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## Controlled polymerisation and purification of branched poly(lactic acid) surfactants in supercritical carbon dioxide

Amy R. Goddard, Sara Pérez-Nieto, Thayse Marques Passos, Brid Quilty, Kim Carmichael, Derek J. Irvine* and Steven M. Howdle*

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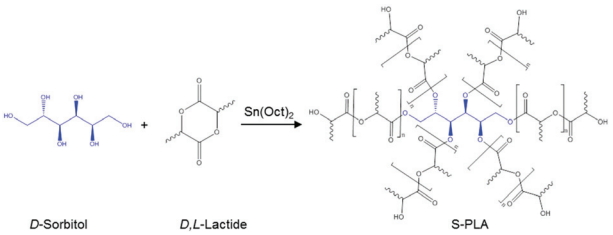


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Green Chemistry

PAPER

# Controlled polymerisation and purification of branched poly(lactic acid) surfactants in supercritical carbon dioxide†

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Product degradability, sustainability and low-toxicity are driving demand for the synthesis of biobased polymers and surfactants. Here we report the synthesis of novel surface active polymers using cyclic esters (D,L-lactide) and temperature sensitive polyols (D-sorbitol) as renewable building blocks. We highlight the modification of chain length and degree of branching to provide a route to tailoring the properties and application performance of these new compounds. High processing temperatures (≥180 °C) and harsh post-reaction treatments are often needed to remove residual monomer and catalysts and these can become barriers to creating materials based on renewable resources. Here we exploit supercritical carbon dioxide ($scCO_2$) as a green solvent to overcome these challenges; significantly reducing reaction temperatures, targeting controlled molecular weights with narrow dispersities and reducing side-product formation. Additionally in the same pot, we can use supercritical extraction to purify the compounds and to efficiently remove unreacted reagents, which could be recovered and recycled. We believe that our approach to the production and purification of these novel branched poly(lactides) is a significant step towards the development of the next generation of biopolymers and green surfactants, combining both the use of bio-sourced raw materials and the potential to use sustainable, low energy processes and techniques.

## 1. Introduction

There has been a steady increase in the research and application of biodegradable and biocompatible polymers and poly (lactic acid) (PLA), derived from renewable resources, has been studied extensively.[1–4] Moreover, in the past decade there has been an increased focus on the synthesis of star-shaped PLA materials as they exhibit highly desirable rheological, mechanical and biomedical properties that are inaccessible from linear polymers.[2,5,6] These branched polyesters offer an increased concentration of functional end groups, which can alter the solubility of the materials and deliver surface active compounds with differentiated application performance.[2] Today, the majority of surfactants are synthesised using petrochemically derived material and their manufacture requires several energy intensive purification steps to reach the specifications required for high value applications.[7] Additionally, concern regarding toxicity and the presence of carcinogenic side-products (such as 1,4-dioxane) post manufacture is also causing a shift towards the demand for milder processing conditions and low-toxicity, biobased alternatives.[8–10] Branched PLA could potentially represent a viable route to delivering such non-petrochemical based replacements. These materials can be synthesised *via* the ring opening polymerisation (ROP) of D,L-lactide using a range of polyhydroxyl co-initiators, including pentaerythritol,[11–16] dipentaerythritol[11,16] and ethylene glycol[5,17] or sugar alcohols, such as glycerol[5,12,14,18] and sorbitol[5,6,19] (Fig. 1) which are renewably sourced and considered to be non-toxic. Ouchi *et al.*[20,21] demonstrated that the incorporation of polyol carbohydrates, such as glucose and dextran, can influence the surface active properties of the resulting polyesters.

In the specific case of D-sorbitol centred star poly(lactic acid) (S-PLA), the materials may have up to 6 hydrophobic PLA arms radiating from the central sorbitol core with each arm

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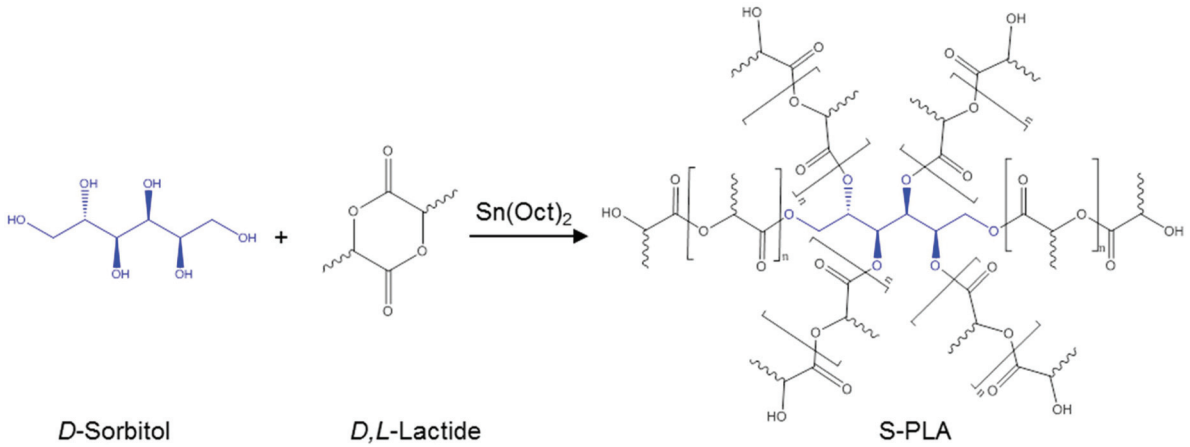


**Fig. 1** ROP of D,L-lactide using D-sorbitol as a co-initiator, leading to branched sorbitol poly(lactic acid) (S-PLA).

containing a hydrophilic hydroxyl end group (Fig. 1). By controlling the synthesis of these compounds it should be possible to control/alter the degree of branching that is achieved, thus modifying their hydrophobic : hydrophilic ratio. This should be sufficient to ensure that the compounds are surface active since an increased number of functional hydroxyl end groups, compared to their linear counterparts, could drive their alignment at the interface between two phases with different polarity.

However, attempts to synthesise S-PLA through condensation polymerisations have yielded only relatively low molecular weights (<4700 Da),[6] while ring-opening polymerisations (ROP) require very long reaction times (up to 120 hours).[19,22] The polymers synthesised exhibit broad dispersities ($Đ$), which have been attributed to side reactions known to take place at high temperatures (≥130 °C), including dehydration of sorbitol.[23–26] Such high temperatures are required because reactions using $Sn(Oct)_2$ are often found to have significant induction periods arising from slow insertion of the first 2–4 monomer units.[27] To overcome this issue and to ensure all reagents are in the melt phase, PLA is typically synthesised commercially at 180–210 °C.[3] This makes the use of temperature sensitive co-initiators (such as sugars) even more challenging.[26]

Hao *et al.*,[5] have attempted to overcome these concerns by using *m*-xylene as a solvent. Narrow polymer distributions are observed ($Đ$ of 1.1), though poor conversions were achieved at lower temperatures (~60% after 5 hours at 100 °C). The addition of an organic solvent also adds additional steps related to the separation and purification of the final product and increases the overall VOC footprint of the process.[23]

An alternative to using toxic organic solvents is the use of supercritical fluids and in particular carbon dioxide ($scCO_2$), which is an environmentally benign, low cost and tuneable solvent that can be easily tuned by altering temperature and pressure.[28] Consequently, there has been significant interest in the ROP of cyclic esters in $scCO_2$,[23,28,29] and also in the purification of the resulting polymers,[30–32] as $CO_2$ can simply be vented to leave a pure, dry, solvent free product.[28] High-pressure $scCO_2$ is able to plasticise and effectively liquefy many monomers and polymers at temperatures below their melting ($T_m$) or glass transition ($T_g$) points,[31,33–35] as particularly demonstrated and measured for polycaprolactone.[36] This allows the synthesis of PLA to be conducted at temperatures as low as 70 °C,[31,33] for D- or L-lactide or slightly higher for the racemic monomer mixture, which has a higher $T_m$, leading to amorphous D,L-lactide, polymer.[37]

Previous literature on the ROP of lactide in $scCO_2$ has focused on the synthesis of linear polyesters, primarily using L-lactide.[30,38–40] Lee *et al.* highlighted how $scCO_2$ extraction could be used to purify PLA by extracting residual L-lactide (80 °C and 200 bar) and also demonstrated a 24 wt% reduction in the residual catalyst.[30] In this particular study the different extractions were assessed individually, and only limited information is available on the conditions required for purification. However, when compared against conventional purification methods clear advantages are seen. In conventional and commercial operations, residual reagents are removed by several purification steps requiring high temperature devolatilisation,[41] or by use of potentially toxic organic solvents (dissolving the crude product in chloroform or DCM, followed by precipitation in methanol) and then drying under high vacuum, often for several days.[13,15,16,22,42]

In this paper we report a new strategy for controlled ROP of D,L-lactide in $scCO_2$ using D-sorbitol as a co-initiator. Our target is to synthesise branched PLA, with targeted molecular weight and also to demonstrate control of the degree of branching by changing the ratio of D,L-lactide : D-sorbitol. Both synthesis and purification are performed in a one-pot process, under comparatively low temperature conditions in the absence of toxic solvents. We highlight the advantages of using this low temperature process to lower polymer dispersity, side-product formation and to target six armed stars. The surface active properties of the compounds are evaluated using the du Noüy ring method, demonstrating the importance of controlling the hydrophobic : hydrophilic ratio of S-PLA in

 

reducing surface tension of water and leading to novel renewable surfactants.

