Electronic Supplementary Information

Photoinduced ring-opening polymerisation of L-lactide *via* a photocaged superbase

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Experimental Part

Materials

All chemicals and solvents, unless otherwise stated, were purchased from Sigma-Aldrich or Fisher Scientific and used without further purification. 1,1,3,3-Tetramethylguanidine, δ-valerolactone, ε-caprolactone and benzyl alcohol were dried over CaH_2, distilled and stored under an inert atmosphere. $CDCl_3$ (Apollo Scientific) was dried over activated 4 Å molecular sieves and left to stand for 24 h before being transferred onto fresh 4 Å sieves and stand for further 24 h. 2-(Nitrophenyl)propoxycarbonyl-1,1,3,3-tetramethylguanidine was prepared as previously reported[1] and dried over P_2O_5 in a vacuum desiccator for one week, in which P_2O_5 was replaced every day. L-Lactide (Purac) was dissolved in CH_2Cl_2 and passed through a silica plug. The solution was transferred to a Schlenk flask and concentrated under vacuum. The resulting solid was recrystallised twice from dry hot toluene (70 °C), sublimed and stored in a glove box. 1-(3,5-Bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU) was synthesised as previously reported[2] and dried over CaH_2 in dry tetrahydrofuran (THF). Dry solvents were obtained by purification over an Innovative Technology SPS alumina solvent column and degassed by repeated freeze-pump-thaw cycles prior to use.

General Considerations

Unless otherwise stated, all polymerisations were performed under an inert nitrogen atmosphere in a glovebox in the dark. Irradiation of samples was conducted in a Metalight QX1 light box equipped with 12 x 9 W bulbs ranging from 320 to 400 nm, with a peak output at 365 nm. Samples were typically placed 10 cm away from the source with the bulbs arranged concentrically around them. ^{1}H NMR spectra were recorded on Bruker AV III HD-300 or AV III HD-500 MHz spectrometers at 298 K. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the residual solvent signal ($CDCl_3$: ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.2 ppm). Matrix-assisted laser desorption ionisation-time of flight mass spectrometry (MALDI-ToF/ MS) analysis was performed on a Bruker Autoflex Speed mass spectrometer using a nitrogen laser delivering 2 ns pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. *Trans*-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) was used as a matrix (a 40 g L^{-1} solution in THF), with sodium trifluoroacetate (NaTFA) used as a cationic agent (10 g L^{-1} solution in THF). Analyte (1 g L^{-1} solution in THF) was mixed with the DCTB and NaTFA solutions (20 μL of each) and applied to form a thin matrix-analyte film. All samples were measured in reflectron mode and calibrated against a 3000 to 8000 g mol^{-1} poly(ethylene glycol) standard. Size exclusion chromatography (SEC) was conducted on systems 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% Et_3N at a flow rate of 1 mL min^{-1}. SEC samples were calibrated against either Varian Polymer Laboratories Easi-Vials linear polystyrene standards (162 – 2.4 × 105 g mol^{-1}) ($CHCl_3$) using Cirrus v3.3 software.

General polymerisation procedure using TMG

L-LA (173 mg, 1.20 mmol) was dissolved in dry $CDCl_3$ (567 μL). A solution of the benzyl alcohol initiator (26.0 μL of a 100 g L^{-1} solution in $CDCl_3$, 24.0 μmol) was added to the monomer solution, followed by TMG (6.9 μL of a 200 g L^{-1} solution in $CDCl_3$, 12.0 μmol).

The reaction solution was transferred to a NMR tube and monitored by ^{1}H NMR spectroscopy. The polymerisation was quenched after 2.5 h by the addition acid Amberlyst and purified by precipitation in hexanes (1 ×) and methanol (2 ×) to yield PLLA as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 7.34 (m, $C_6H_5CH_2O$), 5.16 (q, ^{3}J = 7.0 Hz, O(CO)C*H*CH_3), 4.35 (m, O(CO)C*H*OH), 1.57 (d, ^{3}J = 7.0 Hz, O(CO)CHC*H*$_3$), 1.50 (m, O(CO)CH(C*H*$_3$)OH). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) 169.7 (O(*C*O)CHCH$_3$, 69.2 (O(CO)*C*HCH$_3$), 16.8 O(CO)CH*C*H$_3$.

