Electronic Supplementary Information

Triarylsulfonium Hexafluorophosphate Salts as Photoactivated Acidic Catalysts for Ring-Opening Polymerisation

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Contents

Experimental *Page 3*

Figures

- **Figure S1**: Acid generation as a function of time of UV irradiation of **1** (0.033 g sample size). *Page 5*
- **Figure S2**: (a) Plot of monomer conversion against time and (b) M_n and $Đ_M$ against monomer conversion. ε-CL (■/▼), δ-VL (■/▼) and TMC (■/▼). Reaction conditions $[M]_0/[I]_0$ = 100, 0.66 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 6*
- **Figure S3**: SEC traces of samples of PVL taken at various levels of monomer conversion. Reaction conditions $[M]_0/[I]_0$ = 100, ambient temperature, 90 mins maximum UV irradiation time, (a) 0.66 mol% **1** with respect to monomer and (b) 0.33 mol% **1** with respect to monomer. *Page 7*
- **Figure S4**: SEC traces of samples of PTMC taken at various levels of monomer conversion. Reaction conditions $[M]_0/[I]_0$ = 100, ambient temperature, 90 mins maximum UV irradiation time, (a) 0.66 mol% **1** with respect to monomer and (b) 0.33 mol% **1** with respect to monomer. *Page 8*
- **Figure S5**: Monomer conversion against time (δ-VL (■), ε-CL (■) and TMC (■)) where reaction conditions were $[M]_0/[I]_0$ = 100, 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 9*
- **Figure S6**: Plot of M_n against $[M]_0/[I]_0$ for the ROP of (a) δ-VL, (b) ε-CL and (c) TMC using benzyl alcohol as an initiator. Reaction conditions were 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 10*
- **Figure S7**: MALDI-ToF MS analysis (reflectron mode) of low molecular weight (DP ≈ 20) (a) PVL, (b) PCL and (c) PTMC. Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 11*

- **Figure S8**: ^{1}H NMR spectrum of PVL in $CDCl_3$ (400 MHz, 298 K, * = $CDCl_3$). Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 12*

- **Figure S9:** Overlay of expanded ^{1}H NMR spectra (δ = 5.5 – 1.0 ppm) at various time points of the polymerisation of TMC (400 MHz, 298 K, * = propylene carbonate). Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time. *Page 13*

- **Figure S10**: Overlay of expanded ^{1}H NMR spectra (δ = 2.6 – 1.3 ppm) at various time points of the copolymerisation of L-LA and δ-VL (400 MHz, 298 K). Reaction conditions were $[\text{L-LA}]_0$:$[\delta\text{-VL}]_0$:$[\text{1,4-BD}]_0$:[DBU]:[**1**] = 100:100:1:0.2:0.9 in $CDCl_3$ where [L-LA] = [δ-VL] = 0.5 M. UV irradiation of the reaction occurred at 3 h into the reaction as marked. *Page 14*

- **Figure S11**: SEC trace of the isolated PLLA block (red, M_n ($Đ_M$) = 34 700 g mol^{-1} (1.05) and the subsequently isolated chain extended PVL-*b*-PLLA-*b*-PVL product (blue, M_n ($Đ_M$) = 47 400 g mol^{-1} (1.15)). *Page 15*

- **Figure S12**: Overlay of expanded ^{13}C NMR spectra (δ = 170 – 169 ppm) of isolated PLLA (blue) and PVL-*b*-PLLA-*b*-PVL (red) in $CDCl_3$. *Page 16*

- **Figure S13:** ^{13}C NMR spectra (δ = 220 – 0 ppm) of isolated PVL-*b*-PLLA-*b*-PVL (* = $CDCl_3$). *Page 17*

- **Figure S14:** Differential scanning calorimetric trace of PVL-*b*-PLLA-*b*-PVL. *Page 18*

Experimental

Chemicals

Unless otherwise stated, all chemicals were purchased from Sigma Aldrich and used as received with all transfers performed under an inert nitrogen atmosphere. δ-Valerolactone (δ-VL), ε-caprolactone (ε-CL), benzyl alcohol, propylene carbonate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,4-butanediol (1,4-BD) were freshly distilled into sealable ampoules from CaH_2 under an inert atmosphere. Trimethylene carbonate (TMC) was synthesised according to a literature method,[1] recrystallized three times from methylene chloride/diethyl ether, powdered in a pestle and mortar and subsequently dried over P_2O_5 in a vacuum desiccator for one week, in which the P_2O_5 was replaced every day. L-Lactide (L-LA, Purac) was first dissolved in methylene chloride, passed through a silica plug and then stirred over anhydrous $MgSO_4$. The solution was then filtered and the methylene chloride removed *in vacuo*. The resulting solid was taken up in hot toluene before evaporation to dryness *in vacuo* on a rotary evaporator. The resulting crystalline solid was then transferred to a Schlenk flask and dissolved in anhydrous hot toluene and the solvent was then removed *in vacuo* on a vacuum manifold. The crystalline white solid was then taken up in anhydrous methylene chloride and transferred by cannula onto activated 3 Å molecular sieves and left to stand for 24 h before being transferred for a second time onto fresh 3 Å sieves for a further 24 h. The methylene chloride/L-LA solution was then transferred to a Schlenk flask using a filter cannula and the methylene choride removed *in vacuo*. Finally, the resulting white solid was recrystallised from hot (70 °C) toluene and stored in a glove box at ambient temperature. Triarylsulfonium hexafluorophosphate salts (**1**, 50% in propylene carbonate, Sigma) were dried over three changes of activated 3 Å molecular sieves in the absence of light, each for 24 h per cycle and stored in a light proof glass container over 3 Å molecular sieves. For the purposes of calculation, it was assumed that the ratio of salts in the mixture was 1:1 and as such calculations regarding the quantities of **1** used an average molecular weight of 681 g mol^{-1}. Deuterated chloroform ($CDCl_3$) was purchased from Apollo Scientific Ltd and distilled from CaH_2 before use.

