Supporting Information

Sustainable Synthesis and Precise Characterisation of Bio-based Star Polycaprolactone Synthesised with a Metal Catalyst and with Lipase

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Instrumentation and characterisation techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance spectrometer operating at 400 MHz in deuterated chloroform ($CDCl_3$). The chemicals shifts are given in part per million (ppm) and were referenced to the peak of residual $CHCl_3$ at δ = 7.26 ppm. Multiplicities are given as triplets (t) and multiplets (m). The number, length and molecular weight of the arms of star *D*-sorbitol PCL were quantified by ^{31}P NMR spectroscopy after phosphitylation of the terminal hydroxy and carboxy groups. A stock solution was prepared by dissolving Chromium (III) acetylacetonate [$Cr(acac)_3$] (11.9 mM, 25 mg) and cyclohexanol (17.7 mM, 10.6 mg, internal standard) in 6 ml pyridine : $CDCl_3$ (3:1 volume ratio). Known amounts of samples were dissolved in the stock solution (600 µl), thus including 10.62 µmoles of internal standard (n_{IS}) in each sample. The samples were vortexed until a clear purple solution was obtained. Subsequently, the phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP) (60 µl) was added dropwise, and the samples were left to react on a mechanical shaker at ambient temperature for 60 minutes. Inverse gated decoupled ^{1}H-^{31}P NMR spectra were recorded on a Bruker Avance III at 162 MHz for ^{31}P using $CDCl_3$ as a

locking solvent with an elongated acquisition time (60 min), a 90° pulse angle, 30 s delay time, and 128 scans. The chemical shifts were referenced to δ = 132.20 ppm (H_2O + Cl-TMDP adduct). ^{31}P NMR spectra without ^{1}H-^{31}P decoupling were also recorded to investigate the multiplicity and chemical shifts corresponding to the derivatised functional groups (*e.g.* triplet for primary or doublet for secondary hydroxy groups).

Size exclusion chromatography-multi-angle light scattering (SEC-MALS). SEC measurements were performed on a ^{SEC}Agilent 1260 Infinity triple detection SEC comprising a Wyatt Optilab multi-angle light scattering (MALS) detector, an Agilent differential refractometer (RI). Separation was achieved using 2 PLgel mixed D columns (7.5 mm x 50 mm). The eluent was tetrahydrofuran (THF) at room temperature at a flow rate of 1 ml min^{-1}. The refractive index increment (*dn/dc*) of star *D*-sorbitol PCL was determined using a representative sample, star *D*-sorbitol-$[(PCL)_{9.7}$-$OH]_{5.1}$ (Table 1, Entry 3). Five different concentrations of star *D*-sorbitol-$[(PCL)_{9.7}$-$OH]_{5.1}$ in THF were injected and the resulting RI signals were plotted as a function of concentration. The dn/dc value of 0.074 ± 0.04 mL g^{-1} was obtained as the gradient of a linear fit using the ASTRA software, which is in good agreement with the dn/dc value from the literature for linear PCL in THF at 25 °C (dn/dc = 0.072 mL g^{-1}).[1] Therefore, this value (dn/dc = 0.072 mL g^{-1}) was used for MALS analysis of all samples in this work.

Size exclusion chromatography for the Mark-Houwink Plot. SEC measurements were performed employing refractive index and viscometer detectors on a 390-MSD Agilent system, the eluent was THF at 30°C and a flow rate of 1 mL min^{-1}. Separation was achieved using 2 PLgel mixed D columns 5 µm (300 × 7.5 mm) connected in series. The Universal

[1] Zhou, X. & Hong, L. Controlled ring-opening polymerization of cyclic esters with phosphoric acid as catalysts. *Colloid Polym. Sci.* **291,** 2155–2162 (2013).

Calibration approach was used to calculate the molecular weight average for the star-branched polymers using linear PS standards.

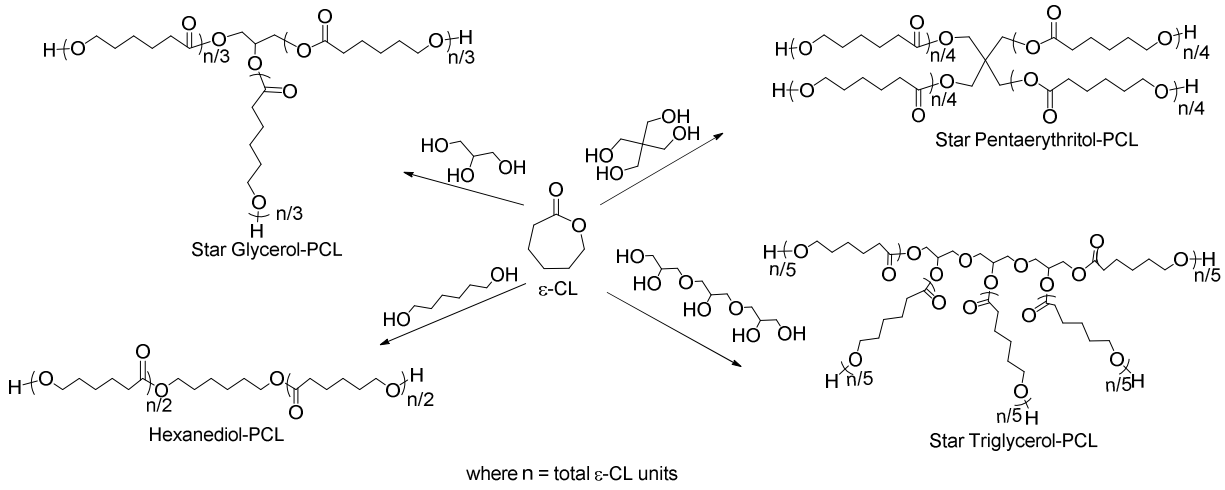
Matrix Assisted Laser Desorption and Ionisation-Time of Flight Mass Spectrometry (MALDI-TOF MS). MALDI TOF MS data were recorded on a Bruker RapiFlex spectrometer operating at the following conditions: Nitrogen laser (337 nm), accelerating potential (20 kV) in positive linear ion mode. Trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was employed as the matrix. An analyte solution and matrix solution with a concentration of 10 g L^{-1} in THF (1:4 v/v analyte-to-matrix solution) were mixed with 1 μL of potassium trifluoroacetate (10 g/L). 1 μL of the resulting mixture was spotted on the MALDI plate for MS analysis. Data were analysed and normalised using the FlexAnalysis version 3.0 (Bruker) software.

