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SUSTAINABLE SYNTHESIS AND POLYCONDENSATION OF LEVOGLUCOSENONE-CYRENE^{TM}-BASED BICYCLIC DIOL MONOMER: AN ACCESS TO RENEWABLE POLYESTERS

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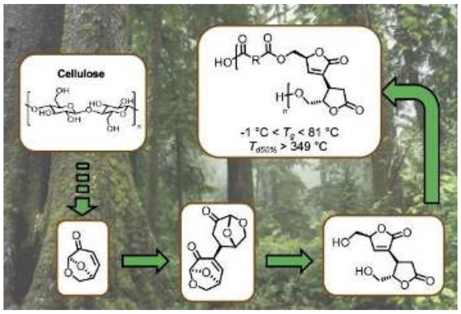


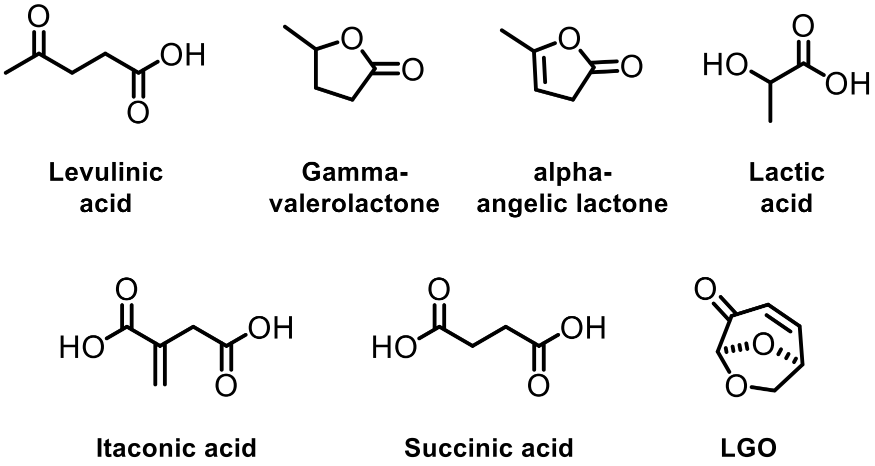
Abstract

The already-reported, low-yielding, and non-sustainable Et_3Nmediated homocoupling of levoglucosenone (**LGO**) into the corresponding **LGO-**Cyrene™ diketone has been revisited and greened-up. The use of methanol as both a renewable solvent and catalyst and K_2CO_3 as a safe inorganic base improved the reaction significantly with regards to yield, purification, and green aspects. **LGO**-Cyrene™ was then subjected to a one-pot, H_2O_2-mediated Baeyer–Villiger oxidation/rearrangement followed by an acidic hydrolysis to produce a new sterically hindered bicyclic monomer, **2H-HBO-HBO**. This diol was further polymerized in bulk with diacyl chlorides to access new promising renewable polyesters that exhibit glass transition temperatures (T_g) from -1 to 81 °C and a good thermostability with a temperature at which 50% of the mass is lost ($T_{d50\%}$) of 349–406 °C.

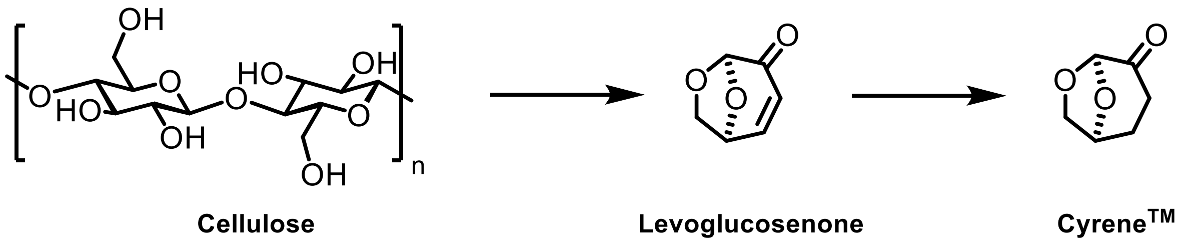
Keywords: biomass, dimerization, oxidation, polymers, synthesis design

Background

The urgent need of sustainable and safe alternatives to replace depleting fossil[1] resources and solve environmental issues such as the “Plastic Continents” in the Pacific Ocean[2] and the severe changes caused by Anthropocene’s[3] polluting gas has driven investigations and creations of bio-synthon databases[4] to substitute the current petroleum-based molecules. The production of the well-known lactic acid from sugar fermentation is a good example of white biotechnology applied to biomass for the production of bio-based monomers. The corresponding material, poly(lactic acid) (PLA), has been commercialized for years and is largely used as the main material for cold beverage cups. Moreover, PLA’s low glass transition temperature (T_g of 55 °C) compared to other commodity plastics, such as poly(ethylene terephthalate), prohibits its utilization at high temperature. Still, PLA remains a good alternative for moderate temperature applications.



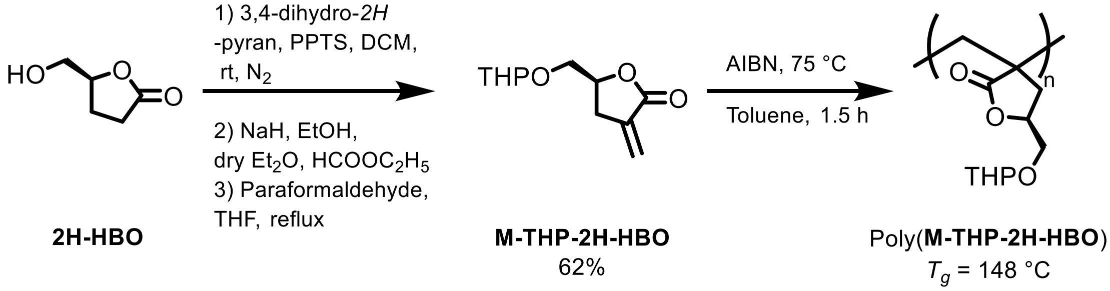
Scheme 2-1. Examples of bio-based synthons



