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Synthesis of water-soluble surfactants using catalysed condensation polymerisation in green reaction media†

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Sustainable and biobased surfactants are required for a wide range of everyday applications. Key drivers are cost, activity and efficiency of production. Polycondensation is an excellent route to build surfactant chains from bio-sourced monomers, but this typically requires high processing temperatures (≥ 200 °C) to remove the condensate and to lower viscosity of the polymer melt. In addition, high temperatures also increase the degree of branching and cause discolouration through the degradation of sensitive co-initiators and monomers. Here we report the synthesis of novel surface-active polymers from temperature sensitive renewable building blocks such as dicarboxylic acids, polyols (D-sorbitol) and fatty acids. We demonstrate that the products have the potential to be key components in renewable surfactant design, but only if the syntheses are optimised to ensure linear chains with hydrophilic character. The choice of catalyst is key to this control and we have assessed three different approaches. Additionally, we also demonstrate that use of supercritical carbon dioxide (scCO₂) can dramatically improve conversion by reducing reaction viscosity, lowering reaction temperature, and driving condensate removal. We also evaluate the performance of the new biobased surfactants, focussing upon surface tension, and critical micelle concentration.

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Introduction

Successful synthesis of linear polyol-polyesters can lead to development of new sustainable surfactants^{1–5} and there is particular focus on the use of carbohydrates as a renewable resource for polymer design,^{3,6,7} because they bring a rich variety of structures with abundant stereochemical diversity.⁸ Carbohydrates such as glucose, glycerol and D-sorbitol contain multiple hydroxyl groups and are emerging as alternative hydrophilic moieties in surfactants.^{1,9} These materials could also offer a renewable alternative to other well-established hydrophilic polymers and macromonomers such as poly(ethylene glycol) (PEG), where there are increased concerns regarding toxicity.¹⁰ Though carbohydrates are viewed as more acceptable, only a small number are currently competitive on price, quality and availability compared to the standard petroleum

derived materials.¹¹ An additional problem is that polyol monomers are often thermally unstable and susceptible to side reactions such as dehydration and decarboxylation which are deleterious, leading to lowered hydrophilicity and colouration.¹²

When employing renewable hydrophiles in surfactant design, the water solubility of the compound is essential and multiple building blocks are therefore used when modifying polymer properties and tailoring end use.¹¹ The number of building-blocks in commercial polyglucosides and polyglycerol is generally between 2–10 repeat units, which increases the number of free hydroxyl groups along the oligomer/polymer backbone.¹³ This number is dependent on the catalyst system employed and it is well known that there is decreased selectivity observed for acid/base catalysed homopolymerisations at high MWs.¹⁴ This limits the number of repeat units, as undesirable branched and cyclic side-products are formed at higher MWs, reducing the hydrophilicity of the end product.^{13,15} Furthermore, when conducting polymerisations using polyols, viscosity build and higher temperatures lead to darkening in colour and this often renders products unsuitable for personal care applications.^{14,15}

To overcome concerns regarding control of molecular weight and side-product formation, the linkage of polyols

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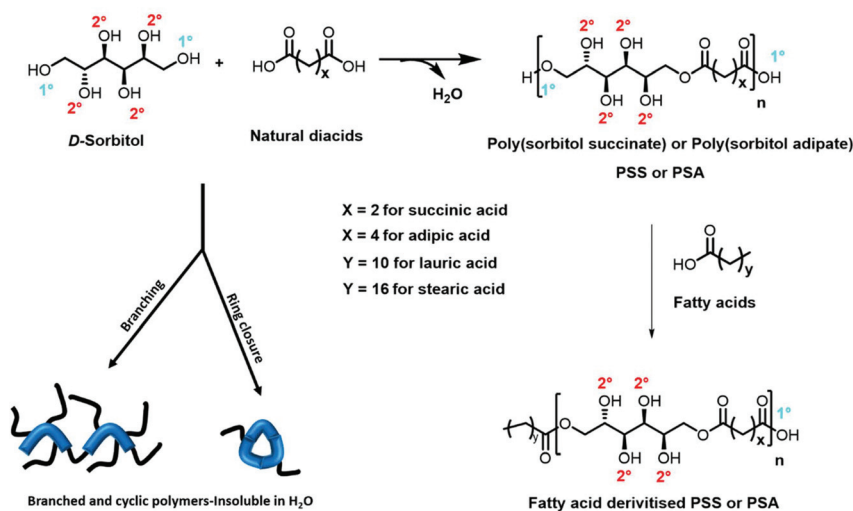


Fig. 1 Condensation polymerisation of diacids with D-sorbitol, followed by end group functionalisation using fatty acids. Note the reaction at the primary hydroxyl groups (1°) is essential to ensure the secondary hydroxyls (2°) are free for hydrogen bonding along the polymer backbone in order to deliver hydrophilicity. Reactions catalysed by *p*TSA are non-selective and result in branched and cyclic polymers that are insoluble in water and highly coloured.

cesses influenced by the presence of contaminants and side-products could have also occurred.⁹ Mass spectrometry indicated that synthesis using *p*TSA also resulted in esterification at the secondary hydroxyl groups (ESI, Fig. S2†), leading to the undesirable deviation from linearity in the product and also causing a decrease in the hydrophilicity and hence water solubility.