General polymerisation procedure using NPPOC-TMG and UV light

L-LA (173 mg, 1.20 mmol) was dissolved in dry $CDCl_3$ (509 µL). A solution of the benzyl alcohol initiator (52.0 µL of a 50 g L^{-1} solution in $CDCl_3$, 24.0 µmol) was added to the monomer solution, followed by NPPOC-TMG (38.7 µL of a 100 g L^{-1} solution in $CDCl_3$, 12.0 µmol). The reaction solution was transferred to a NMR tube and sealed. The solution was then subjected to UV irradiation for 15 minutes and monitored by ^{1}H NMR spectroscopy. The polymerisation was quenched after 3 h by the addition acid Amberlyst and purified by precipitation in hexanes (1 ×) and methanol (2 ×) to yield PLLA as a white powder.

Figures and Table

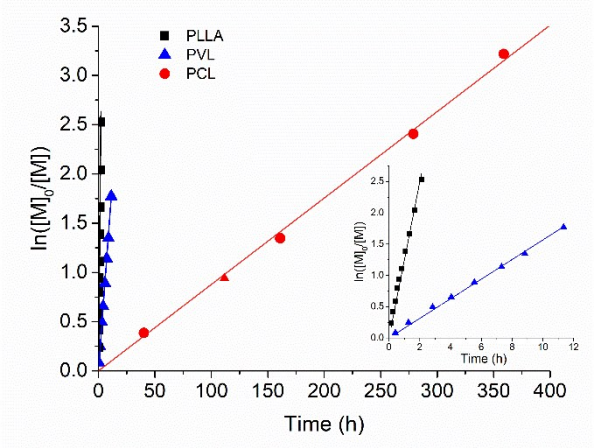

Fig. S1 Plots of ln of initial monomer concentration by monomer concentration (ln([M]$_0$/[M])) against time for the ROP of L-LA (■, [L-LA]$_0$/[BnOH]$_0$/[TMG]$_0$ = 50/1/0.5), δ-VL(▲, ([δ-VL]$_0$/[BnOH]$_0$/[TMG]$_0$/[TU]$_0$ = 30/1/1.5/1.5), and ε-CL (●, [ε-CL]$_0$/[BnOH]$_0$/[TMG]$_0$/[TU]$_0$ = 25/1/1.25/1.25).

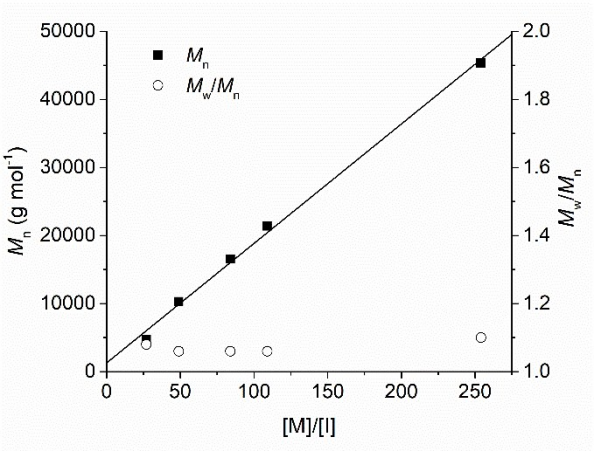

Fig. S2 Number-average molecular weight (M_n; ■) and dispersity ($Đ_M = M_w/M_n$; ○) against monomer-to-initiator concentration ratio ([M]/[I]) for the ROP of L-LA.