Differential scanning calorimetry (DSC). DSC analyses were performed on a Q2000 TA instrument calibrated with an indium standard under N_2 flow. In a standard experiment, the sample (2 – 5 mg) was placed in an aluminium pan with a blank reference pan in the instrument. DSC measurements were performed in a temperature range from -80 to 100 ^{o}C at a heating/cooling rate of 10 °C min^{-1}). The crystallisation temperature (T_c) and the melting temperature (T_m) were taken from the second cycle.

Table S1. The polymerisation of ε-CL using polyols as initiators and $Sn(Oct)_2$ as the catalyst in the bulk.

Entry	I [a]	M_n^{targ} [b] (kg mol^{-1})	T (°C)	t (h)	^{1}H NMR			SEC-MALS		SEC-MALS/ NMR
					Conv [c] (%)	DP_n^{NMR} [d] (arm)	$M_n^{H\text{-}NMR}$ [d] (arm) (kg mol^{-1})	$M_n^{SEC\text{-}MALS}$ (star polymer) [e] (kg mol^{-1})	$Đ$ [e]	$N_{arms}^{SEC\text{-}MALS/NMR}$ [f]
1	HexD	1	95	1	97	4.9	0.50	1.00	1.04	2.0
2	HexD	6	95	6.5	83	17.3	1.97	3.73	1.04	2.0
3	HexD	6	140	1	98	23.6	2.70	5.90	1.07	2.0
4	Gly	6	140	3	98	20.4	2.30	5.90	1.03	2.6
5	PenE	6	140	4	99	15.9	1.82	5.80	1.08	3.2
6	TriG	6	140	9	99	10.9	1.24	5.60	1.04	4.5
7	*D*-Sorb	6	140	10.5	97	9.7	1.10	5.60	1.03	5.1

[a] M: Monomer (ε-CL), I : initiator (1,6-hexanediol (HexD), glycerol (Gly), pentaerythritol (PenE), triglycerol (TriG), *D*-sorbitol (*D*-Sorb)) and C: Catalyst ($Sn(Oct)_2$) is 0.1 mole with respect to the initiator.
[b] $M_n^{targ.}$ = [M]:[I] × $M_{ε\text{-CL}}$ at 100 % monomer conversion. [c] Monomer conversion determined by ^{1}H NMR. [d] Degree of polymerisation and average molecular weight of arms determined by following Eq. (S1) and (S2) respectively. [e] Molecular weight and dispersity ($Đ$) determined by SEC-MALS. [f] Average number of arms estimated by SEC-MALS and ^{1}H NMR.



Scheme S1. ROP of ε-caprolactone from polyols (1,6-hexanediol, glycerol, pentaerythritol, triglycerol) using $Sn(Oct)_2$ catalyst at 140 °C in the bulk to afford polyol-PCL with a variable number of PCL arms.

Equations.

DP_n^{NMR} (arm)	$= \int H_{a'+b'} / \int H_{f'}$	(S1)
$M_n^{H\text{-}NMR}$ (arm)	$= DP_n^{NMR} \times M_{\varepsilon\text{-}CL}$ where $M_{\varepsilon\text{-}CL}$ = molar mass of ε-CL (114.14 g mol^{-1})	(S2)
$M_n^{SEC\text{-}MALS}$ (star polymer)	From SEC-MALS using dn/dc of 0.072 mL g^{-1}	(S3)
$N_{arms}^{SEC\text{-}MALS/NMR}$	$= M_n^{SEC\text{-}MALS}$ (star polymer) / $M_n^{H\text{-}NMR}$ (arm)	(S4)
Mark-Houwink	$[\eta] = K \times M^{\alpha}$	(S5)
$M_n^{P\text{-}NMR}$ (arm)	$= [m_s / n_{PCL\text{-}OP}] \times 1000$	(S6)
$M_n^{P\text{-}NMR}$ (star polymer)	$= M_n^{P\text{-}NMR}$ (arm) $\times N_{arms}^{31P}$	(S7)
%COOH	$= (\int_{PCL\text{-}COOP} / \int_{PCL\text{-}OP}) \times 100$	(S8)
$n_{PCL\text{-}OP}$	$= (n_{IS} \times \int_{PCL\text{-}OP}) / \int_{IS}$	(S9)