General Considerations

Unless otherwise stated, all manipulations were carried out in a nitrogen filled glovebox in darkness. Irradiation of samples was conducted in a Metalight QX1 light box equipped with 12 x 9 W bulbs with a peak output at 365 nm. Samples were typically placed 10 cm away from the source with the bulbs arranged concentrically around them. ^1H and ^{13}C NMR spectra were recorded on either a Bruker DPX-400, AC-400 or DRX-500 spectrometer at 298 K. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances ($CHCl_3$: ^1H $\delta = 7.26$ ppm; ^{13}C $\delta = 77.16$ ppm). Size exclusion chromatography (SEC) was conducted on a system composed of a Varian 390-LC-Multi detector suite fitted with differential refractive index, light scattering, and ultraviolet detectors equipped with a guard column (Varian Polymer Laboratories PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was $CHCl_3$ (HPLC grade) with 2% TEA at a flow rate of 1.0 mL min^{-1}. SEC samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(styrene) standards ($162 – 2.4 \times 10^5$ g mol^{-1}) using Cirrus v3.3 software. MALDI-ToF (matrix-assisted laser desorption ionization – time of flight) spectra were recorded using a Bruker Daltronics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with a positive ion ToF detection performed using an accelerating voltage of 25 kV. Samples were spotted onto a Bruker ground steel MALDI-ToF analytical plate through application of a small portion of a solution containing trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-

propylidene]malonitrile (DCTB) as a matrix (20 μL of a 10 mg mL^{-1} solution in THF), sodium trifluoroacetate as a cationization agent (5 μL of a 10 mg mL^{-1} solution in THF), and analyte (5 μL of a 10 mg mL^{-1} solution in THF) followed by solvent evaporation. The samples were measured in reflectron ion mode and calibrated by comparison to 2 x 10^3 poly(ethylene oxide) standards. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo Thermal Analysis DSC using pre-weighed aluminium pans. In a typical analysis, samples weighing between 2 – 4 mg were subjected to 4 cooling and heating cycles (-90 – 190 °C) at a rate of 10 °C min^{-1}. Analysis of the resulting data was conducted on the final heating cycle using the STARe (Mettler Toledo) software package.

Synthetic Methodology

Typical polymerisation procedure

In a glove box, δ-VL (122 μL, 1.3 x 10^{-3} mol, 50 eq.), **1** (5.95 mg 50% w/w solution (2.98 mg of **1**), 4.4 x 10^{-6} mol, 0.17 eq.), benzyl alcohol (2.8 μL, 2.6 x 10^{-5} mol, 1 eq.) and propylene carbonate (75 μL) were placed into a glass vessel and sealed. The resulting solution was then subjected to UV irradiation for a pre-determined length of time before being quenched by dilution in $CHCl_3$ (100 fold) and precipitated immediately into cold diethyl ether. The precipitate was isolated by filtration before being redissolved in $CHCl_3$ and precipitated a further two times into cold diethyl ether. Finally, the resulting white solid was dissolved in ethyl acetate and passed through a silica plug to remove residual triarylsulfonium hexafluorophosphate salts. Fractions were combined and evaporated to dryness (79 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.31 (m, 5H, $C_6\mathit{H}_5CH_2O$), 5.08 (s, 2H, $C_6H_5C\mathit{H}_2O$), 4.05 (t, 2H, $(C(O)(CH_2)_3C\mathit{H}_2O)_n$), 3.61 (t, 2H, $(C(O)(CH_2)_4O)_nC(O)(CH_2)_3C\mathit{H}_2OH$), 3.36 (t, 1H, $(C(O)(CH_2)_4O)_nC(O)(CH_2)_4O\mathit{H}$), 2.36 (m, 2H, $(C(O)(CH_2)_4O)_nC(O)C\mathit{H}_2(CH_2)_3OH$), 2.32 (t, 2H, $(C(O)C\mathit{H}_2(CH_2)_3O)_n$), 1.65 (m, 4H, $(C(O)CH_2(C\mathit{H}_2)_2CH_2O)_n$), 1.39 (m, 2H, $(C(O)(CH_2)_4O)_nC(O)(CH_2)_2C\mathit{H}_2CH_2OH$), 1.20 (m, 2H, $(C(O)(CH_2)_4O)_nC(O)CH_2C\mathit{H}_2(CH_2)_2OH$). ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ = 173.3, 128.6, 1.28.2, 66.3, 63.9, 62.2, 34.0, 32.1, 28.1, 21.5.

Typical 'one pot' block copolymer polymerisation procedure

In a glove box, δ-VL (46.4 μL, 5.0 x 10^{-4} mol, 100 eq.), L-LA (72 mg, 5.0 x 10^{-4} mol, 100 eq.), 1,4-BD (0.44 μL, 5.0 x 10^{-6} mol, 1 eq.), DBU (0.15 μL, 2.5 x 10^{-7} mol, 0.2 eq.) and **1** (5.95 mg 50% w/w solution (2.98 mg of **1**), 4.4 x 10^{-6} mol, 0.9 eq.) were combined in $CDCl_3$ (0.5 mL) in an NMR tube. The level of monomer conversion was observed by ^{1}H NMR spectroscopic analysis. After 3 h, complete consumption (>98%) of L-LA was observed. The reaction vessel was subjected to UV light (1.5 h). Conversion of δ-VL was monitored by ^{1}H NMR spectroscopic analysis until approximately 70% monomer conversion. The reaction solution was then diluted with chloroform (100 fold) and precipitated into cold diethtyl ether. The precipitate was collected *via* filtration and re-precipitated into cold diethyl ether from chloroform a further two times. The precipitate was then collected *via* filtration, dissolved in ethyl acetate and passed through a silica plug to remove residual triarylsulfonium hexafluorophosphate salts. Fractions were combined and evaporated to dryness (71 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 5.16 (q, 1H, $OC\mathit{H}(CH_3)C(O)$), 4.15 (m, 4H, $OC\mathit{H}_2(CH_2)_2C\mathit{H}_2O$), 4.08 (t, 2H, $C(O)(CH_2)_3C\mathit{H}_2O)_n$), 2.34 (t, 2H, $C(O)C\mathit{H}_2(CH_2)_3O)_n$), 1.68 (m, 4H, $C(O)CH_2(C\mathit{H}_2)_2CH_2O)_n$), 1.58 (d, 3H, $OCH(C\mathit{H}_3)C(O)$). ^{13}C NMR (125 MHz $CDCl_3$, ppm): δ = 173.4, 169.7, 69.1, 64.1, 33.8, 28.2, 21.6, 16.8.