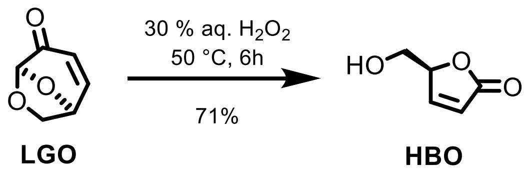
Scheme 2-2. Transformation of Cellulose into Cyrene^{TM}

A few other examples of bio-based molecules used as building blocks in Polymer Science have been described in the literature, including itaconic acid,[4] succinic acid,[4] angelica lactone,[5] levulinic acid, a precursor to methylene-γ-valerolactone,[6,7] and levoglucosenone (**LGO**),[8,9] a promising α,β-unsaturated cyclic ketone (Scheme 2-1). The high potential of **LGO** as both a building block and a precursor of Cyrene^{TM}, a green aprotic polar solvent, has caught the attention of a few research groups and companies. In 2008 Circa developed the Furacell^{TM} technology,[10] a scalable process that allows **LGO** production from cellulose-based feedstocks, such as bagasse and sawdust, and its subsequent hydrogenation to produce Cyrene^{TM} (Scheme 2-2).[11]

Apart from a few works such as the reduction of the ketone moiety of Cyrene™ and its subsequent acrylation proposed by Saito and co-workers[12] to form the corresponding acrylate and polyacrylate, the use of **LGO** and Cyrene^{TM} in material

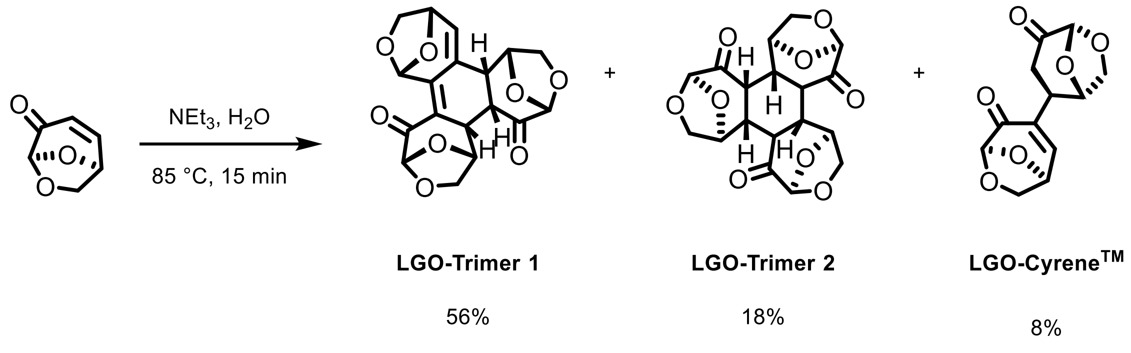


Scheme 2-3. Synthesis of poly(**M-THP-2H-HBO**) from **2H-HBO**



Scheme 2-4. Green synthesis of **HBO** from **LGO**

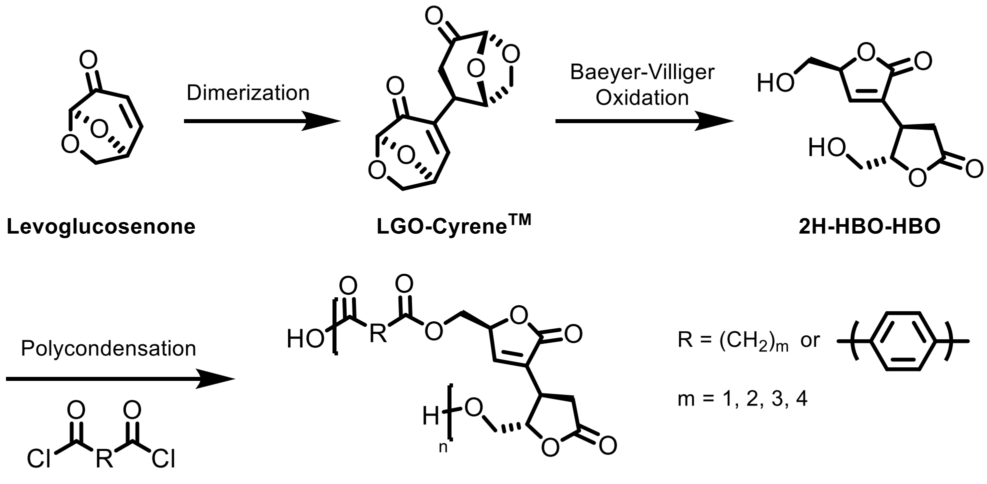
science appears limited. Recently, we reported the synthesis of renewable acrylate monomers with (*S*)-*γ*-hydroxymethyl-*α,β*-butenolide (**HBO**), a bio-based molecule derived from **LGO**, to produce high-T_g biobased polymers with post-polymerization possibilities (Scheme 2-3).[13] Over the last decades, several processes involving either chemical[14],[15] or chemo-enzymatic[16] conditions have been proposed to synthetize **HBO** from **LGO** through Baeyer-Villiger oxidations. For example, in 2018[17] we reported the organic solvent-free oxidation of **LGO** into **HBO** with 30% aqueous H_2O_2 without the presence of any catalyst (Scheme 2-4). Besides its interest as a precursor for the synthesis of such a bio-based acrylate, **HBO** could also be transformed into an AB- or AA'-type monomer if another alcohol or acid function could be added to its structure.



Scheme 2-5. Oligomerization of **LGO** by Stevenson and co-workers[18]

In 1982, Stevenson and co-workers[18] reported the formation of **LGO**-Cyrene™ in 8% yield when **LGO** was heated at 80-85 °C in the presence of triethylamine (Scheme 2-5). In 1995, Peters and coworkers[19] described the self-condensation of **LGO** as a side reaction whenever **LGO** was highly concentrated in the presence of a base and the dimer **LGO**-Cyrene™ was isolated in 32% yield.

To the best of our knowledge, no further optimizations or chemical transformations were carried out to take advantage of this promising molecule that offers a great playground for chemists due to its two ketone moieties. Building on our experience with **LGO** upgrading through sustainable synthetic processes,[16,17,20,21,22] we decided to investigate the implementation of the aforementioned Baeyer-Villiger-based strategy[17] to **LGO**-Cyrene™ to access the corresponding **2HHBO- HBO** as a new bio-based AA'-type diol monomer with the aim to produce renewable polyesters with the **HBO** motif (Scheme 2-6).



