Supporting Information for

Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate)

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Experimental

General procedures

The synthesis of H_2L^1 has previously been reported.[1] Anhydrous complexation reactions were conducted under nitrogen, using either standard anaerobic techniques or in a nitrogen-filled glovebox. All solvents and reagents were obtained from commercial sources (Aldrich and Strem) and used as received unless stated otherwise. THF and hexane were distilled from sodium and stored under nitrogen. Cyclohexene oxide and DCM were distilled from CaH_2 and stored under nitrogen. Zinc trifluoroacetate monohydrate was dried under vacuum at 100 °C for 16 hours, using phosphorus pentoxide as a dessicant. *Rac*-Lactide and *S,S*-Lactide were received from Purac, recrystallised from hot toluene and sublimed under vacuum three times.

^1H and $^{13}C\{^1H\}$ NMR spectra were performed on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a Fisons Analytical (VG) Autospec spectrometer. Elemental analyses were determined by Mr Stephen Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7. SEC data were collected using a Polymer labs PL GPC-50 instrument with THF as the eluent, at a flow rate of $1 mLmin^{-1}$. Two Polymer labs Mixed D columns were used in series. Narrow M_w polystyrene standards were used to calibrate the instrument. MALDI-TOF MS experiments were carried out at the EPSRC NMSCC, Swansea University, using a dithranol matrix in THF at a loading of 1:5 with NaOAc as the cationizing agent. Thermogravimetric Analysis (TGA) measurements were carried out on a Perkin Elmer Pyris 1 TGA instrument under a flow of dry air, heating at a rate of 10 °C min^{-1} to 80 °C, where the sample was held for 30 minutes, before continuing heating at a rate of 10 °C min^{-1} to 350 °C. All DSC experiments were carried out on a Perkin Elmer DSC 400 instrument, heating/cooling at a rate of 10 °C min^{-1} from 25 to 150 °C.

Synthesis of **2**

H_2L^1 (0.25 g, 0.45 mmol) was dissolved in methanol (20 mL) and $Zn(O_2CCF_3)_2$ (0.26 g, 0.90 mmol) was added. The mixture was stirred for 18 hours and the methanol removed *in vacuo*. The product was taken up in dichloromethane (15 mL), filtered, and the solvent removed *in vacuo.* The product, a white powder, was dried in a vacuum oven, in the presence of diphosphorus pentoxide, overnight.

[$L^1Zn_2(O_2CCF_3)_2$] (white powder; 0.30 g, 72%): Found: C, 50.2; H, 6.1; N, 6.1% .Calc. for $C_{38}H_{54}F_6N_4O_6Zn_2$: C, 50.3; H, 6.0; N, 6.2%. ν_{max}/cm^{-1} 3204 (N-H), 1673 (C=O). δ_H (400 MHz; $CDCl_3$) Major isomer: 6.98 (s, 4H, Ar-*H*), 4.15-4.37 (br s, 4H, Ar-CH_2-N), 3.25 (d, *J* = 11.2 Hz, 4H, Ar-CH_2-N), 3.00 (br s, 4H, N-CH_2-C), 2.71 (d, J = 11.5 Hz, 4H, N-CH_2-C), 2.37 (br s, 4H, N*H*), 1.26 (s, 18H, Ar-CH_3) 1.19 (s, 6H N-C-CH_3), 1.05 (s, 6H N-C-CH_3) δ_C (400 MHz; $CDCl_3$) 161.7, 136.9, 127.8, 122.8, 114.7, 62.9, 55.8, 33.9, 33.5, 31.5, 28.4, 20.7. δ_F (400 MHz; d^4-methanol) -78.13 (s). *m/z* (LSIMS 793 ($[M–O_2CCF_3]^+$, 100%).