## 2. Experimental section

### 2.1 Materials

3,6-Dimethyl-1,4-dioxane-2,5-dione (D,L-lactide) (>99%, 144 g $mol^{-1}$), D-sorbitol (≥98%, 182 g $mol^{-1}$) and tin 2-ethylhexanoate ($Sn(Oct)_2$) (92.5–100%, 405 g $mol^{-1}$) were obtained from Sigma Aldrich (UK). All reagents were vacuum dried for 24 hours prior to use. Supercritical Fluid Chromatography (SFC) grade $CO_2$ (minimum purity 99.99%) was obtained from BOC (UK) and was used as received.

### 2.2 View cell plasticisation study

In order to visually observe the effect of $scCO_2$ on the physical state of D,L-lactide, a fixed volume view cell (100 mL) was used.[36,43] The view cell contains two thick sapphire windows located at each end of the cylindrical body, allowing the content to be visually inspected.[36,43] In a typical experiment, 0.5 g of sample was added to a 1 mL glass vial and inserted in the view cell. The windows were sealed and clamped to the body, and $CO_2$ was added up to 50 bar. The temperature and $CO_2$ pressure were raised incrementally, as required (up to 95 °C and 240 bar).

### 2.3 Ring opening polymerisation of D,L-lactide using supercritical carbon dioxide

The high pressure autoclave apparatus used for S-PLA synthesis in $scCO_2$ (ESI Scheme S1†) has been described previously.[29,44]

**2.3.1 Batch experiments: varying molecular weight.** Batch experiments were performed using a 20 mL reaction vessel. For polymers with a theoretical $M_n$ ($M_n^{theo}$) of 6000 Da; D,L-lactide (1 g, 6.94 mmol) and D-sorbitol (32 mg, 0.174 mmol) were added to the autoclave alongside 10 mol% $Sn(Oct)_2$ in relation to the co-initiator (7 mg, 0.017 mmol). In a typical polymerisation the autoclave was degassed for 15 minutes using a flow of $CO_2$ at 2 bar, to ensure removal of air and moisture. The autoclave was sealed and pressurised to 55 bar with the addition of $CO_2$, before heating to 95 °C and increasing the pressure to 240 bar with subsequent addition of $CO_2$. This temperature and pressure was maintained throughout the reaction (3 hours) and the mixture was agitated using an overhead mechanical stirrer (200 rpm) to ensure efficient mixing of the reagents. After 3 hours, the autoclave was cooled to room temperature by turning off the heating unit, and the reactor was typically vented at ≤25 °C and 55 bar.

Reactions were repeated to target polymers with an $M_n^{theo}$ of 500 Da, 1400 Da and 11 700 Da, using D,L-lactide (1 g, 6.94 mmol) and predetermined quantities of D-sorbitol (632 mg, 158 mg and 16 mg) in the molar ratio of 2 : 1, 8 : 1 and 80 : 1. In addition, 10 mol% $Sn(Oct)_2$ in relation to the co-initiator was used.

**2.3.2 Kinetic experiments: varying reaction temperature.** Kinetic experiments were conducted using a 60 mL reactor, modified to include a sample collection valve to allow periodic collection of samples during polymerisation. For kinetic experiments D,L-lactide (5 g, 34.7 mmol) and D-sorbitol (158 mg, 0.868 mmol), at a 40 : 1 ratio, were added to the autoclave alongside 10 mol% $Sn(Oct)_2$ in relation to the co-initiator (35 mg, 0.085 mmol).

The same reaction protocols were followed (see above). Samples were taken periodically throughout the reaction (24 hours) by briefly opening a tap at the base of the autoclave, for ≤5 seconds, to allow the pressure to expel a small quantity of the product through the sample tap, which was collected in glass vials.

For kinetic studies at 120 °C the procedure was repeated, but in this case the catalyst was only added to the reaction once the desired temperature and pressure was achieved (120 °C and 240 bar). This was ensured by delivering the catalyst (35 mg) in a sealed glass capillary tube mounted inside the autoclave, between the overhead stirrer blades, in such a way that it would break only when the stirrer was engaged. In this way exact time of addition of the catalyst to the reaction was controlled. The mechanical stirrer was switched on when the desired reaction conditions were reached (240 bar, 120 °C).

The products obtained were glassy powders for higher molecular weight polymers and tacky foams at lower molecular weight. Conversions of >80% were obtained for all reactions.

### 2.4 Ring opening polymerisation of D,L-lactide in the bulk

D,L-lactide (1 g, 6.94 mmol), D-sorbitol (32 mg, 0.174 mmol) and 10 mol% $Sn(Oct)_2$ in relation to the co-initiator (7 mg, 0.017 mmol) were placed in a 20 mL round bottomed flask. The mixture was degassed using Ar for 15 minutes prior to submerging the round bottom flask in a pre-heated oil bath set at 140 °C. The reactions were conducted for 3 hours and the reaction was terminated by decanting the viscous mixture into a ceramic crucible. Upon standing the reaction mixture solidified and once cooled to room temperature was ground to a fine powder using a pestle and mortar.

As for the $scCO_2$ experiments, the reactions were repeated to target polymers with an $M_n^{theo}$ of 500 Da, 1400 Da and 12 000 Da, using D,L-lactide (1 g, 6.94 mmol) using predetermined quantities of D-sorbitol (632 mg, 158 mg and 15 mg) in the molar ratio of 2 : 1, 8 : 1 and 82 : 1 along with 10 mol% $Sn(Oct)_2$ with respect to the co-initiator. Reactions were also attempted in the bulk at the lower temperature of 95 °C.

### 2.5 Purification of sorbitol-poly(lactic acid) (S-PLA)

To purify the polymer the autoclave was purged with $scCO_2$ (ESI Scheme S1†). A particularly attractive feature of this process is that the S-PLA product is insoluble in $scCO_2$ under the investigated conditions, and this helps to ensure only monomer and catalyst are removed. In a typical purification: 1 g polymer was placed in the 20 mL autoclave base and degassed for 15 minutes using a flow of $CO_2$ at 2 bar, to ensure

all air and moisture is removed. The reaction vessel was sealed and pressurised to 55 bar with the addition of $CO_2$, then heated to the desired temperature and pressurised (typically 45 °C and 240 bar) with subsequent addition of $CO_2$. Once the conditions were reached the exit and inlet tap were opened and $scCO_2$ was flowed through the reaction vessel at a constant flow rate, typically for 15 minutes. The extracted material was collected in a trap submerged in an ice-bath, attached at the autoclave outlet tap and subsequently identified *via* $^1$H-NMR. After extraction the autoclave was cooled to room temperature (≤25 °C, 55 bar) before depressurisation and collection of the purified sample. The purification was repeated at pressures of 55 bar, 105 bar and 140 bar, at longer purification times (up to 45 minutes) and also at a higher temperature of 80 °C (at 240 bar).

To aid removal of residual amounts of D,L-lactide (<20 mg $g^{-1}$ sample) a small quantity of ethanol (0.5 mL) was added to the autoclave after initial purification (15 minutes, 45 °C, 240 bar). The autoclave was repressurised following the same procedure as detailed above (45 °C, 240 bar), and $scCO_2$ was flowed through the reaction vessel for a further 30 minutes.

### 2.6 Polymer characterisation

The molecular weight distribution of the polymers was obtained by GPC (Polymer Laboratories GPC-50 Plus) using a refractive index (RI) detector. The columns (PLGel Mixed-D columns, two in series) were eluted by $CHCl_3$ (Sigma, 99.8%) and calibrated against polystyrene standards. Analysis was performed at 40 °C and at a flow rate of 1 ml $min^{-1}$. Samples (10 mg $ml^{-1}$) were passed through syringe filters (Whatman, 25 mm, 0.2 μm) prior to analysis.

$^1$H-NMR and $^{13}$C-NMR spectra were typically recorded in DMSO-$d_6$ using a Bruker DPX 300 MHz and Bruker AV 400 MHz spectrometer. The molecular weight of S-PLA was determined by $^1$H-NMR ($M_n^{NMR}$) (ESI Fig. S1†) taking the conversion of the polymer into account, assuming linear growth (ESI eqn (S1A)†). Peaks corresponding to PLA end groups (methine protons) are shifted further upfield compared to when incorporated in the polymer backbone ($\delta$ = 4.17–4.25 *vs.* 5.08–5.21 ppm), identified previously when synthesising branched PLA (with 2 to 22 initiating hydroxyl groups).[12–14,45–47] This shift is used to determine the chain length of each PLA arm (ESI eqn (S1B)†).[12–14,45]

DSC analysis was performed using a TA-Q2000 DSC (TA Instruments). In a standard experiment, the sample (3–4 mg) was subject to a first heating ramp up to 150 °C and then cooled down to −90 °C (10 °C $min^{-1}$). A second identical heating scan was then conducted, with the same temperature ramp settings and the $T_g$ of the polymer was determined from this second cycle.

Matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-ToF MS) was conducted using a Bruker Ultraflex II spectrometer in reflectron mode. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) was used as the matrix.

**2.6.1 Sample preparation for $^{31}$P-NMR analysis.** Analysis was performed following the procedure reported by Spyros *et al.*[48] A stock solution was prepared by dissolving 520 mg chromium(III) acetylacetonate ($Cr(acac)_3$) and 150 mg cyclohexanol (internal standard) in 50 ml pyridine : $CDCl_3$ (2.3 : 1 v/v), protected from moisture using 4 Å molecular sieves. 20–30 mg sample was dissolved in 0.6 ml stock solution in a NMR tube, before adding 50 μl 2-chloro-4,4,5,5-tetramethyldioxaphospholane (TMDP). The mixture was left to react for 30 minutes at room temperature before acquiring the $^{31}$P-NMR spectra, using a Bruker AV 400 MHz spectrometer (128 scans). The inverse gated decoupling technique was used with a 10 second delay time. Spectra were referenced in relation to the product of TMDP reacted with water, at $\delta$ = 132.2 ppm.

### 2.7 Toxicity assessment

A broth micro-dilution method was adopted as a preliminary test to indicate the differences in toxicity between reagents and polymer products. The aim was to determine the $LC_{50}$, the lethal concentration where 50% of bacterial growth is inhibited, determined by the descending line of best fit between concentrations where no inhibition (100% bacterial growth) and full inhibition (0% bacterial growth) was observed. This test examined the susceptibility of *Staphylococcus aureus* (*S. aureus*, ATCC 6538) and *Escherichia coli* (*E. coli*, ATCC 25922) to S-PLA (1800 Da) before and after purification using $scCO_2$. D,L-Lactide and $Sn(Oct)_2$ were also assessed in comparison, to give an indication of the toxicity of each compound toward the bacteria tested. These microbes were used for the initial screen as the growth of *E. coli* is known to be inhibited by tin, whilst PLA has previously been evaluated against *S. aureus*.[49–51] Sample preparation is included in the ESI.†

### 2.8 Tensiometry

Equilibrium surface tensions ($\sigma$) of S-PLA at 800 Da, 1800 Da and 6800 Da, synthesised using $scCO_2$, were measured using the du Noüy ring method on a Lauda Tensiometer TD3 using water (60 mL) at a concentrations of 0.5% w/v. A platinum ring was submerged into the aqueous solution and then slowly pulled through the liquid–air interface, to measure the surface tension (mN $m^{-1}$).[52] All measurements were performed at room temperature (20 °C) and analysis was automated, with repeats made ≥5 times until a standard deviation of ≤0.1 mN $m^{-1}$ was obtained. The commercial surfactants Tween™ 20 ($PEG_{20}$-sorbitan laurate, ~1200 Da), Tween™ 80 ($PEG_{20}$-sorbitan oleate, ~1300 Da) and Pluronic™ L35 ($PEG_{25}$-$PPG_{50}$-$PEG_{25}$) were assessed as a comparison.

### 2.9 Micelle formation

**2.9.1 Critical micelle concentration (CMC).** The CMC was determined tensiometrically following the same procedure as described above, measuring the surface tension at varying concentrations of S-PLA 800 Da (at 1%, 0.5%, 0.25%, 0.125%, 0.063% and 0.031% w/v). A plot of surface tension *vs.* concentration (log scale) was used to determine the CMC value.

**2.9.2 Loaded micelles.** An effective way to visualise micelle formation is to disperse the yellow dye coumarin 6 in an aqueous solution using a surfactant. This was attempted using S-PLA (800 Da), synthesised using $scCO_2$. S-PLA (800 Da) was dissolved in 1 ml $H_2O$ (1% w/v) and separately 1% w/v coumarin 6 was dissolved in DCM. Coumarin 6 solution (0.1 ml) was added to the aqueous solution and placed on a rotary evaporator for 1 hour allowing the solution to mix and for the DCM to evaporate. Once the DCM was evaporated the sample was placed on an orbital shaker overnight. Coumarin 6 is hydrophobic and its native solubility in water is very low (0.25 μg $ml^{-1}$). As a control a sample was run in parallel containing no S-PLA (800 Da) in the aqueous phase. The samples were photographed under UV light after standing for 15 minutes.

# 3. Results & discussion

$ScCO_2$ has been reported to strongly depress the melt temperature of L-lactide from ~95 °C to ~50 °C,[31,33,37] and through view cell studies we were able to visualise a similar trend for D,L-lactide, which has a higher $T_m$ (~130 °C). D-Sorbitol has an ambient $T_m$ of 95 °C.

These view cell studies clearly show that at ambient pressure and temperature D,L-lactide and D-sorbitol are white powders (Fig. 2-I), but in the presence of $scCO_2$ (240 bar) at 95 °C their mixture is fully liquefied (Fig. 2-II). This demonstrates that the melt temperature of D,L-lactide is significantly lowered under $scCO_2$ conditions, both with and without D-sorbitol (ESI Fig. S2C†). The majority of D,L-lactide remains in this liquefied form and is not miscible with the $scCO_2$. D-Sorbitol when mixed with D,L-lactide is fully liquefied and without stirring lies as droplets at the bottom of the vial (Fig. 2-II). Without agitation the reagents form two immiscible liquids. Upon depressurisation both reagents foam, with D-sorbitol expanding significantly as the $scCO_2$ solubilised within the compound is released (Fig. 2-III).

As D,L-lactide has a relatively high $T_m$, the standard approach is to perform polymerisations in the bulk at temperatures of ≥140 °C,[6,12,53] or industrially at ≥180 °C.[3] Our contention is that use of $scCO_2$ could allow these reactions to be performed at significantly lower temperatures, an important aspect to consider when using temperature sensitive co-initiators.

### 3.1 Comparison of synthesis in the bulk and using $ScCO_2$

Polymerisations were carried out in $scCO_2$ (at 95 °C, 240 bar) and in the bulk (at 95 °C and 140 °C) using different monomer to co-initiator concentrations, to control the degree of branching and final molecular weight of S-PLA (Table 1).

Polymerisations using $scCO_2$ yielded white glassy powders for higher molecular weight polymers, with lower molecular weight compounds being tacky white foams (as they have lower $T_g$ values – Table 1, entries 1 and 2). By contrast, products from polymerisations in the bulk at 140 °C were off-white glassy polymers (Table 1 entries 8 and 9), while low molecular weight compounds were pale yellow to off-white in colour and sticky (Table 1, entries 6 and 7).

Polymerisations carried out in $scCO_2$ at 95 °C and in the bulk at 140 °C (Table 1, entries 1–4 and entries 6–9) typically proceeded to 80–90% conversion, where the conversions plateau.

The presence of a conversion ceiling was expected and has been reported in the prior literature.[54–57] This has been attributed to the reaction reaching the ring-chain equilibrium state where the amount of remaining monomer corresponds to the equilibrium monomer concentration, which is known to increase at higher reaction temperatures.[54,55] In this equilibrium state, transesterification reactions becoming dominant resulting in the generation of both species of lower and higher molecular weight than the target, producing an increase in the

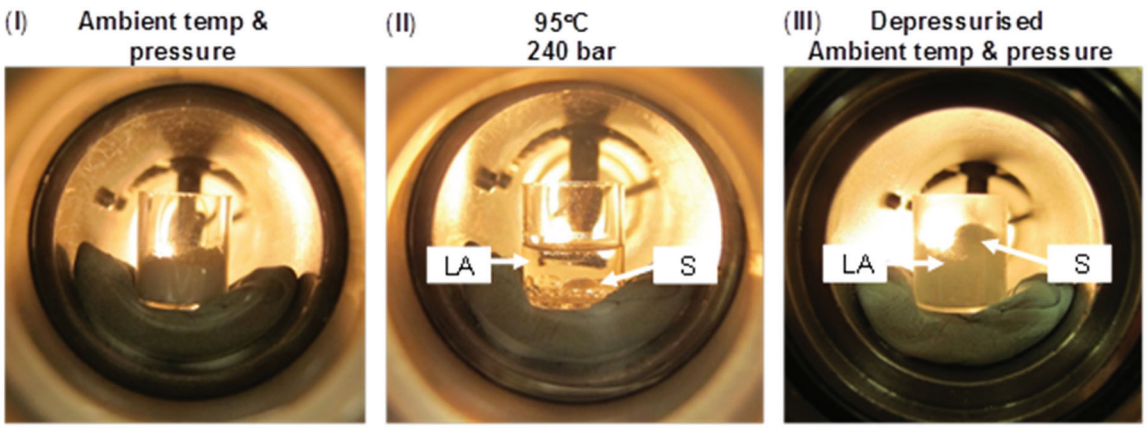


**Fig. 2** Transitions observed for a mixture of D,L-lactide (LA) and 10 wt% D-sorbitol (S) in the view cell at increasing temperatures & pressure; (I) the mixture in the form of a white powder (room temperature and ambient pressure); (II) sample fully plasticised at 95 °C and 200 bar, note immiscible drops of liquefied D-sorbitol at the base of the vial; (III) the foamed mixture after depressurisation, highlighting the significant expansion of D-sorbitol.