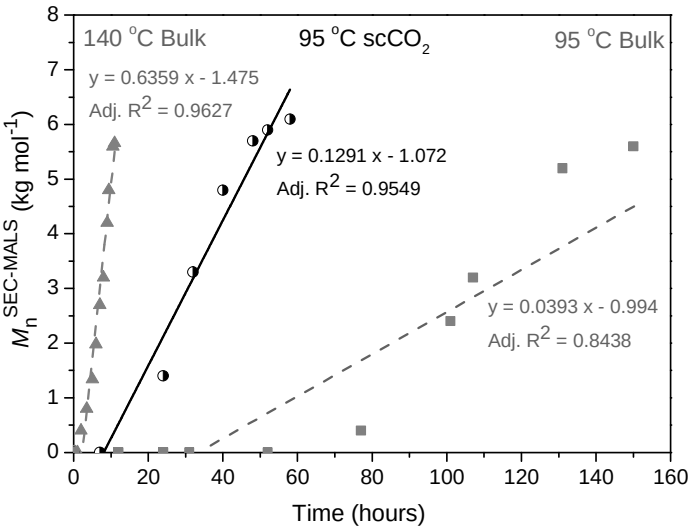


Figure S1. Evolution of M_n $^{SEC\text{-}MALS}$ *vs.* time for the synthesis of star *D*-sorbitol-PCL catalysed by $Sn(Oct)_2$ in $scCO_2$ (95 °C, round symbols) or in the bulk (95 °C, grey square symbols and 140 °C, grey triangle symbols).

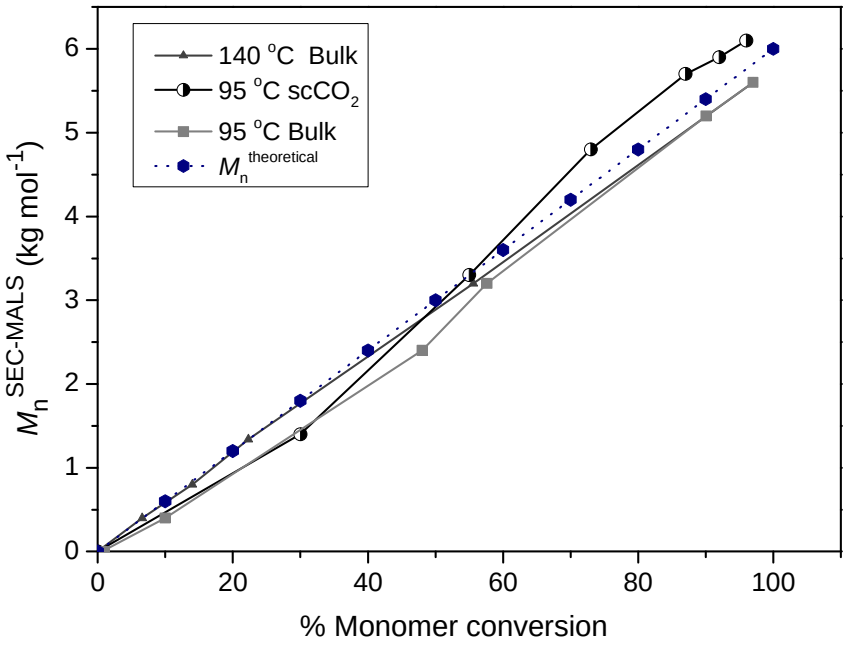


Figure S2. Evolution of molecular weight (M_n $^{SEC\text{-}MALS}$) with monomer conversion for the synthesis of star *D*-sorbitol-PCL in the presence of $Sn(Oct)_2$, in $scCO_2$ (95 °C) or in the bulk (95 °C, 140 °C). The theoretical molecular weight is included as well.

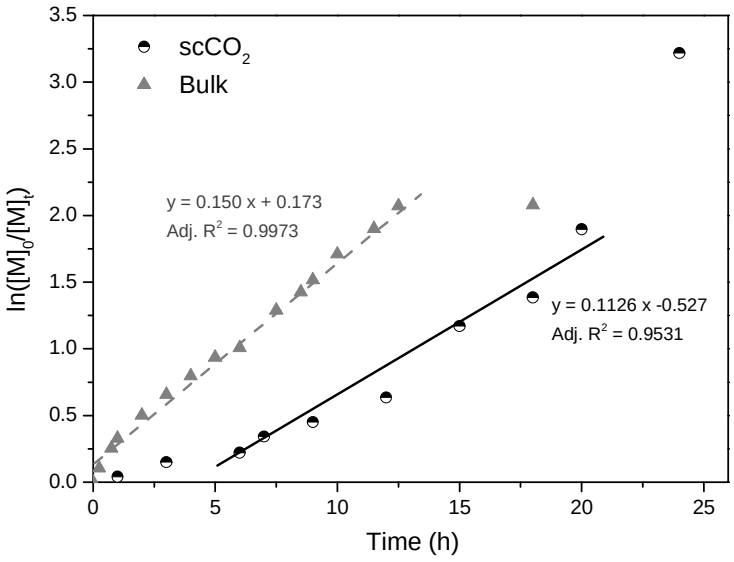


Figure S3. Evolution of $\ln([M]_0/[M]_t)$ *vs.* time for the synthesis of star *D*-sorbitol-PCL catalysed by 3 wt% Novozym 435 relative to ε-CL in the bulk (grey symbols) and in $scCO_2$ (black symbols) at 60 °C.

