_n=1,300 g/mol; M_w/M_n = 2.505. The solution was further stirred at 50 °C for 1 day under vacuum. GPC: M_n=4,600 g/mol; M_w/M_n = 2.423. The product mixture was dissolved in a small amount of THF was precipitated in *n*-hexane, and the brown product (3.49g) was obtained. The brown product was purified by alumina column chromatography to remove Ru. GPC: M_n=5,729 g/mol; M_w/M_n = 2.190. The yellow product was azeotropically dried with anhydrous benzene three times. The final yield of poly(butenediol) is 57 % (1.9 g, 0.027 mol). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.82 (m, 5H); 5.73 (m, 191H); 5.30 (m, 11H); 4.41 (d, 1H); 4.06 (m, 398H) ; 3.92 (m, 7H) ; 3.47 (m, 14H) (**Figure S7**). ^{13}C-NMR (300 MHz, $CDCl_3$) δ 135.6, 132.6, 129.3, 125.4, 118.4, 79.4, 73.0, 70.1, 67.0, 66.4, 65.9, 65.5, 64.2, 58.4 (**Figure S8**). GPC: M_n=5,970 g/mol; M_w/M_n = 2.203. DSC: see below

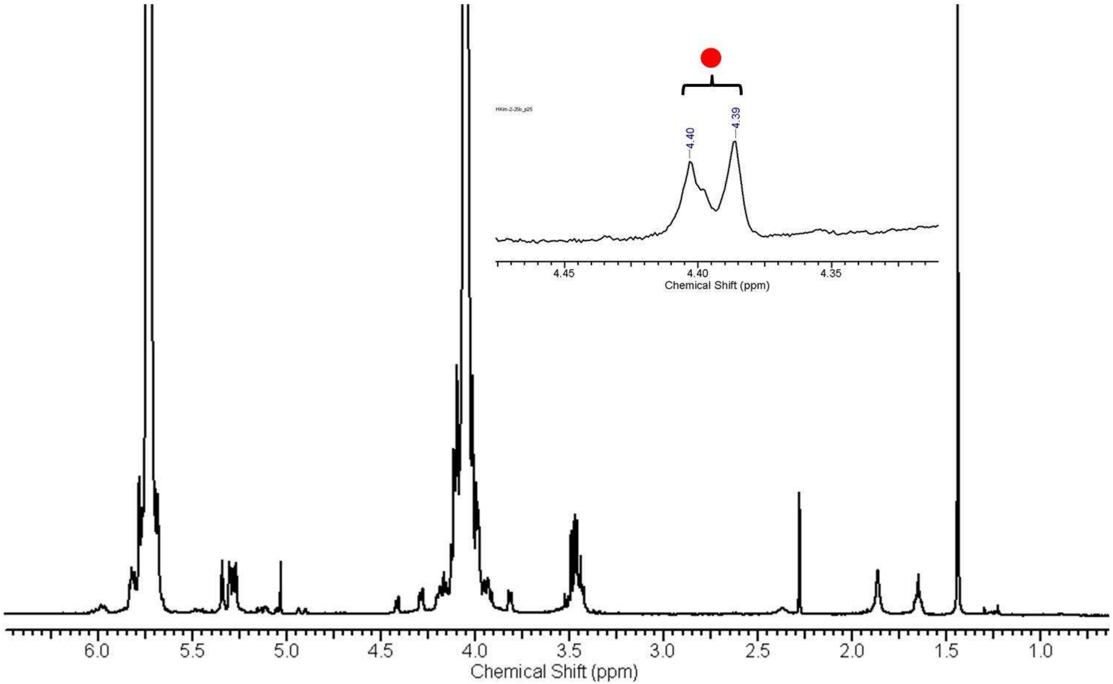

Figure S7. ^{1}H-NMR data of poly(butenediol) (entry 4, Table 1), note ● which occurs in the poly(butenediol) backbone