Ring closed sorbitan is an indicator of dehydration and also shows that ring closure side reactions took place alongside polymerisation in the presence of *p*TSA.^{3,9} Peaks corresponding to sorbitan derivatives were detected exclusively in the product synthesised with *p*TSA. The darkening in colour would make these products undesirable for personal care applications, and their reduced solubility would make them unsuitable as hydrophilic components in surfactant design. For these reasons *p*TSA was not further investigated. On the other hand, reactions catalysed using Novozym 435 and K₂CO₃ were much more promising; the products were found to be soluble in aqueous environment and considerably lighter in colour. In addition, the enzyme could be washed and re-used as has been previously demonstrated.^{31,32} Potentiometric titrations showed that there are considerably more hydroxyl groups than carboxylic acid groups in the samples from the enzymatic and carbonate catalysed polymerizations (Table 1). This excess of hydroxyl groups suggests that ring closure and branching,

which are a consequence of the reaction of the secondary alcohol groups of sorbitol, have been minimised. Clearly, this also explains the high aqueous solubility of these compounds. However, with both Novozym 435 and K₂CO₃, it can be seen that the OH:COOH ratio is slightly less than their expected (theoretical) values (see ESI Table S1†) indicating that reactions at the secondary hydroxyl groups may not have been eliminated completely. It is also possible that the titrations could be giving slightly lower hydroxyl values because acetylation of the secondary hydroxyl groups can be challenging due to steric hindrance. We can see this in the titration of pure D-sorbitol, which gave an average of 5.8 hydroxyl groups instead of the theoretical value of 6. It is also important to note that there is very likely a contribution from reactions at the secondary hydroxyl groups of sorbitol. This is something that we have investigated in the past and there is clear evidence that the enzyme does deliver a small level of esterification at the secondary alcohol moiety as measured by phosphorylation.^{33,34} However, the mass spectrometry data strongly hint that over esterification, and degradation of sorbitol was minimized when using Novozym 435 and K₂CO₃ (ESI, Fig. S2†) and it is surprising that K₂CO₃ would catalyse the polymerization with such close specificity to Novozym.

Table 1 Comparing synthesis of poly(sorbitol adipate) (PSA) using bio- and chemo-catalysts, synthesised at 95 °C and 120 °C under solvent free conditions for 48 hours

Entry	Catalyst	Conversion ^a (%)	Ratio OH : COOH ^b	<i>M</i> _n (g mol ⁻¹) ^b	Appearance
1	<i>p</i> TSA	93	n/a	1600 ± 50	Sticky dark brown solid
2	N435	82	13 : 1	1100 ± 100	Yellow oil
3	K ₂ CO ₃	83	20 : 1	1700 ± 100	Pale yellow oil

^a Determined by H-NMR. ^b Determined by potentiometric titration.



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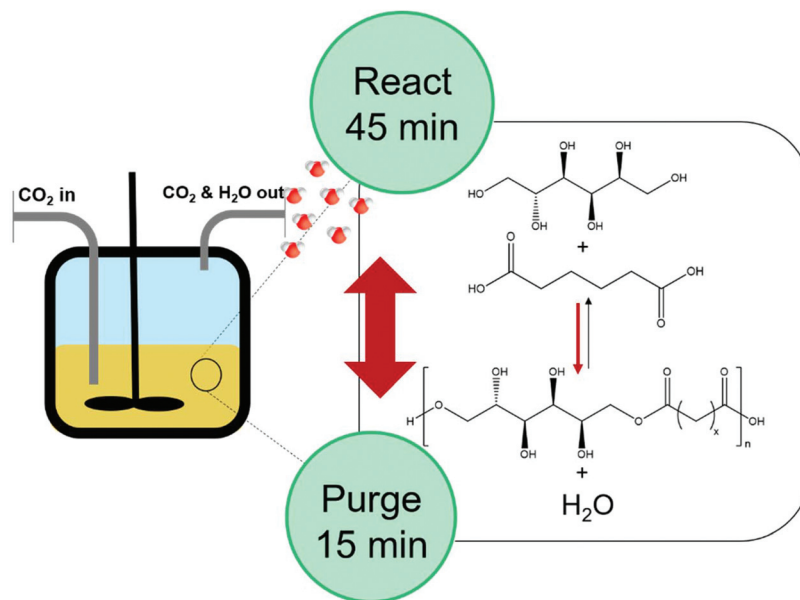


Fig. 2 Schematic representation of the condensation polymerisation of adipic acid with D-Sorbitol in scCO_2 in a reactor vessel. The reactor is filled with CO_2 through an inlet while CO_2 and H_2O exit through the outlet on the right when the reactor is purged.