Figures

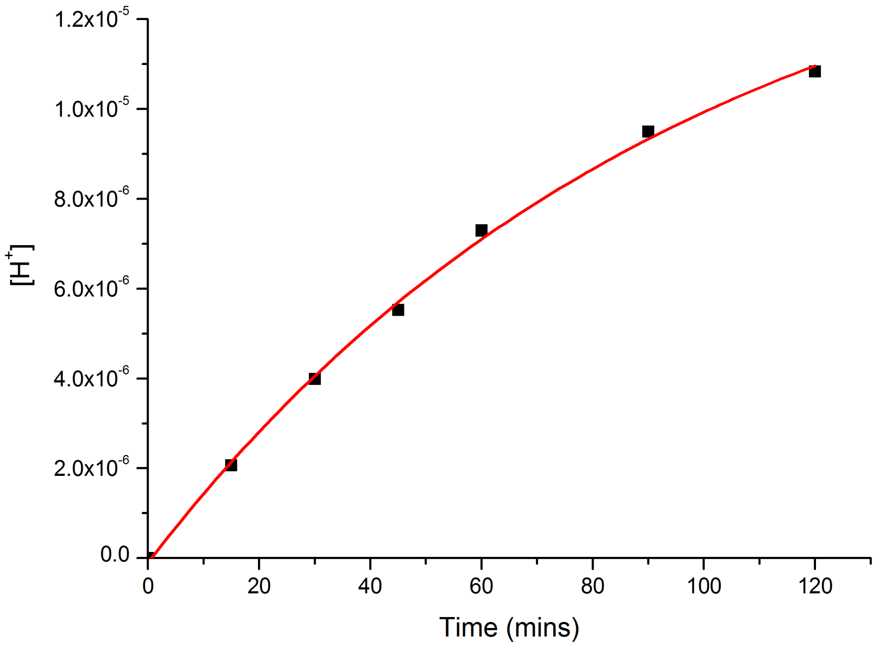

Fig. S1 Acid generation as a function of time of UV irradiation of **1** (0.033 g sample size).

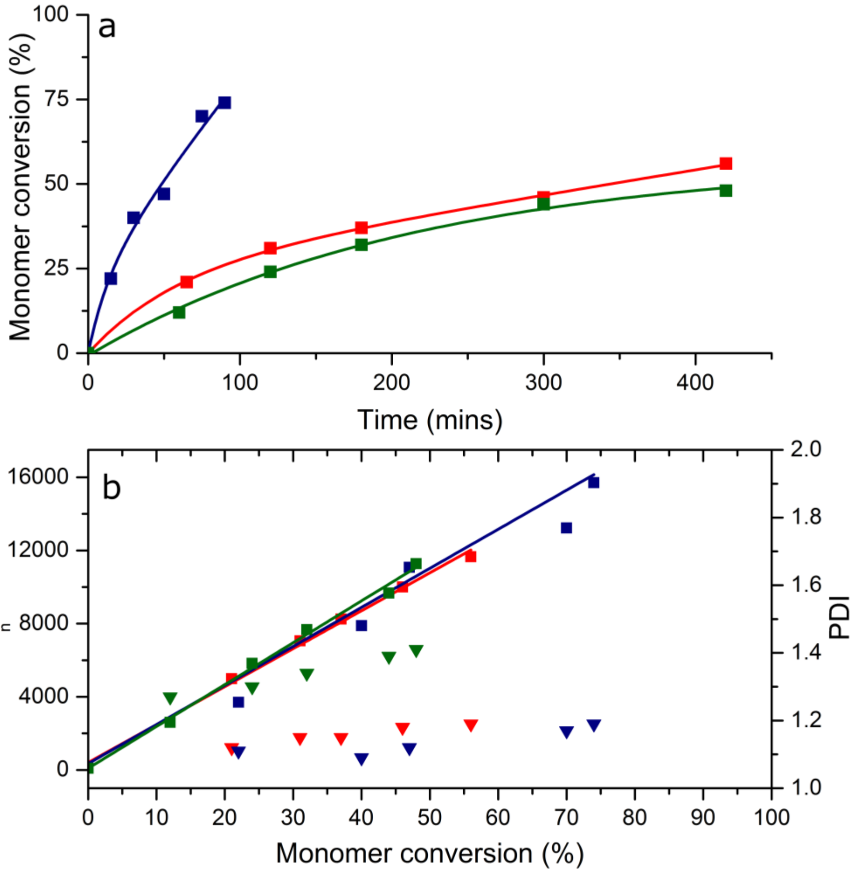

Fig. S2 Plot of (a) monomer conversion against time and (b) M_n and $Đ_M$ against monomer conversion. ε-CL (🟥/▼), δ-VL (🟦/▼) and TMC (🟩/▼). Reaction conditions $[M]_0/[I]_0 = 100$, 0.66 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

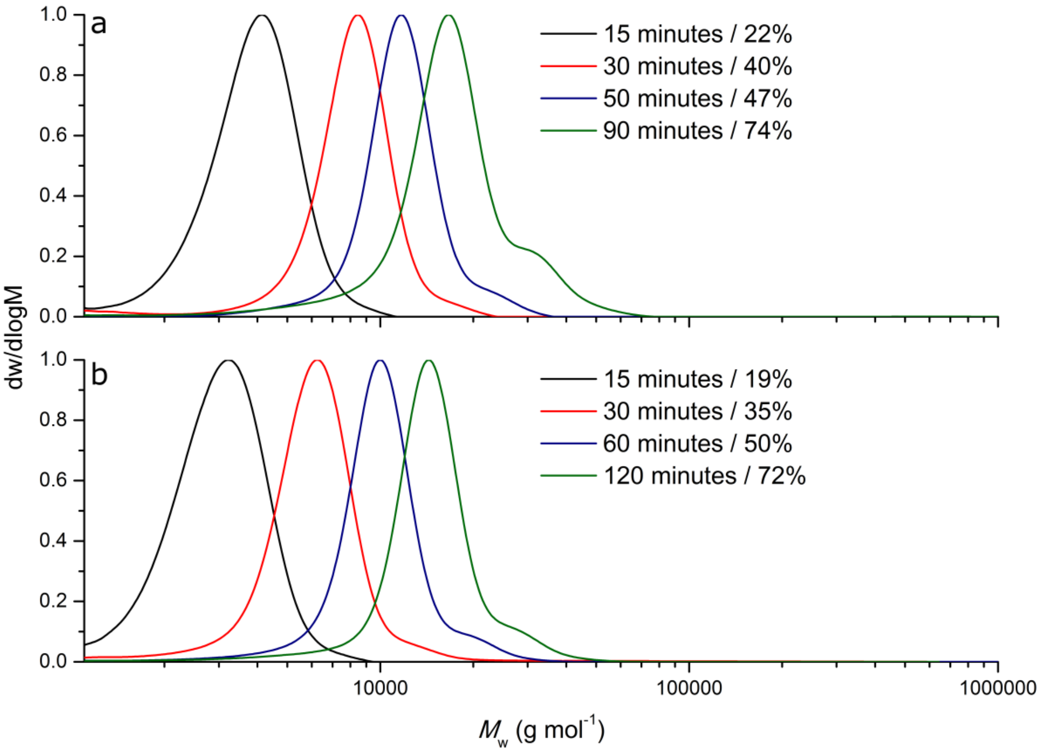

Fig. S3 SEC traces of samples of PVL taken at various levels of monomer conversion. Reaction conditions $[M]_0/[I]_0 = 100$, ambient temperature, 90 mins maximum UV irradiation time, (a) 0.66 mol% **1** with respect to monomer and (b) 0.33 mol% **1** with respect to monomer.