Copolymerization conditions

Cyclohexene oxide (2.5 mL, 25 mmol) and **2** (22 mg, 0.025 mmol) were added to a Schlenk tube. The vessel was evacuated, and charged with 1 atm CO_2 after which it was left stirring at 80 °C for 24 hours. The crude reaction mixture was then taken up in CH_2Cl_2 (10 mL) and evaporated in air. The product was then dried *in vacuo* overnight. This proved sufficient to remove unreacted monomer, no further purification was necessary. Isolated yield, 47%. Shorter reaction times (16 h and 8 h) were used to generate lower weight samples (M_n = 6000 and 2500 g/mol)

Block copolymerization conditions

Under a nitrogen atmosphere in a glovebox, (*rac*/*S*,*S*)-Lactide was placed in a vial with a stirrer bar and dissolved in THF (1.5 mL). Separately, poly(cyclohexene carbonate) (0.05 mmol) was placed in a vial with **3** (5.4 mg, 0.1 mmol) and dissolved in THF (0.5 mL). This solution was then added to the lactide solution, and stirred for approximately 5 minutes, until the viscosity increased such that stirring could no longer continue. The reaction was terminated and the polymer precipitated by the addition of hexane (~2 mL). The polymer was filtered and dried under vacuum.

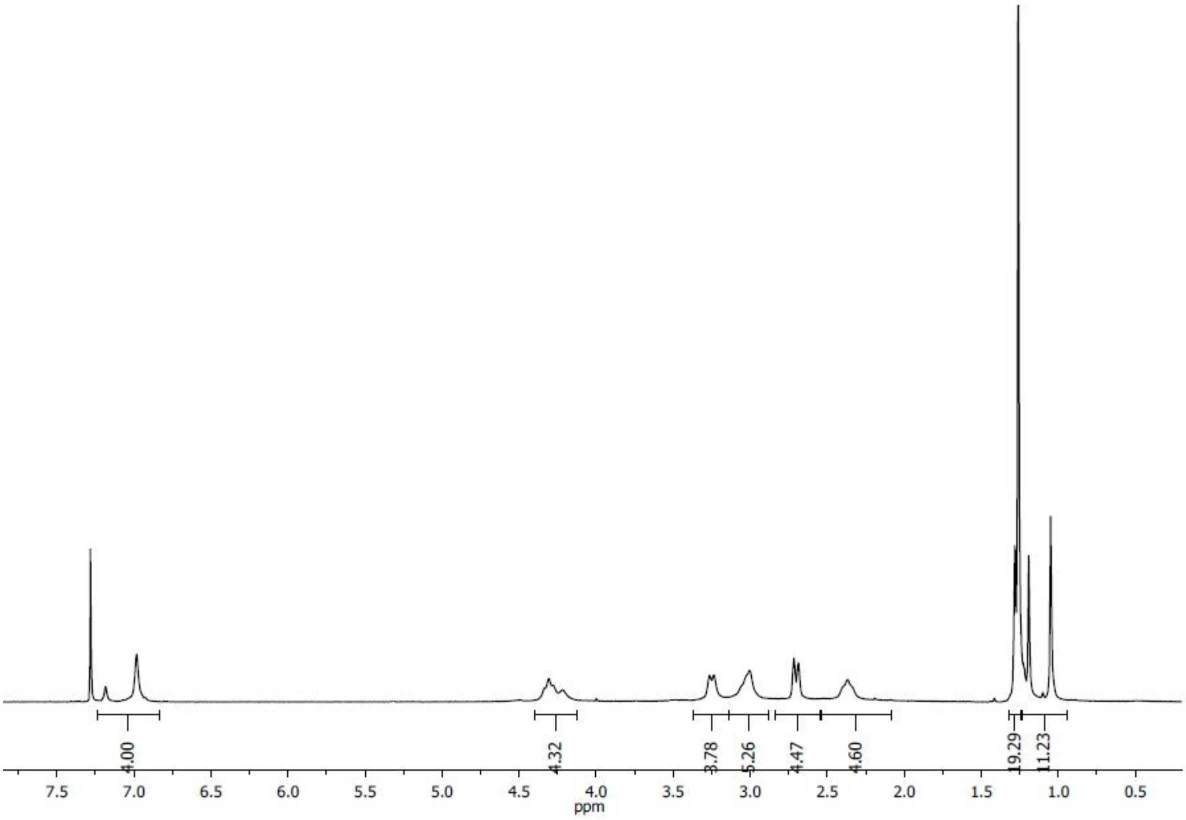

Figure S1: ^{1}H NMR spectrum of **2** in $CDCl_3$

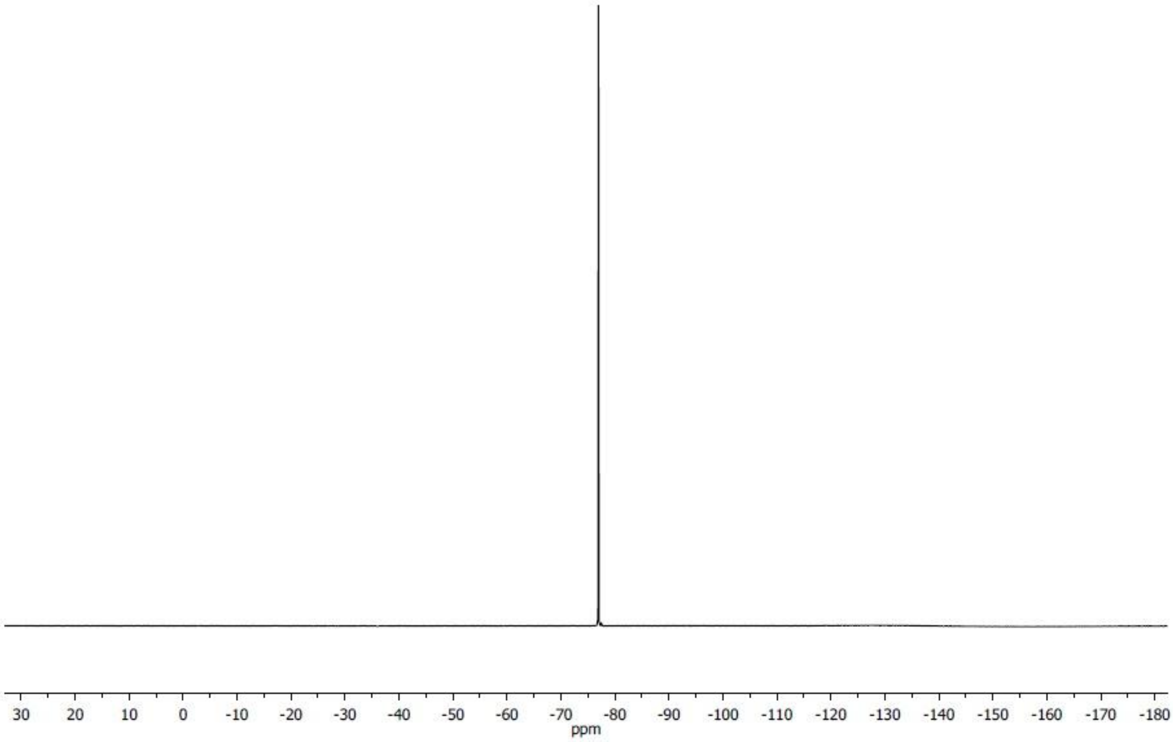

Figure S2: ^{19}F{^{1}H} NMR spectrum of **2** in *d*^{4}-methanol.

