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Sustainable one-pot synthesis and polycondensation of a Levoglucosenone-derived cyclic acetal diol

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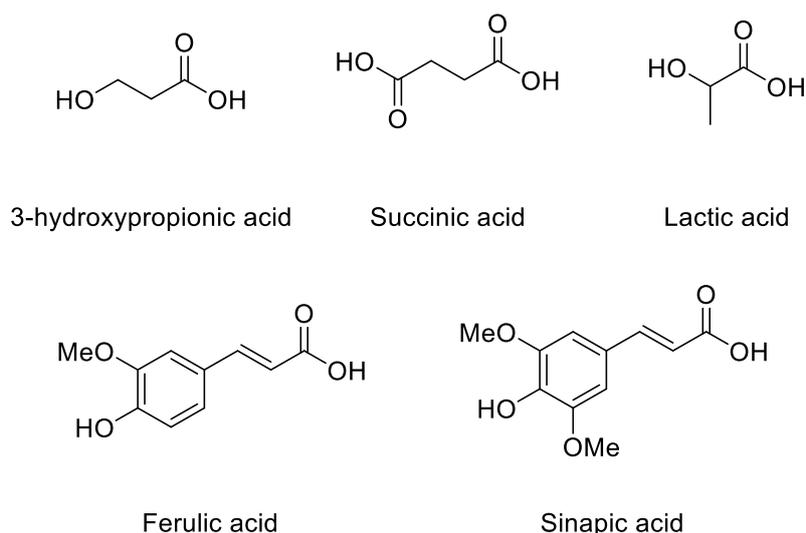
Abstract

The already described one-pot two-step hydration/reduction of levoglucosenone (**LGO**) into (1*R*,2*S*,5*R*)-6,8-dioxabicyclo[3.2.1]octane-2,4-diol (**HO-LGOL**) was improved by replacing 50 mol% of Et₃N by 5 mol% of K₃PO₄, a more sustainable base. The sterically hindered diol was then subjected to polycondensations with aliphatic co-monomers to prepare new bio-based polyesters that exhibit glass transition (*T_g*) values between 12 and 54 °C and high thermal stability greater than 200 °C. Two different strategies were implemented to perform the polymerizations: (1) utilization of aliphatic diacyl chlorides or (2) a method involving aliphatic diethyl esters in presence of metal catalyst. Those methods were then subjected to life cycle assessment (LCA) to study their environmental impacts.

Keywords: levoglucosenol, reduction, diol, polycondensation, polyester, LCA

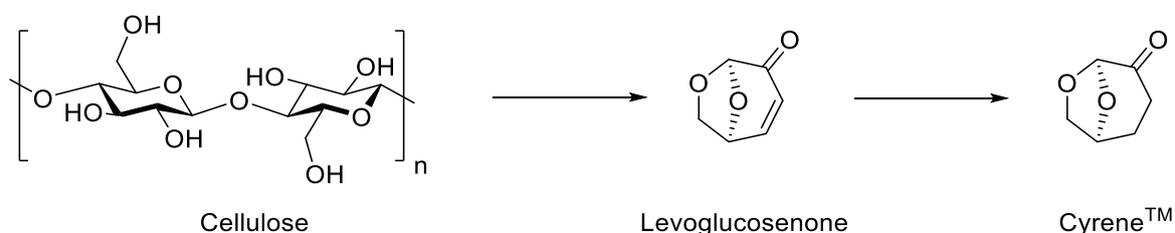
Introduction

While awareness regarding climate change and the environment is rising, the global production of fossil fuel-based goods is soaring. In an attempt to slow down the subsequent growth of polluting chemical emissions that leads us to suffocating and dangerous outcomes, sustainable alternatives based on the exploitation of bio-renewable sources are being explored. Fermentation processes allow access to platform chemicals of interest such as 3-hydroxypropionic acid^{1,2} and succinic acid^{3,4} while lignocellulosic material has been extensively used to source building blocks of interest such as *p*-hydroxycinnamic acids (Scheme 1).⁵



Scheme 1. Examples of bio-renewable chemical platforms

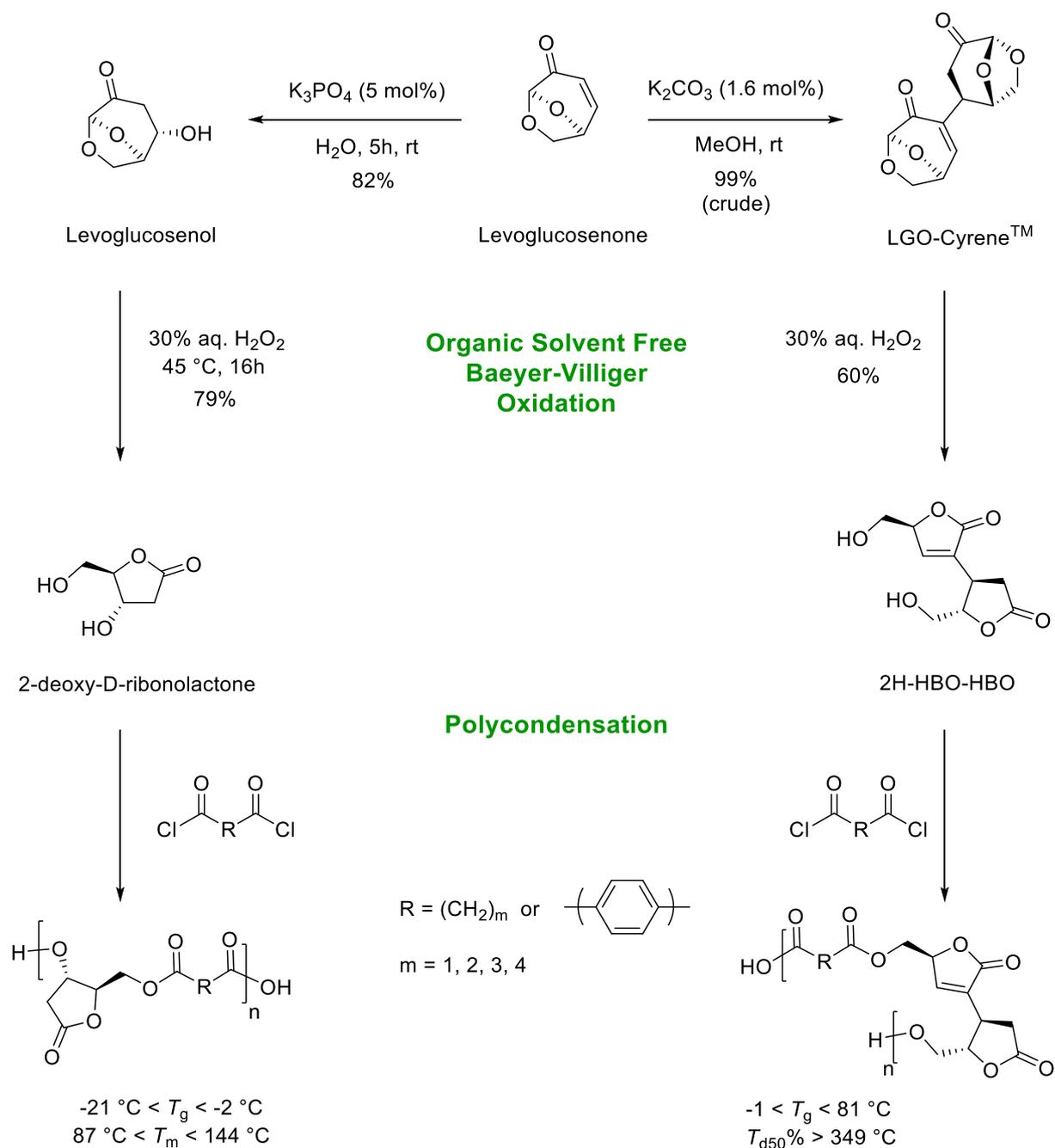
Despite the absence of official bio-based building blocks libraries-apart from the DOE⁶ list- the number of valuable biomass-derived building blocks reported and reviewed in the scientific literature is increasing. From lactic acid to CyreneTM, those molecules have been used in many fields as innovative bio-based alternatives. The first is known for the successful poly(lactic acid) (PLA)^{7,8} while CyreneTM is advertised as a cellulose-derived green polar aprotic solvent that could advantageously replace toxic solvents such as dichloromethane (DMC) and dimethylformamide (DMF).^{9,10}