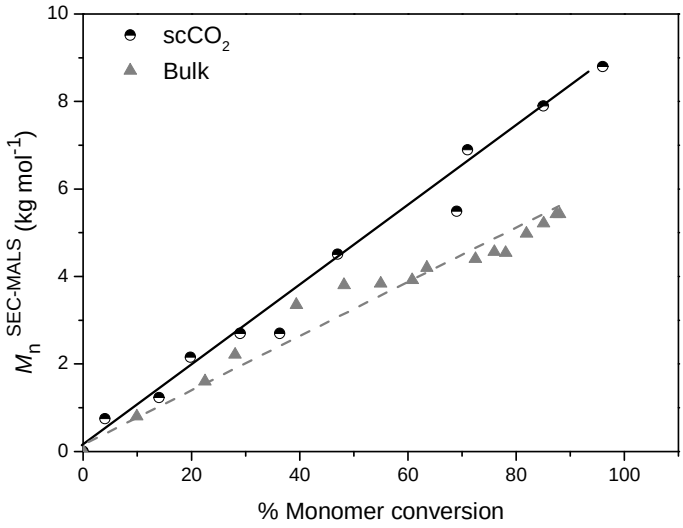


Figure S4. Evolution of M_n $^{SEC\text{-}MALS}$ (kg mol^{-1}) with increasing monomer conversion for the synthesis of star *D*-sorbitol-PCL catalysed by 3 wt% Novozym 435 in the bulk (grey symbols) and in $scCO_2$ (black symbols) at 60 °C.

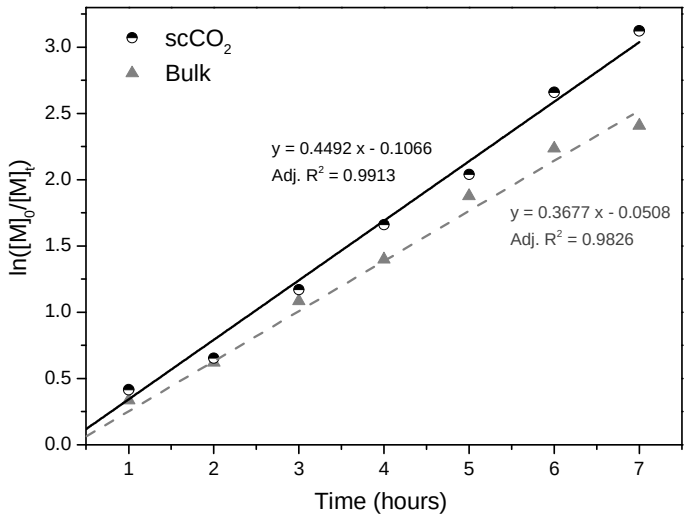


Figure S5. Evolution of $\ln([M]_0/[M]_t)$ versus time for the synthesis of star *D*-sorbitol-PCL catalysed by 10 wt% Novozym 435 relative to ε-CL in the bulk (grey symbols) and in $scCO_2$ (black symbols) at 60 °C.

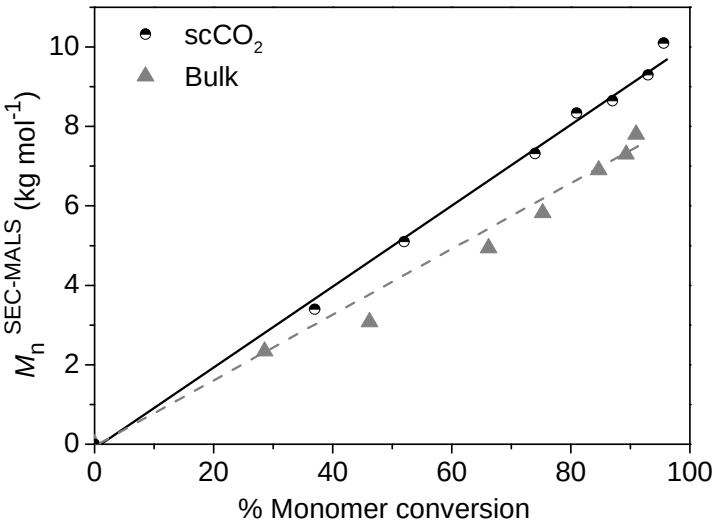


Figure S6. Evolution of M_n $^{SEC\text{-}MALS}$ (kg mol^{-1}) with increasing monomer conversion for the synthesis of star *D*-sorbitol-PCL catalysed by 10 wt% Novozym 435 in the bulk (grey symbols) and in $scCO_2$ (black symbols) at 60 °C.

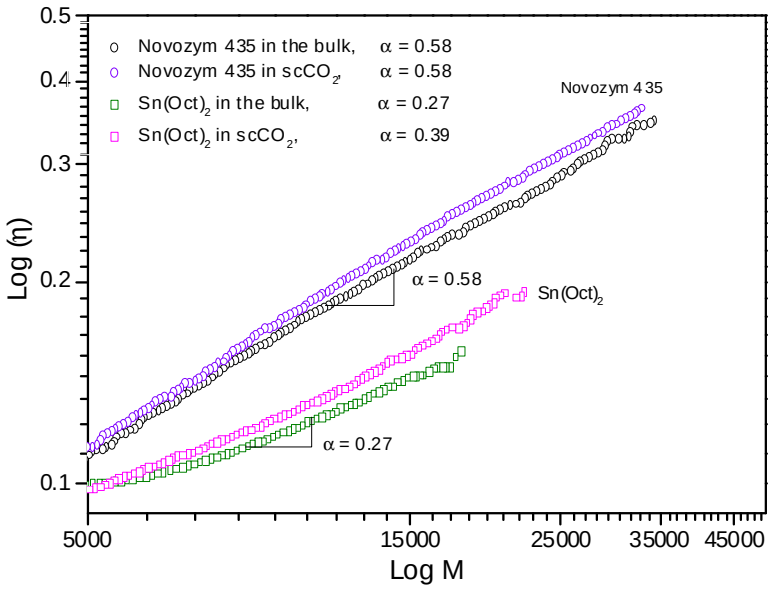
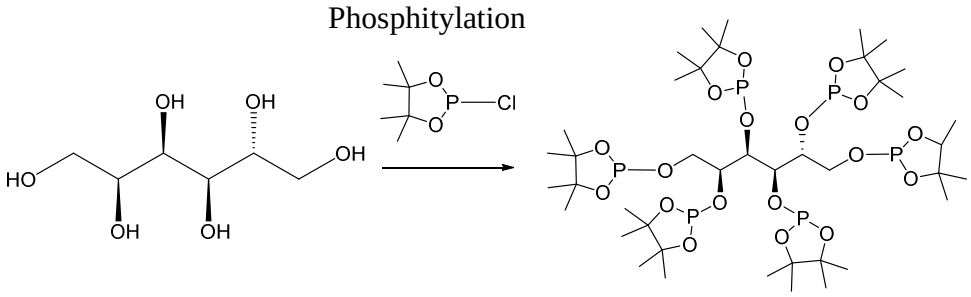