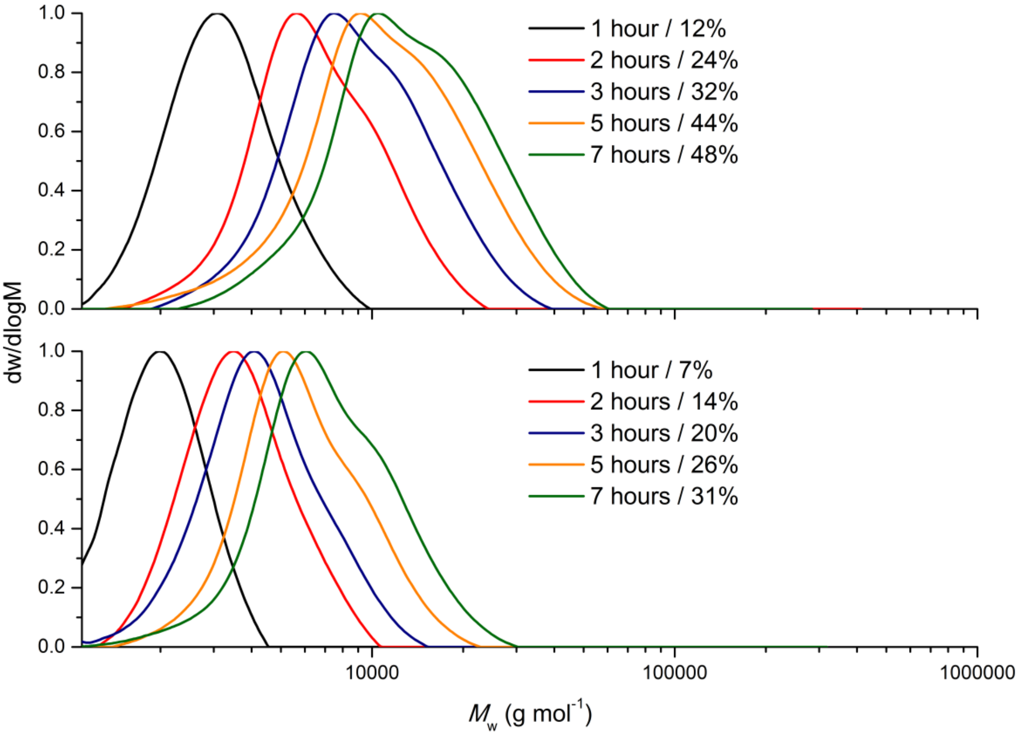

Fig. S4 SEC traces of samples of PTMC taken at various levels of monomer conversion. Reaction conditions $[M]_0/[I]_0$ = 100, ambient temperature, 90 mins maximum UV irradiation time, (a) 0.66 mol% **1** with respect to monomer and (b) 0.33 mol% **1** with respect to monomer.

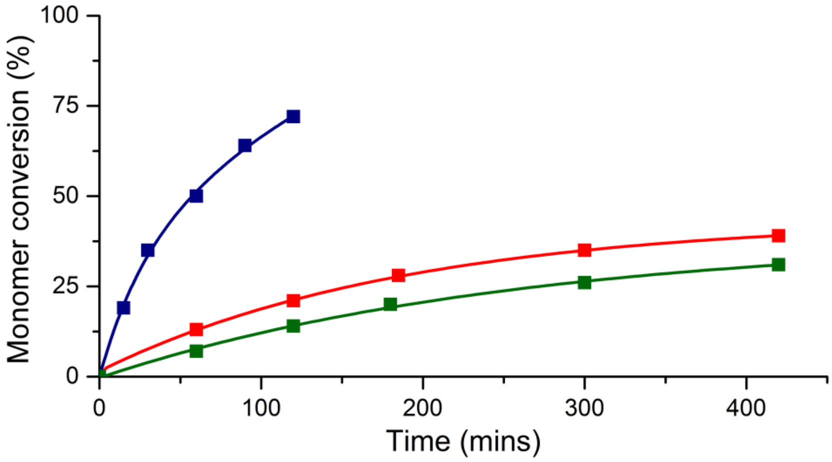

Fig. S5 Monomer conversion against time (δ-VL (🟦), ε-CL (🟥) and TMC (🟩)) where reaction conditions were $[M]_0/[I]_0$ = 100, 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