Scheme 2-6. Syntehsis of **2H-HBO-HBO** polyesters from **LGO**

Experimental

Chemicals and regeants

Levoglucosenone was graciously provided by the Circa Group. Potassium carbonate 99% (Acros), hydrogen peroxide 30% (Fischer), diethyl succinate 98% (Alpha Aesar), malonyl chloride 97% (Sigma Aldrich), succinyl chloride 95% (Sigma Aldrich), adipoyl chloride 98% (Sigma Aldrich), glutaryl chloride 97% (Sigma Aldrich), terephthaloyl chloride >99% flakes (Sigma Aldrich) were used without further purification unless mentioned. NMR solvents including deuterated chloroform, deuterated methanol, and deuterated dimethyl sulfoxide were purchased from Cambridge Isotopes Laboratories.

Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy

^{1}H NMR spectra of samples were recorded at 300 MHz ($CDCl_3$, CD_3OD, DMSO-d_6 and Acetone-d_6 residual signal at 7.26, 3.31, 2.50 and 2.05 ppm respectively). ^{13}C NMR spectra of samples were recorded at 75 MHz ($CDCl_3$, CD_3OD, DMSO-d_6 and Acetone-d_6 residual signal at 77.2, 49.0, 39.5 and 29.8, 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)

TGA was performed under nitrogen with a TGA Q500 from TA Instruments. About 1-5 mg of each sample was 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)

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-coolheat cycle at 10 °C/min. The temperature ranged from -80 °C to 100 °C.

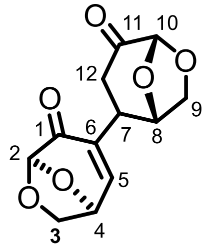
Gel Permeation Chromatography (GPC)

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 Polystyrene Standards (M_w: 620, 1,320, 2,930, 4,730, 10,190, 19,650, 29,870, 75,000, 123,700 and 278,700 g.mol^{-1}). The samples were prepared by solubilizing around 5 mg of material in 1 mL of the aforementioned solvent.

Monomer synthesis

Synthesis of (1*S*,1'*S*,2*R*,5*R*,5'R*)*-6,6',8,8'-tetraoxa[2,3'-bi(bicyclo[3.2.1]octan)]-2'-ene-4,4'-dione (LGO-Cyrene™)

LGO (2.59 g, 2 mL, 20.5 mmol) was solubilized in methanol (2.2 mL) and 45 mg (0.3 mmol) of K_2CO_3 were added. The solution was stirred at room temperature until the precipitate hinders the stirring. The reaction was filtered to obtain an orange solid that could be engaged in the next step without further purification (2.56 g, 99% yield).

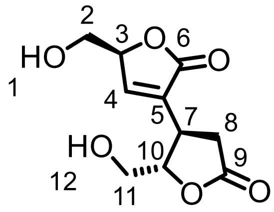


LGO-Cyrene

^{1}H NMR (DMSO-d_6, 300 MHz): δ_H 2.17 (d, 1H, J = 17.0 Hz, H_{12}), 3.09 (dd, 1H, J = 8.6 and 17.0 Hz, $H_{12'}$), 3.38 (m, 1H, H_7), 3.75 (m, 2H, H_3 & H_9), 3.90 (m, 1 H, $H_{9'}$), 4.27 (m, 1H, $H_{3'}$), 4.52 (m, 1H, H_8), 5.10(s, 1H, H_{10}), 5.27 (t, 1H, J = 4.5 Hz, H_4), 5.45 (s, 1H, H2), 7.12 (dd, 1H, J = 1.2 & 5.0 Hz, H_5). ^{13}C NMR (DMSO-d_6, 75 MHz): δ_c 34.7 (C_{12}), 38.1 (C_7), 66.4 (C_9), 67.7 (C_3), 72.4 (C_8), 74.9 (C_4), 100.5 (C_{10}), 101.1 (C_2), 136.1 (C_6), 146.1 (C_5), 189.1 (C_1), 201.2 (C_{11}).

Synthesis of (*S*)-5-(hydroxymethyl)-3-((2S,3S)-2-(hydroxymethyl)-5-oxotetrahydrofuran-3-yl)furan-2(5H)-one (2H-HBO-HBO)

To **LGO**-Cyrene™ (1.50 g, 6.58 mmol) was added 30% aqueous H_2O_2 (1.48 mL, 14.5 mmol). The system was stirred at 45 °C until full consumption of the starting material. After concentration of the reaction, the crude product was purified over silica gel chromatography (Eluent: Ethyl Acetate/Methanol: 100/0 to 90/10) to give a colorless oil (900 mg, 60% yield).



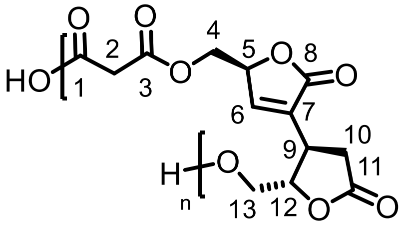
2H-HBO-HBO

^{1}H NMR (Acetone-*d*$_6$, 300 MHz): δ_H 2.72 (dd, 1H, *J* = 8.1 & 17.5 Hz, $H_{8'}$), 2.87 (dd, 1H, *J* = 8.1 & 17.5 Hz, H_8), 3.53 (m, 1H, H_7), 3.80 (m, 4H, $H_{2,11}$), 4.25 (m, 2H, $H_{1,12}$), 4.55 (m, 1H, H_{10}), 5.12 (m, 1H, H_3), 7.54 (d, 1H, *J* = 1Hz, H_4). ^{13}C NMR (Acetone-*d*$_6$, 75 MHz): δ_c 33.3 (C_7), 33.5 (C_8), 61.6 (C_2), 62.2 (C_{11}), 82.7 (C_3), 83.6 (C_{10}), 133.4 (C_5), 148.3 (C_4), 172.3 (C_6), 174.9 (C_9).