Table 1 Synthesis of S-PLA at targeted molecular weights after 3 hours. Polymerisations carried out in $scCO_2$ and in the bulk are shown for comparison

| Entry | Sample | Temp. | $[M]_0/[I]_0$ | $M_n^{theo\ a}$ (Da) | Conv.$^b$ | $M_n^{NMR\ b}$ (Da) | $M_n^{arm\ b}$ (Da) | # Arms$^c$ | $M_n^{GPC\ c}$ (Da) | $Đ^c$ | $T_g$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $scCO_2$ | 95 °C | 2 : 1 | 500 | 81% | 450 | 170 | 1.8 | 800 | 1.2 | 10 °C |
| 2 | $scCO_2$ | 95 °C | 8 : 1 | 1400 | 85% | 1200 | 280 | 4.0 | 1800 | 1.2 | 22 °C |
| 3 | $scCO_2$ | 95 °C | 40 : 1 | 6000 | 85% | 5100 | 830 | 5.9 | 6800 | 1.1 | 40 °C |
| 4 | $scCO_2$ | 95 °C | 80 : 1 | 11 700 | 85% | 10 200 | 1510 | 6.0 | 9800 | 1.1 | 42 °C |
| 5 | Bulk | 95 °C | 40 : 1 | 6000 | 2% | 300 | n/a | n/a | n/a | n/a | n/a |
| 6 | Bulk | 140 °C | 2 : 1 | 500 | 81% | 400 | 110 | 1.8 | 600 | 1.5 | 14 °C |
| 7 | Bulk | 140 °C | 8 : 1 | 1400 | 78% | 1100 | 270 | 3.9 | 1800 | 1.5 | 23 °C |
| 8 | Bulk | 140 °C | 40 : 1 | 6000 | 87% | 5300 | 880 | 5.3 | 6500 | 1.4 | 40 °C |
| 9 | Bulk | 140 °C | 82 : 1 | 12 000 | 93% | 11 200 | 1780 | 5.7 | 14 800 | 1.3 | 43 °C |

M: monomer (D,L-lactide), I: co-initiator (D-sorbitol). $^a$ Theoretical weight, based on monomer : co-intiator ratio. $^b$ Determined by $^1$H-NMR, $M_n^{NMR}$ has been calculated assuming linear growth, $M_n^{arm}$ gives an indication of the average chain length of each of the PLA arms, determined by end-group integration. $^c$ The # arms has been determined by phospholane end group derivatisation and subsequent $^{31}$P-NMR analysis. $^d$ Gel Permeation Chromatography (GPC) data in $CHCl_3$ reported relative to polystyrene standards, n/a: not assessed.

$Đ$ along with a residual level of monomer.[56,57] By contrast, all of the reactions attempted in the bulk at 95 °C yielded no polymer product. (Table 1, entry 5).

The S-PLA products were analysed using $^1$H-NMR and GPC analysis. The $scCO_2$ polymerisations were observed to yield polymers with good dispersities ($Đ$ of 1.1–1.2) (Table 1, entries 1–4), as has been observed previously for linear polymers synthesised using $scCO_2$.[2,44] This narrow distribution is most likely a result of the lower processing temperatures and reduced viscosity, as the polymer phase will remain plasticised throughout the reaction.[58]

S-PLA synthesised in the bulk has a high dispersity ($Đ$ of 1.3–1.5) (Table 1, entries 6–9) and a low molecular weight tail is observed. By contrast the S-PLA synthesised in $scCO_2$ has a narrower, more controlled and targeted molecular weight distribution (Fig. 3).

Comparing in detail the $scCO_2$ and bulk reactions (Table 1, entries 4 and 9) the increased conversion in the bulk may well be responsible for the observed higher molecular weight polymers (14 800 Da *vs.* 9800 Da). However, higher branching in the $scCO_2$ case could also lead to the PLA being more globular in shape resulting in a smaller hydrodynamic volume than expected and hence a lower apparent measured MW by GPC.[59]

The number of hydroxyl groups participating in the ROP (# arms) was determined by reacting the remaining free hydroxyl groups on the co-initiator with a phospholane reagent, TMDP (ESI Fig. S3†).[48] Chung *et al.* have previously used this method for end group analysis of lignin initiated PLA.[60] This technique can be used to differentiate end-group hydroxyls found on the PLA chain and to clearly identify primary and secondary hydroxyl groups related to D-sorbitol, after phosphorylation (Fig. 4).[60,61] This comparison, cross referenced with $^{13}$C-NMR (ESI Fig. S4†), allowed the determination of the number of PLA arms radiating from our central D-sorbitol core and consequently the degree of branching.

It was observed that the number of PLA arms increased alongside the ratio of $[M]_0 : [I]_0$ as more D,L-lactide becomes available to react with the initiating hydroxyl groups on D-sorbitol. This number increases from 2 arms to 4 arms at a 2 : 1 and 8 : 1 ratio (Table 1, entries 1, 2 and 8, 9), respectively, before plateauing at ~6 arms for higher ratios (40 : 1 and 80 : 1) (Table 1, entries 3, 4 and 8, 9), which is the maximum number of branching points. This is also reflected in the $T_g$ value of the polymers as they increased from 10 °C to ~20 °C to ~40 °C, for polymers with 2, 4 and 6 PLA arms respectively, plateauing at 40 °C for higher molecular weight polymers (Table 1, entries 1–4). When assessing the $^{31}$P-NMR spectra of lower molecular weight S-PLA (Fig. 4A and B) we clearly identify a larger number of peaks corresponding to unreacted secondary hydroxyl groups of D-sorbitol, compared to primary hydroxyl groups.

This suggests that the primary hydroxyls are the initial branching points for PLA. As the ratio of D,L-lactide : D-sorbitol is increased from 2 : 1 to 8 : 1 to 40 : 1 to 80 : 1 the secondary hydroxyl groups on the co-initiator also participate in the ROP reaction and we observe branching at multiple points (Fig. 5). Additionally, using this technique the number of arms determined for S-PLA synthesised in the bulk at 140 °C was demonstrated to be consistently lower than the equivalent compounds synthesised at 95 °C using $scCO_2$. This is likely a result of higher viscosities slowing down the co-initiation from secondary hydroxyls on D-sorbitol, or as a result of side-product formation at the higher temperatures, reducing the number of initiating hydroxyl groups. To investigate these

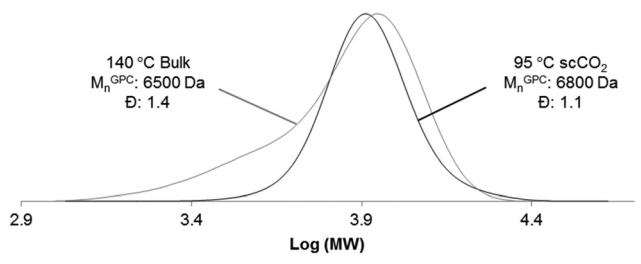


Fig. 3 Overlay of GPC traces of S-PLA synthesised in $scCO_2$ (95 °C) and in bulk (140 °C). Note the low molecular weight tail observed in the sample synthesised at 140 °C and the broader $Đ$. The response has been normalised.