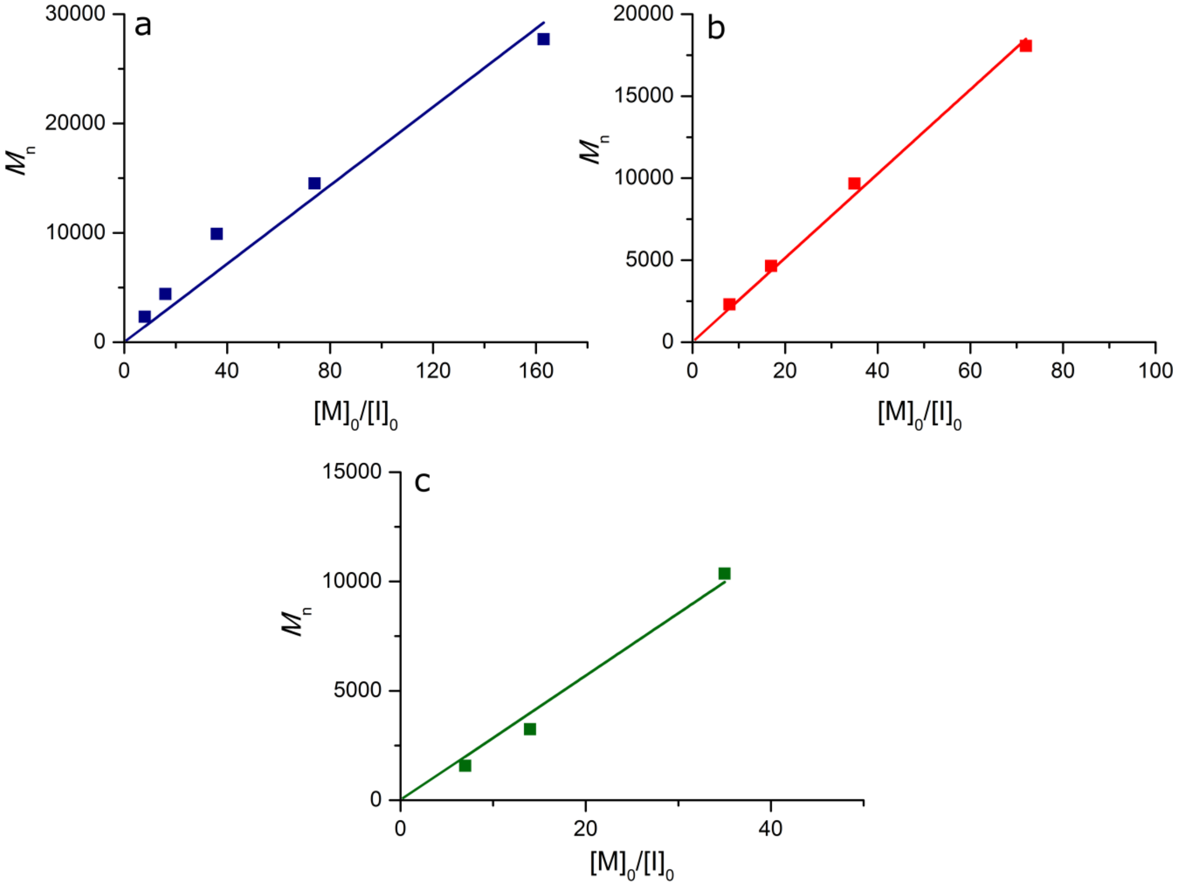

Figure S6: Plot of M_n against $[M]_0/[I]_0$ for the ROP of (a) δ-VL, (b) ε-CL and (c) TMC using benzyl alcohol as an initiator. Reaction conditions were 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

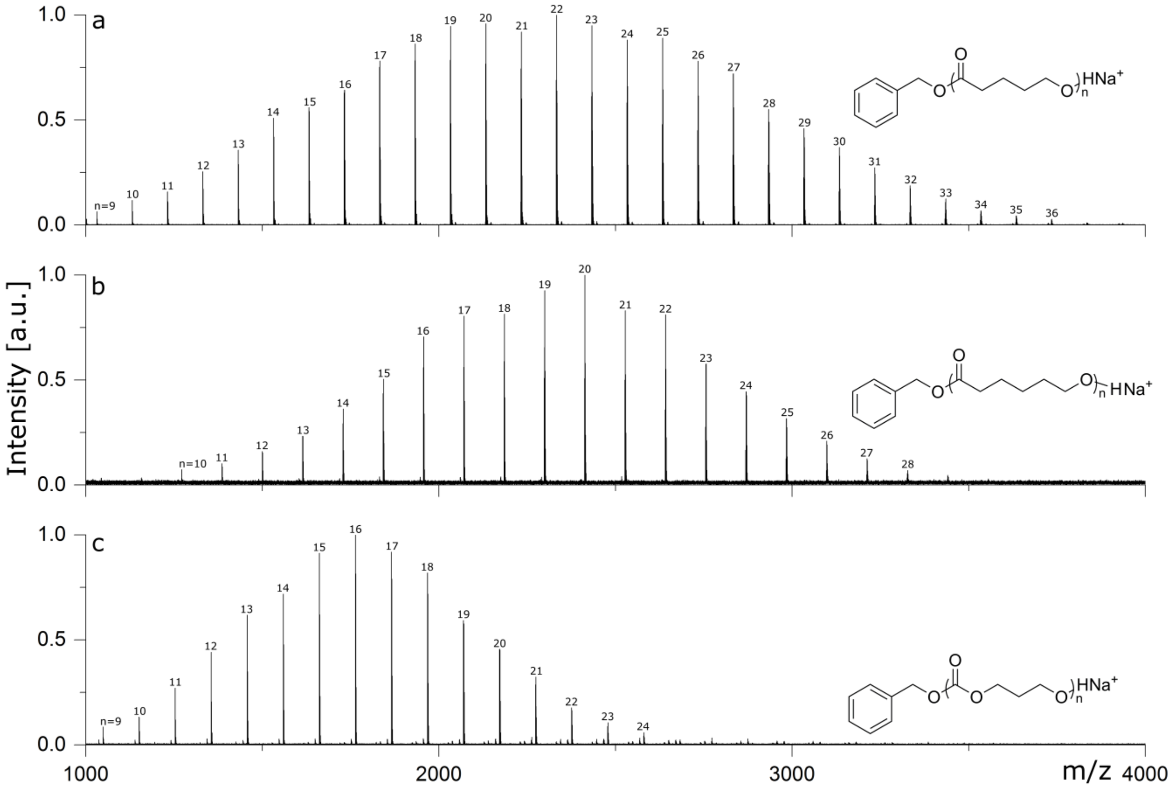

Fig. S7 MALDI-ToF MS analysis (reflectron mode) of low molecular weight (DP ≈ 20) (a) PVL, (b) PCL and (c) PTMC. Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