Polymerizations

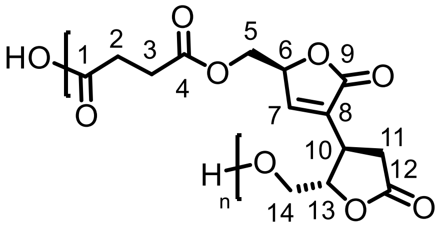
In a 10 mL round bottom flask, **2H-HBO-HBO** (885 mg, 3.75 mmol) was charged and malonyl chloride (0.37 mL, 3.80 mmol) was added under nitrogen. The system was stirred at room temperature until the viscosity hindered the stirring, and then the temperature was increased up to 40 °C to decrease the viscosity. Then, the temperature was increased by 20 °C, up to 80 °C, whenever the stirring was hindered. Finally, vacuum was applied for one hour and the resulting renewable polyesters were solubilized in DMSO and was precipitated in water. After filtration, the biobased polymers were freeze-dried overnight. Additional polyesters were prepared with this protocol employing alternate diacyl chlorides.

Poly(2H-HBO-HBO malonate)



40% yield after reprecipitation. ^{1}H NMR (DMSO-d_6, 300 MHz): δ_H 2.74 (m, 3H, $H_{9,10}$) 3.56 (m, 2H, H_2), 4.28 (m, 4H, $H_{4,13}$), 4.64 (m, 1H, H_{12}), 5.28 (m, 1H, H_5), 7.51 (m, 1H, H_6). ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 33.6 (C_{10}), 41.8 (C_9), 52.7 (C_2), 63.8 (C_{13}), 65.4 (C_4), 79.7 (C_{12}), 80.3 (C_5), 133.0 (C_7), 148.3 (C_6), 166.5 (C_3), 168.4 (C_1), 172.4 (C_8), 175.3 (C_{11}).

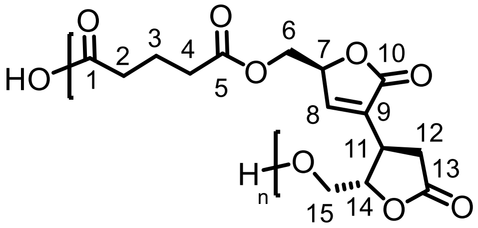
Poly(2H-HBO-HBO succinate)



45% yield after reprecipitation. ^{1}H NMR (DMSO-d_6, 300 MHz): δ_H 2.52 (t, 4H, J = 12.7 Hz, $H_{2,3}$), 2.76 (m, 2H, H_{11}), 3.34 (m, 1H, H_{10}), 4.24 (m, 4H, $H_{5,14}$) 4.62 (m, 1H, H_{13}), 5.27 (m, 1H, H_6), 7.52 (m, 1H, H_7). ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 28.7 ($C_{2,3}$), 33.5 (C_{11}), 33.6

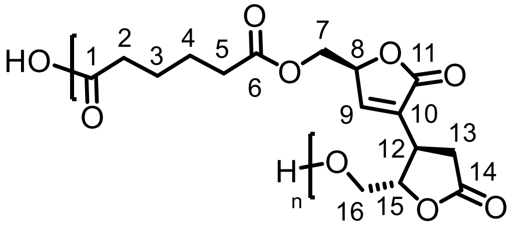
(C_{10}), 63.2 (C_{14}), 64.7 (C_{14}), 80.0 (C_{13}), 80.4 (C_6), 132.8 (C_8), 148.4 (C_7), 172.0 (C_4), 172.4 (C_1), 173.8 (C_9), 175.3 (C_{12}).

Poly(2H-HBO-HBO glutarate)



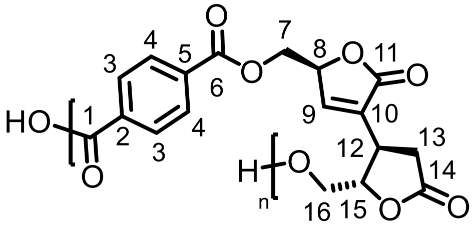
45% yield after reprecipitation. ^{1}H NMR (DMSO-d_6, 300 MHz): δ_H 1.72 (m, 2H, H_3), 2.32 (m, 4H, $H_{2,4}$), 2.81 (m, 2H, H_{12}), 3.38 (m, 1H, H_{11}), 4.29 (m, 4H, $H_{6,15}$), 4.67 (m, 1H, H_{14}), 5.34 (m, 1H, H_7), 7.62 (m, 1H, H_8). ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 20.2 (C_3), 32.6 (C_4), 33.7 (C_2), 51.8 ($C_{11,12}$), 62.9 (C_{15}), 64.5 (C_6), 80.0 (C_{14}), 80.6 (C_7), 132.8 (C_9), 148.6 (C_8), 172.4 (C_5), 172.6 (C_1), 174.5 (C_{10}), 175.3 (C_{13}).

Poly(2H-HBO-HBO adipate)



38% yield after reprecipitation. ^{1}H NMR (DMSO-d_6, 300 MHz): δ_H 1.50 (m, 4H, $H_{3,4}$), 2.19 (m, 2H, H_2), 2.32 (m, 2H, H_5), 2.79 (m, 2H, H_{13}), 3.39 (m, 1H, H_{12}), 4.28 (m, 4H, $H_{7,16}$), 4.67 (m, 1H, H_8). ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 24.3 ($C_{3,4}$), 33.7 (C_5), 33.8 (C_2), 51.7 ($C_{12,13}$), 62.8 (C_{16}), 64.4 (C_7), 79.9 (C_{15}), 80.5 (C_8), 132.7 (C_{10}), 148.7 (C_9), 172.4 (C_6), 172.9 (C_1), 174.8 (C_{11}), 175.3 (C_{14}).