Scheme 2. Transformation of cellulose into CyreneTM 11,10,12

The development of the Furacell technology in 2006¹¹ by Circa has been the cornerstone of success for CyreneTM since it drastically lowered the cost to produce the key cellulose-derived precursor levoglucosenone (**LGO**), a versatile cyclic α,β -unsaturated ketone (Scheme 2). Besides its potential as a chemical intermediate for the synthesis of high value-added chemicals¹³, **LGO** has been recently used for the preparation of novel monomers and polymers. For instance, Saito and co-workers reported the formation of **LGO**-based acrylates through reduction of the ketone moiety of CyreneTM followed by acrylation to form polyacrylates with desirable thermal properties.¹⁴ Recently, we reported a sustainable optimization of **LGO** dimerization into **LGO**-CyreneTM that was oxidized through an organic solvent- and catalyst-

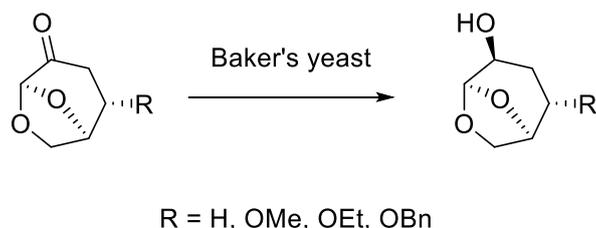
free process to form a new 100% biobased diol, **2H-HBO-HBO**, and a series of corresponding polyesters (Scheme 3).¹⁵ Still dedicated to the development of greener access to novel bio-based **LGO**-based monomers, we optimized the **LGO** hydration into levoglucosenol and oxidized the later by using the aforementioned method. The resulting 2-deoxy-D-ribonolactone was then subjected to polycondensation to yield a new set of 100% bio-based polymers (Scheme 3).¹⁶



Scheme 3. Synthesis of **2H-HBO-HBO** and **HO-HBO** polyesters from **LGO**

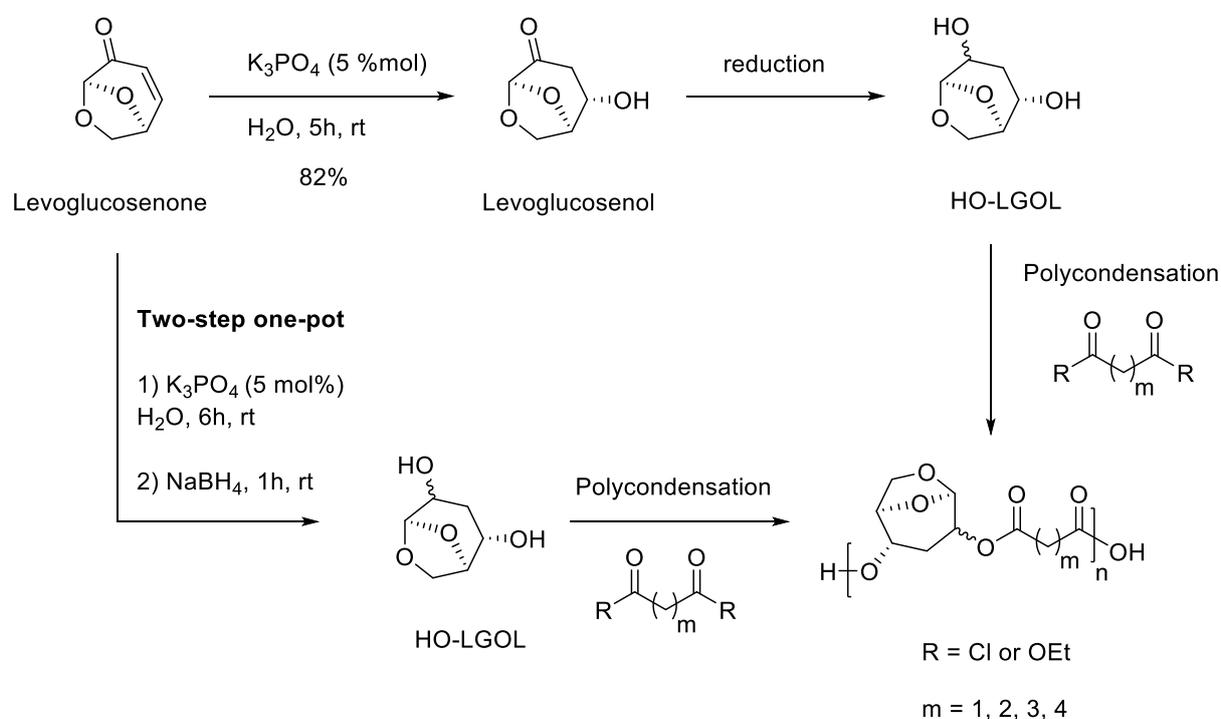
In 2018, Carr *et al.* described the isolevoglucosenone¹⁷ synthesis from **LGO** and performed the chemical reduction of levoglucosenol (**LGOL**) with NaBH₄ in methanol to obtain the

corresponding diol (hydrated levoglucosenol, **HO-LGOL**) in 72% yield. Recently, this reduction was optimized by Valeev and co-workers, who not only increased the yield to 90% but also partially greened the process by replacing methanol with water.¹⁸ In a second report, they implemented a chemo-enzymatic pathway involving baker's yeast in an aqueous D-glucose solution.¹⁹ Even though this strategy lowered the yield significantly to 39%, it offers a promising and greener alternative to NaBH₄ (Scheme 4).



Scheme 4. Reduction of Cyrene derivatives catalyzed by baker's yeast.¹⁹

To the best of our knowledge, hydrated levoglucosenol (**HO-LGOL**) has never been used as a diol for polyester production. Having extensively worked on **LGO**-based monomers and their subsequent polymerizations, we decided to focus our efforts on (1) the improvement of **LGOL** reduction to **HO-LGOL**, (2) the polycondensation of the latter to offer a new series of polyesters bearing acetal functionality, and (3) the optimization of the polymerization process (Scheme 5).



Scheme 5. Synthesis of **HO-LGOL** polyesters from levoglucosenone (**LGO**)

Materials and Methods

Chemicals and Reagents: Levoglucosenone was graciously provided by the Circa Group. Potassium phosphate tribasic >98% (Sigma Aldrich), malonyl chloride 97% (Sigma Aldrich), succinyl chloride 95% (Sigma Aldrich), glutaryl chloride 97% (Sigma Aldrich), adipoyl chloride 98% (Sigma Aldrich), diethyl malonate > 99% (TCI), diethyl succinate 98% (alfa aesar), diethyl glutarate > 99% (Sigma Aldrich), diethyl adipate 99% (Sigma Aldrich), tin (II) 2-ethylhexanoate > 85% (TCI), *p*-toluenesulfonic acid monohydrate > 98.5% (Sigma Aldrich), zinc (II) acetate dehydrated 98+% (Acros Organics), antimony (III) oxide 99+% (Acros Organics), and sodium borohydride >98% (Sigma Aldrich) were used without further purification unless mentioned. NMR solvents including deuterated chloroform, deuterated methanol, and deuterated dimethyl sulfoxide were purchased from Cambridge Isotope Laboratories.

Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy. ¹H NMR spectra of samples were recorded at 300 MHz (CDCl₃, CD₃OD, DMSO-*d*₆, and acetone-*d*₆ residual signal at 7.26, 3.31, 2.50, and 2.05 ppm respectively). ¹³C NMR spectra of samples were recorded at 75 MHz (CDCl₃, CD₃OD, DMSO-*d*₆, and acetone-*d*₆ residual signal at 77.2, 49.0, 39.5, and 29.8 ppm respectively). Chemical shifts are reported in parts per million (ppm). Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Thermogravimetric Analysis (TGA) was performed under nitrogen with a TGA Q500 from TA Instruments. About 1-5 mg of each sample were equilibrated at 50 °C for 30 min. Then, the samples were heated at 10 °C/min from 50 °C to 500 °C. The reported values (*T*_{d5%} and *T*_{d50%}) represent the temperature at which 5% and 50% of the mass is lost, respectively.

Differential Scanning Calorimetry (DSC) thermograms were obtained with a DSC Q20 from TA Instruments. Typically, 5-10 mg of sample were weighed and charged into a sealed pan that passed through a heat-cool-heat cycle at 10 °C/min. The temperature ranged from -80 °C to *T*_{d5%}.

Gel Permeation Chromatography (GPC) was performed at 60 °C using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector, a viscometer detector, a laser, UV lamp and two PLgel columns (5μm MIXED-D 300x7.5mm) using 10mM lithium bromide (LiBr) in HPLC grade dimethylformamide (DMF) as the mobile phase at a flow of 1.0 mL/min. Calibration was

performed with narrow dispersity poly(methyl methacrylate) standards (M_n : 640, 970, 1,790, 2,930, 4,660, 6,380, 10,100, 18,220, 30,350, and 45,730 $\text{g}\cdot\text{mol}^{-1}$). The samples were prepared by solubilising around 8 mg of material in 1 mL of the aforementioned solvent.

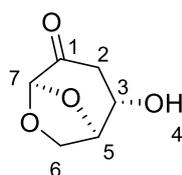
Comparative life cycle analysis applied to both HO-LGOL preparations and both polycondensation methods: The life cycle analysis (LCA) has been performed using openLCA (software), EcoInvent 3.4 (database), and CML 2001 (method from Leiden University). This study is a comparative analysis between two polycondensation routes to HO-LGOL-based polyesters from LGO. This implies that HO-LGOL preparation was also modelled and included in the final calculations. Poly(HO-LGOL succinate) was chosen as model to perform this analysis. Two polycondensation strategies were investigated: (1) a method using succinyl chloride as co-monomer, (2) a process involving diethyl succinate as co-monomer in the presence of $\text{Zn}(\text{OAc})_2$. Each polymerization approach was divided into 4 studies: (a) no energy considered in the entire modelled process, (b) no solvent considered in the entire modelled process, (c) no energy and no solvent considered in the entire modelled process, (d) energy and solvents considered in the entire modelled process. The LCA was performed by choosing a functional unit of 1 g of targeted material. In this LCA, priority was given to primary data from laboratory experiments but assumptions were made regarding energy consumption. Indeed, energy consumption was calculated from the different device powers and was also based on processes available in Ecoinvent 3.4 described in the ESI. The data used are divided into several categories in order of importance: primary data from laboratory-scale experiments including HO-LGOL one-pot two-step preparation (without considering the purification step), polymerization of HO-LGOL through either the diacyl chloride route or the diethyl ester route except for the energy consumption. Secondary data from Ecoinvent 3.4 database using acetone, wood chips, water, sodium tetrahydridoborate, venting of nitrogen, liquid nitrogen, DMF, phosgene, succinic acid, toluene, ethanol, sulfuric acid and different sources of energy. Secondary data modelled based on the literature were used for chemicals specific to this study. Levoglucosenone production was evaluated based on a patent describing the preparation of LGO from lignin waste²⁰ and the generated waste was estimated by using a publication that describes the environmental effects of CyreneTM and LGO production.²¹ Potassium phosphate tribasic was modelled based on the production of trisodium phosphate described in Ecoinvent 3.4. Diethyl succinate production was evaluated by using a publication describing esterification of succinic acid²² and the necessary heat quantity was based on ethyl acetate production described in Ecoivent 3.4; the ethanol, which is both solvent and reagent, was estimated at 20 equivalents with respect to succinic acid loading. Succinyl chloride production was evaluated by using a patent describing carboxylic acid chloride production²³ and the energy consumption

was based on trimesoyl chloride production described in Ecoinvent 3.4 since no information regarding energy was reported in the patent. $\text{Zn}(\text{OAc})_2$ production was estimated by using a patent describing the salt production²⁴ and the energy of the cooling system was approximated by a 50L refrigerator with an annual consumption of 200kWh. The energy consumption of poly(HO-LGOL succinate) production from diethyl succinate was approximated by polyethylene terephthalate production described in Ecoinvent 3.4. The energy consumption of poly(HO-LGOL succinate) production from succinyl chloride was approximated by polydimethylsiloxane production described in Ecoinvent 3.4.

Synthesis of monomers

Synthesis of (1*R*,2*S*,5*R*)-2-hydroxy-6,8-dioxabicyclo[3.2.1]octan-4-one (Levoglucofenol)¹⁶:

Levoglucofenone (LGO) (1.037 g, 8.2 mmol) was solubilised in water (100 mL) and K_3PO_4 (90 mg, 0.42 mmol) was added. The solution was stirred at room temperature for 5 hours. HCl (1 M) (420 μL) was added to neutralize the base. Water was evaporated under vacuum and the crude product was purified by silica gel chromatography (Eluent: cyclohexane/ethyl acetate: 8/2 to 5/5, $R_f = 0.5$ in ethyl acetate) to obtain a yellow oil (970 mg, 82% yield).



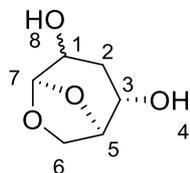
^1H NMR (DMSO- d_6 , 300 MHz): δ_{H} 2.14 (dt, 1H, $J = 1.2$ & 16.8 Hz, H_2), 2.91 (dd, 1H, $J = 5.4$ & 16.8 Hz, H_2), 3.75 (m, 1H, H_6), 3.96 (m, 1H, H_6), 4.11 (m, 1H, H_3), 4.58 (m, 1H, H_5), 5.05 (s, 1H, H_7), 5.40 (d, 1H, $J = 4.5$ Hz, H_4). ^{13}C NMR (DMSO- d_6 , 75 MHz): 40.9 (C_2), 65.1 (C_3), 69.3 (C_6), 77.6 (C_5), 100.8 (C_7), 201.1 (C_1). $[\alpha]_{\text{D}}^{23} = -196^\circ$ ($C = 0.10$, EtOH).