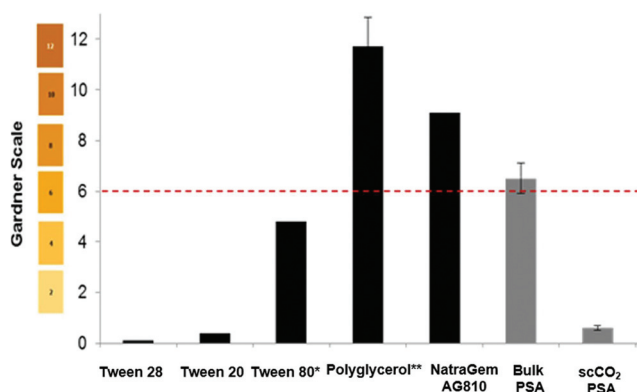


Fig. 3 Gardner values for a range of commercial surfactants (■) compared against poly(sorbitol adipate) synthesised in the bulk and in scCO_2 (□), at 50% solids in aqueous solutions. The bio-based surfactant NatraSense™ AG810, polyglucose derivatised with C8–C10 fatty alcohol, has been bleached with $\text{NaOH}/\text{H}_2\text{O}_2$ post derivatisation. The Gardner colour scale is displayed for the values on the left. * At 100% solids, ** average of three samples synthesised in-house at Croda. The dashed line indicates the colour target for bio-based surfactants. Note the low colour achieved for the synthesis of poly(sorbitol adipate) in scCO_2 .

to NatraSense™ AG810, a substantial improvement in colour is observed without the need for bleaching. This colour is improved even more significantly to a value of 2 when using scCO_2 with extraction. This is a significant finding, highlighting a method of minimizing discolouration without the need for harsh post-reaction bleaching steps that often used to improve colour of surfactants for personal care products.

Polymerisations were also attempted at a lower temperature of 100 °C, but only a low conversion of 37% was achieved after

24 hours (Table 2, entry 1). The low conversion is likely to be caused by the reagents not being fully liquefied at this temperature. Although it is desirable to work at lower temperatures, this is clearly not efficient and so all further reactions were carried out at 120 °C. The “react, extract, repeat” approach in scCO_2 was therefore also applied to synthesise poly(sorbitol succinate) at 120 °C. Results of this reaction are shown in Table S3 of the ESI.†

Functionalising with fatty acid end groups – developing a surfactant

Sorbitol based polyesters, PSA and PSS were explored as hydrophilic components in surfactant design. The aim was to selectively end-cap the terminal primary hydroxyl groups on the polyol-polyesters *via* esterification with hydrophobic fatty acids.¹ Simultaneously maintaining aqueous solubility and molecular weight but avoiding over- and transesterification.

Derivatisation of the PSA and PSS chains was controlled by targeting the polyester chain to end-cap feed ratios. When observed through a view cell as illustrated for PSA synthesis in (ESI Fig. S4†), the reactants were seen to be initially heterogeneous, possessing distinct fatty acid and polyester layers. With time, these phases morphed into a homogeneous emulsion as the polyol-polyester derivatives which act as surfactants were formed. This is supported by findings from Ducret *et al.*³⁶ who identified increased solubility of D-sorbitol in an oleic acid phase as soon as small amounts of monomer were produced. Post reaction, the samples were washed with chloroform to remove unreacted fatty acid and the final products were found to be light amber water soluble solids. The reaction was monitored using $^1\text{H-NMR}$, though exact conversions could not be estimated as resonances from the fatty acid (c,



2.33 ppm) and the poly(sorbitol adipate) backbone (a, 2.2–2.4 ppm) overlap (ESI Fig. S5†). This overlap is also apparent for poly(sorbitol succinate) end-groups (2.22–2.43 ppm). However, the percentage of fatty acid integrated into the polyester backbone could be determined by assessing the integrals of the triplet at 0.85 ppm (g, terminal methyl group in lauric and stearic acid) against peaks at 1.35–1.60 ppm (b, b', poly(sorbitol diacid) backbone protons). Results from the end-capping of the polymers are summarised in Table 3.