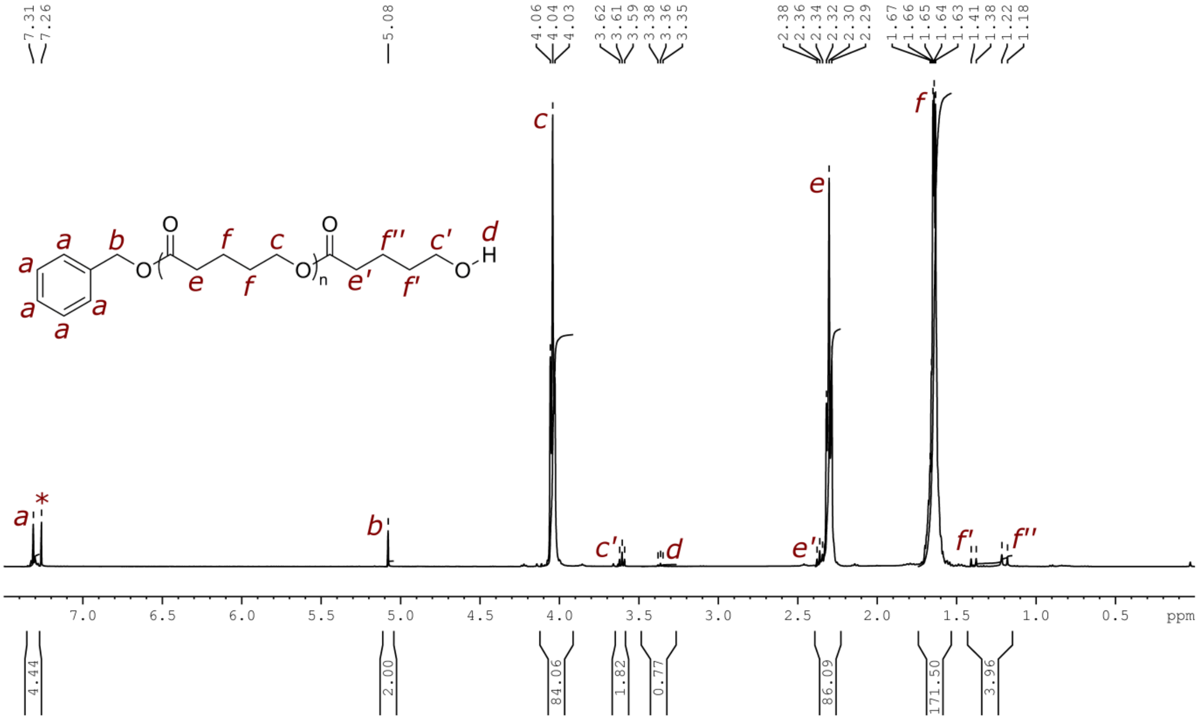

Fig. S8 ^{1}H NMR spectrum of PVL in $CDCl_3$ (400 MHz, 298 K, * = $CDCl_3$). Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

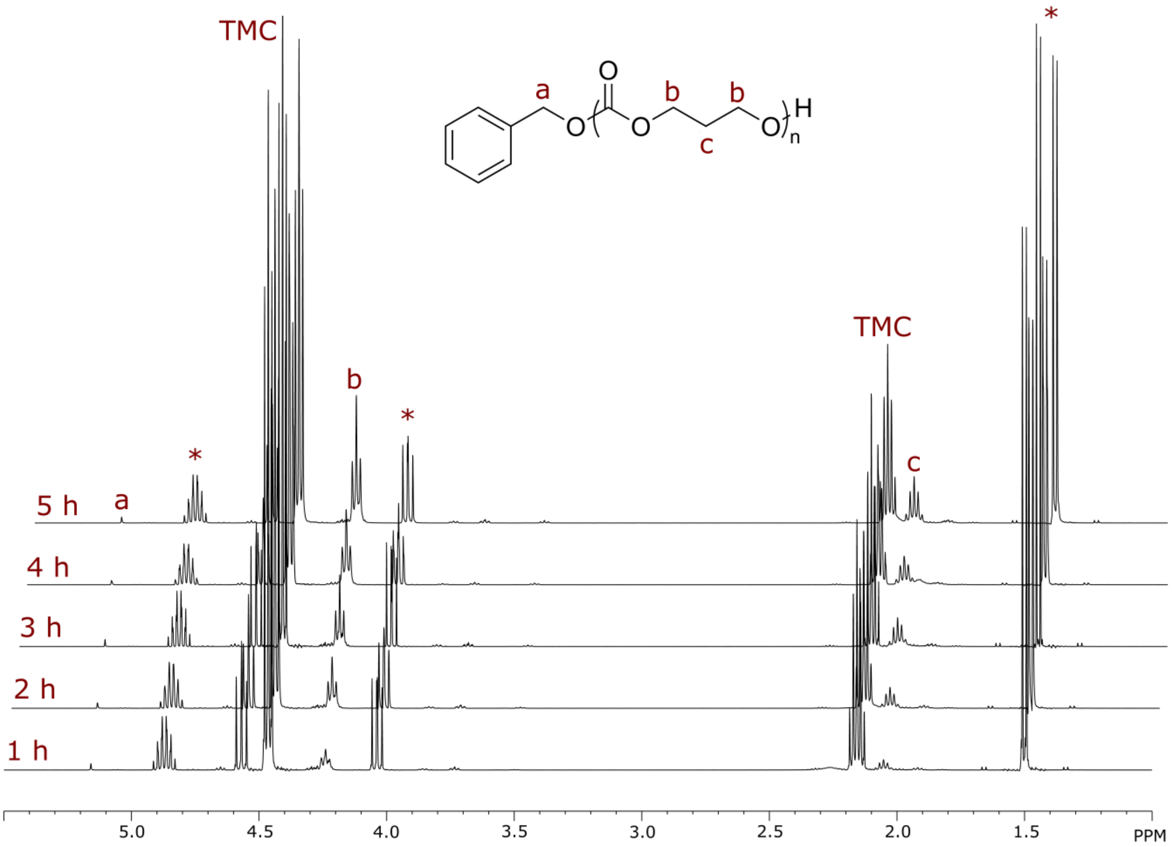

Fig. S9 Overlay of expanded ^{1}H NMR spectra (δ = 5.5 – 1.0 ppm) at various time points of the polymerisation of TMC (400 MHz, 298 K, * = propylene carbonate). Reaction conditions: 0.33 mol% **1** with respect to monomer, ambient temperature, 90 mins maximum UV irradiation time.