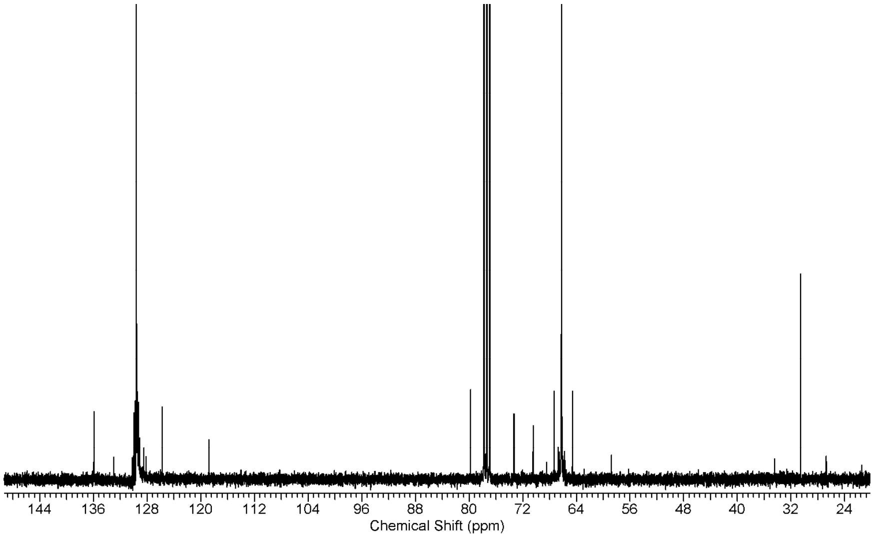

Figure S8. ^{13}C-NMR data of poly(butenediol)

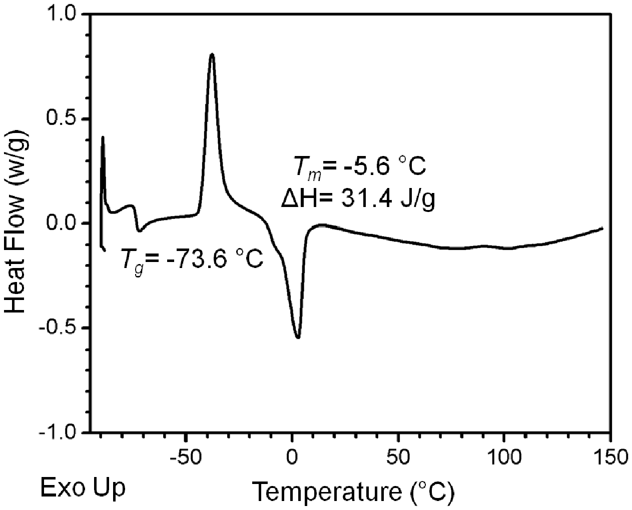

Figure S9. DSC data of poly(butenediol,entry 4, Table 1) with the second cycle after annealing at 150 °C for 5 mins.

Synthesis of 3 (ROP of LA from the macroinitiator 2)

To a 20 ml oven-dried vial containing a stir bar, poly(oxy-2-butenylene) (202 mg; 0.035 mmol, M_n = 6,000 g/mol, M_w=13,200 g/mol, M_w/M_n = 2.20), L-lactide (417 mg; 2.89 mmol) and TBD (4 mg, 0.0029 mmol) was added dichloromethane (DCM) (2.89 mL). The vial was sealed and stirred for 2 hours at room temperature. The reaction was quenched by the addition of 30 mg (0.25 mmol) benzoic acid with stirring for 30 mins, and solvent was removed under vacuum. GPC: M_n=10,910 g/mol; M_w/M_n = 2.077. The crude product dissolved in minimal amount of THF was added to methanol to get a white precipitate. The precipitate was collected by decanting, and THF was removed under vacuum. The final yield of triblock copolymer was 51% (307 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.74 (m, 173H); 5.19 (m, 154H); 4.42 (d, 1H); 4.37 (q, 2H) ; 4.07 (m, 359H) ; 3.47 (m, 14H) ; 1.61 (m, 472H) (**Figure S10**). ^{13}C-NMR (300 MHz, $CDCl_3$) δ 169.6, 129.6, 69.2, 66.2, 16.9 (**Figure S11**). GPC: M_n=12,700 g/mol; M_w/M_n = 1.966.