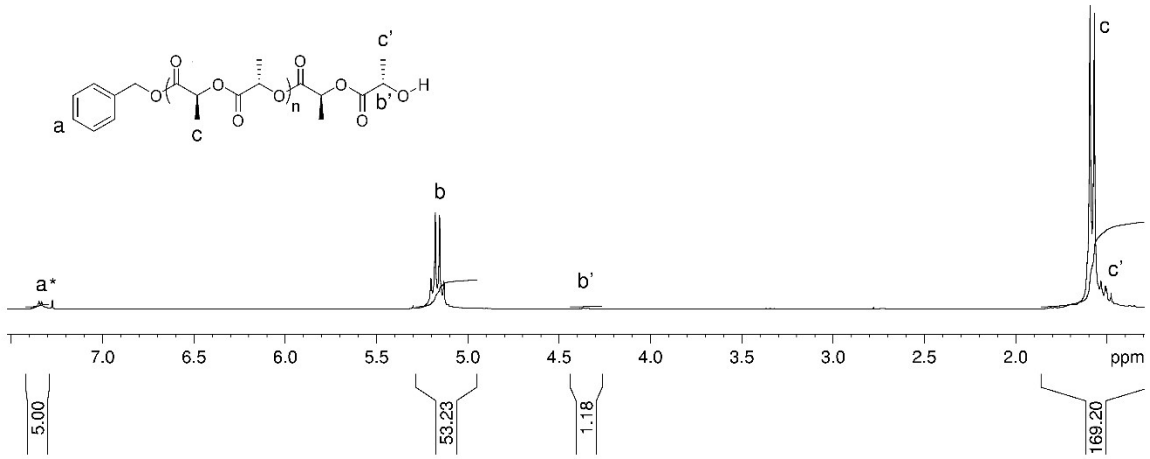

Fig. S3 ^{1}H NMR spectrum of PLLA ($CDCl_3$, 300 MHz, 298 K, * = residual $CHCl_3$). Reaction conditions: [L-LA]$_0$/[BnOH]$_0$/[TMG]$_0$ = 30/1/0.3.

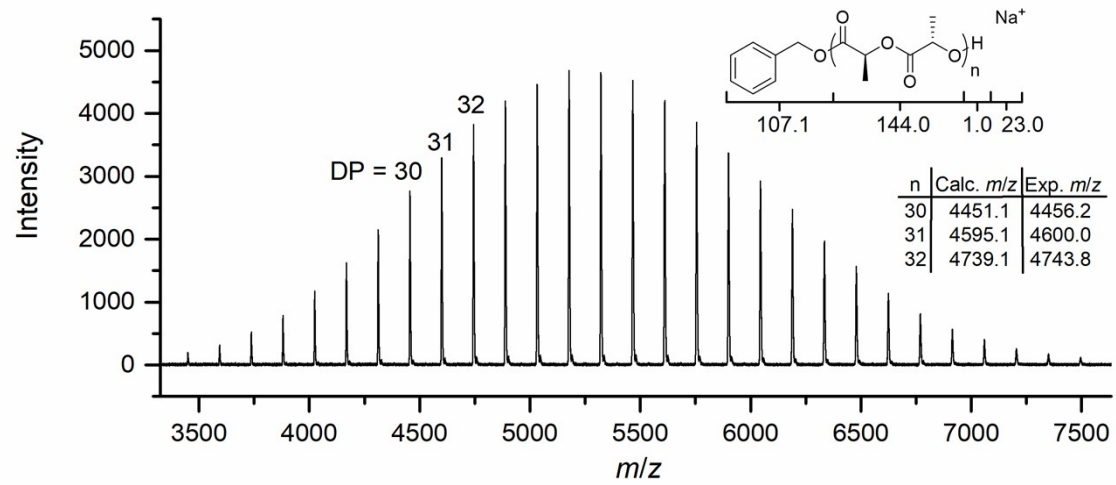

Fig. S4 MALDI-ToF MS spectrum of PLLA. Reaction conditions: [L-LA]$_0$/[BnOH]$_0$/[TMG]$_0$ = 50/1/0.5.