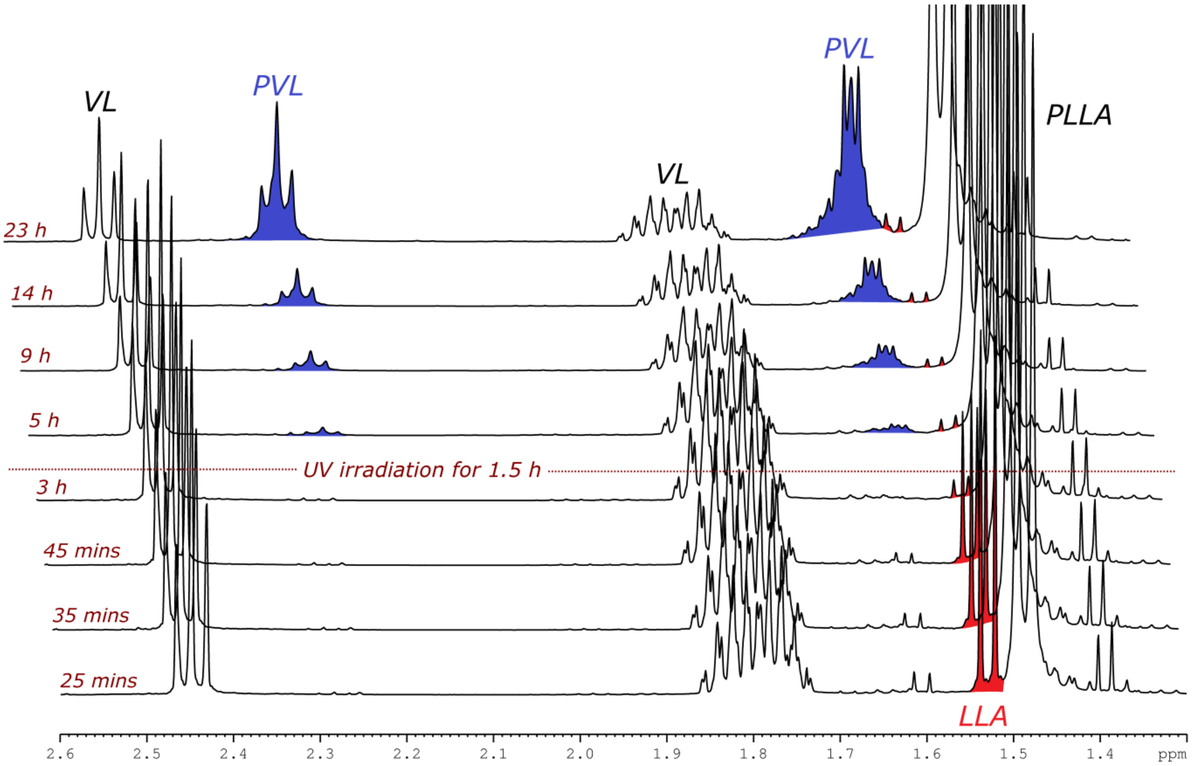

Fig. S10 Overlay of expanded ^{1}H NMR spectra (δ = 2.6 – 1.3 ppm) at various time points of the copolymerisation of L-LA and δ-VL (400 MHz, 298 K). Reaction conditions were [L-LA]$_0$:[δ-VL]$_0$:[1,4-BD]$_0$:[DBU]:[**1**] = 100:100:1:0.2:0.9 in $CDCl_3$ where [L-LA] = [δ-VL] = 0.5 M. UV irradiation of the reaction occurred at 3 h into the reaction as marked.

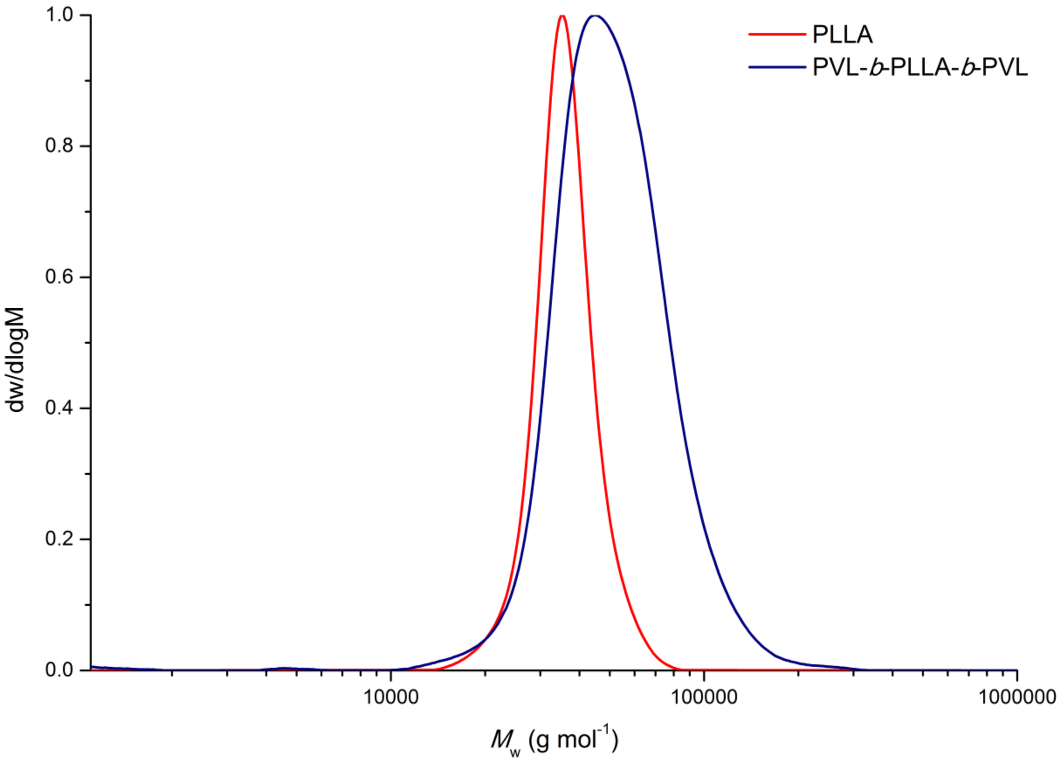

Fig. S11 SEC trace of the isolated PLLA block (red, M_n ($Đ_M$) = 34 700 g mol^{-1} (1.05) and the subsequently isolated chain extended PVL-*b*-PLLA-*b*-PVL product (blue, M_n ($Đ_M$) = 47 400 g mol^{-1} (1.15)).