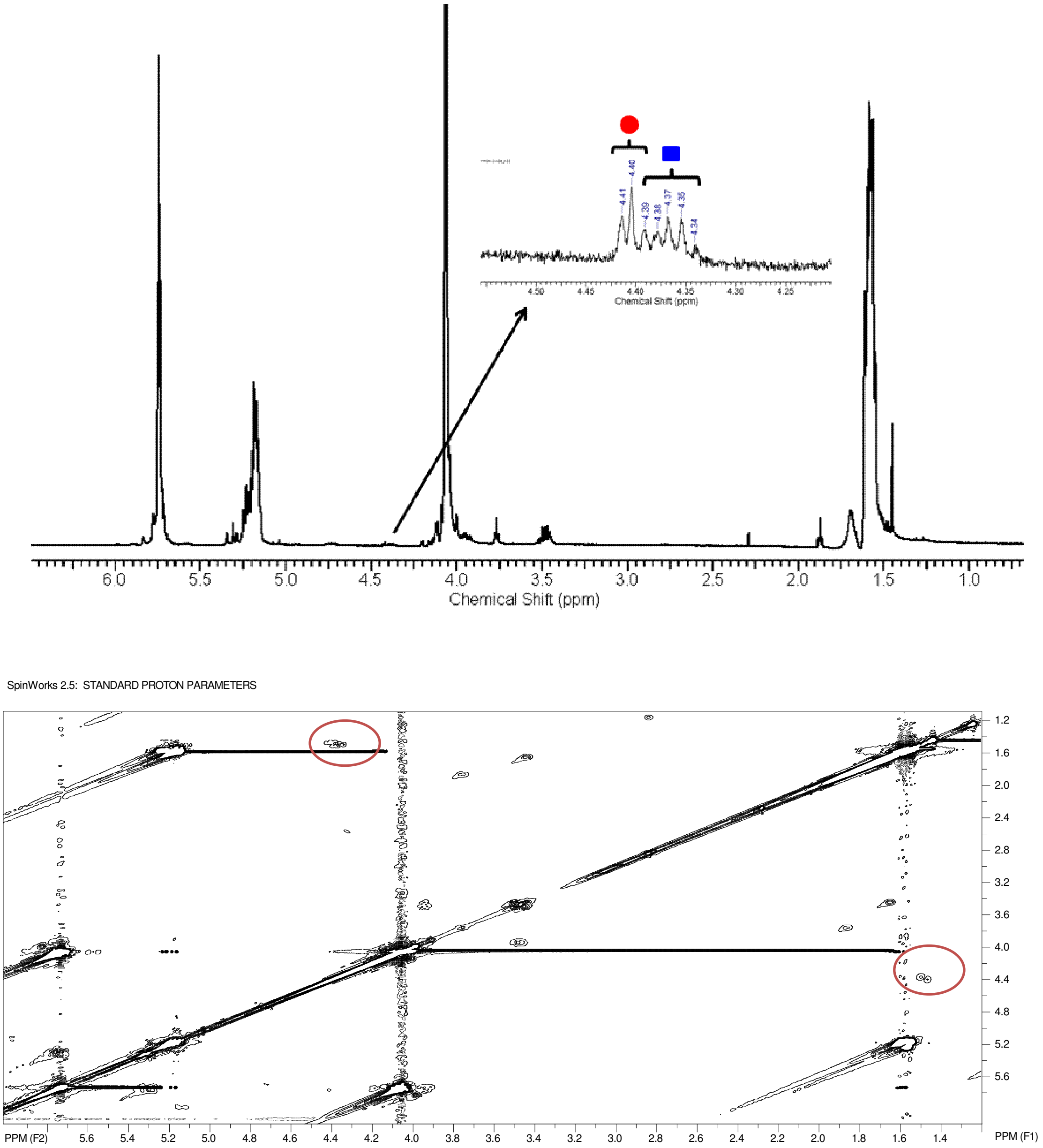

Figure S10. (upper) ^{1}H-NMR data of triblock copolymer where ● originates in the poly(butenediol) backbone (see Figure S7) and ■ represents the PLLA endgroups. (lower) ^{1}H-^{1}H COSY of the triblock copolymer. The circles indicate the cross peaks (4.43 ppp, 1.48 ppm).