Poly(2H-HBO-HBO terephthalate)

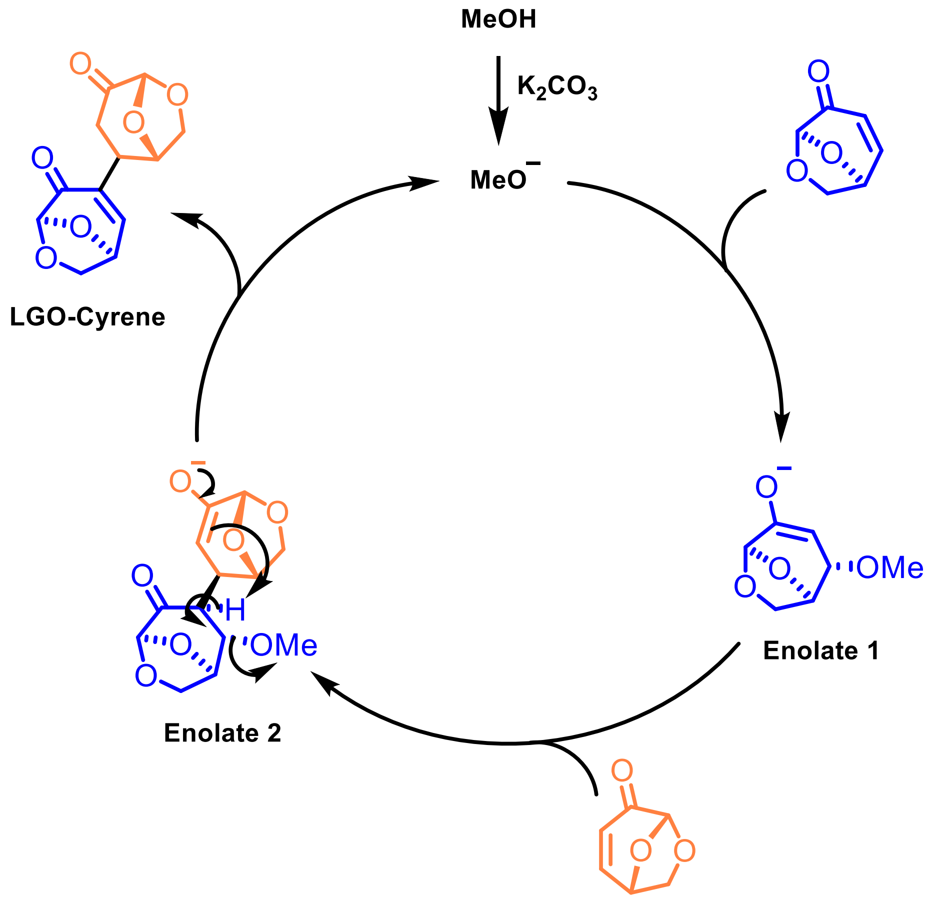


42% yield after reprecipitation. ^{1}H NMR (DMSO-*d*$_6$, 300 MHz): δ_H 2.77 (m, 2H, H$_{13}$), 3.51 (m, 1H, H$_{12}$), 4.55 (m, 4H, H$_{7,16}$), 4.78 (m, 1H, H$_{15}$), 5.48 (m, 1H, H$_8$), 7.73 (m, 1H, H$_9$), 7.99 (m, 4H, H$_{3,4}$). ^{13}C NMR (DMSO-*d*$_6$, 75 MHz): δ_C 33.5 (C$_{12}$), 33.8 (C$_{13}$), 63.8 (C$_{16}$), 65.6 (C$_7$), 79.9 (C$_{15}$), 80.4 (C$_8$), 129.9 (C$_4$), 130.2 (C$_3$), 132.7 (C$_{10}$), 134.9 (C$_2$), 135.5 (C$_5$), 149.2 (C$_9$), 165.0 (C$_6$),167.1 (C$_1$), 172.4 (C$_{11}$), 175.3 (C$_{14}$). (NB: optimal solubility of the polymer in the NMR solvent was reached)

Results and discussions

Michael addition is a valuable 100% atom economical reaction that is often performed under mild conditions and generally proceeds in high yields. Having extensively used **LGO**, we knew its unsaturated ketone exhibits high reactivity towards nucleophilic attack. Our first efforts were thus focused on the design and optimization of a high yielding Michael additionmediated homocoupling of **LGO** under green conditions to access **LGO**-Cyrene^{TM}.

Peters and coworkers[19] showed that the formation of **LGO**Cyrene^{TM} was possible if **LGO** was concentrated enough in the medium (32% yield at [**LGO**] **=** 5.33 M). Stevenson and coworkers[18] suggested that the generation of hydroxide through acid-base reaction between water and Et$_3$N, would lead to the hydration of **LGO** thus initiating



Scheme 1. Proposed catalytic cycle for **LGO**-Cyrene^{TM} formation

its homocoupling, the proposed mechanism relying on the abstraction of the proton in the α position of the resulting saturated ketone. Although we fully agree with the first step of the mechanism, namely the generation of the methoxide and its Michael addition on **LGO**, we believe that the enolate intermediate **1** (Scheme 2-7) resulting from the Michael addition of the methoxide would itself add onto another **LGO** molecule through Michael addition, thus providing the corresponding enolate **2**. Finally, for the final step, we envision the abstraction of the proton in the α position of the ketone by enolate **2** and the concomitant regeneration of the hydroxide ion that will initiate a new catalytic cycle (Scheme 2-7). It is noteworthy to mention that the addition of enolate **1** proceeds with high diastereoselectivity, providing detectable amnounts of only one **LGO**-Cyrene^{TM} diastereomer.