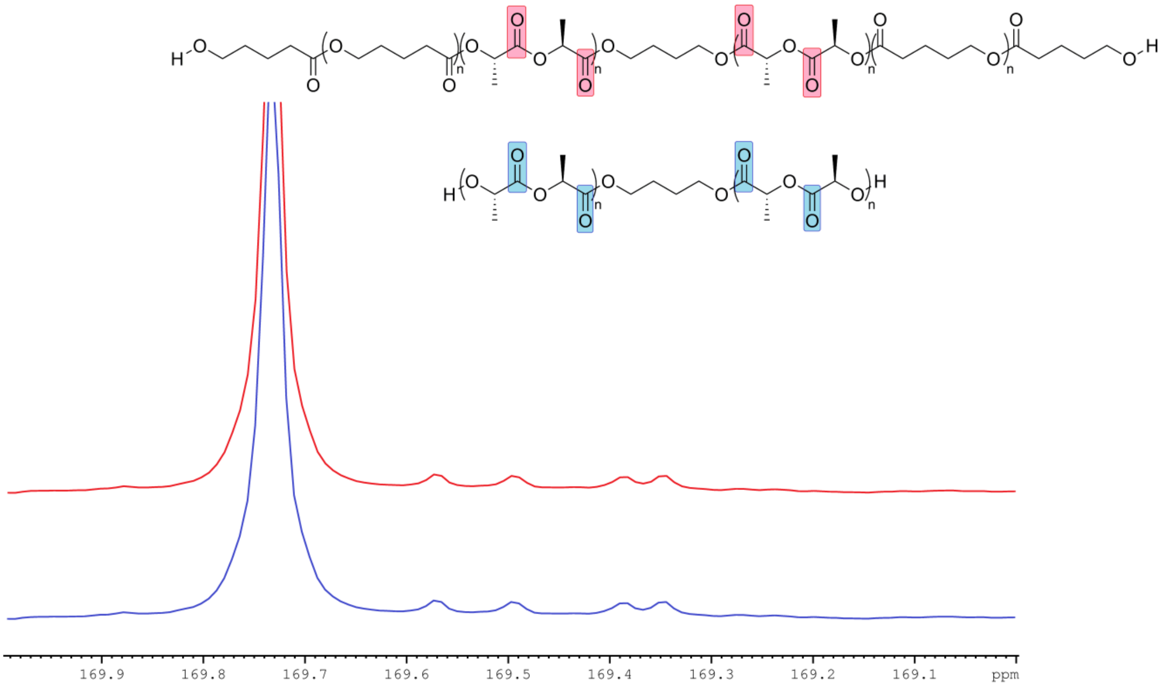

Fig. S12 Overlay of expanded ^{13}C NMR spectra (δ = 170 – 169 ppm) of isolated PLLA (blue) and PVL-*b*-PLLA-*b*-PVL (red) in $CDCl_3$.

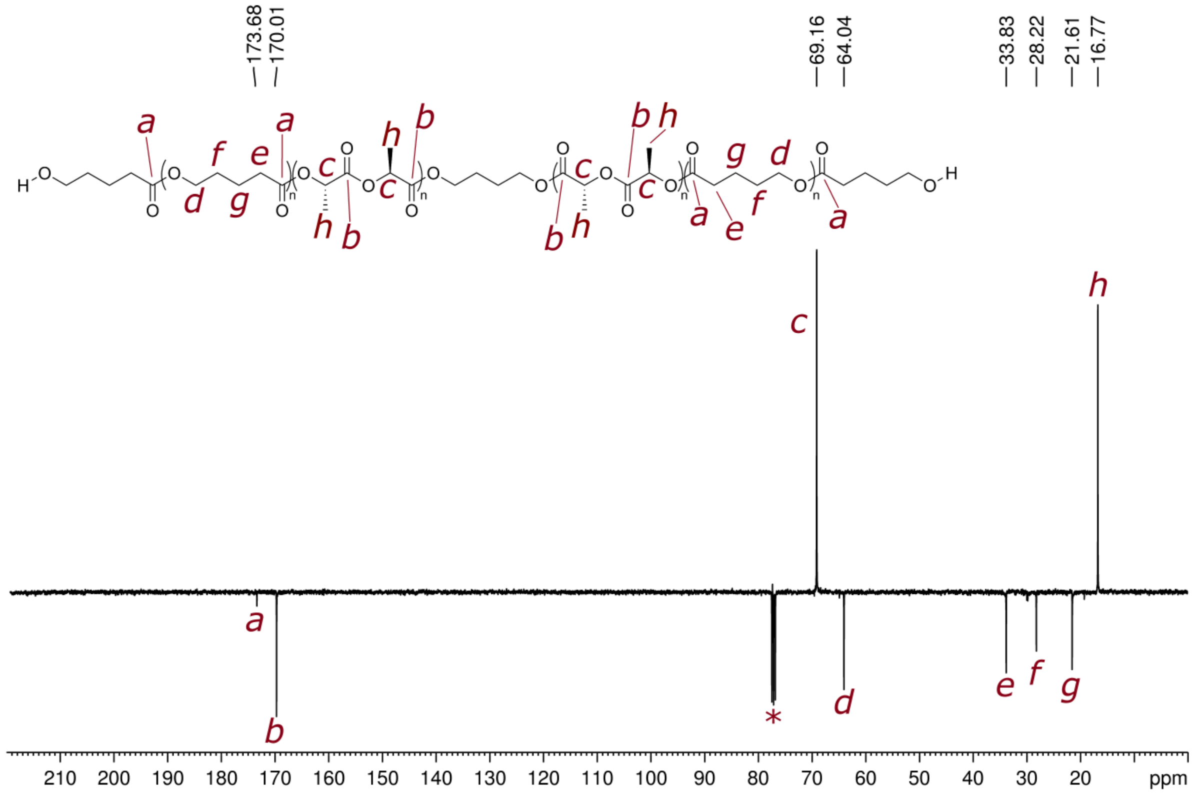

Fig. S13 ^{13}C NMR spectra ($\delta = 220 – 0$ ppm) of isolated PVL-*b*-PLLA-*b*-PVL (* = $CDCl_3$).

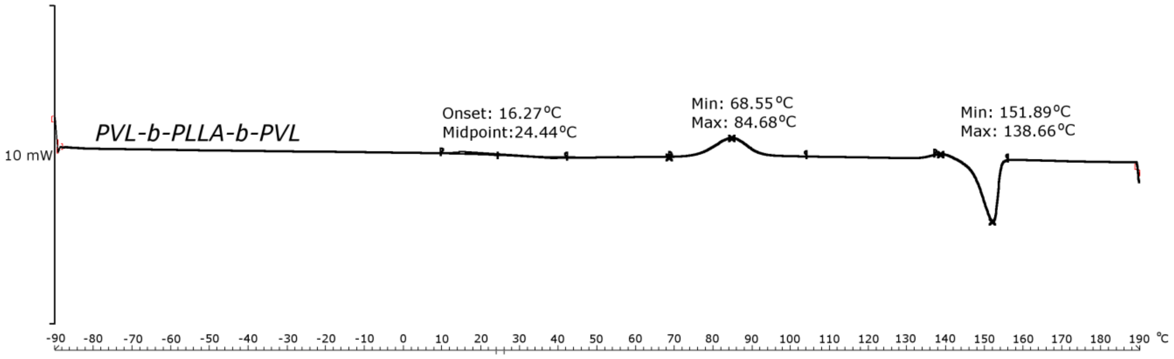

Fig. S14 Differential scanning calorimetric trace of PVL-*b*-PLLA-*b*-PVL.

References

1. T. F. Al-Azemi, H. H. Dib, N. A. Al-Awadi and O. M. E. El-Dusouqui, *Tetrahedron*, 2008, **64**, 4126-4134.