Synthesis of (1*R*,2*S*,5*R*)-6,8-dioxabicyclo[3.2.1]octane-2,4-diol (HO-LGOL):

From Levoglucofenol: Levoglucofenol (1.889 g, 13.1 mmol) was solubilized in methanol (45 mL) and NaBH_4 (511 mg, 13.2 mmol) was added at once at 0 °C. Magnetic stirring was maintained for 30 minutes at 0 °C and the reaction mixture was then warmed to room temperature before being concentrated under reduced pressure. The crude product was then purified by silica gel chromatography (Eluent: cyclohexane/ ethyl acetate: 10/90, then 100% ethyl acetate, and finally ethyl acetate/methanol: 90/10) to obtain a viscous white solid (1.793 g, 94% yield).

Two-step one-pot synthesis of HO-LGOL from LGO: Levoglucofenone (LGO) (1.000 g, 8.0 mmol) was solubilised in 250 mL of distilled water and K_3PO_4 (89 mg, 0.4 mmol) was

added. The mixture was stirred at rt for 6 h. Then NaBH₄ (350 mg, 9.0 mmol) was added at 0 °C and the system was then stirred for 1 hour at room temperature. Acetone (3 mL) was added to quench the excess NaBH₄ and the solvent was removed under reduced pressure. The crude product was purified over silica gel (Eluent: cyclohexane/ethyl acetate: 10/90 then 100% ethyl acetate, and finally 90/10: ethyl acetate/methanol) to obtain an oil (876 mg, 75% yield).



¹H NMR (DMSO-d₆, 300 MHz): δ_H 1.69 (dt, 1H, H₂), 1.88 (m, 1H, H₂), 3.79 (m, 5H, H_{1,3,5,6}), 4.04 (m, 1H, H₈), 4.35 (m, 1H, H₄), 5.16 (m, 1H, H₇). ¹³C NMR (DMSO-d₆, 75 MHz): 33.7 (C₂), 66.0 (C₆), 66.4 (C₃), 67.6 (C₁), 76.9 (C₅), 103.2 (C₇).

Polymerizations

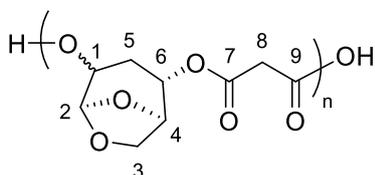
Diacyl chloride method: In a 10 mL round bottom flask under nitrogen, **HO-LGOL** (479 mg, 3.28 mmol) was charged and malonyl chloride (0.33 mL, 3.39 mmol) was added. The mixture was stirred at room temperature until the viscosity hindered the magnetic stirring, and then the temperature was increased gradually up to 100 °C. Finally, vacuum was applied for one hour and the resulting renewable polyester was solubilized in a minimum volume of DMSO (NB: DMSO can be slightly warmed up if the polymer does not readily solubilize) and was then precipitated in cold water. After filtration, the bio-based polymer was freeze-dried overnight. Additional polyesters were prepared with this protocol employing alternative diacyl chlorides.

Diethyl ester method: In a 10 mL round bottom flask under inert atmosphere, **HO-LGOL** (490 mg, 3.36 mmol) was charged with diethyl malonate (0.5 mL, 3.36 mmol) and 5 mol% of metal-catalyst. The system was immediately heated at 160 °C under N₂ flow and stirred for 17 h (overnight). Then dynamic vacuum was applied and the temperature was gradually increased up to 220 °C.

Poly(**HO-LGOL** malonate)

Yield, diacyl chloride method: 91%

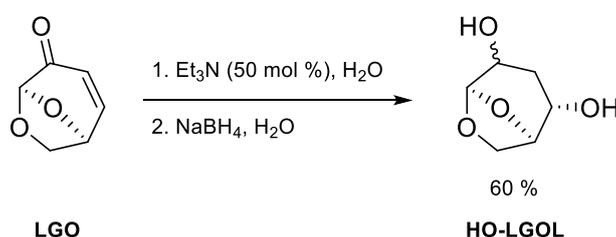
Yield, diethyl ester method: 45%



^1H NMR (DMSO- d_6 , 300 MHz): δ_{H} 1.54 (m, 5H, H_{5,10,9}), 1.92 (m, 1H, H₅), 2.33 (m, 4H, H_{8,11}), 3.65 (m, 1H, H₃), 4.00 (m, 1H, H₃), 4.54 (m, 1H, H₄), 4.71 (m, 1H, H₆), 4.85 (m, 1H, H₁), 5.35 (s, 1H, H₂). ^{13}C NMR (DMSO- d_6 , 75 MHz): 24.2 (C_{9,10}), 27.3 (C₈), 33.4 (C₁₁), 33.6 (C₅), 66.4 (C₃), 69.4 (C₁), 74.5 (C₆), 99.7 (C₄), 103.0 (C₂), 172.6 (C₇), 172.7 (C₁₂).

Results and discussion

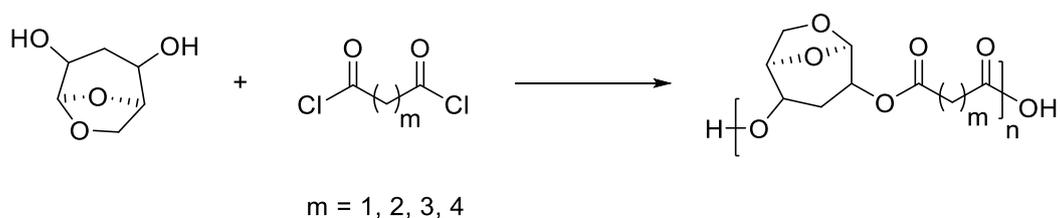
Recently, Sharipov and co-workers¹⁸ proposed the one pot synthesis of **HO-LGOL** where they used 50 mol% of Et₃N to catalyze **LGO** hydration and, after 2 h of reaction, added 1 equivalent of sodium borohydride to reduce the ketone (Scheme 6).



Scheme 6. One pot synthesis of **HO-LGOL** proposed by Sharipov *et al.*¹⁸

First, we directly implemented this procedure but only reached 60% yield compared to the 90% yield claimed by Sharipov. Building on this attractive strategy, we decided to explore the two-step one-pot synthesis of **HO-LGOL** by using our own hydration conditions. **LGO** was thus subjected to hydration in the presence of 5 mol% K₃PO₄-rather than 50 mol% of Et₃N-and the system was stirred for 6 hours at room temperature. Then NaBH₄ was added at 0 °C and the mixture was stirred at room temperature for 1 additional hour. After purification by silica gel chromatography, the desired diol was obtained in 75% yield. In our hands, compared to Sharipov's procedure, we clearly observed a yield increase of 75% *vs.* 60%. In addition, our hydration method only requires 5 mol% of a green base while they used 50 mol% of a toxic organic base.

HO-LGOL synthesis being successfully improved, we brought our attention to its polymerization. We proceeded through the same method used for **2H-HBO-HBO**¹⁵ and 2-deoxy-D-ribonolactone¹⁶-namely, the utilization of diacyl chlorides as co-monomers with chain length from $m = 1$ (malonyl chloride) to $m = 4$ (adipoyl chloride) in solvent free conditions under inert conditions (Scheme 7).