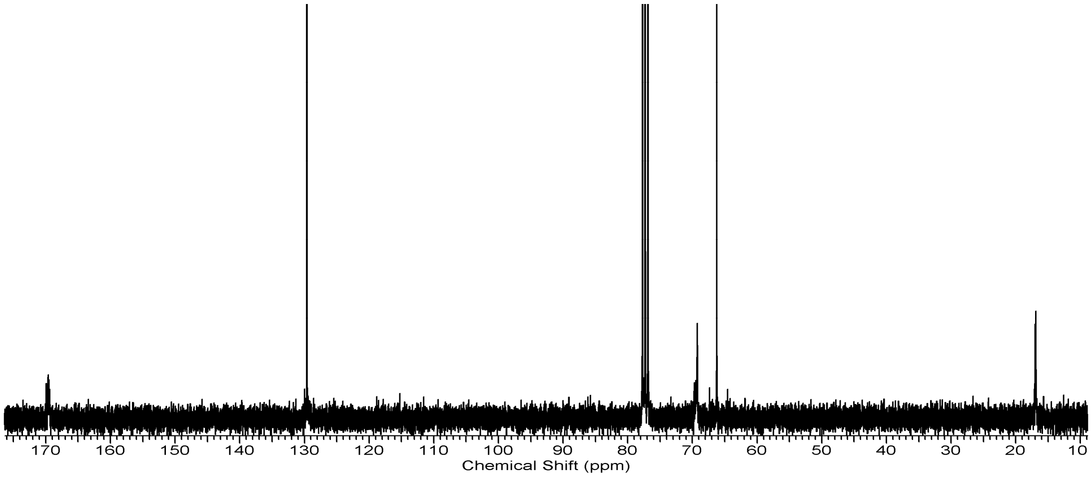

Figure S11. ^{13}C-NMR data of triblock copolymer.

Metathesis of triblock copolymer

The triblock copolymer (102 mg, 0.0080 mmol) and Grubb II catalyst ((1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro(phenylmethylene)-(tricyclohexylphosphine) ruthenium) (2 mg, 0.0024 mmol) were added to a 20 ml oven-dried vial, and anhydrous benzene (2 ml) and 1-hexene (2ml) were added to the vial. The reaction was stirred at RT for 12 hrs,, quenched with ethyl vinyl ether (0.2 ml) and stirred for 30 mins. After removal of volatiles under vacuum, ^{1}H-NMR (**Figure S12**) and GPC data of the crude product were obtained. GPC: M_n=6,700 g/mol; M_w/M_n = 1.844.

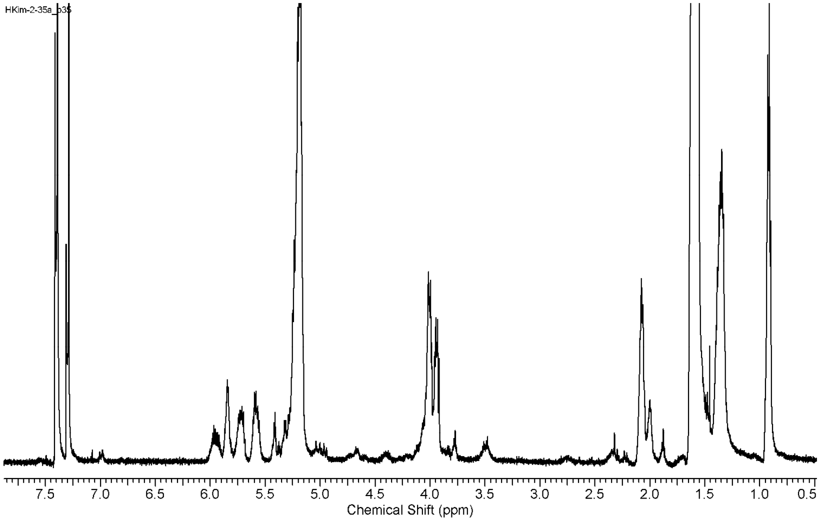

Figure S12. ^{1}H-NMR of crude triblock copolymer after the metathesis reaction

Supporting Information References:

(1) Kiesewetter, M. K.; Waymouth, R. M. *Organometallics* **2010**, *29*, 6051-6056.
(2) Rottger, S.; Waldmann, H. *Eur. J. Org. Chem.* **2006**, 2093-2099.
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(4) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353-3361.
(5) Alexakis, A.; Normant, J. F.; Villieras, J. *J. Mol. Catal.* **1975**, *1*, 43-58.