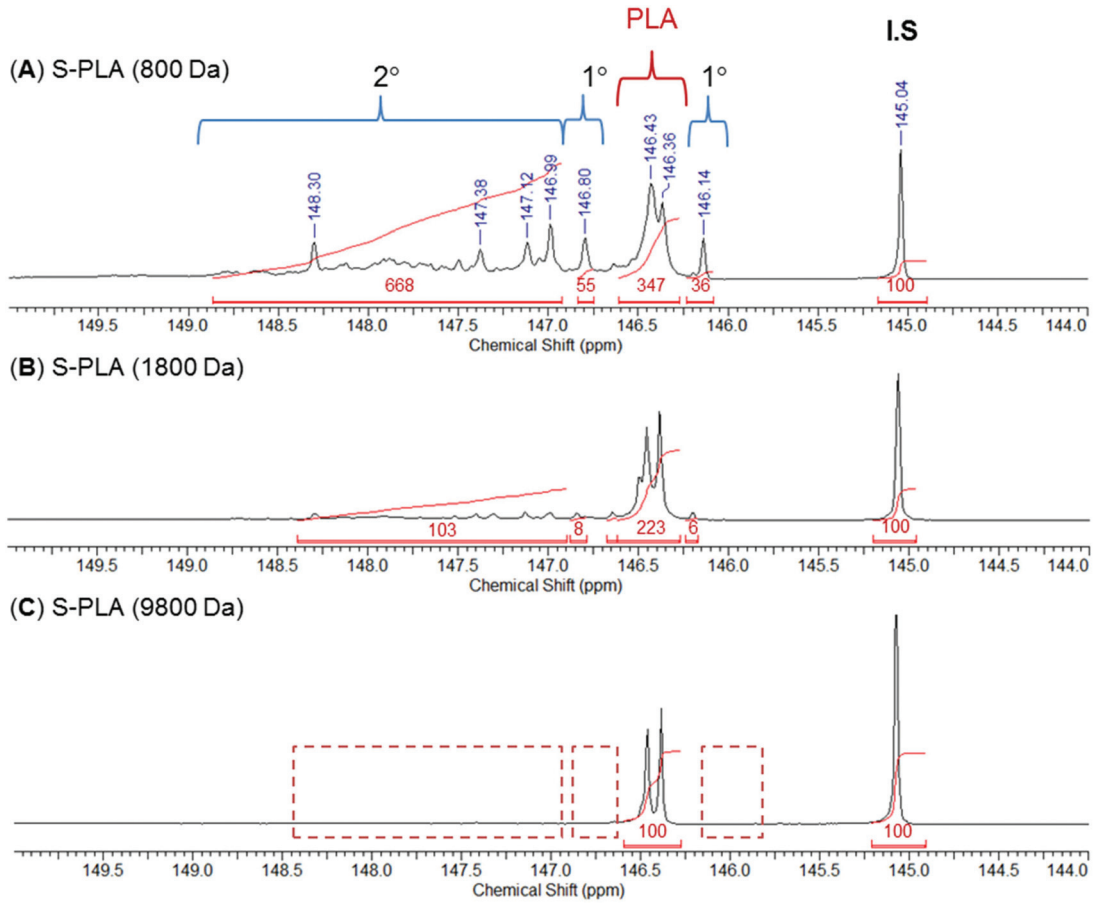


**Fig. 4** $^{31}$P-NMR spectra comparing S-PLA synthesised in $scCO_2$ at (A) 800 Da, (B) 1800 Da and (C) 9800 Da. Peaks corresponding to PLA end groups (PLA) and primary and secondary hydroxyl groups on D-sorbitol (1° and 2°, respectively) have been highlighted. IS = Cyclohexanol. Note the decrease in peaks associated with the co-initiator hydroxyl groups as the molecular weight increases, highlighted by the dashed boxes in spectrum (C).

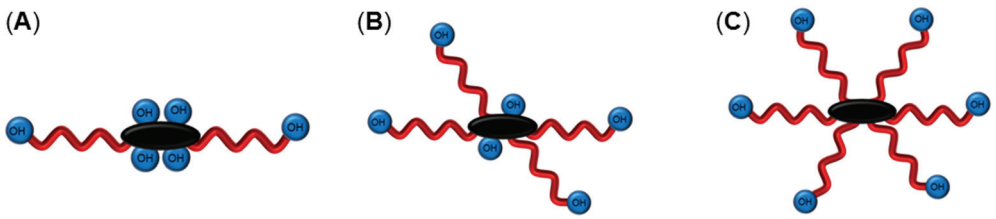


**Fig. 5** Schematic diagram of S-PLA synthesised with varying degrees of PLA branching; (A) 2 arms, (B) 4 arms and (C) 6 armed structures. The sorbitol core (black), hydrophobic PLA arms (red) and hydrophilic hydroxyl groups (blue) are displayed.

observations further, lower molecular weight S-PLA (1800 Da) was analysed using MALDI-ToF-MS.

When evaluating compounds synthesised using $scCO_2$ only peaks corresponding to D-sorbitol initiated PLA were observed (a and b, Fig. 6-I) as expected. When analysing the equivalent compound synthesised at 140 °C in the bulk, the same peaks are observed (peaks a and b) (Fig. 6-II) along with additional peaks (series c and d), which are not detected in S-PLA synthesised using $scCO_2$. Series c is observed 18 $m/z$ downfield from series b and is attributed to the dehydration of D-sorbitol, forming sorbitan which is known to occur under acidic conditions and is accelerated by elevated temperatures.[62] Sorbitan can then itself act as a co-initiator to ring open D,L-lactide leading to another unwanted side reaction. Series d is attributed to the esterification of sorbitan-PLA with the 2-ethylhexanoic acid. These compounds have also been identified by Kowalski *et al.*[63] when synthesising linear PLA in the bulk. The identification of these side-products by MALDI-ToF-MS (Fig. 6) helps to explain the broader $Đ$ observed for S-PLA synthesised in the bulk that was demonstrated by GPC (Fig. 3).

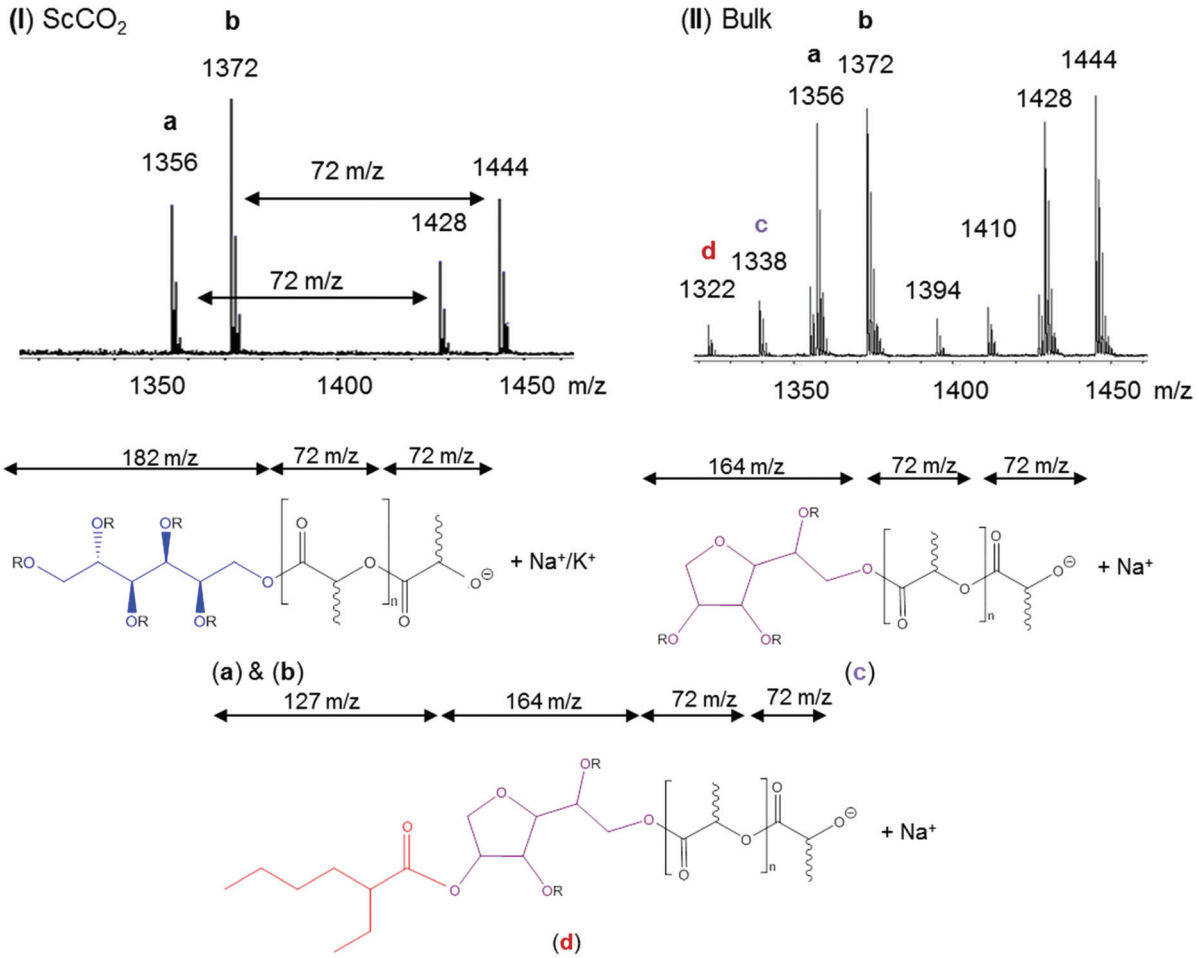


Fig. 6 MALDI-TOF mass spectra acquired in reflectron-mode of S-PLA synthesised using an 8 : 1 ratio in (I) $scCO_2$ and (II) bulk, after 3 hours. Peaks corresponding to S-PLA with $Na^+$ and $K^+$ adducts labelled (a) and (b) respectively. Note additional peaks observed in spectrum (II), assigned to side-products related to products initiated with sorbitan (c) and sorbitan-PLA derivatised with 2-ethylhexanoate, from the catalyst (d). The proposed structures of the side-products are shown below the spectra, where R = lacotyl repeat unit, H.