High gravimetric yields (>94%) were achieved in all cases except for entry 1 where it was found that 6 hours was too brief a time to achieve a significant amount of end-capping. Consequently, the reaction mixture was unable to form a single homogeneous phase on this timescale. Low end capping efficiency means a biphasic system persists, hampering the reaction between the hydrophobe and hydrophile. Reactions that were allowed to proceed for 24 hours were able to overcome the initial biphasic period of the reaction and form a homogeneous phase.

Surfactant tension measurements of D-sorbitol-based polyesters: dynamic and static

To confirm the surface activity of the synthesised D-sorbitol based polyesters, dynamic and static surface tension measurements were performed. Results were compared to surface tension reductions achieved using commercial Tween™ and Pluronic™ surfactants that are based on petrochemical sourced PEG (polyethylene glycol) and PPG (polypropylene glycol). Neither the starting materials (D-sorbitol and dicarboxylic acids), nor the polyesters PSA and PSS reduced the surface tension of water below 60 mN m⁻¹, when measured dynamically (Fig. 4). However, all the end-capped polyesters reduced the surface tension significantly as has been shown previously.¹⁵ The end-capped PSAs reduced the surface tension of water to ~30 mN m⁻¹, with the compounds quickly migrating to the surface interface, identified by a rapid drop in surface tension (bubble was present only for short period of time; lifetime ~5000 seconds). PSS based compounds appeared to migrate to the surface at a slower rate, with a maximum reduction in surface tension being ~50 mN m⁻¹ for the laurate and ~40 mN m⁻¹ for the stearate derivative (where a reduction in surface tension was apparent at bubble lifetimes up to ~18 000 seconds). These values are comparable to the

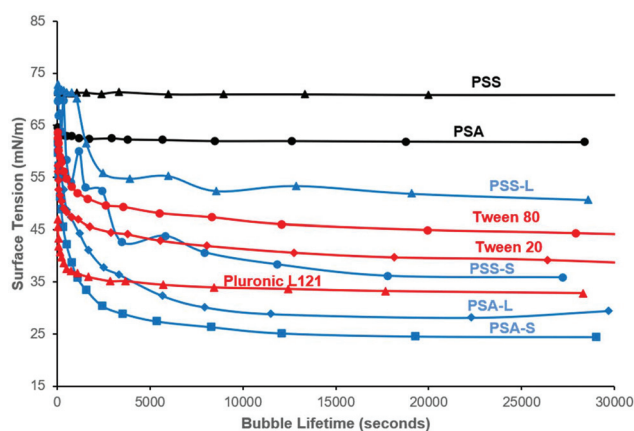


Fig. 4 Bubble Tensiometer determination of surface tension at increasing bubble lifetimes for synthesised polyesters PSA (poly(sorbitol adipate)) and PSS (poly(sorbitol succinate)) (black curves), their stearate and laurate derivatives (blue curves) and commercial surfactants (red curves). The method shows how fast the compounds migrate to the bubble-water interface. Note the reduction in surface tension for the derivatised polyesters, and that they are competitive with PEG-based commercialised surfactants Tween™ and Pluronic™.

Tween™ surfactants which reduced the surface tension to ~40–50 mN m⁻¹, while Pluronic™ 121 reduced the surfaced tension to ~35 mN m⁻¹ (Fig. 4).⁴ The Pluronic™ surfactants quickly migrated to the interface causing a sharp drop in surface tension, at low water-bubble lifetimes (<2500 seconds). The surface tension therefore quickly reaches a plateau as the equilibrium surface tension is achieved. This drop in surface tension was found to be slower for the Tween™ surfactants and a decrease in surface tension was observed at bubble lifetimes as low as ~480 seconds. The rate of reduction before reaching a plateau is dependent on the concentration and the structure of the compound evaluated. The surface tension is likely to plateau within a shorter timeframe with increased concentrations (>1 wt%), as identified previously for cationic and non-ionic surfactant systems.³⁰

In all cases the static (equilibrium) surface tension measurements were lower than the equivalent measurements using the dynamic tensiometer (Fig. 5). This would be expected as the aqueous surfactant system will be in equilibrium using the static test method. PSA and PSS were measured and found to reduce the surface tension of water slightly to 50 mN m⁻¹ and 56 mN m⁻¹ respectively. This apparent surface activity is likely caused by the difference between the hydrophilic D-sorbitol repeat units and the hydrophobic hydrocarbon backbone on the dicarboxylic acid. Thus, as the carbon chain is increased from C4 to C6 (for succinic and adipic acid, respectively) a greater reduction in the surface tension is identified. When they are end-capped with fatty acids this alters the amphiphilic balance, and a considerably greater reduction in surface tension is observed (Fig. 5). Derivatisation of PSS with lauric and stearic acids leads to surface tension measurements of 41 mN m⁻¹ and 36 mN m⁻¹