Figure S7. Intrinsic viscosity [η] as a function of the molar mass M for star *D*-sorbitol-PCL polymers catalysed by Novozym 435 in the bulk (black symbols) and in $scCO_2$ (blue symbols) and of star *D*-sorbitol-PCL polymers catalysed by $Sn(Oct)_2$ in the bulk (green symbols) and in $scCO_2$ (pink symbols).



D-sorbitol Phospholane ester of *D*-sorbitol

Scheme S2. Phosphitylation reaction of *D*-sorbitol by 2- chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP).

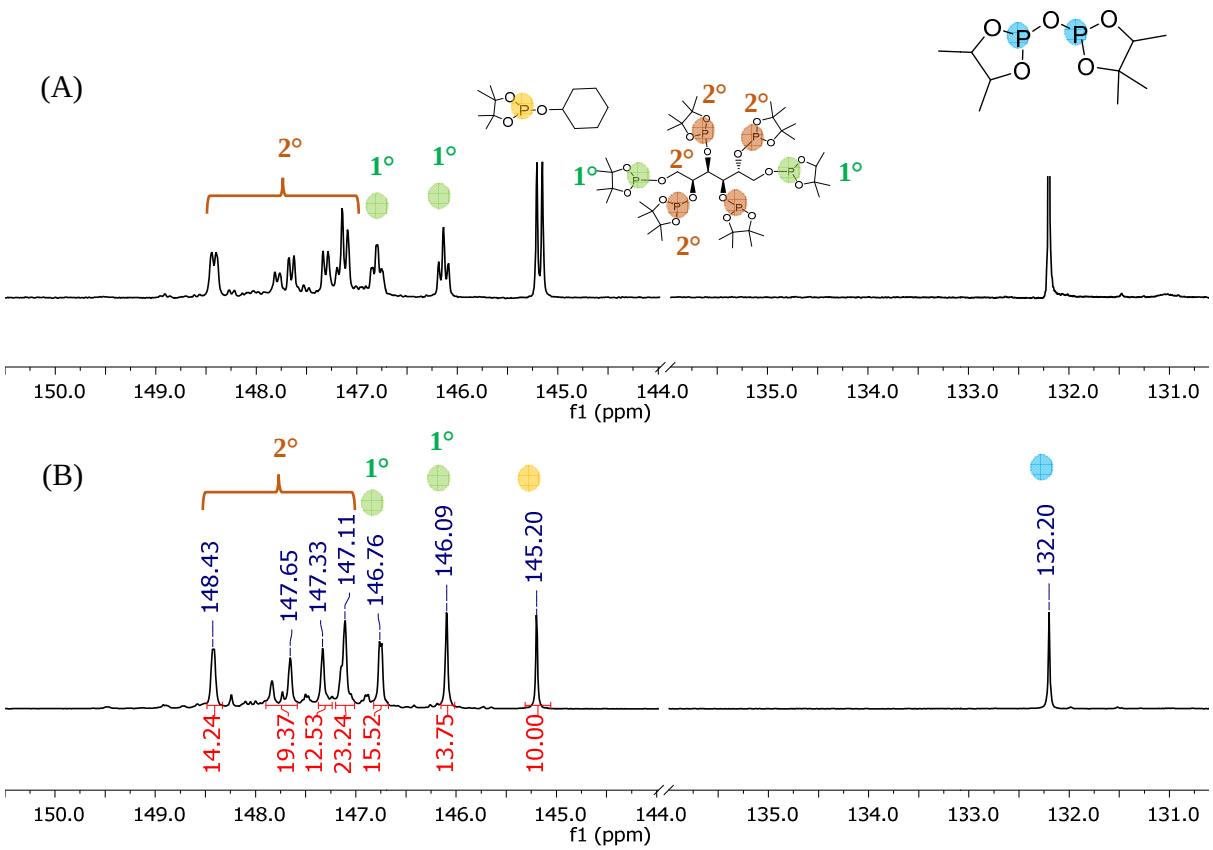


Figure S8. ^{31}P NMR spectra of *D*-sorbitol derivatised by 2- chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. (A) ^{31}P NMR spectrum without decoupling, where the phospholane ester of the primary (1°) and secondary (2°) hydroxy group show triplet (●) and doublet (●) resonances, respectively. (B) The corresponding inverse gated decoupled ^{31}P NMR spectrum used for quantification. IS: internal standard (cyclohexanol). Note that one would expect four 2˚ hydroxyl features, but there are additional peaks which clearly represent the presence of other minor species perhaps from less than fully quantitative phosphitylation of sorbitol.