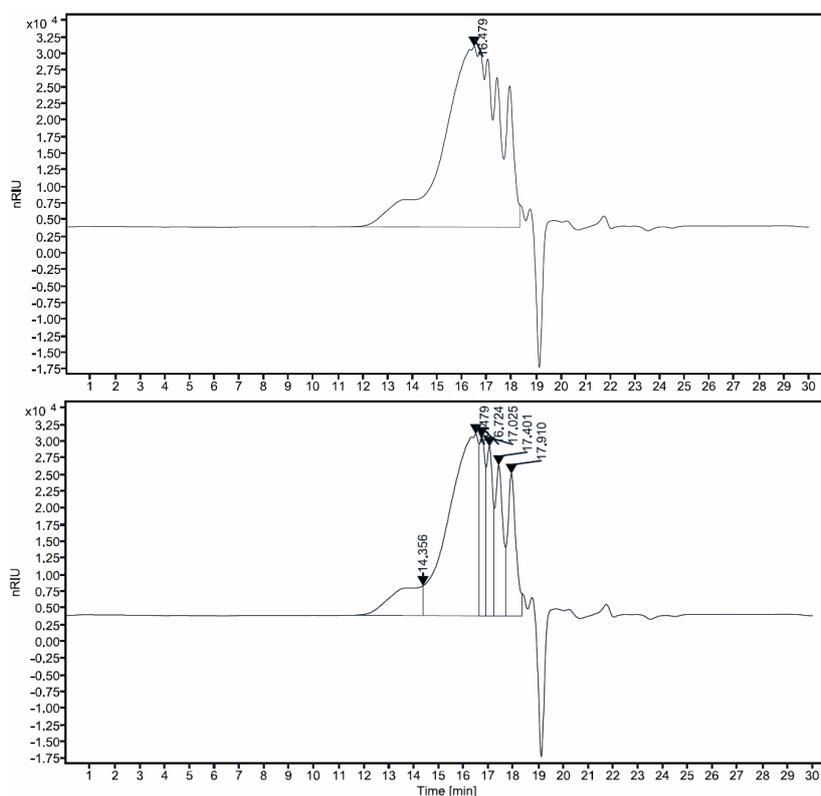


Scheme 7. Polyesters from HO-LGOL and diacyl chlorides

Polymerizations started at room temperature and the temperature was gradually increased to 100 °C to allow better magnetic stirring while the viscosity increased because of polymer chain formation. Finally, we applied dynamic vacuum for 1h at 100 °C to remove residual HCl as well as the small oligomer chains. The dark brown solids were solubilized in DMSO and the bio-based materials were precipitated in cold water through careful addition.

The entire set of polyesters was highly insoluble in GPC solvents such as THF and CDCl_3 . Only poly(HO-LGOL malonate) presented descent solubility in DMF while partial solubility was observed for the remaining materials. The samples were analyzed by GPC with the aim to observe the molecular weights of the soluble polymer chains. It is noteworthy to mention that two different types of integration have been performed: a full integration to have a true and fair view of the molecular weight and dispersity of the polymers, and the integration of the area corresponding to the longer chain length polymers (Figure 1).

Figure 2. Illustrative example for the integration of the GPC chromatograms (poly(HO-LGOL adipate) from diethyl adipate): full integration (top), integration of the area corresponding to the longer chain polymers (bottom)



As expected, all the samples described in Table 1 showed low molecular weights from 1.3 kDa for poly(**HO-LGOL** adipate) ($m=4$, Table 1, Entry 4) to 2.9 kDa for poly(**HO-LGOL** malonate) ($m=1$, Table 1, Entry 1). Apart from the malonate-based polyester that presented a wide bell curve, tails were observed in the low retention times for the other samples. We assumed the presence of higher polymer chains that probably hindered significantly the solubility. Such heterogeneity regarding chain lengths is noticed occasionally when bulk conditions are applied, especially in presence of highly reactive co-monomers such as diacyl chlorides. Indeed, reaction between the diacyl chlorides and the diol tends to rapidly form high molecular weight material, generating a significant viscosity increase. As a consequence, magnetic stirring is slowed down or even hindered and both oligomers and unreacted monomers are trapped in a highly viscous medium, or in a solid, and cannot react further. In addition, the acetal can be potentially opened (with adventitious water), unlocking 2 additional hydroxyl functionalities that could react and create crosslinks.

Table 1: Molecular weight of **HO-LGOL**-based polyesters prepared with diacyl chlorides

Entry	Polymer ^[a]	Full integration			Integration for the longer chain length polymers			Yield (%)
		M_n (kDa) ^[b]	$DP^{[c]}$	$\bar{D}^{[b]}$	M_n (kDa) ^[b]	$DP^{[c]}$	$\bar{D}^{[b]}$	
1	Poly(HO-LGOL malonate)	2.9	14	2.7	6.9	32	1.7	91
2	Poly(HO-LGOL succinate)	1.4	6	1.9	3.1	14	1.7	46
3	Poly(HO-LGOL glutarate)	1.4	6	2.1	3.2	13	1.8	48
4	Poly(HO-LGOL adipate)	1.3	5	1.5	2.2	9	1.3	37

^[a] Partially soluble. ^[b] GPC: DMF (10 mM LiBr) at 60 °C vs poly(methyl methacrylate) standards. ^[c] Calculated by GPC

In order to better control the polyester formation, as well as to avoid utilization of toxic diacyl chlorides, polycondensations in the presence of the corresponding diethyl esters and metal or acid catalyst were considered. Four different catalysts were investigated with diethyl malonate as the model: Sb_2O_3 , $Sn(Oct)_2$, $Zn(OAc)_2$, and *p*-TSA. The co-monomers were mixed with 5 mol% of catalyst and the system was heated at 160 °C for 17h under inert atmosphere to prevent polymer chain oxidation. Then vacuum was applied and the temperature was gradually increased to 220 °C. Use of *p*-TSA resulted in formation of a black and charcoal type solid indicating degradation and therefore unsuccessful polymerization. This outcome may be explained by the opening of the ketal moiety of LGO and the release of two hydroxyls that can further react and generate crosslinks. The best results were obtained in the presence of $Zn(OAc)_2$ and $Sn(Oct)_2$ that gave malonate-based polyesters with glass transition temperatures of 54 °C and 48 °C, respectively (Table 2, Entries 2 & 4). GPC analysis of the partially soluble poly(**HO-LGOL** malonate) made from $Zn(OAc)_2$ gave a single bell curve with a M_n of 3.7 kDa (Table 2, Entry 2). A similar bell curve around 3.9 kDa was observed when $Sn(Oct)_2$ was used; however, another signal at 51.1 kDa was noticed. This indicated that high molecular weight chains were formed during the polycondensation but tended to be retained in the filter.

Table 2: Effect of catalyst on polyester formation from **HO-LGOL** and diethyl malonate.

Entry	Catalyst	Yield (%)	M_n (kDa) ^a	D^a	$T_{d5\%}$ (°C) b	T_g (°C) ^c
1	Sb ₂ O ₃	-	-	-	-	-
2	Zn(OAc) ₂	45	3.7	1.6	224	54
3	p-TSA	28	-	-	303	-
4	Sn(Oct) ₂	30	3.5	-	245	48

^a GPC: DMF (10 mM LiBr) at 60 °C vs. poly(methyl methacrylate) standards. ^b TGA temperatures at which 5% and 50% mass loss were observed under nitrogen; temperature ramp 10 °C/min from 50 to 500 °C. ^c Determined by DSC under N₂; temperature ramp 10 °C/min from -80 °C to $T_{d5\%}$; margin of error: ± 2 °C

Polycondensations of **HO-LGOL** following the previously described method were then performed with diethyl esters from $m=2$ to $m=4$ in the presence of Zn(OAc)₂ to study the influence of the aliphatic chain length on the thermal properties. The resulting materials were partially soluble and GPC analysis mainly showed oligomers. For instance, poly(**HO-LGOL** succinate) and poly(**HO-LGOL** glutarate), showed M_n values of 1.1 kDa and 1.9 kDa, respectively. Even though those values were low, less intense signals at shorter retention time (higher molecular weight) were observed in each chromatogram. For example, the second bell curve noticed for poly(**HO-LGOL** adipate) ($m=4$) corresponds to a M_n of 35.2 kDa (Table 3, Entry 3) meaning that high molecular weights were formed but significantly retained in the filter due to poor solubility.