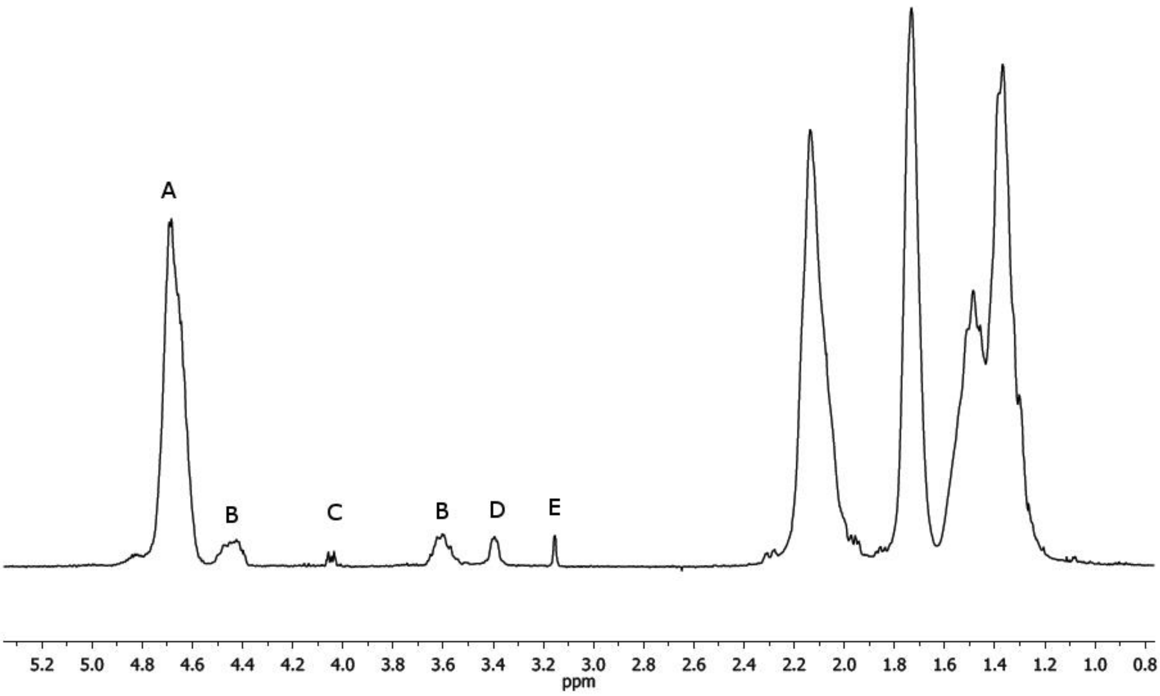

Figure S3: ^{1}H NMR spectrum of PCHC produced by **2**. Peak A assigned to methyne protons of polycarbonate linkages. Peaks B are assigned to the methyne protons of the terminal hydroxyl end group. Peak C is assigned to the cyclic carbonate by-product CHC. Peak D is assigned to the methyne protons of ether linkages. Peak E is assigned to unreacted CHO.