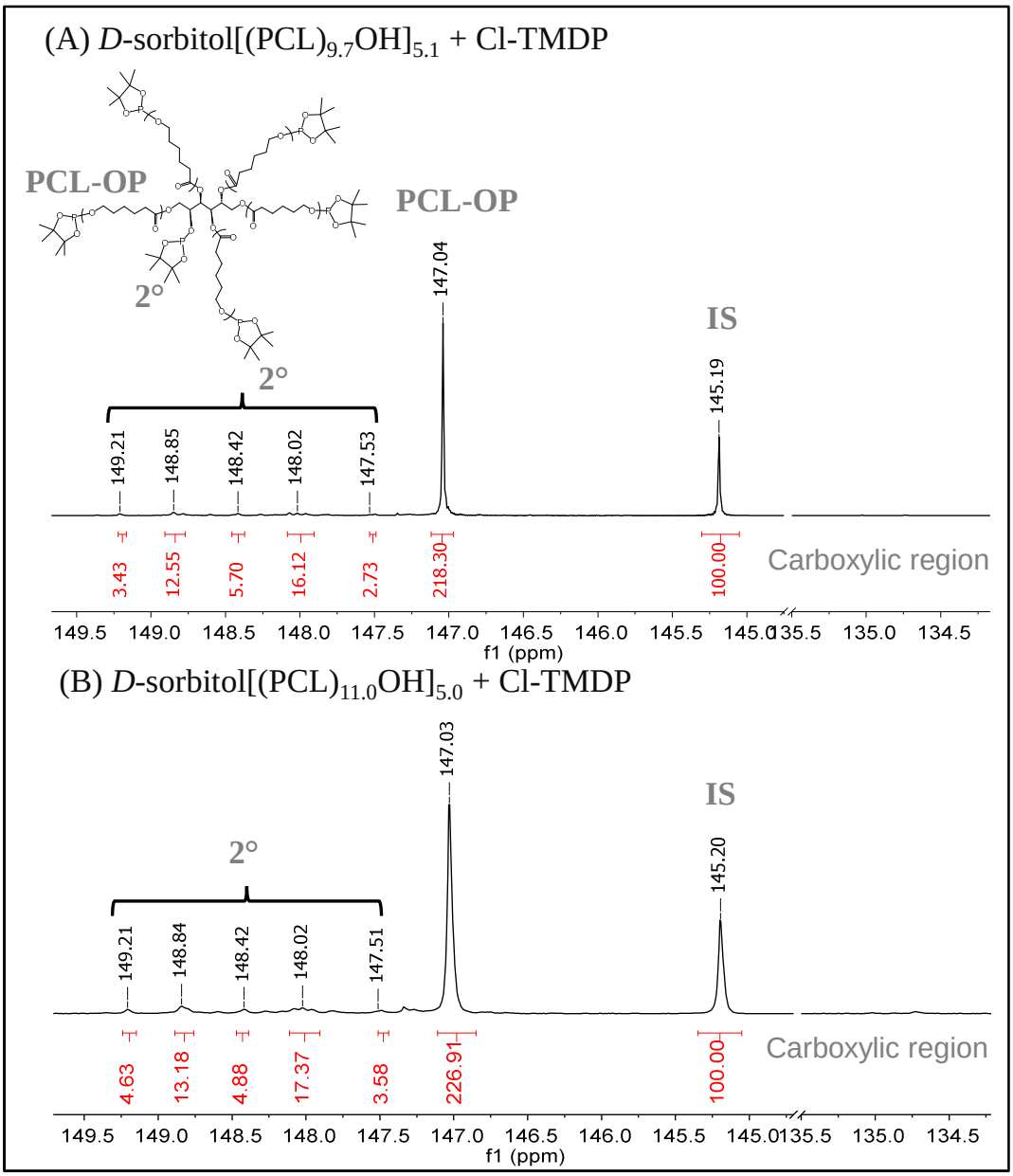


Figure S9. Inverse gated decoupled ^{31}P NMR spectra of $Sn(Oct)_2$ catalysed star samples after phosphitylation by Cl-TMDP. (A) star *D*-sorbitol[$(PCL)_{9.7}OH]_{5.1}$ synthesised in the bulk (Table 3, Entry 3) and (B) star *D*-sorbitol[$(PCL)_{11.0}OH]_{5.0}$ in $scCO_2$ (Table 3, Entry 4) using $Sn(Oct)_2$ as the catalyst. IS: internal standard (cyclohexanol).

Table S2. Analytical results from ^{31}P NMR analysis of star *D*-sorbitol-PCL synthesised using Novozym 435 as the catalyst (Table 4 Entries 1-4).

Sample (S)	Each Sample	^{31}P NMR spectrum			^{31}P NMR calculation		$\int_{COOP}$ [f]	%COOH (linear chains) [g]	N_{arms} (^{31}P) [h]	$M_n^{P\text{-}NMR}$ (star polymer) [i] (g mol^{-1})
	n_{IS} (μmol)	m_s [a] (mg)	$\int_{IS}$ [b]	$\int_{PCL\text{-}OP}$ [c]	$n_{PCL\text{-}OP}$ [d] (μmol)	$M_n^{P\text{-}NMR}$ (arm) [e] (g mol^{-1})				
Entry 1	10.6	25.7	100	121.2	12.8	2000	1.73	1.4	3.1	6200
Entry 2	10.7	25.5	100	73.68	7.88	3200	3.86	5.2	3.3	10600
Entry 3	10.8	26.3	100	81.39	8.79	3000	4.42	5.4	3.2	9600
Entry 4	10.4	26.0	100	86.39	8.98	2900	9.74	11.3	2.9	8400

[a] Mass of the sample (m_s) used for derivatisation with Cl-TMDP and subsequent NMR analysis. [b] Integral corresponding to the resonance of internal standard (δ = 147.04 ppm). [c] Integral of star sample relative to the IS. [d] Moles of hydroxy groups determined by following Eq. (S9). [e] Number average molecular weight of arms determined by following Eq. (S6). [f] Integrals corresponding to COOH in the sample. [g] Amount of linear PCL chains quantified by following Eq. (S8). [h] Average number of arms determined by following Eq. (2). [i] Molecular weight of star polymer determined by following Eq. (S7).