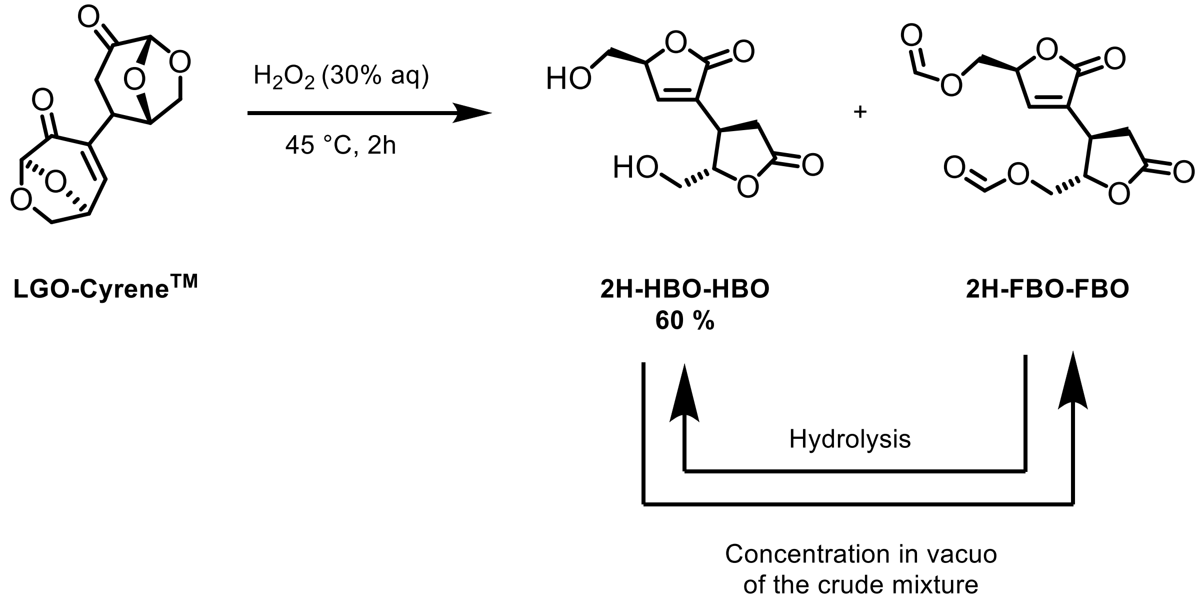
For the design and optimization of the novel sustainable synthetic procedure towards **LGO**-Cyrene^{TM}, as the presence of a nucleophilic species is essential for the reaction to occur, methanol was chosen as both the solvent and the source of methoxide. It is noteworthy to mention that even though ethanol is a greener alternative to methanol, the preliminary results obtained with that solvent provided low yields. Aiming at an ecofriendly and safe process, we decided to replace Et_3N with potassium carbonate, a greener and less toxic base. The optimization of this process was performed using the One Variable at A Time approach (OVAT), focusing on the effect of the temperature, the concentration and the reaction duration. We first looked at the influence of the **LGO** concentration at room temperature for a catalytic amount of base fixed at 1.6 mol% (Table 2-1, entries 1 to 6). Below 2 M, there was no significant impact of [**LGO**] on the yield. Indeed, 0.5 M of **LGO** (Table 2-1, Entry 1) provided a yield of 32% whereas 38% yield was obtained with [**LGO**] = 2 M (Table 2-1, Entry 4). Nonetheless, an important increase up to 58% yield (Table 2-1, Entry 6) was observed for [**LGO**] = 2.9 M. Having reached an honorable yield of 58% in 24 h at [**LGO**] = 2.9 M, the influence of the time was investigated. Table 2-1, Entry 7 shows that a yield of only 25% was obtained after 6 hours of reaction, confirming that the reaction needs to be performed for longer times. The obtention of a 55% yield for 48 h (Table 2-1, Entry 8) versus 40% (Table 2-1, Entry 5) raised the question about the relevance of a time superior to 24 h. In an attempt to accelerate the reaction, we studied the dimerization at higher temperature. Table 2-1, entries 9 to 11 show that a temperature of 40 °C did not significantly impact the yield. At

Table 2-1. Optimization of **LGO** dimerization[a]

Entry	T (°C)	C (mol/L)	t (h)	Yield (%)
1	25	0.5	24	32[b]
2	25	1.0	24	30[b]
3	25	1.5	24	35[b]
4	25	2.0	24	38[b]
5	25	2.5	24	40[b]
6	25	2.9	24	58[b]
7	25	2.9	6	25[b]
8	25	2.5	48	55[b]
9	40	1.0	24	33[b]
10	40	2.0	24	54[b]
11	40	2.9	24	60[b]
12	25	9	2	99[c]
13	25	12	2	92[c]
14	40	9	2	67[c]
15	40	12	2	99[c]

[a]Conditions: K_2CO_3 1.6 mol%.[b]Purified product (column chromatography purification). [c]Crude product (unwashed cake).

theses concentrations (Table 2-1, Entries 12 to 15) and at room temperature (Table 2-1, Entries 12 to 13), precipitation of a product started to hinder the stirring after a few hours. Based on that observation, the cake was filtered and we found out that the unwashed crude solid was mainly composed of the targeted product and a few impurities. Even though washing with coldmethanol partially eliminated the latters, we decided to engage this crude product in the next step without further purification. It is important to note that, for [**LGO**] below 9 M, remaining **LGO** was observed at the end of the reaction whereas no more **LGO** was left when more concentrated reaction medium was used. In all cases, the monitoring of the reaction using ^{1}H NMR spectroscopy showed the appearance of extra peaks at the beginning of the reaction - besides that from **LGO**-Cyrene^{TM} - that gradually decreased during the course of the reaction, thus indicating that the aforementioned impurities are, most likely, reaction intermediates. The dimerization being optimized, we then focused our efforts on the 2nd step of the synthetic pathway, the oxidation of **LGO**-Cyrene™ into **2H-HBO-HBO**.