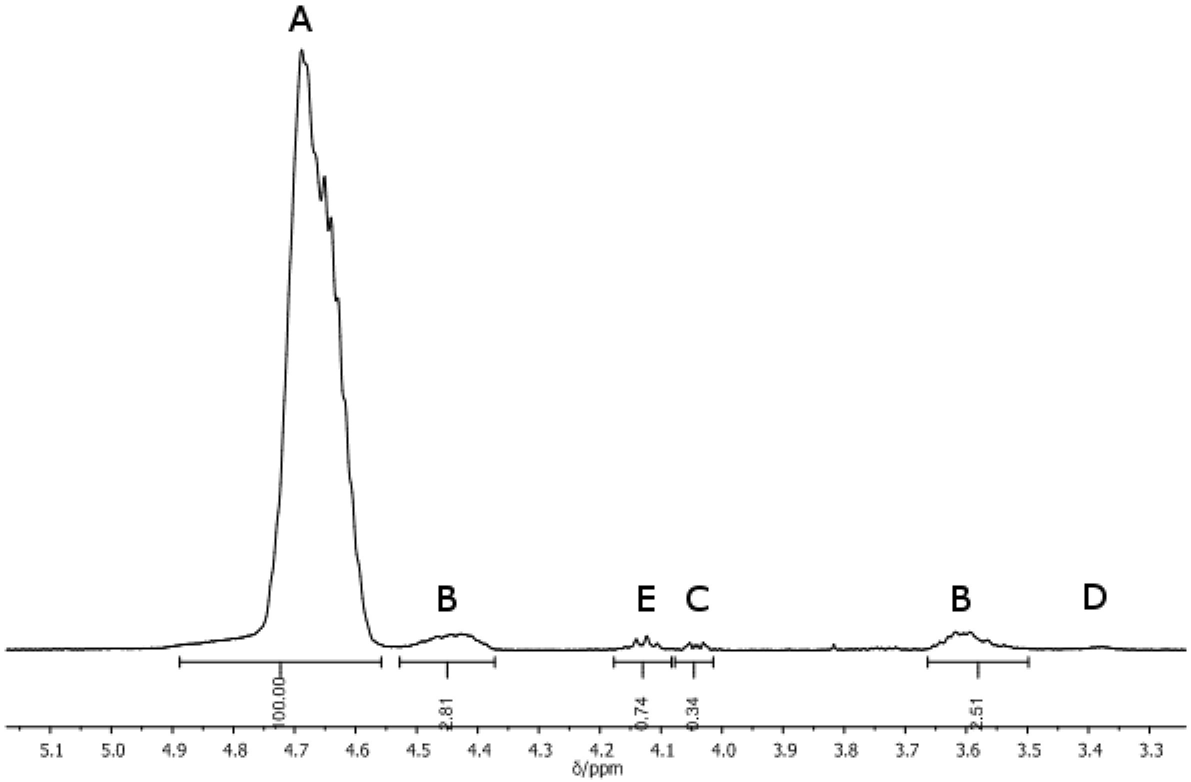

Figure S4: Expanded ^{1}H NMR spectrum of PCHC produced by **1**. Peak A assigned to methyne protons of polycarbonate linkages. Peaks B are assigned to the methyne protons of the terminal hydroxyl end group. Peak C is assigned to the cyclic carbonate by-product CHC. Peak D is assigned to the methyne protons of ether linkages. Peak E is assigned to methyne protons on acetate terminated polymer units.