Table 3 Synthesis of end-capped poly(sorbitol diacid), using lauric acid and stearic acid

Entry	Polyester	Fatty acid	[Polyester] : [FA] ^a	Reaction time (h)	Yield ^b (%)
1	PSA	Lauric	1 : 1.3	6	88%
2	PSA	Lauric	1 : 1.3	24	96%
3	PSA	Stearic	1 : 1.2	24	94%
4	PSS	Lauric	1 : 1.5	24	98%
5	PSS	Stearic	1 : 1.5	24	97%

^a Based on M_n^{AV} of polyester. ^b Yield: weight of collected product/theoretical weight.



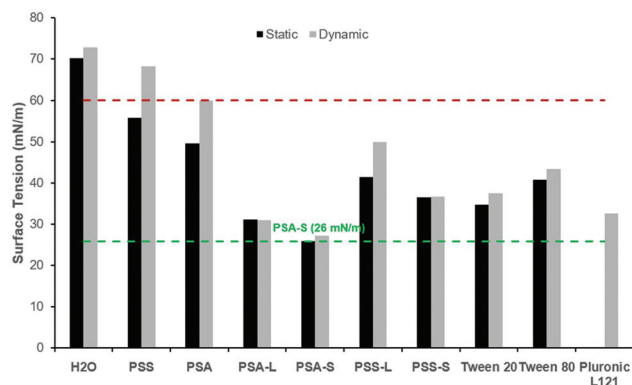


Fig. 5 Static (■) (0.5 wt%) and dynamic (▣) (1 wt%) surface tension (σ) measurements of synthesised polyesters compared to a range of commercialised surfactants. Compounds reducing $\sigma \leq 60 \text{ mN m}^{-1}$ (red dashed line) are classed as surfactants. The lowest surface tension measurement obtained is 26 mN m^{-1} for PSA-S, highlighted (green dashed line) to aid visual comparison. PSS: poly(sorbitol succinate), PSA: poly(sorbitol adipate), L: laurate, S: stearate, Tween™ 20: PEG_{20/80}-sorbitan laurate, Tween™ 80: PEG₂₀-sorbitan oleate and Pluronic™ L121: PEG₅-PPG₆₀-PEG₅.

respectively, decreasing as the fatty acid chain length increased.

As identified using the dynamic surface tension test, the greatest reduction in surface tension was observed for PSA derivatives at 26–31 mN m⁻¹. In this case, the reduction is more than doubled compared to the underivatised polyester. These results are very competitive to commercial petrochemical-based surfactants (Tween™ and Pluronic™) and are lower than D-sorbitol esters previously reported (38–46 mN m⁻¹).¹⁷ The results are also closely matched with the commercial bio-based surfactant NatraGem™ E145 (polyglycerol succinate laurate), at 29 mN m⁻¹. This is expected as their structures are relatively similar; both based on sugar polyols, dicarboxylic acids and oleochemical building blocks.

Surfactant aggregation and micellisation

Critical micelle concentration (CMC). CMC, the concentration at which the surfactant molecules self-organize in solution into micelles can be detected from surface tension vs. concentration graphs at the point where the surface tension reaches a plateau or remains fairly constant.³⁷ With the synthesized polyesters, the surface tension of PSA-S was identified to drop to $\sim 29 \text{ mN m}^{-1}$, before plateauing at this value allowing the CMC value to be determined at 0.003 wt% (ESI, Fig. S6†). For the non-capped polyesters (PSA and PSS), no drop or plateau was identified at concentrations $\leq 1 \text{ wt\%}$ (Table 4, entries 1 and 2). This is in line with expectation as they are highly hydrophilic, easily dissolve in the water and do not significantly alter the surface tension.

By contrast, the derivatised polyesters containing the smallest hydrophilic segments; PSA-L and PSA-S (Table 4, entries 3 and 4), displayed the lowest CMC values. PSS derivatised products (Table 4, entries 5 and 6) displayed higher CMC values

Table 4 CMC of the synthesised polyester surfactants determined by automated surface tension measurements using a Wilhelmy plate at concentrations from 0.1–10 000 mg L⁻¹

Entry	Product	M_n (g mol ⁻¹) ^a	CMC		
			mg L ⁻¹	wt%	μM
1	PSA	1700	>10 000	>1%	>5900
2	PSS	5900	>10 000	>1%	>1700
3	PSA-L	1900	220	0.022%	120
4	PSA-S	2000	30	0.003%	15
5	PSS-L	6100	5080	0.508%	830
6	PSS-S	6200	2040	0.204%	330
7	Tween TM 28 ^b	3900	2650	0.265%	680
8	Tween TM 80 ^c	1300 Da	1.2	0.002%	—
9	Tween TM 20 ^c	1200 Da	5.9	0.007%	—