Table 3: Molecular weight of polyesters from **HO-LGOL** and diethyl esters.

Entry	Polymer ^[a]	Full integration			Integration for the longer chain length polymers			Yield (%)
		M_n	$DP^{[c]}$	$\bar{D}^{[b]}$	M_n	$DP^{[c]}$	$\bar{D}^{[b]}$	
		(kDa) ^[b]			(kDa) ^[b]			
1	Poly(HO-LGOL succinate)	1.1	5	1.1	10.4	46	1.88	59
2	Poly(HO-LGOL glutarate)	1.9	8	1.4	36.0	149	1.48	69
3	Poly(HO-LGOL adipate)	2.9	11	2.6	32.5	127	1.2	50

^[a] Partially soluble. ^[b] GPC: DMF (10 mM LiBr) at 60 °C vs poly(methyl methacrylate) standards. ^[c] Calculated by GPC.

Table 4: Thermal properties of polyesters from **HO-LGOL** and diethyl esters.

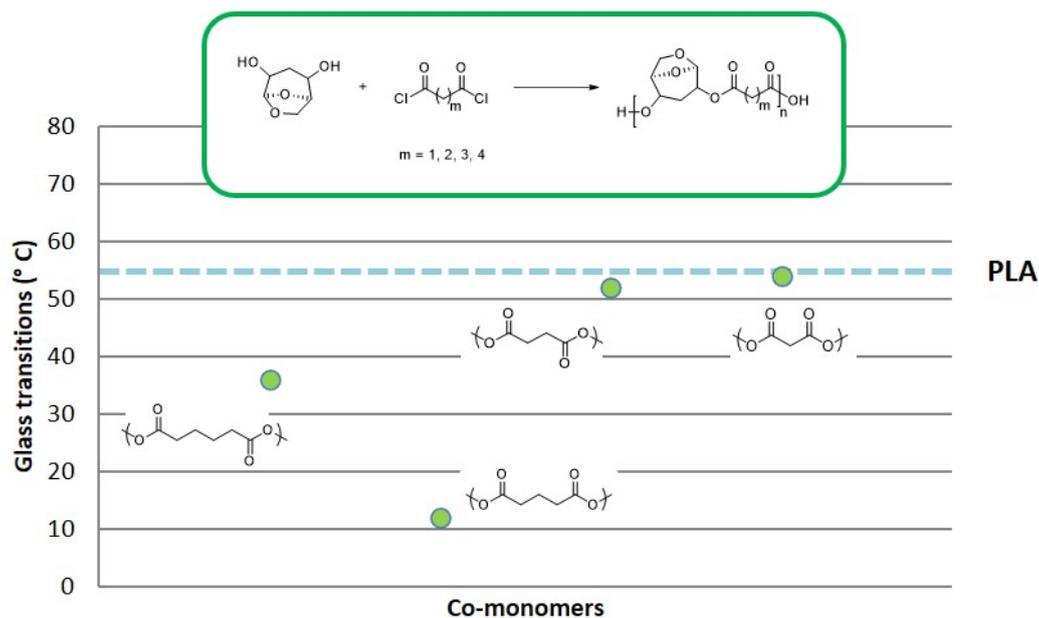
Entry	Polymer	$T_{d5\%}$ (°C) ^a	$T_{d50\%}$ (°C) ^a	T_g (°C) ^b
1	Poly(HO-LGOL malonate)	225	327	54
2	Poly(HO-LGOL succinate)	283	344	53
3	Poly(HO-LGOL glutarate)	214	369	12
4	Poly(HO-LGOL adipate)	315	391	36

^a TGA temperatures at which 5% and 50% mass loss were observed under nitrogen; temperature ramp 10 °C/min from 50 to 500 °C. ^b Determined by DSC under N₂; temperature ramp 10 °C/min from -80 °C to $T_{d5\%}$; margin of error: ±2 °C

The series of bio-based polyesters was then subjected to TGA and DSC thermal analysis to determine T_g -values and decomposition temperatures $T_{d5\%}$ and $T_{d50\%}$ (Table 4). Most of the polyesters have good thermal stability; for instance, poly(**HO-LGOL** malonate) (m=1, Table 4, Entry 1) exhibits a $T_{d5\%}$ of 225 °C and poly(**HO-LGOL** adipate) (m=4, Table 4, Entry 4) reaches 315 °C. Considering the $T_{d50\%}$, all of them were above 325 °C. Figure 2 describes the glass transition value evolution vs. the selected co-monomers. Despite the low T_g value of 12

°C for poly(**HO-LGOL** glutarate) (Table 4, Entry 3), the glass transition temperatures tended to increase as the co-monomer shortened, as expected,. Nonetheless, for $m=1$ and $m=2$ similar values were observed forming a threshold around 54 °C.

Figure 2. T_g values (margin of error: ± 2 °C) of **HO-LGOL**-based polyesters compared to that of PLA (55 °C, PLLA)²⁵



With the aim to study the environmental impacts of the two polycondensation processes employed to access **HO-LGOL**-based polyesters and compare them, life cycle analysis (LCA) was performed by using the CML 2001 method (Leiden University) available in openLCA software. The routes from **LGO** production to sustainable polyesters via **HO-LGOL** polymerization were modelled based on data from (1) Ecoinvent 3.4, (2) the scientific literature including both patents and publications, and (3) experimental work performed in our lab. Using this information, CML 2001 calculates midpoint indicators divided in numerous categories such as acidification potential and marine ecotoxicity. Those indicators do not relate to direct effects such as coral reef bleaching or increase of lung diseases, which are considered endpoint indicators, but they focus on more upstream consequences in the cause-effect chain.

Figure 3. Effect on acidification potential, climate change, stratospheric depletion, and photochemical oxidation for poly(**HO-LGOL succinate**) made from either diethyl succinate (blue) or succinyl chloride (dark green).

