Supporting Information

RAFT solution polymerisation of bio-based γ-methyl-α-methylene-γ-butyrolactone monomer in DMSO and Cyrene

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Experimental details

Materials

All reagents were used as received. γ-methyl-α-methylene-γ-butyrolactone (γMeMBL, 97%) was obtained from TCI. 2-Cyano-2-propyl benzodithioate (CPBD, >97%), 4-cyanopentanoic acid dithiobenzoate (CPADB), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%), 4,4′-azobis(4-cyanovaleric acid) (ACVA, ≥98%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%) and Cyrene (≥ 98.5%) were purchased from Merck. DMSO (99+%), t-butanol (99.5%) and chloroform-d (CDCl$_3$, 99.8 atom% D) were purchased from ThermoScientific. THF (99%, stabilised with 250-350 ppm BHT) was obtained from Alfa Aesar and Methanol (99.6%) was purchased from Honeywell.

RAFT Solution Polymerisation of γMeMBL

Details of a typical experiment are given, exemplified here targeting the synthesis of P(γMeMBL)$_{100}$ in DMSO at 70 °C, using CPDB and AIBN as the CTA and initiator, respectively.

AIBN (2.9 mg, 0.018 mmol), CPDB (19.7 mg, 0.089 mmol) and γMeMBL (1.00 g, 8.918 mmol) were weighed into a round bottom flask and DMSO (1.54 g) was added to give a final solids content of 40% w/w. The reaction vessel was sealed and degassed with N$_2$ for 20 minutes. Following degassing the reaction vessel was sealed and placed into an oil bath 70 °C. After 24 h the reaction mixture was removed from the oil bath, exposed to the air and allowed to cool to room temperature. A sample was removed for ^{1}H NMR spectroscopy to determine conversion and for GPC analysis to determine molecular weight and dispersity. Polymers were purified by first diluting the mixture with THF to approximately 20% w/w solids then precipitating twice into methanol. Pure P(γMeMBL) polymers were obtained as fine, pink coloured powders.

For kinetic evaluation, a small sample (<0.1 mL) was extracted from the reaction mixture at specific time intervals using a degassed syringe while under a flow of N$_2$. For all RAFT screening experiments (see Table S1) a solids content of 40% w/w was maintained in all cases.

When targeting different degrees of polymerisation, the amount of CPDB and AIBN were varied, while maintaining a final solids content of 40% w/w.

Polymerisations in Cyrene were conducted under identical reaction conditions, except that Cyrene was used as the solvent instead of DMSO. Generally crude reaction mixtures had high viscosities when high conversions were obtained, more so for Cyrene than DMSO due to the increased viscosity of Cyrene, compared with DMSO. Kinetic evaluation of the polymerisation of γMeMBL in Cyrene was conducted concurrently in separate vials for each time point due to issues with sampling due to high solution viscosities. Polymerisations were stopped at pre-determined time points by removing from the oil bath and exposing to air and diluting for ^{1}H NMR and GPC analyses.

Characterisation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a JEOL ECS 400 MHz spectrometer at 21 °C on sample dissolved in CDCl$_3$. Spectra were processed using Delta 5.3.1 software.

Gel permeation chromatography (GPC) analysis was performed using an Agilent 1260 Infinity GPC system, equipped with both refractive index and UV detectors, with chloroform eluent containing 2% v/v triethylamine. Samples were injected at a flow rate of 1.0 mL/min through a guard column, followed by two separation columns (Agilent PL gel 5 μm Mixed-C) at 40 °C. All samples were prepared to an approximate concentration of 5 mg/mL. The system was calibrated using near-monodisperse poly(styrene) standards (M_p ranging from 162 to 364,000 g mol^{-1}). Chromatograms were analysed using Agilent GPC/SEC software.

Differential scanning calorimetry (DSC) was performed using TA Instruments Q2000 DSC under an N$_2$ atmosphere. A heat-cool-heat program between 0 and 250 °C (10 °C min^{-1} ramp) was performed, with glass transition temperatures (T_g) recorded from the second heat cycle. Analysis of results was performed

using TA Instruments Universal Analysis software. Glass transition temperatures (T_g) were determined using the half height method.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 550 using platinum crucibles over a temperature range of 30 to 700 °C, at a heating rate of 10 °C min^{-1} under an argon atmosphere. Analysis of results was performed using TA Instruments Trios software and the onset of degradation was determined using the software from the inflection point.

Supplementary figures and tables

Table S1. Reaction conditions, conversions and molecular weight data (M_n, M_w, $Đ$) obtained from initial screening of the RAFT solution polymerisation of γMeMBL, targeting a degree of polymerisation of 100, conducted at 70 °C for 24 h.