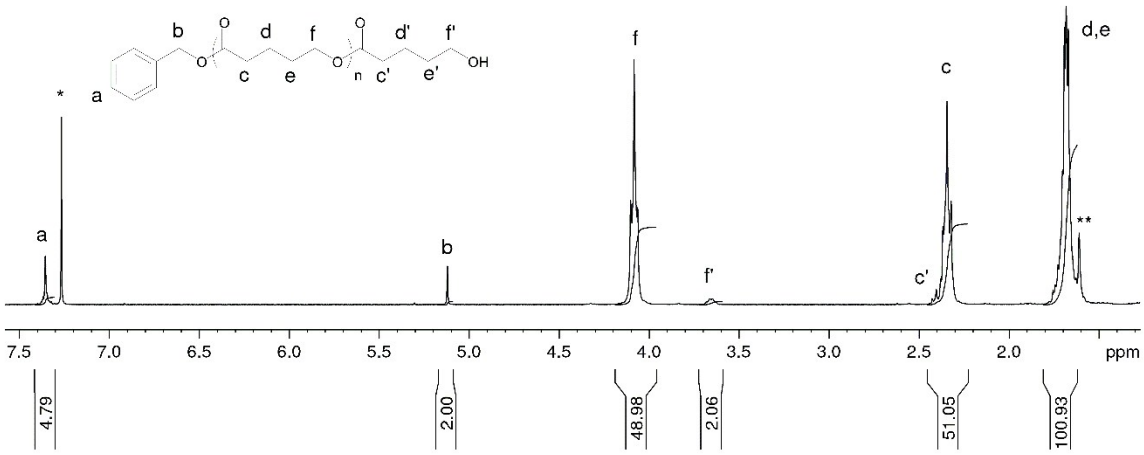

Fig. S5 ^{1}H NMR spectrum of PVL ($CDCl_3$, 300 MHz, 298 K, * = residual $CHCl_3$, ** = residual H_2O). Reaction conditions: $[\delta\text{-VL}]_0/[\text{BnOH}]_0/[\text{TMG}]_0/[\text{TU}]_0$ = 30/1/1.5/1.5.

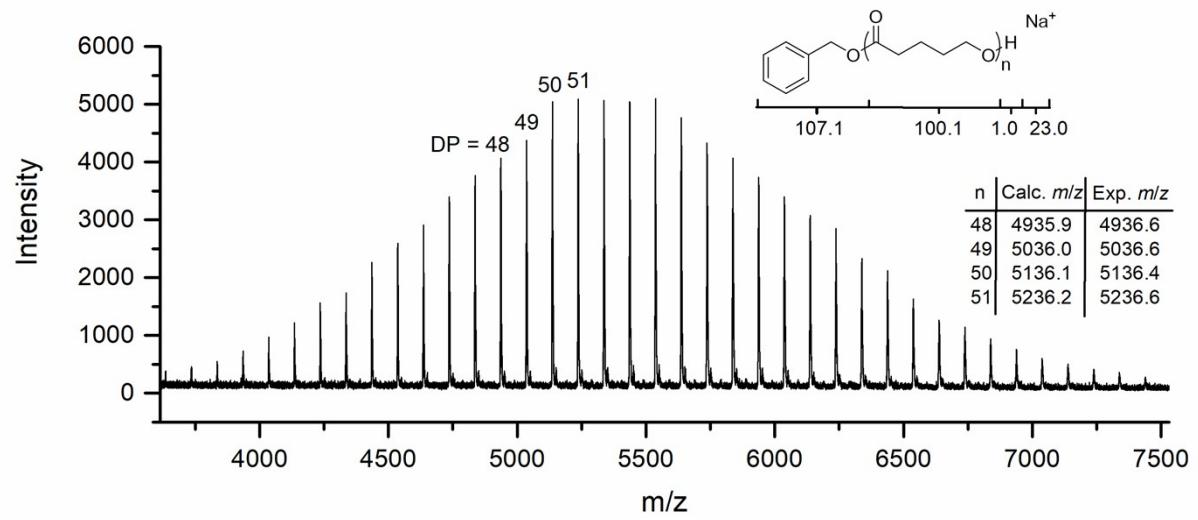

Fig. S6 MALDI-ToF MS spectrum of PVL. Reaction conditions: $[\delta\text{-VL}]_0/[\text{BnOH}]_0/[\text{TMG}]_0/[\text{TU}]_0$ = 55/1/2.8/2.8.