### 3.2 Kinetic measurements of S-PLA synthesis in $ScCO_2$

A linear increase in molecular weight with time was observed when conducting kinetic measurements on the synthesis of S-PLA (40 : 1 ratio) in $scCO_2$ (Fig. 7A). This is consistent with a controlled polymerisation, and is temperature dependent, as observed by taking kinetic measurements at 80 °C, 95 °C and 120 °C.

When synthesis was conducted at 120 °C, 88% conversion was achieved in only 5 minutes after which the molecular weight was observed to plateau due to a ring-chain equilibrium state (Fig. 7A). However, it is interesting to note that the reaction still commences at much lower temperatures despite D,L-lactide and D-sorbitol only visually being liquefied at 95 °C (Fig. 2-II). This suggests that the monomers must be partly liquefied and/or soluble in the $scCO_2$ at lower temperatures. The fact that the monomer could be soluble in the $scCO_2$ at 95 °C is supported by the prior literature. Stassin and Jérôme[33] investigated enantiomerically pure L-lactide and they identified that ~48% of the monomer was soluble in $scCO_2$ at 70 °C and 300 bar, while the excess formed droplets of melted monomer. This finding for L-lactide is supported by Gregorowicz[34] who studied the solid–liquid–vapour equilibria between L-lactide and $scCO_2$. At 80 °C and 240 bar the monomer was observed to be in a vapour and liquid phase. However, reducing temperature to 50 °C, at a constant pressure, gave a vapour and solid phase. Although these reports concerned L-lactide a very similar solid–vapour relationship is thought to occur with D,L-lactide at 80 °C. Thus we can reasonably infer why the reaction continues even at this low temperature despite the fact that the reactants visually remain solid. As the reaction progresses, the $scCO_2$ is thought to lower the viscosity and reduce the $T_g$ of the S-PLA product,[58] aiding both further polymerisation (lowering viscosity), solubilisation and mass transport of the monomers, allowing the reaction to continue.

$^1$H-NMR measurements allow us to follow the levels of conversion and in doing so the apparent rate of polymerisation ($k_{app}$) could be monitored, allowing us to visualise the influence of temperature. The kinetic plots for the polymerisation of S-PLA at temperatures of 80–120 °C are shown in Fig. 7B. At

 

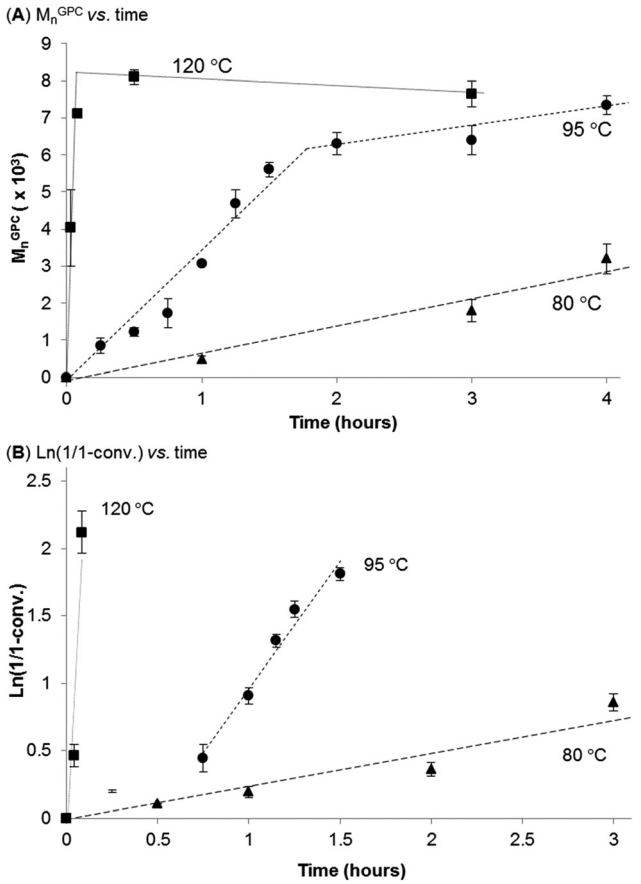


Fig. 7 Plots of (A) molecular weight of S-PLA and (B) Ln(1/1-conv.) as a function of the polymerisation time for reactions conducted at 80 °C (●), 95 °C (■) and 120 °C (▲) in $scCO_2$.

120 °C the apparent rate of polymerisation is over 13 times greater than the same reaction conducted at 95 °C ($k_{app}$ = 24.4 *vs.* 1.9), while the reaction at 80 °C is approximately 8 times slower than at 95 °C ($k_{app}$ = 1.9 *vs.* 0.24).

When conducting the reaction at 95 °C the increase in conversion is noted to produce two different linear relationships as the projected trend line will not intersect the origin of the graph (Fig. 7B). The causes of these two separate rate regions were attributed to the low reaction temperature lengthening the time for the *in situ* coordination of $Sn(Oct)_2$ and the co-initiator. This generates an induction period where little polymerisation is achieved in addition there is likely to be an impact of the limited solubility of the lactide at lower temperature.

By increasing the temperature to 120 °C no induction period was observed either because the "*in situ*" coordination rate has been increased and/or the monomer solubility has increased. If this is a solubility effect these data would suggest that the system needs to build polymer rich regions in the reaction mixture which will then aid monomer compatibilisation. In the bulk, reactions using $Sn(Oct)_2$ are often characterised by significant induction periods arising from a slow insertion of the first 2–4 monomer units,[27] and increasing reaction temperature is the solution adopted to overcome this commercially.[3]

Interestingly, the induction period is almost impossible to observe for the polymerisation at 80 °C because the low reaction rate at this temperature slows down the insertion of all monomer units, not only the first 2–4 units.

Reactions conducted in $scCO_2$ at 95 °C show a highly controlled (*Đ* of 1.1–1.2) increase in molecular weight determined by GPC and MALDI-ToF-MS (Fig. 8). An increase in molecular weight can be identified when comparing samples taken after 1 and 3 hours (Fig. 8-I–II). It is interesting to note that spectra from S-PLA synthesised in $scCO_2$ are dominated by the distribution with a mass separation of 144 *m*/*z*.

A secondary distribution with a mass separation of 72 *m*/*z* only becomes apparent at later times (Fig. 8-II). Meanwhile, the MALDI spectrum of S-PLA synthesised in the bulk (Fig. 8-III–IV) is dominated by a mass separation of 72 *m*/*z*. This would suggest that transesterification is considerably enhanced in the bulk compared to $scCO_2$, which could be a result of the increased temperatures (140 °C *vs.* 95 °C) or is a consequence of the reduced viscosity in $scCO_2$ leading to a slower rate of chain–chain scissioning between PLA arms.

### 3.3 Purification of sorbitol poly(lactic acid)

When synthesising S-PLA the conversion plateaus at 80–90% and unreacted monomer will therefore be present in the final product. The conventional purification of PLA requires either thermal devolatilisation or use of organic solvents and both are energy intensive, increase the VOC footprint and are difficult to apply to S-PLA as it exhibits similar organic solvent profiles to the monomers used.

Lee *et al.*,[30] demonstrated that L-lactide could efficiently be removed using $scCO_2$ extraction at 80 °C after 1 hour. Reactions were conducted at these conditions (80 °C and 240 bar), demonstrating that a reduction in D,L-lactide from a crude sample was possible in only 15 minutes. However, whilst L-lactide is in the vapour and liquid phase at these conditions,[34] D,L-lactide is a solid (ESI Fig. S2†). At 80 °C and 240 bar $scCO_2$ has a density of 670 kg $m^{-3}$, whereas at 45 °C the density increases to 850 kg $m^{-3}$. For this reason we explored purification at this lower temperature (45 °C, 240 bar, 15 minutes).

To assess the efficiency of D,L-lactide removal from S-PLA at these mild conditions (45 °C, 240 bar), the product was spiked with known quantities of D,L-lactide monomer which could be quantified by $^1$H-NMR by comparison to a known concentration of an internal standard (dimethyl sulphone, $\delta$ = 2.99) (ESI Fig. S5†). Samples were purified using $scCO_2$ for 15 minutes and a direct correlation was observed between the amount of D,L-lactide added (from 10–30 weight% in respect to the polymer) and the quantities removed (90–340 mg) was observed (ESI Fig. S6†). Furthermore, it was concluded that in order to ensure efficient extraction the pressure was required to be ≥140 bar (ESI Fig. S7†). Increasing pressure from 140 bar to 240 bar only increases removal by a few %, while reducing