Entry	Solvent	CTA	Initiator	CTA/In	Conv [a] (%)	$M_{n\ th}$ [b] (g mol⁻¹)	M_n [c] (g mol⁻¹)	M_w [c] (g mol⁻¹)	$Đ$ [c]
1	MeOH	CPDB	AIBN	5	>99	5800	6000	11300	1.88
2	*t*-butanol	CPDB	AIBN	5	98	5700	3900	20600	5.27
3	DMSO	CPDB	AIBN	5	95	5600	7900	10000	1.26
4	Cyrene	CPDB	AIBN	5	78	4600	7100	9400	1.32
5	DMSO	CPDB	ACVA	5	90	5300	6500	9000	1.37
6	DMSO	CPADB	AIBN	5	86	5100	5500	7600	1.32
7	DMSO	CPDT	AIBN	5	97	5800	6100	8600	1.41
8	DMSO	CPDB	AIBN	10	89	5200	7500	9400	1.25
9	DMSO	CPDB	AIBN	2.5	>99	5800	8000	10300	1.27

[a] Conversion determined by ¹H NMR Spectroscopy. [b] Theoretical M_n ($M_{n\ th}$) calculated as follows: $M_{n\ th} = ((M_{w\ mon} \times$ target DP) $\times$ (Conv/100)) + $M_{w\ CTA}$. [c] Determined by CHCl₃ GPC analyses.
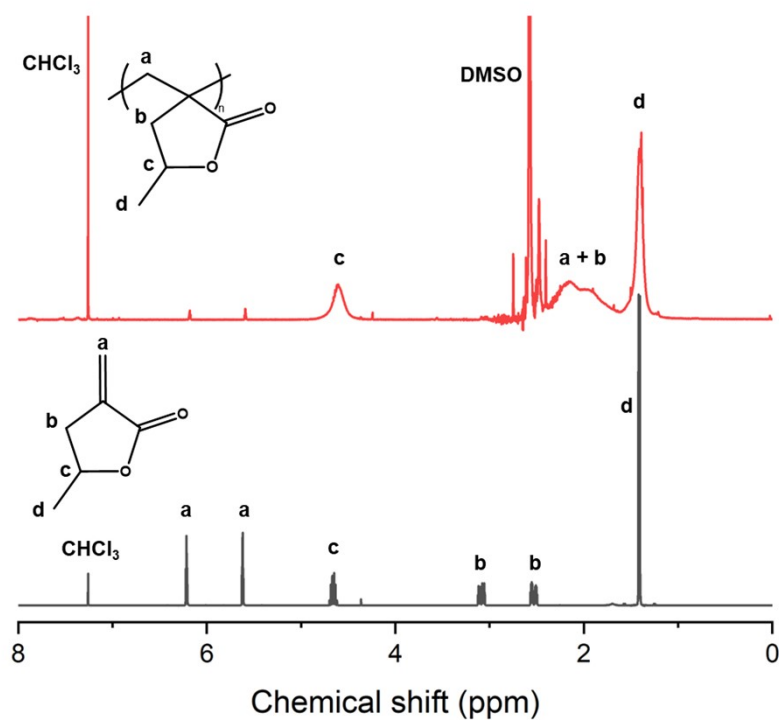