^a Calculated from M_n^{AV} of poly(sorbitol diacid) + fatty acid. ^b PEG₈₀ sorbitan laurate. ^c Reported CMC values.⁴

than their PSA analogues. The difference in CMC values expressed in mg L^{-1} is reduced when expressed in the molar concentration, μM (accounting for the higher MW of the PSS based surfactants). In both cases the stearate derivatives displayed a lower CMC compared to their laurate counterparts (Table 4, entries 4 and 6 compared to entries 3 and 5).

This can be explained by the presence of a larger hydrophobic segment, as reported for similar systems elsewhere. Moreover, the CMC values determined for the PSA derivatives and PSS-S are much lower than the values observed for Tween™ 28 (Table 4, entry 7). On the other hand, Tween™ 80 and Tween™ 20 display low CMC values, at 0.002 and 0.007 wt% respectively (Table 4, entries 8 and 9). Of the synthesized surfactants, PSA-S shows a comparable CMC value of 0.003 wt% (Table 4, entry 4). When comparing molar concentrations, the CMC of PSA-S is slightly higher (at 15 μ M) compared to Tween™ 80 and Tween™ 20 at 1.2 and 5.9 μ M respectively (Table 4, entries 8 and 9).

Dynamic light scattering

DLS measurements indicate that the sizes of the self-assembled structures range from 130 to 220 nm (Table 5, entries 1-4). This suggests that the self-assembly of the end-

Table 5 Size distribution of surfactant micelles measured by DLS, plotting size distribution by intensity. PSS and PSA represent poly(sorbitol succinate) and poly(sorbitol adipate), whereas L/S refer to the corresponding laurate and stearate derivatives. PDI gives an indication of the width of the overall distribution, assuming a single mean

Entry	Compound	Concentration (wt%)	Z-average (<i>d</i> , nm)	PDI
1	PSS-L	0.25% ^a	220 ± 15	0.31 ± 0.02
2	PSS-S	0.50% ^a	197 ± 9	0.34 ± 0.05
3	PSA-L	0.06%	171 ± 9	0.30 ± 0.02
4	PSA-S	0.06%	129 ± 2	0.287 ± 0.003
5	Pluronic TM L121	0.06%	169 ± 2	0.160 ± 0.008
6	Tween TM 20	0.06%	820 ± 30	0.730 ± 0.004

^a Concentrations close to CMC value.

aggregation size identified for sodium capped PLA oligomers.⁴² These compounds were identified to increase in diameter over a 24-hour period from 100–300 nm, suggesting the formation of larger aggregated structures with time.

Dispersing a hydrophobic dye

The surfactant properties of the poly(sorbitol diacid) derivatives were further probed with a fluorescent dye, coumarin 6, used as a hydrophobic drug model to encapsulate into the core and to better visualize the self-assembled aggregates. Samples were prepared by making a solution of the dye in DCM then adding the dye solution dropwise to an aqueous solution of the surfactants. The mixture was then stirred for an hour at atmospheric pressure and for 30 min under reduced pressure (75 mbar) to remove DCM. Once the DCM was evaporated, the samples were placed in an orbital shaker overnight before filtering through membrane syringe filters (0.45 μm , Millex. L.G, Millipore, USA), to exclude larger aggregates and undissolved coumarin 6. The D-sorbitol based polyesters were compared to TweenTM 20 and PluronicTM L121, two commercially available amphiphilic surfactants used for emulsification, solubilisation and stabilisation. In particular, TweenTM 20 was used for oil-in-water systems (HLB >10) whereas PluronicTM L121 forms water-in-oil solutions (HLB <10).³⁰ Visual observations of filtered solutions of a blank sample containing no polymer and a control sample containing D-sorbitol gave a direct insight into the ability of the compounds to disperse and solubilise the dye in water (Fig. 7A and B).