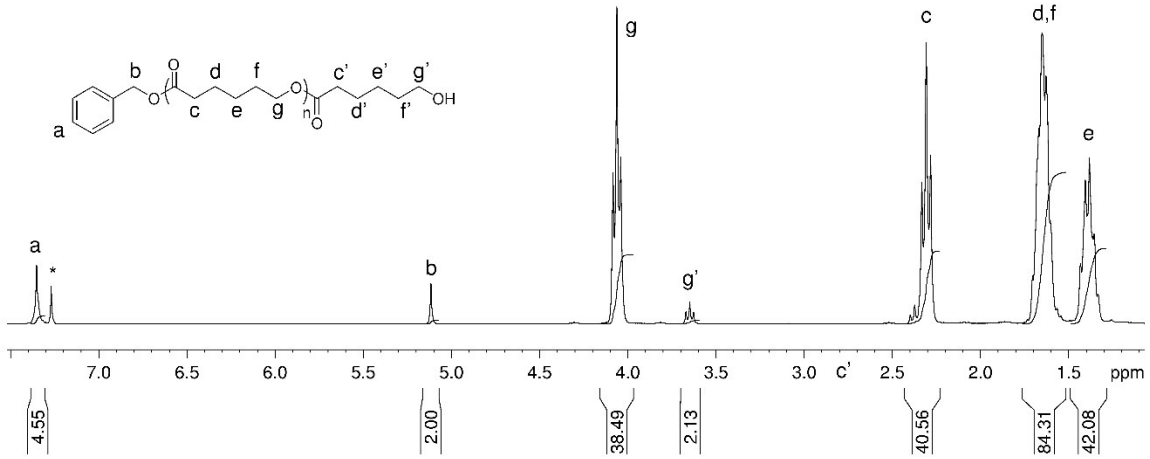

Fig. S7 ^{1}H NMR spectrum of PCL ($CDCl_3$, 300 MHz, 298 K, * = residual $CHCl_3$). Reaction conditions: $[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{TMG}]_0/[\text{TU}]_0$ = 25/1/1.25/1.25).

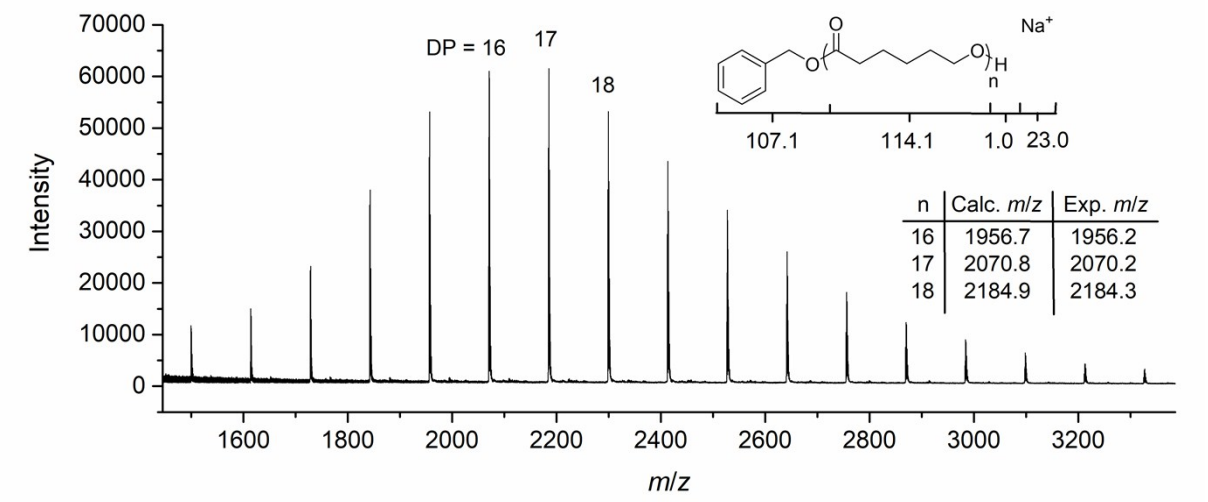

Fig. S8 MALDI-ToF MS spectrum of PVL. Reaction conditions: $[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{TMG}]_0/[\text{TU}]_0$ = 25/1/1.25/1.25).

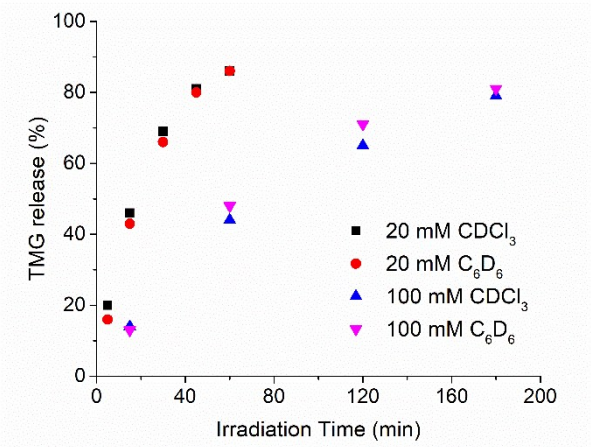

Fig. S9 Photolysis of NPPOC-TMG under 320-400 nm UV irradiation.