Figure S1. Assigned ¹H NMR (400 MHz, d_6-DMSO) spectra for the γMeMBL monomer (bottom) and the resulting P(γMeMBL) polymer after conducting RAFT solution polymerisation in DMSO for 24 h.
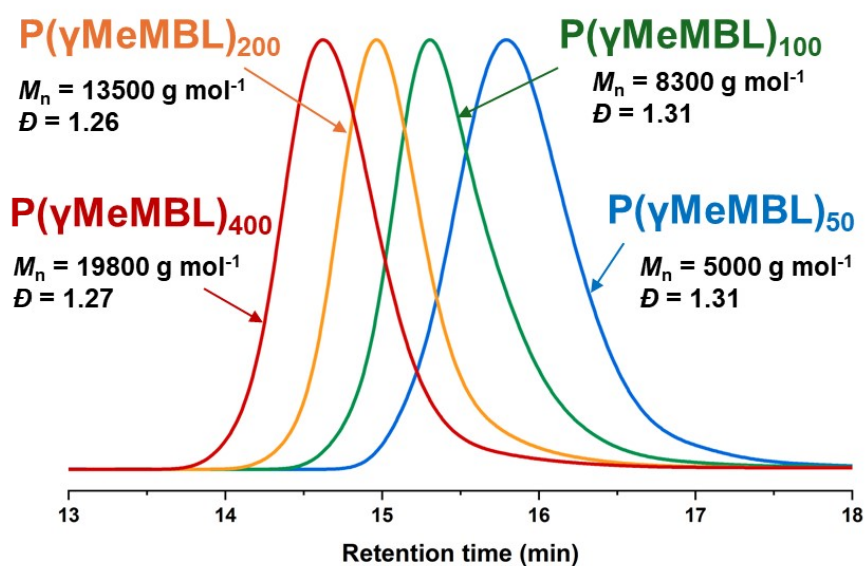
Figure S2. Normalised overlaid GPC chromatograms for P(γMeMBL)$_x$ synthesised by RAFT solution polymerisation of γMeMBL in DMSO at 70 °C for 24 h, using CPDB.
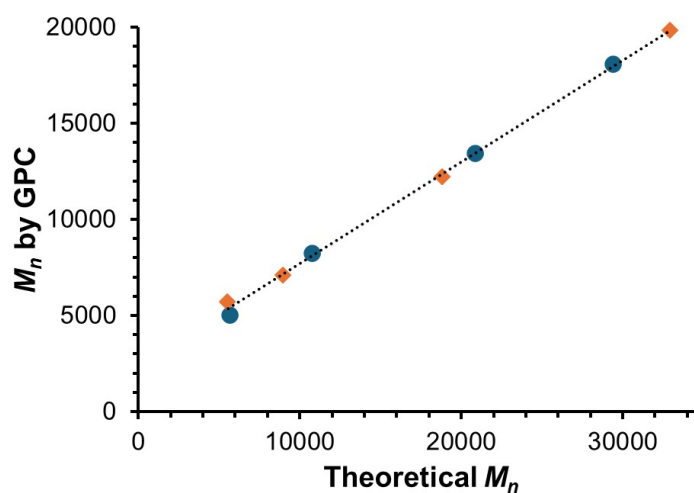

Figure S3. M_n determined by GPC analyses versus theoretical M_n for P(γMeMBL)$_x$ synthesised by RAFT solution polymerisation of polymerisation of γMeMBL in DMSO (orange diamonds) and Cyrene (blue circles) at 70 °C for 24 h, using CPDB.
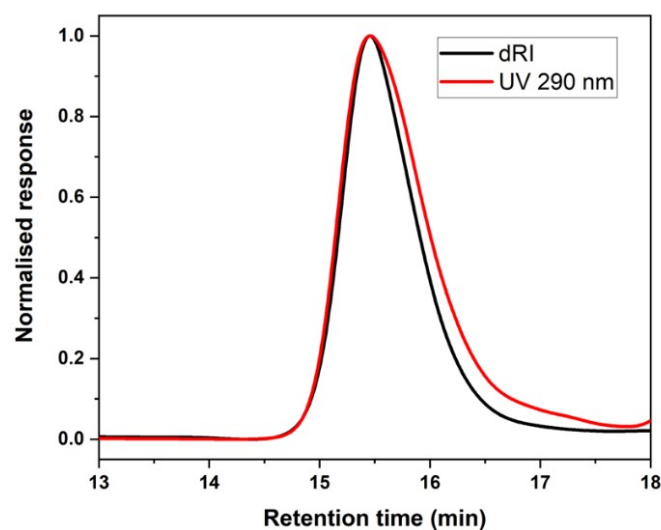
Figure S4. GPC data for P(γMeMBL)$_{100}$ synthesised in Cyrene, showing both the normalised differential refractive index (dRI) and UV (collected at 290 nm) detector responses. The data is representative of all P(γMeMBL) samples synthesised in this work.

Table S2. Conversions and molecular weight data (M_n, M_w, $Đ$) obtained the synthesis of P(γMeMBL)$_{50}$ and subsequent chain extension of the macro-RAFT with an additional 50 units of γMeMBL. Reactions were conducted at 70 °C for 24 h in DMSO using a CTA/initiator ratio of 5.

Target Composition	CTA	Monomer/CTA	Conv [a] (%)	$M_{n\ th}$ [b] (g mol^{-1})	M_n [c] (g mol^{-1})	M_w [c] (g mol^{-1})	$Đ$ [c]
P(γMeMBL)$_{50}$	CPDB	50	>99	5800	5200	6700	1.29
P(γMeMBL)$_{100}$	P(γMeMBL)$_{50}$	50	96	11200	12200	17700	1.45