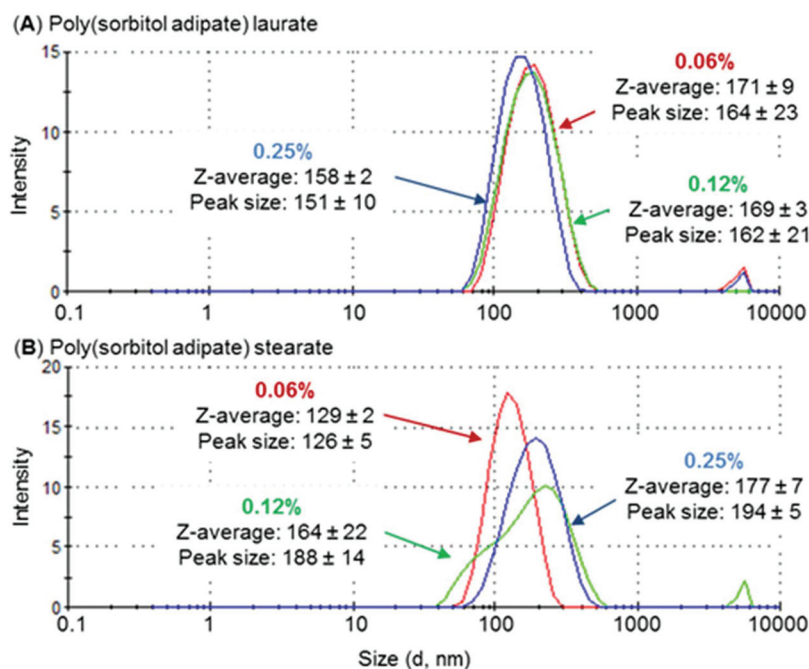
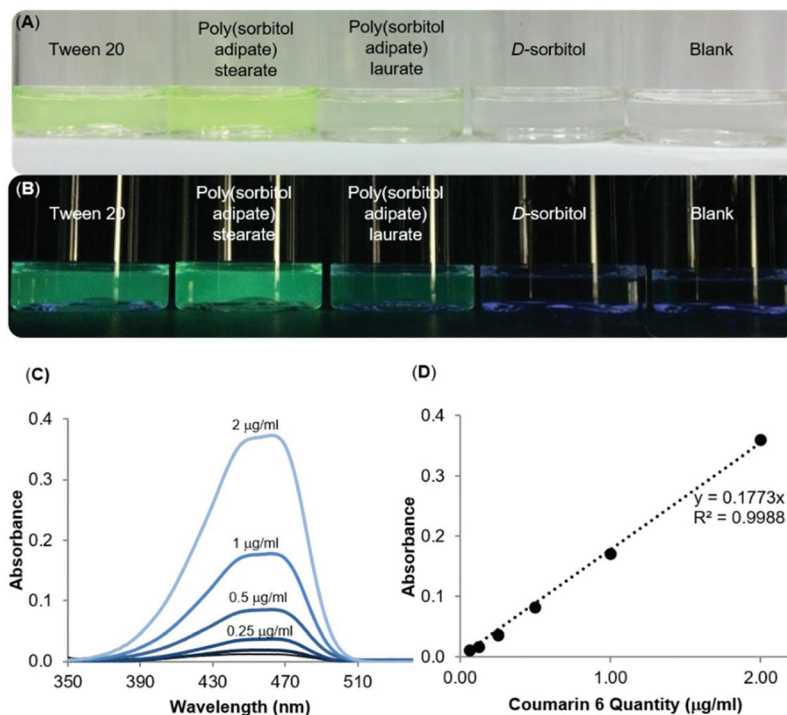


Fig. 6 DLS measurement of (A) poly(sorbitol adipate) laurate and (B) poly(sorbitol adipate) stearate at increasing concentrations 0.06 (→), 0.12 (→) and 0.25 (→) wt%, plotting size distribution (d , nm) by intensity. Note the increase in size for the stearate derivative, whereas the laurate polyester remains relatively constant. Peaks at higher hydrodynamic volumes (<2%) are thought to be caused by dust particles interfering with the reading.

Condition	Coumarin 6 Quantity (mg/mL)
Control	~0.2
D	~0.4
D-sorbitol	~0.4
jen 20	~4.2
Pluronic	~2.0
PSA-S	~8.0
PSA-L	~1.8
PSS-S	~3.2
PSS-L	~0.8

times higher than commercial Pluronic™ L121, almost double the concentration of the commercial Tween™ 20 (at 4.28 $\mu\text{g mL}^{-1}$) and around 35 times the measured native solubility of coumarin 6 in water (0.23 $\mu\text{g mL}^{-1}$). These data support the hypothesis that the dye is packed differently into the core of the self-assembled aggregates based on the hydrophilic: hydrophobic ratio of the polyester alongside the size of the micelles/aggregates formed.