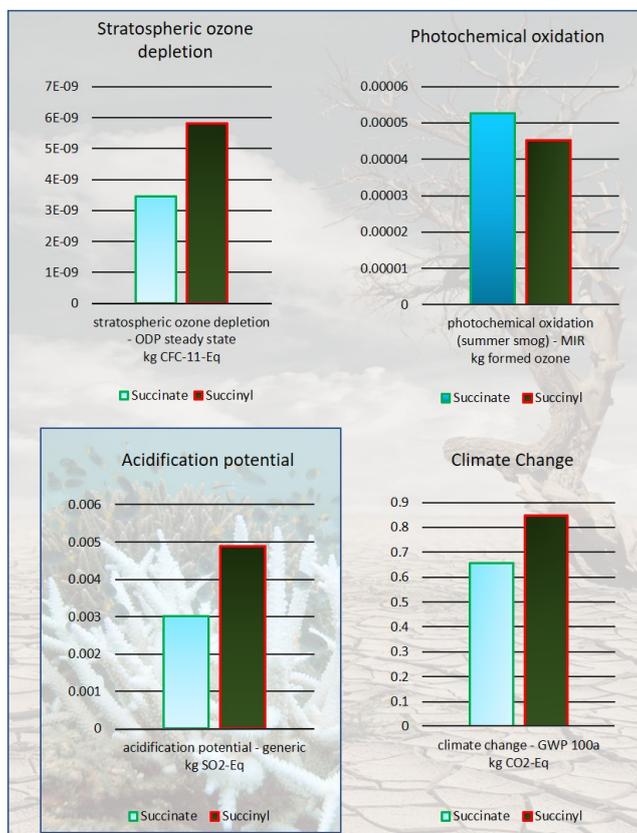


Figure 3 describes the impacts of the two polycondensation strategies on categories related to greenhouse gases emissions such as the stratospheric ozone depletion expressed in CFC-11, namely trichlorofluoromethane, or the acidification potential. For three of the four categories, we observe that utilization of the diethyl succinate-based method results in less harm than the counterpart strategy involving succinyl chloride. For example, 0.003 kg SO₂ equivalents are generated per 1g of poly(**HO-LGOL succinate**) when using diethyl succinate. On the other hand, the succinyl chloride method releases 1.6 times more SO₂ equivalents. A similar trend is observed for the stratospheric ozone depletion category; diethyl ester and diacyl chloride processes produce 3.5E⁻⁹ and 5.8E⁻⁹ (1.7 times more) kg of CFC-11 respectively per 1g of polymer made. The climate change midpoint also tends to favor the utilization of diethyl succinate, even if the difference is less significant compared to the aforementioned categories at low scale. Finally, calculations show that the succinyl chloride process has a smaller impact on photochemical oxidation which means that a smaller amount of ozone is emitted compared to the other process. Even though ozone generation might seem interesting because of the

stratospheric ozone depletion, this is counterintuitive as ozone emissions are dangerous at “ground level” and contribute to the formation of toxic smog.

Figure 4. Effect on land use and resources for poly(**HO-LGOL succinate**) made from either diethyl succinate (light green) or succinyl chloride (black).

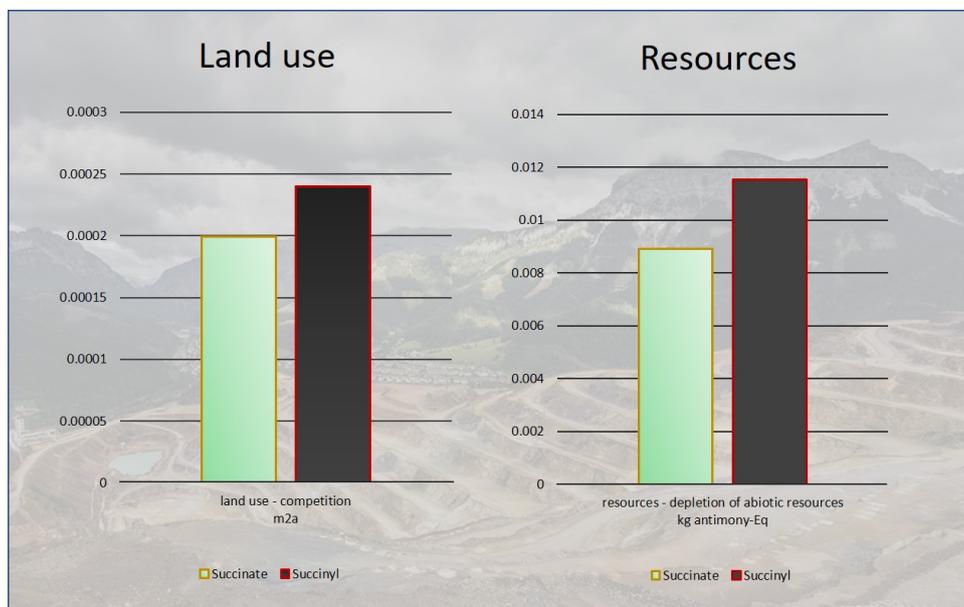


Figure 4 covers two other significant categories related to the uses of land and resources. We observe that, once again, the process involving succinyl chloride has more negative impacts than the one with diethyl succinate. For instance, the resource category, which covers the depletion of abiotic resources such as fossil fuels and minerals, shows a depletion of 0.009 kg antimony equivalents for the diethyl ester method versus 0.011 kg for the succinyl chloride route. In other words, based on the calculations, the utilization of diethyl succinate rather than succinyl chloride to produce 1 g of poly(**HO-LGOL succinate**) appears more sustainable and requires a smaller amount of land.

Figure 5. Effect on ecotoxicity and human health for poly(HO-LGOL succinate) made from either diethyl succinate (light green) or succinyl chloride (black)