[a] Conversion determined by ^{1}H NMR Spectroscopy. [b] Theoretical M_n ($M_{n\ th}$) calculated as follows: $M_{n\ th}$ = ((M$_{w\ mon}$ x target DP) x (Conv/100)) + M$_{w\ CTA}$. [c] Determined by CHCl$_3$ GPC analyses.
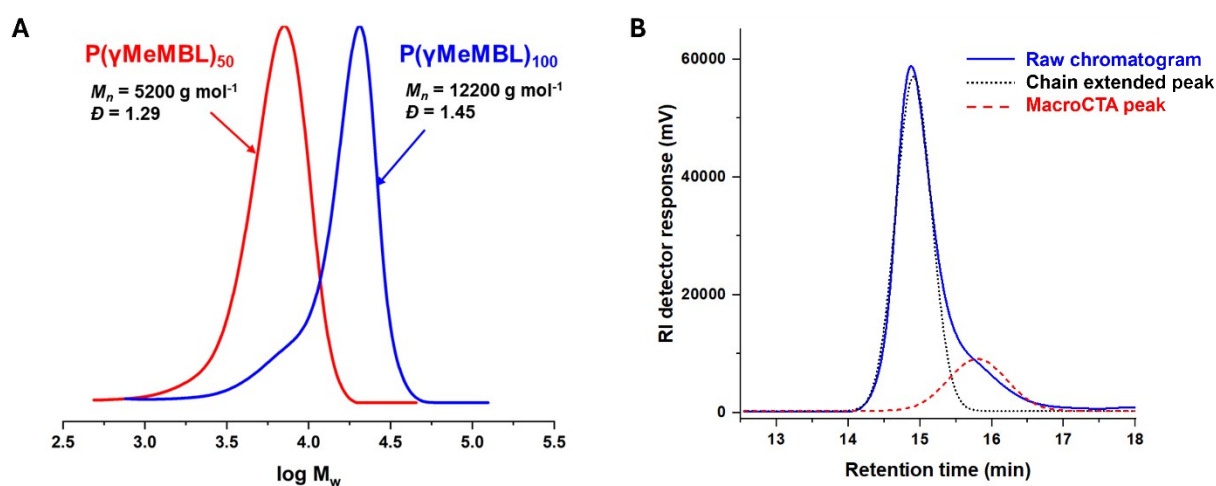

Figure S5. A) Normalised molecular weight distributions, obtained via GPC, for P(γMeMBL)$_{50}$ synthesised in DMSO (red) and the subsequent P(γMeMBL)$_{100}$ (blue) synthesised using the previous polymer as a macro-CTA and growing a target of 50 additional monomer units. B) Deconvolution of the P(γMeMBL)$_{100}$ GPC chromatogram, showing the raw RI detector response (blue solid line), deconvoluted peaks for the chain extended P(γMeMBL)$_{100}$ (dotted black line) and deconvoluted P(γMeMBL)$_{50}$ macroCTA peak (red dashed line). The ratio of the chain extended P(γMeMBL)$_{100}$:P(γMeMBL)$_{50}$ macroCTA was 0.8:0.2 determined by the area of peak.

Table S3. Thermal characterisation data, T_g and onset of thermal degradation, for P(γMeMBL)$_x$ synthesised in Cyrene at 70 °C for 24 h.

Target Composition	T_g [a] (°C)	Onset of thermal degradation [b] (°C)
P(γMeMBL)$_{50}$	206	345
P(γMeMBL)$_{100}$	210	354
P(γMeMBL)$_{200}$	218	362
P(γMeMBL)$_{400}$	221	366

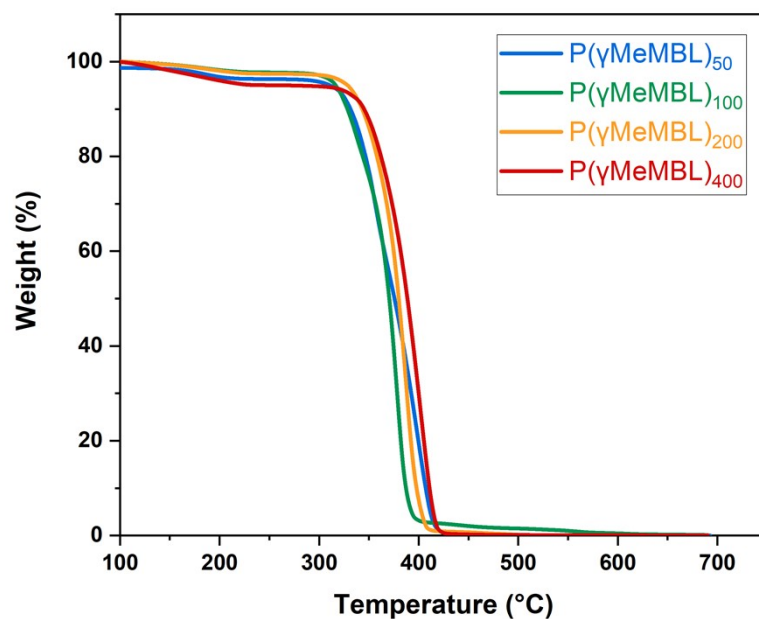*[a] Determined by DSC analyses. [b] Determined by TGA.*

Figure S6. TGA profiles for P(γMeMBL) of various molecular weights synthesised by RAFT solution polymerisation in Cyrene.