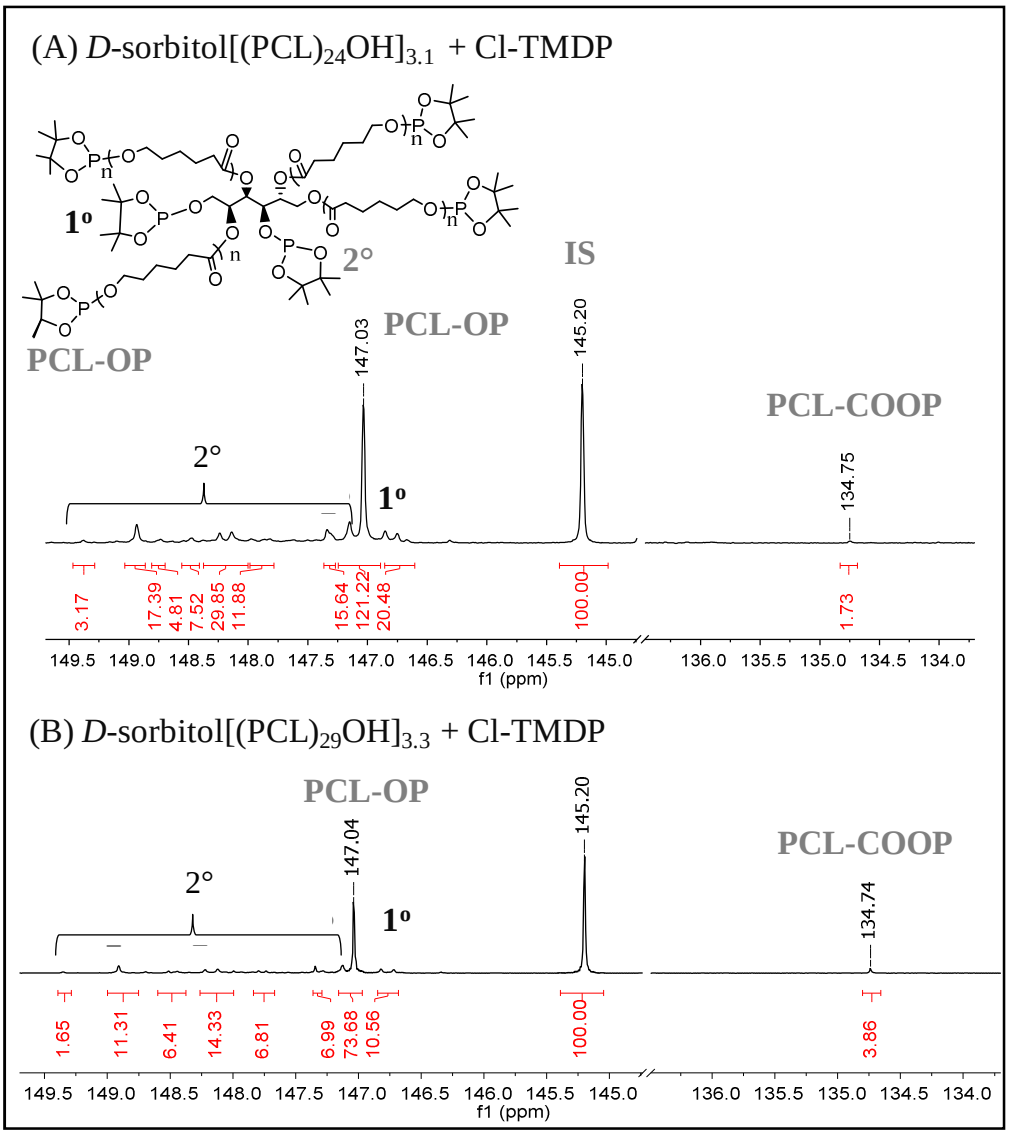


Figure S10. Inverse gated proton-decoupled ^{31}P NMR spectra after phosphitylation by Cl-TMDP. (A) star *D*-sorbitol[(PCL)$_{24}$OH]$_{3.1}$ synthesised in the bulk using Novozym 435 (3 wt%) as the catalyst (Table 4 Entry 1 and Table S2 Entry 1) and (B) star *D*-sorbitol[(PCL)$_{28}$OH]$_{3.3}$ synthesised in the bulk using Novozym 435 (10 wt%) as the catalyst (Table 4 Entry 2 and Table S2 Entry 2). IS: internal standard (cyclohexanol).