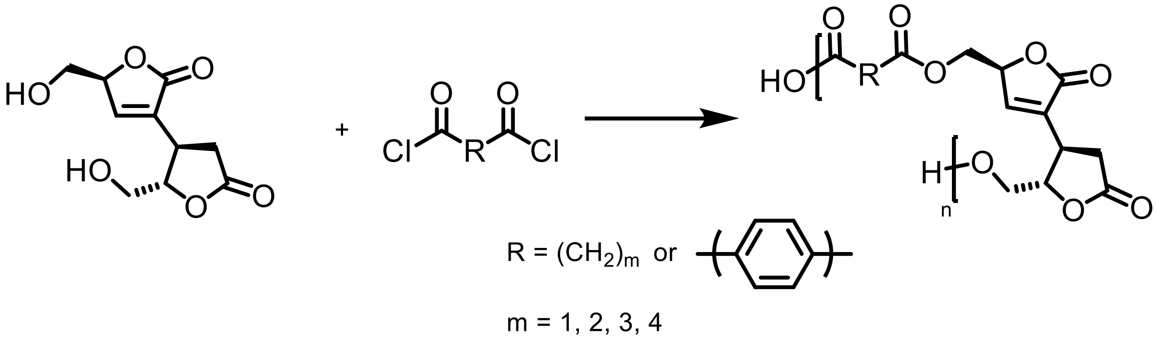


Scheme 2-8. 2H-HBO-HBO formation from **LGO**-Cyrene^{TM}

To oxidize **LGO**-Cyrene^{TM}, our strategy relied on the well-established Baeyer–Villiger oxidation. This well-known reaction usually involves a peracid, such as meta-chloroperbenzoic acid (*m*-CPBA)[23] or peracetic acid,[14] that reacts with a cyclic ketone to form an intermediate that rearranges into a lactone. Several groups have investigated the use of chemoenzymatic conditions to make this process greener and more sustainable. For instance, Chavez and co-workers[24] proposed the in situ generation of peracetic acid by using ethyl acetate and a lipase, *Candida antarctica* Lipase B.

In 2015, we implemented and optimized this strategy for the synthesis of **HBO** to avoid the use of toxic chemicals such as m-CPBA. Even though this process is greener and proceeds in good yield, scalability may be an issue if the cost of the enzyme is considered. Recently,[22] we proposed an alternative to this chemoenzymatic method that consists of performing the Baeyer–Villiger oxidation of **LGO** in the presence of only H_2O_2 in water. This new procedure drastically simplified and further greened-up the previous protocol as it avoids the use of the costly enzyme and ethyl acetate. Additionally, it has been efficiently scaled up to kg quantities. This strategy was thus applied directly to **LGO**-Cyrene^{TM} with the aim to oxidize the two ketone groups to form **2H-HBO-HBO** (Scheme 2-8). After 2 h of reaction, we used TLC to reveal the full consumption of **LGO**-Cyrene^{TM}, however, intermediates remained, and the reaction was continued for another 4 h. Along with **2H-HBO-HBO**, its formate (**2H-FBO-FBO**), an intermediate of the reaction, was also observed. Even though an acid treatment was attempted to hydrolyze **2H-FBO-FBO**, it reformed readily during the concentration of the reaction mixture, which limited the yield of **2H-HBO-HBO** to 60% after purification.

With this new diol in hand, its polycondensation in the presence of suitable comonomers was attempted. To determine the impact of the chain length and flexibility of the diacid monomer, aliphatic comonomers malonyl chloride (m= 1) or adipoyl chloride (m=4) and the aromatic monomer terephthaloyl chloride, respectively, were chosen (Scheme 2-9).



Scheme 2-9. Polycondensation of **2H-HBO-HBO** in the presence of diacyl chlorides.

As a result of the poor solubility of **2H-HBO-HBO** in most organic solvents, except polar solvents such as alcohol or DMSO, a solvent-free process was selected. Diacyl chlorides were added to the sticky **2H-HBO-HBO** under N_2 flow at room temperature, and the system was kept free of air. An increase in the viscosity because of the formation of polymer chains was noticed after a few minutes, and this time depended on the nature of the comonomer engaged in the polycondensation. The temperature of the polymerization was set at 40 °C to decrease the viscosity and to allow facile stirring. The temperature was increased gradually up to 80 °C. Finally, vacuum was applied for 1 h to remove unreacted monomers and residual HCl gas. The resulting dark-brown materials were dissolved in DMSO, and the renewable polyesters were precipitated by dropwise addition into a poor solvent such as cold water or cold methanol.

Table 2-2. Molecular weights and thermal properties of the **2H-HBO-HBO**-based polyesters.

Entry	Polymer	M_n (kDa)[a]	DP[b]	$Đ$ [a]	$T_{d5\%}$ (°C)[c]	$T_{d50\%}$ (°C)[c]	T_g (°C)[d]
1	Poly(**2H-HBO-HBO** malonate)	4,600	16	1.44	183	363	60
2	Poly(**2H-HBO-HBO** succinate)	3,500	11	1.42	241	395	70
3	Poly(**2H-HBO-HBO** glutarate)	3,500	11	1.24	184	389	26
4	Poly(**2H-HBO-HBO** adipate)	3,400	10	1.19	142	349	-1
5	Poly(**2H-HBO-HBO** terephthalate)	4,700	13	1.47	208	406	81

[a]GPC: DMF (10 mM LiBr) at 60 °C *vs* poly(styrene) standards. [b]Calculated by GPC. [c]TGA temperatures at which 5% and 50% mass loss were observed under nitrogen, temperature ramp 10 °C/min from 50 to 500 °C. [d] Determined by DSC under N_2, temperature ramp 10 °C/min from -80 to 100 °C.

We analyzed the products by using gel permeation chromatography (GPC). As expected, we did not obtain a neat Gaussian distribution but we observed overlapping peaks caused by the presence of oligomers with different chain lengths. This may be explained by the bulk conditions used to perform the polymerization as the high viscosity tends to decrease the homogeneity of the medium. The GPC chromatograms were first analyzed by considering the peaks as a single region to determine the M_n values listed in Table 2-2. Then, peaks were separated and experimental M_n values were evaluated for each region. For example, poly(**2H-HBO-HBO** malonate) has a reported M_n of 4600 Da (Table 2-2, Entry 1) with a dispersity ($Đ$) of 1.44. This molecular weight corresponds to 16 repeat units. In contrast, we could split the region into two distinct areas to give Peak 1 and Peak 2, which had a M_n of 7600 and 3000 Da with a $Đ$ of 1.22 and 1.03, respectively. Similar results were obtained with the other renewable polyesters. For instance, poly(**2H-HBOHBO** succinate) and poly(**2H-HBO-HBO** terephthalate) have experimental M_n values of 3500 and 4700 Da, respectively, with $Đ$

of approximately 1.4–1.5. As mentioned previously, several peaks were observed in the chromatograms (Figures S27, S29, S31, S33, and S35) and molecular weights reached 8000–10000 Da.