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Upon derivatisation with a fatty acid hydrophobe, the compounds were found to aggregate. This leads to a reduction in polyester-water interactions. This self-assembly could therefore

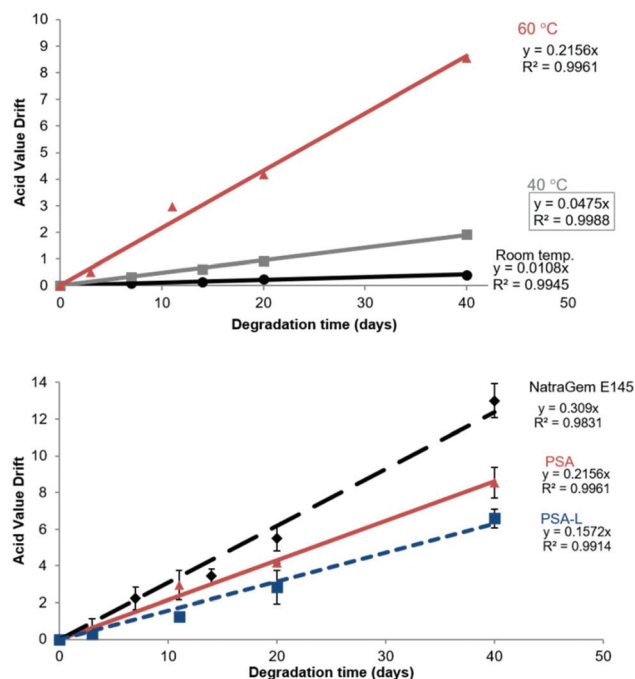


Fig. 9 Acid value drift of (A) poly(sorbitol adipate) stored in 50:50 MeOH : H₂O (v/v) at 10 g L⁻¹ over 40 days at RT (●), 40 °C (■) and 60 °C (▲) and (B) Acid Value drift comparison of: poly(sorbitol adipate) (PSA, ▲), derivatised poly(sorbitol adipate) laurate (PSA-L, ■) and the commercial NatraGem™ E145 (polyglycerol succinate laurate, ◆) at 60 °C. Note the reduction in acid value drift upon derivatisation.

explain the reduced acid value drift identified post-derivatisation. Interestingly, a greater AV drift was identified for NatraGem™ E145 (polyglycerol succinate laurate) compared to PSA and its laurate derivative. This improved stability of the D-sorbitol based polyesters compared to the glycerol-based polyesters could be caused by increased steric hindrance around the ester bonds making the hydrolysis reaction more challenging. This reduction compared to the commercial sugar-based polyesters indicates that an acceptable (even improved) level of hydrolytic degradation is occurring. However, it still shows that degradation will still occur with time ensuring an environmentally benign end of life option.

Conclusion

We have developed an efficient and clean synthesis of α -sorbitol and diacid based polyesters by combining the use of the inexpensive K_2CO_3 as selective catalyst in the green medium scCO_2 . The resulting renewable polyesters were evaluated as components in surfactant design. The “react, extract, repeat” approach facilitated moderate temperatures ($\leq 120^\circ\text{C}$) and higher conversions allowing the removal of the condensate. This catalytic strategy enabled the synthesis of linear water soluble poly(sorbitol adipate) and poly(sorbitol succinate) without the need to use high temperature and protection-deprotection chemistry which are often barriers to commercialisation. Our synthesis of poly(sorbitol adipate) using K_2CO_3 under supercritical conditions (synthetic and as an extraction medium) showed a selectivity of about 68% towards the primary hydroxyl groups; close to that obtained with Novozym 435 (80% selectivity). This promising selectivity when using K_2CO_3 was unexpected and the consistently higher molecular weights of the polyesters (compared to those obtained using the enzyme) allow synthesis of polyesters similar to those frequently used in surfactant design. Our approach ensured the targeted synthesis of linear poly(sorbitol adipate) and poly(sorbitol succinate) by selectively reacting the α -sorbitol as a diol at the more acidic sorbitol terminal primary hydroxyls, which are also less sterically hindered. This retention of linearity ensured that the polyesters were rich in pendant secondary hydroxyl groups and were consequently water soluble. The water-soluble polyesters were further derivatised using hydrophobic lauric and stearic acids giving rise to competitive surface-active properties with very promising reductions in surface tension (as low as 26 mN m^{-1}) compared to a range of commercial petrochemical and bio-based surfactants currently on the market. CMC values were identified to be dependent on the hydrophilic : hydrophobic ratio of the surfactants, ranging from 0.003 to 0.5 wt%.

Poly(sorbitol adipate) stearate efficiently dispersed the hydrophobic dye coumarin 6 in water, almost doubling the loading of this compound compared to the commercial Tween™ 20. These polyol-polyester surfactants were all identified to aggregate with hydrodynamic sizes of 130–225 nm. Poly(sorbitol adipate) based surfactants displayed sizes ranging

In conclusion, a cost-effective catalyst system and straightforward synthesis route towards linear and hydrophilic polyol-polyesters makes them interesting candidates for the next generation of bio-based surfactants.

There are no conflicts of interest to declare.

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