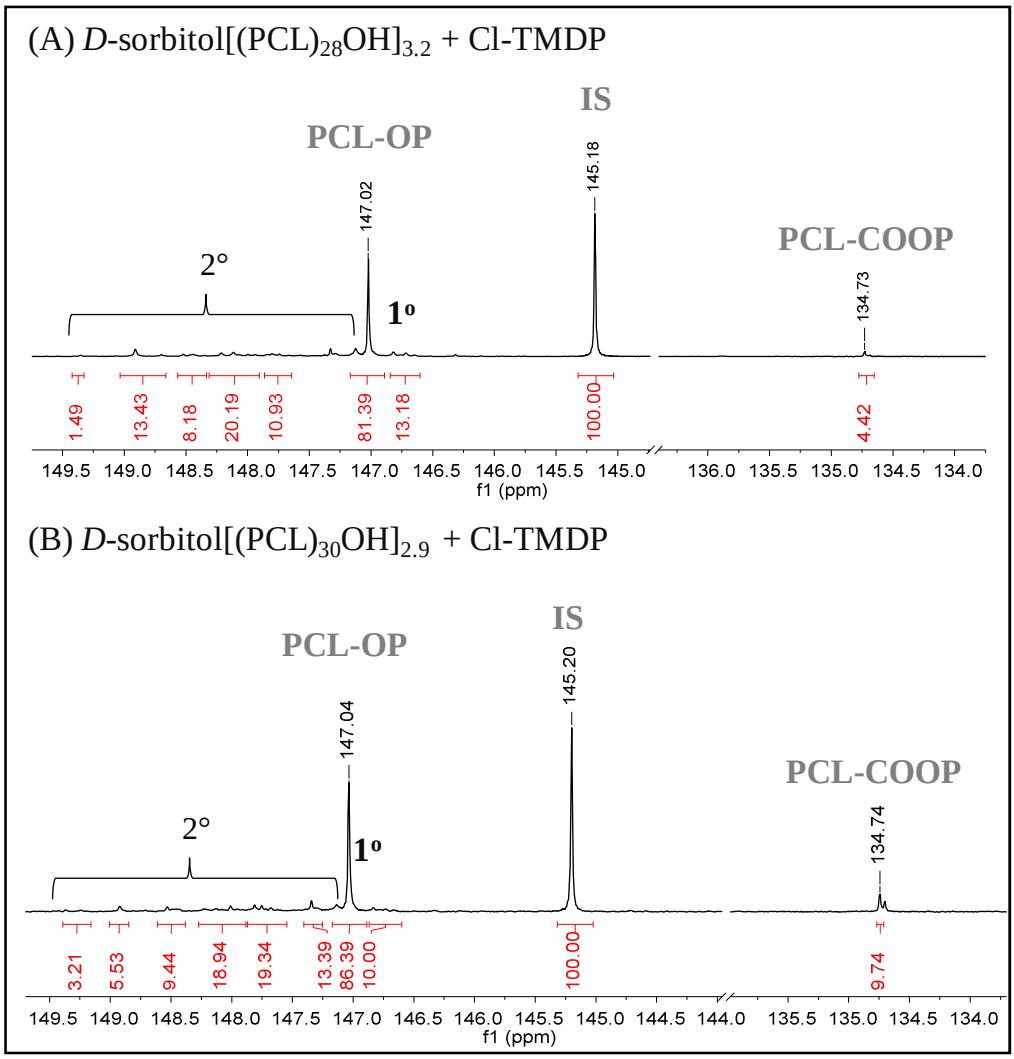


Figure S11. Inverse gated proton-decoupled ^{31}P NMR spectrum after phosphitylation by Cl-TMDP. (A) star *D*-sorbitol[(PCL)$_{28}$OH]$_{3.2}$ synthesised in scCO$_2$ using Novozym 435 (3 wt%) (Table 4 Entry 3 and Table S2 Entry 3) and (B) star *D*-sorbitol[(PCL)$_{30}$OH]$_{2.9}$ synthesised in scCO$_2$ using Novozym 435 (10 wt%). (Table 4 Entry 4 and Table S2 Entry 4). IS: internal standard (cyclohexanol).

Table S3. DSC thermal analysis of star polyol-PCL of a variable number of arms catalysed by $Sn(Oct)_2$ and star *D*-sorbitol-PCL synthesised using Novozym.435.

Sample [a]	M_n SEC-MALS (star polymer) [b] (kg mol^{-1})	N_{arms} (^{31}P) [c]	T_m (°C) [d]	T_c (°C) [d]	ΔH (J/g) [e]
Hexanediol-PCL	5.90	2.0	45	38	68
Glycerol-PCL	5.90	2.6	43	33	40
Pentaerythritol-PCL	5.80	3.0	40	32	72
Triglycerol-PCL	5.60	4.5	38	30	68
D-Sorbitol-PCL	5.60	5.1	35	24	62
N435 *D*-Sorbitol-PCL	5.65	3.1	42	33	72
N435 *D*-Sorbitol-PCL	8.80	3.2	41	31	64

[a] Polyol-PCL (polyol = hexanediol, glycerol, pentaerythritol, triglycerol, *D*-sorbitol) and N 435 (Novozym 435). [b] Molecular weight determined by SEC-MALS. [c] Average number of arms by phosphitylation. [d] Melting temperature and crystallisation temperature measured by DSC under nitrogen at a heating/cooling rate of 10 °C min^{-1}. [e] Melting enthalpy measured by DSC.

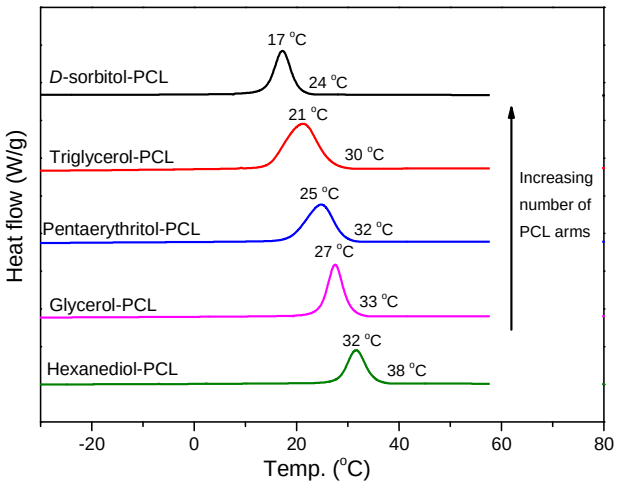


Figure S12. Comparison of DSC thermograms of polyol-PCL. The cooling scan from the melt after holding the sample at 120 °C for 10 min is shown.