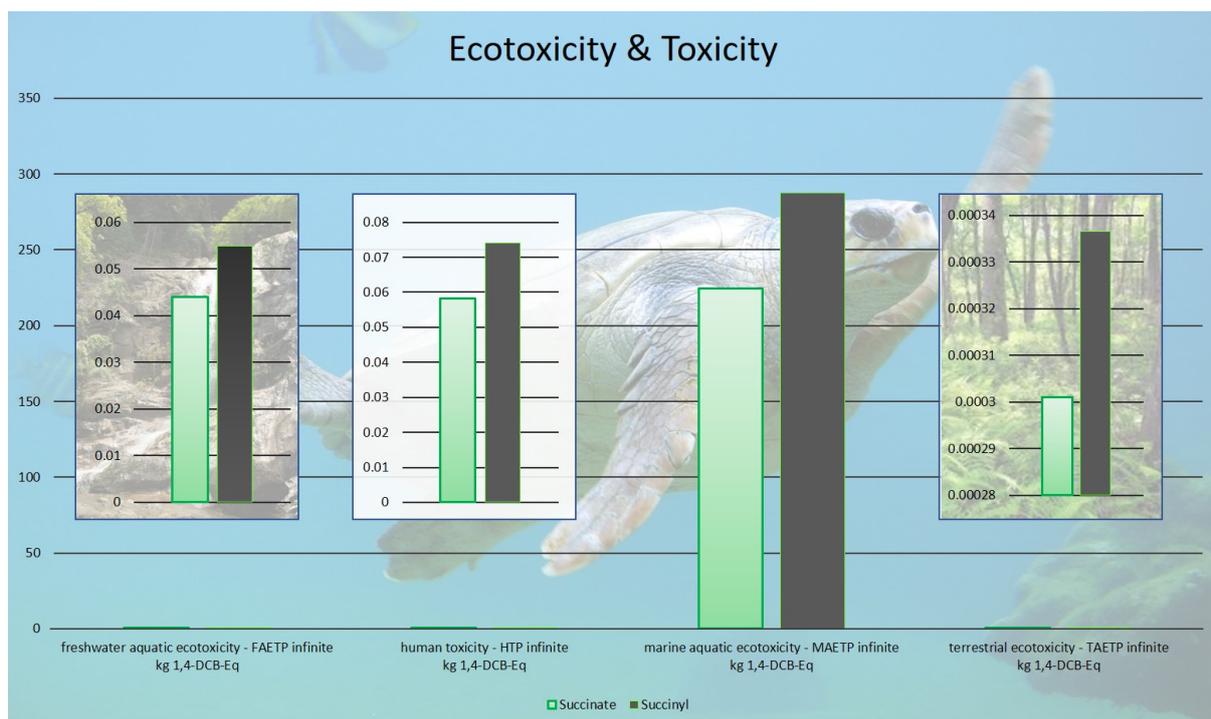
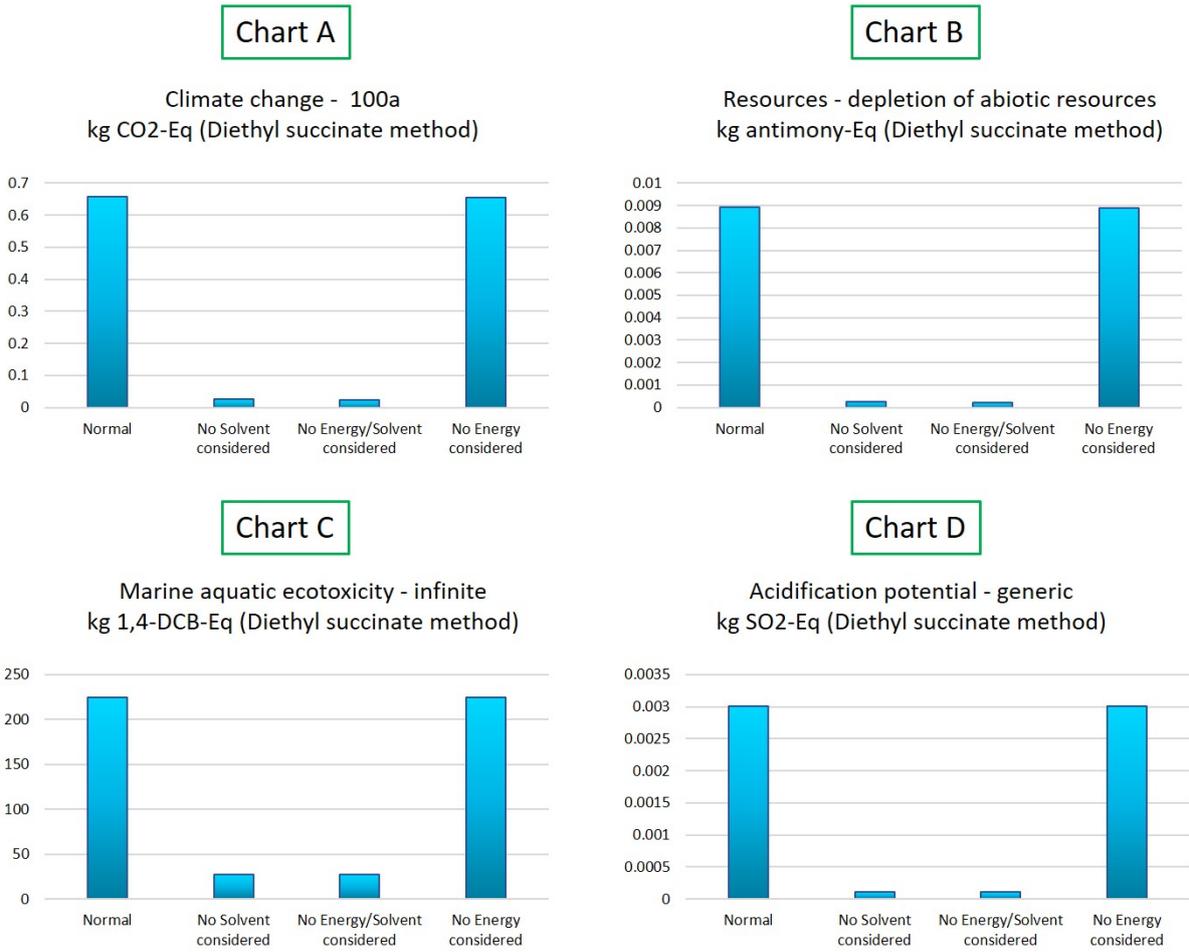


Figure 5 covers three types of ecotoxicity: freshwater aquatic, marine aquatic, and terrestrial, as well as human toxicity, all expressed in kg 1,4-DCB (1,4-dichlorobenzene) equivalents. Overall, we observe that the polycondensation with succinyl chloride is worse than the process using diethyl succinate. It is extremely important to note that the most impacted ecosystem is the marine ecosystem. Indeed, the amount of 1,4-DCB generated is at least 3000 times more important than the other categories. The multiplier between marine ecotoxicity and terrestrial ecotoxicity even reaches 750,000.

With a good overview of the impacts of the two methods on the different midpoint indicators, we decided to investigate the contribution of both the energy and the solvent to the calculations. To do so, we performed the calculations (1) ignoring the solvents, (2) ignoring the solvents and the energy, and (3) ignoring the energy and we compared the results for the four categories described in Figure 6. We clearly observe that no matter the midpoint indicator, a trend is observed for all the displayed categories. For instance, in Chart A, the case study that does consider solvent gives 0.025 kg CO₂ equivalents while the results for the normal calculations give 0.66 kg CO₂ equivalents implying a multiplier of approximately 26. This clearly shows the significant impact of the amount of solvents on each category. Surprisingly, based on our calculations, energy does not seem to have such substantial impact. For example, Chart C that describes the marine aquatic ecotoxicity shows comparable values between the result from

normal calculation and the one from the calculation that does not consider energy. Of course, it is important to note that in this study, the amount of energy is more difficult to model due to the scale and the lack of information.

Figure 6. Study of the energy and solvent impact of the production of 1 g of poly(HO-LGOL succinate), using the diethyl succinate method, on climate change (Chart A), resources – depletion of abiotic resources (Chart B), marine aquatic toxicity – infinite (Chart C), and acidification potential – generic (Chart D)



Conclusion

Wood waste-based levoglucosenone can easily undergo hydration followed by reduction through a one-pot two-step process to access a bio-based diol (**HO-LGOL**). The previously reported procedure was made more sustainable by substituting Et₃N with K₃PO₄, a less toxic inorganic base. Polycondensation of **HO-LGOL** was explored through two strategies, (1) a method involving diacyl chlorides, and (2) a procedure using diethyl esters in the presence of metal catalysts. The resulting polyesters present promising properties, including high thermal stabilities and attractive glass transition temperatures between 12 and 54 °C, depending on the co-monomer engaged in the polycondensations. High molecular weights up to 36.0 kDa were observed, but improvements of the polymerization process are to be developed to lower the dispersity as well as to increase the solubility of the resulting bio-based polyesters.

The two aforementioned polymerization approaches were then subjected to comparative LCA to determine which one has the lesser detrimental impact on the environment and human health. The calculations showed that the strategy based on utilization of diethyl esters in the presence of Zn(OAc)₂ was more eco-friendly. Further analysis performed through LCA demonstrated that no matter the procedure considered solvents were, by far, the most impactful considerations on the majority of the midpoint indicators. Interestingly, based on the calculations, energy did not seem to be as significant as expected regarding environmental impact. This may be explained by the complexity of correctly including energy in the model, due to a lack of information. Those results demonstrated the impact of the solvents is often more significant than the nature of the reagents; of course, this does not dissuade us to replace toxic reagents to minimize the environmental impacts. Nevertheless, for now, solvents, and probably energy, seem to be keystones to decrease our environmental impact. Further work on these **LGO**-based polyesters, their biodegradation, and water-degradability will be reported in due course.

Associated content

NMR spectra, DSC and TGA traces, as well as GPC data are available in the supporting information.

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FA, LMMM and FD-N: conceived the research. FA: supervised the research. FD-N and CV: performed the monomer synthesis, the polycondensations and the characterization. FA, LMMM and FD-N: provided the technical guidelines. FD-N: performed the Life Cycle Analysis. JC: reviewed the Life Cycle Analysis results and provided technical guidelines. FA, LMMM and SAM: reviewed the results. LMMM and FD-N: wrote and drafted the article. FA, LMMM and SAM: reviewed and approved the article.

Notes

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