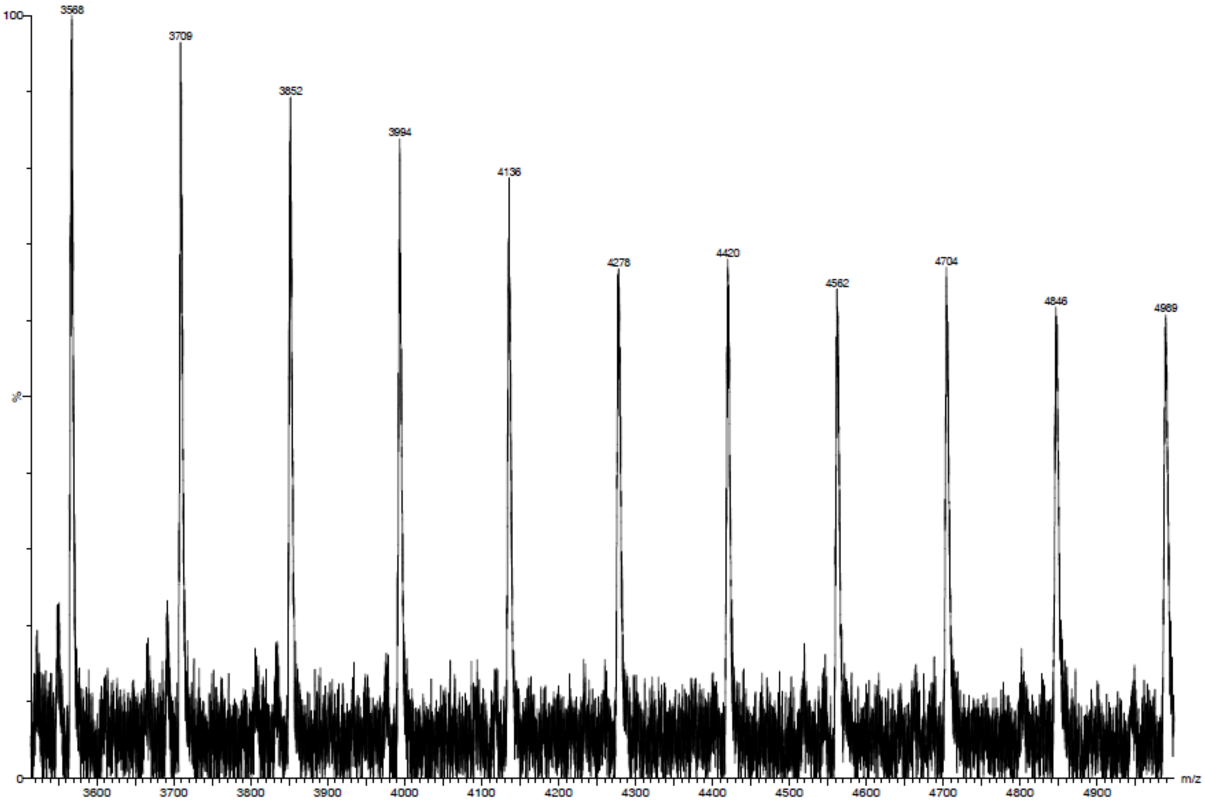

Figure S5: MALDI-ToF spectrum of PCHC produced by 2, showing the polymer series $[HO(C_7H_{10}O_3)_nC_6H_{11}O_2]K^+$. [17.01 + (142.15)n + 99.15 + 39.1].

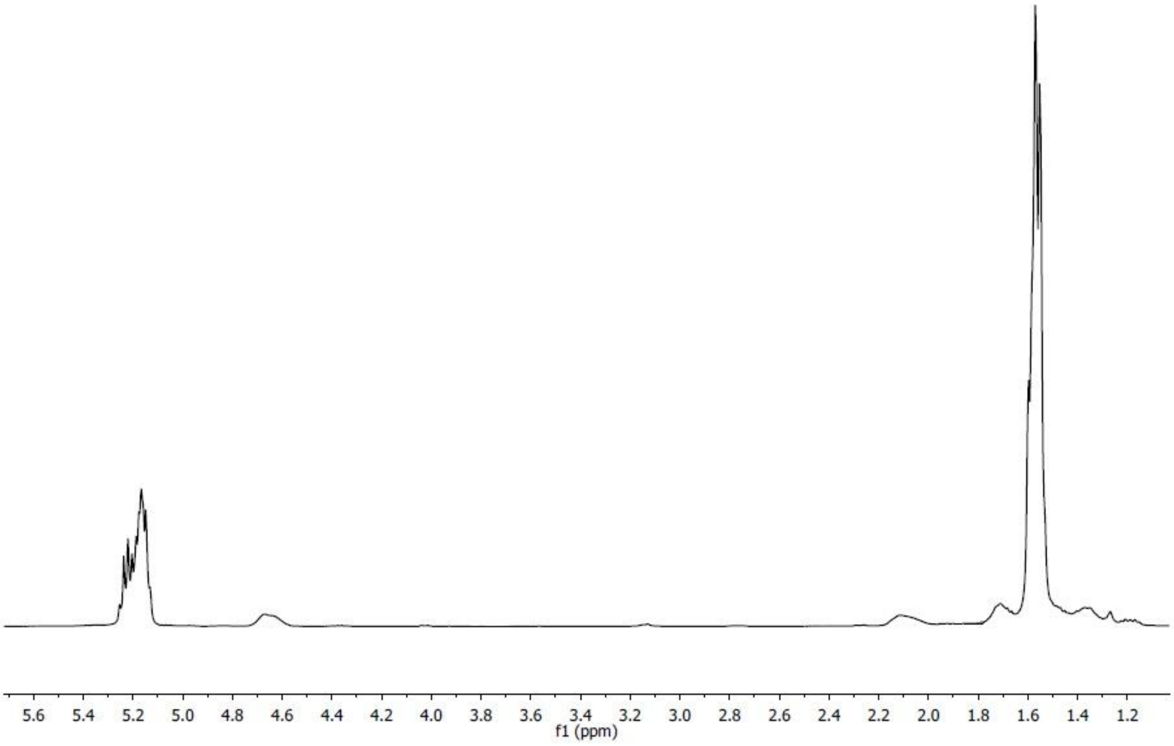

Figure S6: ^{1}H NMR spectrum of precipitated PLA-PCHC-PLA (PCHC M_n = 9000 g/mol, 400 equiv. PLA, PLA-PCHC-PLA M_n = 51,000 g/mol). See Fig. 2 for assignments.