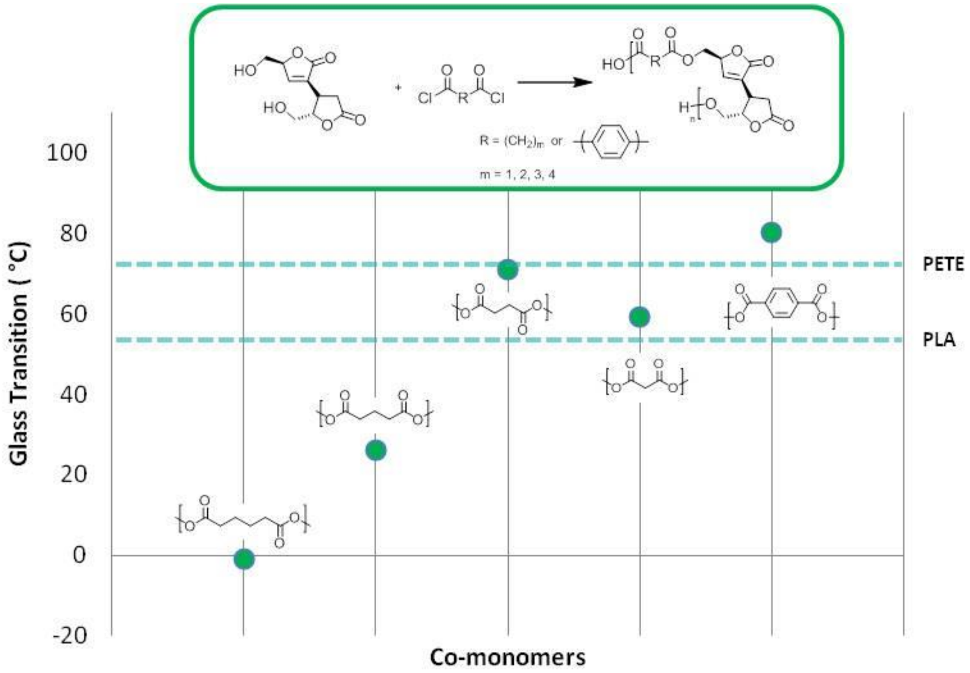


Figure 1-1. T_g values of our renewable polyesters and compared to those of commodity polyesters PETE (71 °C)[25] and PLA (55 °C).[26]

Although this bulk polycondensation did not provide polymers with high molecular weights, it did demonstrate the potential of **2H-HBO-HBO** as a monomer and it validated the proof of concept. We used thermogravimetric analysis (TGA) to investigate the thermal degradation of the polymers. Most of the renewable polyesters were quite stable with a temperature at which 5% of the mass is lost ($T_{d5\%}$) higher than 180 °C, except for poly(**2H-HBO-HBO** adipate), which exhibits a $T_{d5\%}$ value of 140 °C. Poly(**2H-HBO-HBO** succinate) (Table 2-2, Entry 2, m=2) even reaches a $T_{d5\%}$ of 241 °C. We also measured the temperature at which 50% of the mass is lost ($T_{d50\%}$), and the values of all of the materials are above 300 °C.

The evolution of T_g with respect to the diacyl chlorides engaged in the process is shown in Figure 2-2. As expected, the higher the number of carbon atoms in the aliphatic chain, the lower the T_g, even though a slight decrease is observed for poly(**2H-HBO-HBO** malonate) (Table 2-2, Entry 1, m=1). This trend is also observed for poly(ethylene malonate), which exhibits a T_g of -15 °C,[27] whereas poly(ethylene succinate) has a T_g of -6 °C.[28] For instance, poly(**2H-HBO-HBO** glutarate) (Table 2-2, Entry 3, m=3) exhibited a T_g of 26 °C, whereas poly(**2H-HBO-HBO** succinate) (Table 2-2, Entry 2, m=2) showed a T_g of 71 °C, and thus competes with poly(ethylene terephthalate)(PETE). Compared to ethylene glycol, **2H-HBO-HBO** exhibited a higher T_g if used as a diol with succinate and terephthalate motifs. Indeed, poly(ethylene succinate) and poly(ethylene terephthalate) have T_g values of -6 and 71 °C,[28,25] respectively, whereas the corresponding bio-based polymers that incorporate **2H-HBO-HBO** rather than ethylene glycol showed T_g values of 70 and 81 °C, respectively. These higher T_g values may be explained by the high steric hindrance and rigidity of the new **HBO**-based diol brought by the two lactone moieties.

Conclusion

Levoglucosenone (**LGO**), a renewable cellulose-based building block produced at a sufficient scale to be industrially relevant, can be transformed easily into **2H-HBO-HBO**, a new bio-based, sterically hindered bicyclic diol. Indeed, **2H-HBO-HBO** can be readily obtained through a sustainable two-step process that involves **LGO** homocoupling in methanol in the presence of K_2CO_3 followed by a H_2O_2-mediated Baeyer–Villiger oxidation in water. **2H-HBO-HBO** was then subjected to a series of solvent-free polycondensations with common diacyl chlorides. Even though the polymerization conditions must be improved to use diacids or diesters instead of diacyl chlorides and to reach higher molecular weights, the resulting materials show promising properties, especially the glass transition values, which, for some of them, compete with commercially available commodity plastics that include polyesters such as poly(ethylene terephthalate) and poly(lactic acid). Moreover, these polyesters are stable at a high temperature with a temperature at which 50% of the mass is lost above 300 °C. In addition to these valuable thermal properties, the chemical versatility brought by **2H-HBO-HBO** can be further exploited through post-polymerization and expand the scope of applications. Indeed, as already investigated with itaconate-based polymers,[29] the α,β-unsaturated lactone moieties in the bio-based **2H-HBO-HBO**-based polyesters allow Michael additions. We are building on this proof-of-concept to further expand our library of **LGO**-based monomers, and new sustainable **LGO**-derived monomers and their corresponding bio-based polymers are currently under investigation and will be reported in due course.

Associated Content

The Supporting Information is available free of charge on the editor website at DOI: https://doi.org/10.1002/cssc.202000680. NMR spectra, GPC, DSC and TGA traces.

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