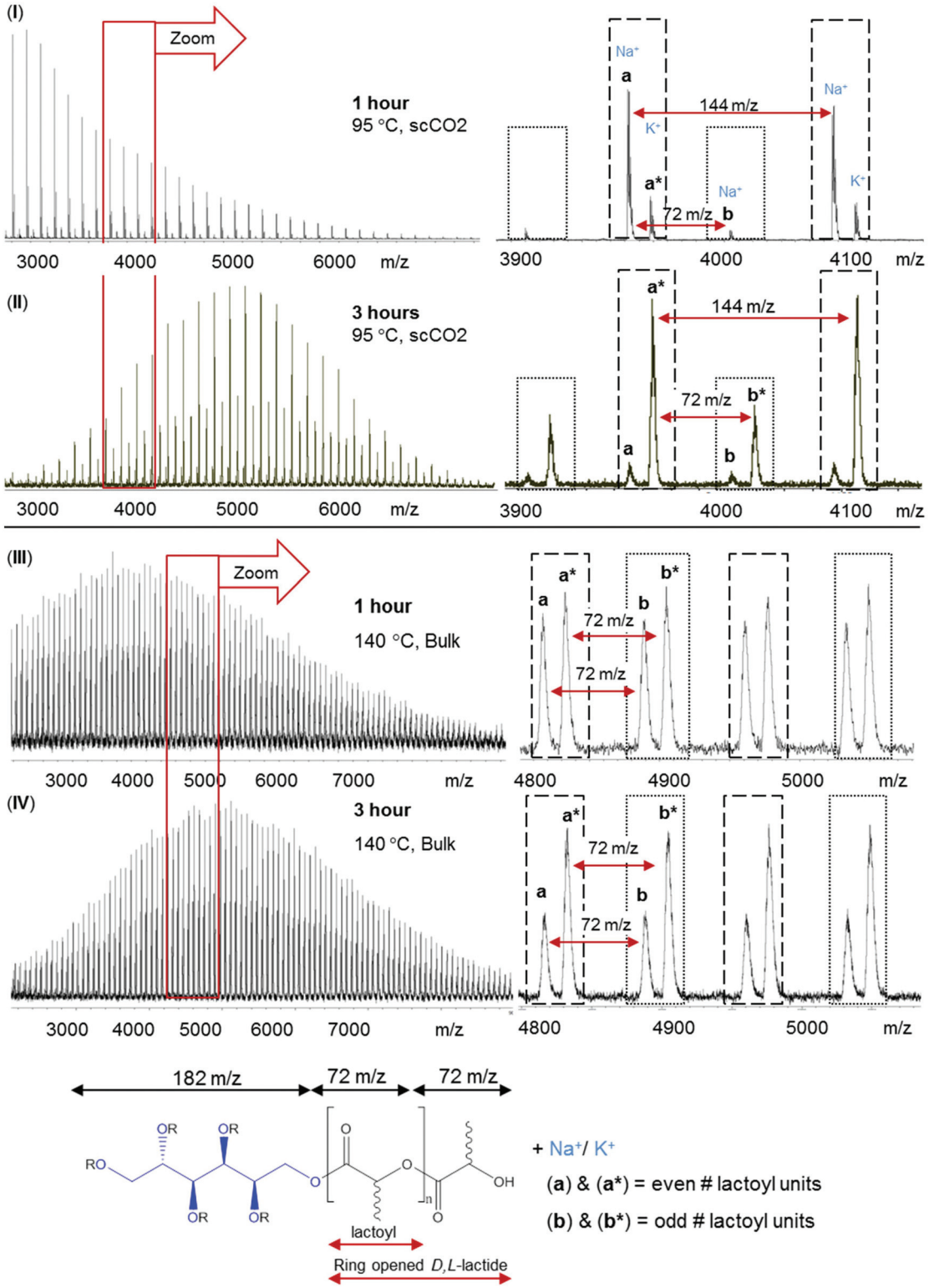


**Fig. 8** MALDI-ToF-MS of S-PLA synthesised at 95 °C using $scCO_2$ (I & II) and at 140 °C in the bulk (III & IV) after 1 and 3 hours. The full spectra (left) and zoomed regions (right) are shown. Peaks a and a* correspond to the same compound but with $Na^+$ and $K^+$ ion adducts. This is also the case for peaks labelled b and b*. Note the increase in transesterification (peaks differing by 72 *m/z*) observed for reactions conducted in the bulk.

the pressure from 140 bar to 110 bar results in a 20% reduction in the amount of monomer removed. This was attributed to the changes in $scCO_2$ density, where a significant increase in density is observed from ~50–130 bar, (70 to 550 kg $m^{-3}$) while density remains relatively constant from 140 to 240 bar, at 45 °C (715 to 850 kg $m^{-3}$).[28,64]

Despite being able to efficiently remove the majority of the monomer in a very short time it proved challenging to increase the final product purity above 98% using just $scCO_2$. Even increasing purging times from 15 minutes to 45 minutes did not remove the remaining ~15–20 mg $ml^{-1}$ D,L-lactide, and the quantities removed were observed to plateau (Fig. 9B and ESI Fig. S8†).

Therefore, to enhance the extraction of the residual quantity of D,L-lactide, ethanol was added as a co-solvent. After initially purifying the polymer with $scCO_2$ for 15 minutes, a small amount of ethanol (0.5 ml) was added to the reaction vessel. The sample was purged for a further 30 minutes to ensure the co-solvent (and remaining monomer) was fully removed (Fig. 9). This resulted in complete removal of D,L-lactide, determined by $^1$H-NMR, and demonstrates a viable route to the low-energy purification of PLA polymers. The extracted monomer was collected in a vial and potentially provides a method of recycling and reusing the reagent.

The typical level of tin in the final polymer samples was assessed through ICP-EOS measurements, where a method in which the material was degraded using microwave digestion was found to be the most reliable. This data compared samples both pre- and post-purification using $scCO_2$ and ethanol as a co-solvent. These results were found to be 2890 ppm ± 5% and 1670 ppm ± 5% which represents an overall Sn reduction of 42%. When synthesising polycaprolactone (PCL) Stjerndahl *et al.*[65] identified a 32% reduction in tin post-purification, when dissolving the sample in chloroform followed by precipitation in cold hexane and methanol (90 : 10 v/v). In comparison, the use of supercritical fluid extraction for purification is very competitive, without the need for VOC solvents. Further measurements will be required to define the effect of different processing conditions on the level of reduction that is achieved *e.g.* to determine the impact of pressure, temperature and time on tin removal. The GPC and MALDI data for both the pre- and post-purified samples were collected to ensure that no degradation or post-functionalisation had occurred during processing (ESI Fig. S9 and S10†) and showed that the pre and post treatment materials are identical.

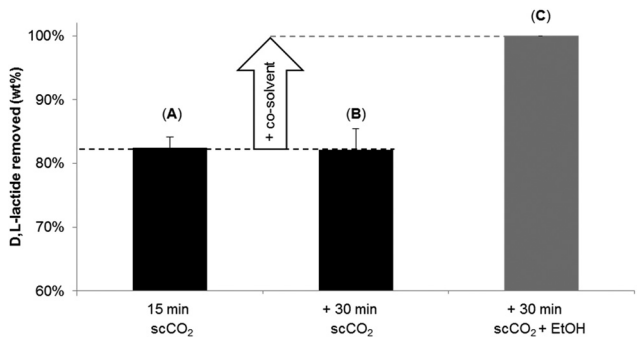


**Fig. 9** Purification of S-PLA after (A) 15 minutes using $scCO_2$. This sample was then purified for a further (B) 30 minutes using $scCO_2$, and (C) 30 minutes using $scCO_2$ and EtOH as a co-solvent. Using a co-solvent we can efficiently remove all D,L-lactide from S-PLA, below the detection limit of the $^1$H-NMR.

### 3.4 Product toxicology assessment

When considering the next generation biobased surfactants, low-toxicity and hence the purity and toxicology of the final product are attributes that are becoming increasingly important, especially in end-use applications in biomedical and personal care.[66–69] The toxicity of tin containing compounds has previously been assessed using a broth dilution method against *E. coli*,[49] while Sobczak *et al.*,[70] evaluated the toxicity of branched PCL and PLA using a bacterial luminescence test and two protozoan assays. Although cell culture assays with mammalian cells are currently the most popular *in vitro* tests for evaluating toxicity, other assays involving bacteria and lower Eurkaryotes are often used as preliminary methods to indicate differences in toxicity between compounds.[70]

As the growth of *E. coli* is known to be inhibited by tin,[49] and as PLA has previously been evaluated against *S. aureus*[50,51] these Gram negative and Gram positive bacteria, respectively, were used as a preliminary screen to gain an insight into the toxicity of the catalyst, monomer and products synthesised before and after purification using $scCO_2$. Before purification, lower quantities of our S-PLA product would be expected to inhibit bacterial growth, since they contain higher levels of lactide and $Sn(Oct)_2$.

As expected $Sn(Oct)_2$ was found to be relatively toxic (at low concentrations) when screened against *S. aureus* and *E. coli* (ESI Table S1†), while in comparison D,L-lactide was found to be 5–6 fold less toxic to both bacteria. Our assessment of crude S-PLA (1800 Da) showed that a 10 mmol sample inhibits 50% of the growth ($LC_{50}$) of *S. aureus* (Fig. 10).