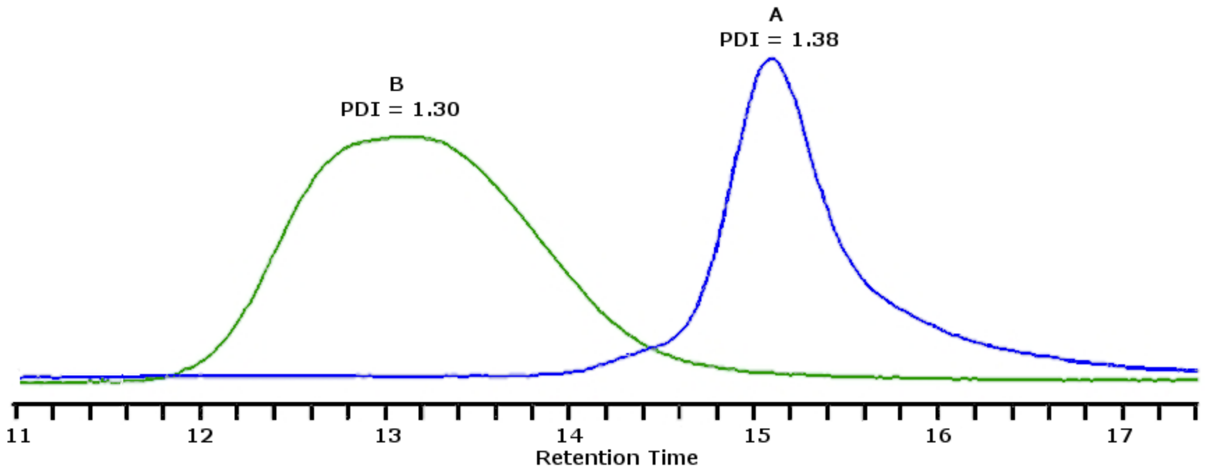

Figure S7: Expanded overlaid GPC traces of PCHC (M_n = 9200, A - blue) and PLA-PCHC-PLA (M_n = 55,000, B - green) using THF as an eluent.

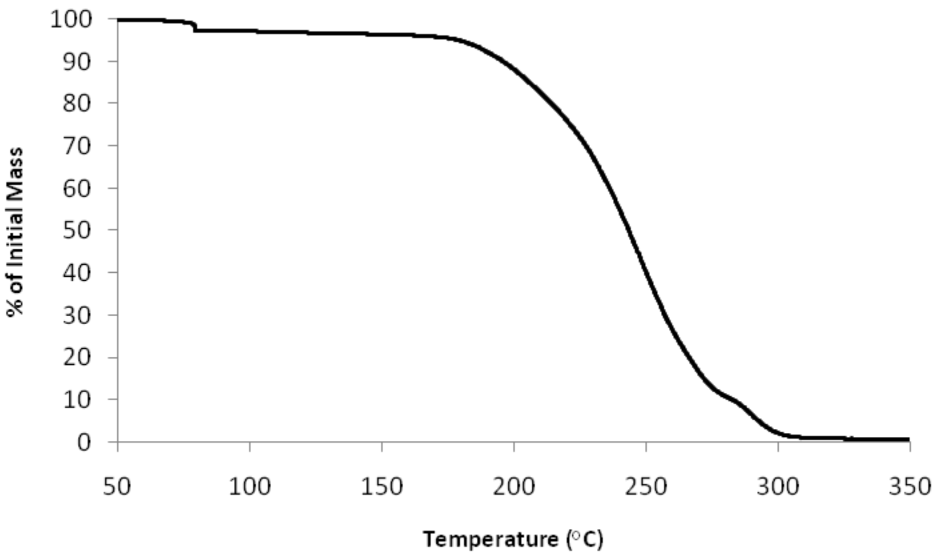

Figure S8: Thermogravimetric analysis (TGA) trace for PLA-PCHC-PLA (PCHC 9000 g/mol, 200 equiv. lactide per end).