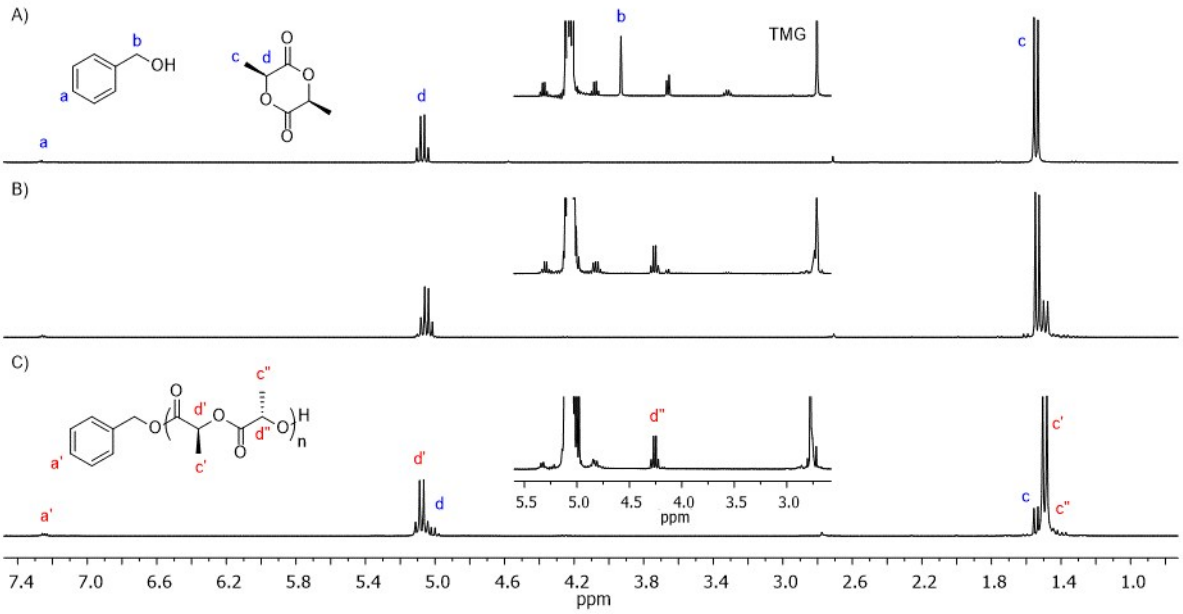

Fig. S10 ^{1}H NMR spectra of polymeric solution of L-LA in the presence of NPPOC-TMG before A) before and B) after 320−400 nm irradiation for 15 minutes and C) further 175 minutes in the absence of light ($CDCl_3$, 300 MHz, 298 K).

Table S1 Monomer conversion and molecular weight of PLLA prepared by irradiating the polymeric solutions containing NPPOC-TMG that were initially kept in the dark over 1, 2, 5 and 9 days.

Day	Monomer Conversion[a] (%)	M_n[b] (kg mol^{-1})	$Đ_M$[b]
1	90	9.9	1.05
2	90	10.0	1.05
5	91	10.0	1.05
9	91	10.3	1.06

[a] Determined by ^{1}H NMR spectroscopy. [b] Obtained from SEC analysis in $CHCl_3$, calibrated against polystyrene standards.

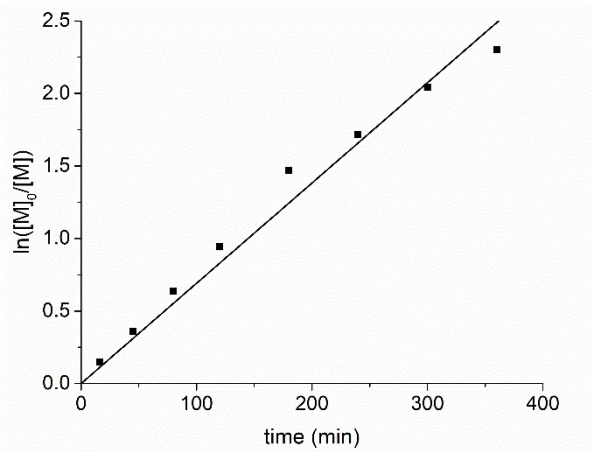

Fig. S11 Plots of ln of initial monomer concentration by monomer concentration ($\ln([M]_0/[M])$) against time for the ROP of L-LA ($[L\text{-LA}]_0/[BnOH]_0/[NPPOC\text{-}TMG]_0$ = 100/1/1, 15 minutes under 320-400 nm irradiation).

References

1. W. Xi, H. Peng, A. Aguirre-Soto, C. J. Kloxin, J. W. Stansbury and C. N. Bowman, *Macromolecules*, 2014, **47**, 6159.
2. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 7863.