Increasing the purity of this polymer by only 10% reduces the toxicity of S-PLA 3 fold meaning that 30 mmol is now required to achieve the same inhibition. This reduction in toxicity after only 15 minutes purification is thought to be attributed to the removal of D,L-lactide and $Sn(Oct)_2$ and highlights that purification can significantly improve the toxicity profile of the polymers. By increasing the purity of the polymer >90% (as conducted for S-PLA 6800 Da using a co-solvent) we would expect the toxicity to drop even further. This trend was also observed when screening against *E. coli* (ESI Fig. S11†) and is similar to observations made by Sobczak *et al.*,[70] who identified L-lactide to be slightly toxic against the bacteria and protozoa assessed, while purified PLA displayed no toxicity.

### 3.5 Product application assessment

A good indicator of surface active properties in an aqueous system is to measure the ability of a compound to reduce the

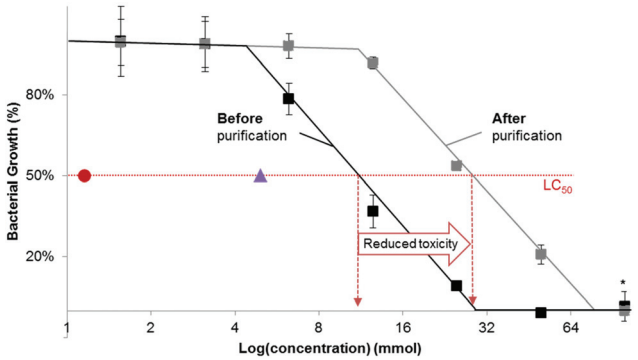


**Fig. 10** Bacterial growth (*S. aureus*) at varying concentrations of S-PLA (1800 Da), before (—) and after (—) purification with $scCO_2$. The dashed horizontal line indicates the $LC_{50}$ and the vertical dashed arrows clearly show the shift for the purified compound. $LC_{50}$ values for $Sn(Oct)_2$ (●) and D,L-lactide (▲) have been included to aid interpretation. *Points excluded in $LC_{50}$ calculations.

surface tension of water. Water has a surface tension ($\sigma$) of ~70 mN $m^{-1}$ and any compound which can reduce this tension is generally classed as a surfactant (typically ≤60 mN $m^{-1}$) (ESI Fig. S12†). D-Sorbitol and D,L-lactide do not reduce the surface tension and neither does high molecular weight S-PLA (6800 Da) (Fig. 11). The high proportion of hydrophobic lactoyl arms in relation to a small number of hydrophilic hydroxyl end groups is thought to be the reason for this observation. However, lower MW samples of S-PLA with an $M_n^{GPC}$ of 800 Da and 1800 Da clearly do reduce $\sigma$ to 42 mN $m^{-1}$ and 54 mN $m^{-1}$, respectively.

These results are promising when benchmarked against a range of commercial petrochemical surfactants (where $\sigma$ ranged from 35–50 mN $m^{-1}$), and the data also highlight how modifying chain length and degree of branching of S-PLA is an essential route to tailoring the surface active properties of these biobased dispersants.

The ability of the compounds to aggregate and micellise in an aqueous solution depends on their concentration. The surface tension will drop until the critical micelle concentration (CMC) has been reached.[71] At concentrations below this level only single surfactant molecules exist while above the CMC these molecules will form aggregates.[72] The CMC value of the most promising compound synthesised (S-PLA 800 Da, ESI Fig. S13†) was determined to be 327 μM (0.26% w/v), consistent with commercial surfactants which typically have CMC values ≤1% w/v (Table 2). When comparing to the petrochemically derived commercial compounds it is clear that Tween™ surfactants are efficient at much lower concentrations (<6 μM). However Pluronic™ L35, when compared to S-PLA (800 Da) (synthesised using $scCO_2$), requires approx. 40% higher concentrations to reach the CMC value. The knowledge of these CMC values is important when using surfactants to give an indication of the concentration required for the compound to be efficient.

The ability of S-PLA (800 Da) to disperse particles can also be visualised when adding a hydrophobic dye (coumarin 6) to an aqueous system (Fig. 12). By itself, coumarin 6 lacks the solubility to be retained and will lie on top of the water phase. However when small quantities of SPLA (800 Da) are present (1% w/v) these compounds efficiently disperse the dye in the water phase, which can clearly be visualised under UV light.

**Table 2** Comparison of CMC values of synthesised and commercial surfactants

| Compound | Molecular weight | CMC (μM) | CMC (% w/v) | Ref. |
|---|---|---|---|---|
| S-PLA (800 Da) | 800 Da | 327 | 0.26% | — |
| Pluronic L35 | 1900 Da | 530[a] | 1.00% | 73 |
| Tween 80 | 1300 Da | 1.2 | 0.002% | 72 |
| Tween 20 | 1200 Da | 5.9 | 0.007% | 72 |

[a] Determined by fluorescence spectroscopy at 25 °C, technique shows good agreement with surface tension measurements.[71]

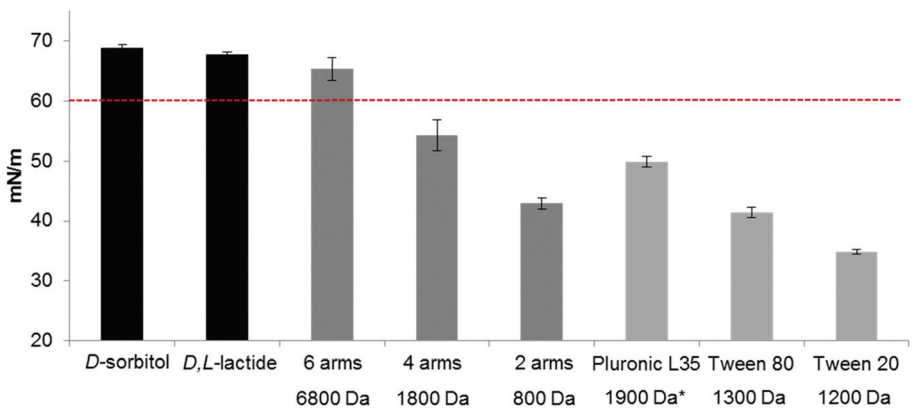


**Fig. 11** Equilibrium surface tension of starting material (■) and synthesised compounds (■) benchmarked against a range of commercial surfactants (■). Compounds below the dashed line are considered to have surface active properties. *1% w/v used.

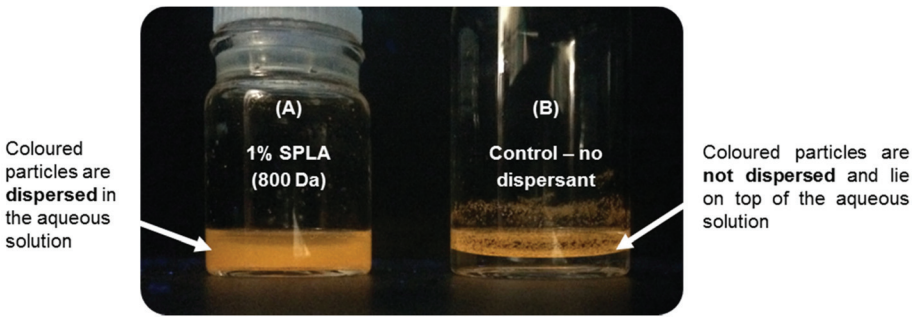


**Fig. 12** Dispersion of coumarin 6 in water (A) with and (B) without S-PLA (800 Da), viewed under UV light.

## 4. Conclusion

A green, low energy, sustainable one-pot process for the synthesis and purification of branched PLA has been demonstrated using controlled ring opening polymerisation of D,L-lactide in $scCO_2$ with D-sorbitol as a co-initiator. The process can be performed at significantly reduced temperatures (as low as 80 °C) compared to bulk reactions (140 °C) detailed analysis by MALDI-ToF-MS, GPC and $^1$H-NMR demonstrate that the $scCO_2$ approach reduces the formation of side-products, and leads to narrower polymer dispersities, and good control of the degree of branching.

We additionally demonstrate the ability to purify these compounds using a low energy extraction process (using $scCO_2$ and small quantities of ethanol as a co-solvent), achieving complete removal of the D,L-lactide in only 45 minutes, at low temperatures of 45 °C and 240 bar, eliminating the need for multi-step purification methods, toxic solvents and high energy vacuum devolatilisation. In practice, the synthesis and purification could be performed in a one pot process potentially opening up a new low temperature synthetic route that up till now could only be achieved with considerable use of conventional organic solvents on the large scale.

Initial toxicity screens highlight that these purification steps can significantly improve the toxicity profile of the polymers, an important aspect to consider when assessing end use. The multi-armed branched products display interesting surface active properties which are competitive when benchmarked against a range of commercial petrochemical alternatives, highlighting their potential as biobased surfactants. This method of tailoring the number of PLA branching points and hence the ratio of hydrophilic hydroxyl groups to the hydrophobic PLA backbone may prove to be a viable route to biobased replacements for petrochemically derived poly(ethylene oxide) and poly(propylene oxide) (the building blocks used in the synthesis of commercial Pluronic™ and Tween™ surfactants), where concerns regarding toxicity and sustainability are becoming paramount.

## Acknowledgements

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