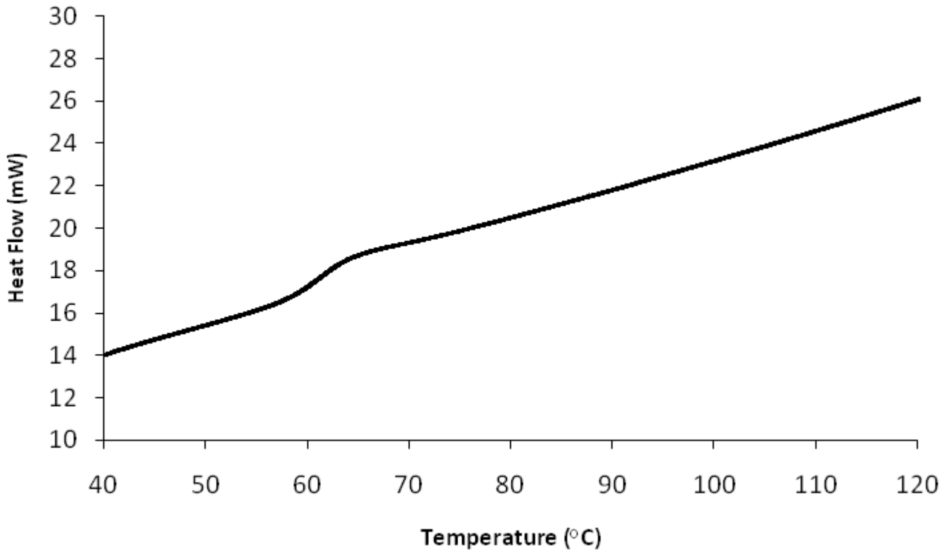

Figure S9: Representative DSC trace for PLA-PCHC-PLA (PCHC 9000 g/mol, lactide 400 equiv.). Exo down.

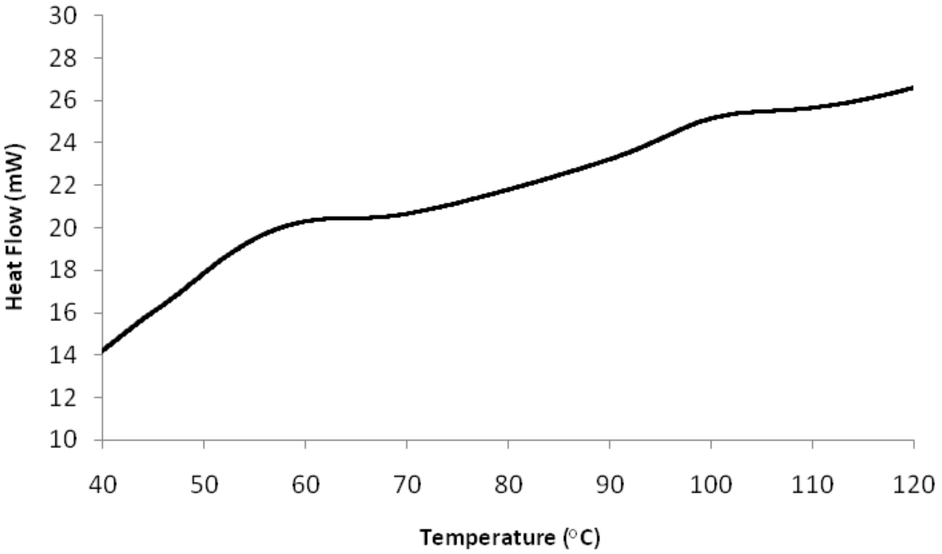

Figure S10: DSC trace of PLA-PCHC-PLA (PCHC 6000 g/mol, 200 equiv. Lactide) showing slight hump at 90-110 °C, corresponding to PCHC block. Exo up.

1. M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem.-Int. Edit.*, 2009, **48**, 931-933.