Sustainable hyperbranched functional materials *via* green polymerization of readily accessible levoglucosenone-derived monomers

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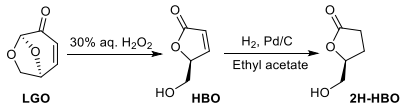
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Abstract: The homopolymerization in basic conditions of the recently reported bis(γ-lactone), 2H-HBO-HBO, is herein described for the first time. The solvent-free polymerization of this pentafunctional levoglucosenone (LGO) derivative afforded fully renewable poly(vinyl-ether lactone) copolymers with a highly hyperbranched structure. This investigation stemmed from the polycondensation trials between 2H-HBO-HBO and di(methyl carbonate) isosorbide (DCI) that failed to give the anticipated polycarbonates. Such unexpected behavior was ascribed to the higher reactivity of the 2H-HBO-HBO hydroxy groups towards its α,β-conjugated endocyclic C=C, rather than the DCI methylcarbonate moieties. The different mechanistic scenarios involved in 2H-HBO-HBO homopolymerization have been addressed and a possible structure of poly(2H-HBO-HBO) was suggested. Furthermore, the readily accessible (*S*)-γ-hydroxymethyl-α,β-butenolide (HBO) was also polymerized for the first time at a relatively large-scale, without any prior modification, resulting in a new hyperbranched polymer with an environmental factor (*E* factor) ~ 0. These new HBO-based polymers have a great potential for industrial-scale production due to their interesting properties and easy preparation *via* a low-cost, green and efficient process.

Introduction

Levoglucosenone (**LGO**) is a renewable chiral molecule produced at an industrial scale from cellulosic feedstocks (*e.g.* sawdust, straw and bagasse).[1–3] The presence of different reactive functional moieties in the **LGO** structure, *i.e.* α,β-unsaturated ketone and ketal, allows many chemical modifications leading to highly valuable compounds.[4] For instance, (*S*)-γ-hydroxymethyl-α,β-butenolide (**HBO**), a chiral α,β-unsaturated lactone, is readily achievable by Baeyer-Villiger oxidation of **LGO.**[5]-[6] Moreover, the catalytic hydrogenation of **HBO** leads to the quantitative formation of (*S*)-γ-hydroxymethyl-γ-butyrolactone (**2H-HBO**)[5,7] (Scheme 1), another interesting bio-based molecule. Owing to its high chemical versatility, **LGO** showed also great potential as a building block in diverse synthetic processes[8] such as polymer syntheses.[9–13]

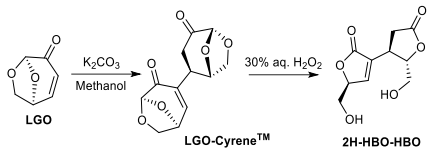


Scheme 1. Synthesis of **HBO** and **2H-HBO** from **LGO**

The rapidly evolving field of **LGO**-derived monomers and polymers was recently reviewed with a special focus on the green aspects of the monomer syntheses and polymerization processes.[9] Indeed, the production of bio-based polymers that can compete with petrochemical-based commodity polymers is highly relevant for biorefinery progress.[14] Replacing polymers derived from fossil fuels by sustainable biopolymers is crucial, not only given the inevitable progressive depletion of fossil feedstock but also to protect our planet from climate change and severe environmental issues.[15,16] Nevertheless, renewable carbon content cannot be the only metric in assessing an alternative bio-based material,[17–19]. Sustainable factors, such as green metrics, must also be taken into consideration to evaluate the greenness of a chemical reaction.[17–20] Although not all green metrics are easily accessible, the environmental factor (*E* factor) - expressed as kg of waste per kg of product - is largely accepted as a simple and useful quantitative measure of the amount of waste generated from a process.[21,22]

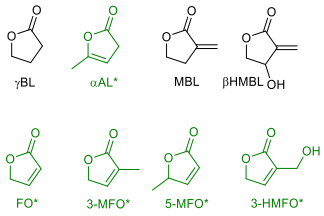
As an example, we recently reported a one-pot synthesis of a new bicyclic diol, **2H-HBO-HBO**, *via* H_2O_2-mediated Baeyer-Villiger oxidation/rearrangement of **LGO**-Cyrene™[23]; the *E* factor of this synthetic approach was 3.8 (Scheme 2).[9] The presence of two reactive primary hydroxy groups in **2H-HBO-HBO** structure renders this compound potentially suitable for polycondensation reactions. The solvent-free polycondensation of **2H-HBO-HBO** with diacyl chlorides (*E* factor ~ 1.5) led to polyesters with glass

transition (T_g) values ranging from −1 to 81 °C and good thermostability.[23]



Scheme 2. Synthesis of **2H-HBO-HBO** from **LGO**

2H-HBO-HBO structure incorporates two multifunctional 5-membered lactone cycles, *i.e.* a trifunctional **HBO** (endocyclic double bond, lactone ring and hydroxy) and a bifunctional **2H-HBO** (lactone ring and hydroxy). Although *γ*-lactone monomers have been traditionally considered as "non-polymerizable" due to the low ring-strain energy, recently, Carlotti, Peruch *et al*. reviewed several examples of the ring-opening polymerization (ROP) of these compounds.[24,25] Indeed, long chains γ-butyrolactone (γBL) polymers were prepared through ROP using alkali metal and alkoxide/urea as catalytic systems.[24] Furthermore, unsaturated polyesters were synthesized from the ROP of γBL derivatives having endocyclic C=C bond (α-angelica lactone; αAL)[26] or exocyclic C=C bond (α-methylene-γ-butyrolactone; MBL)[27] (Scheme 3). Chen *et al.* showed that MBL polymerization can lead to three types of polymers depending on the catalyst/initiator ratio that affects the polymerization pathway(s), *i.e.* ROP, vinyl addition polymerization (VAP) or a combination of both.[27]



Scheme 3. Structures of selected γ-lactone monomers (to the best of our knowledge, those marked with * are the only γ-lactone that contain endocyclic C=C known for polymerization)

Chen *et al.* also reported that, under nucleophilic and basic conditions, the polymerization of hydroxy-functionalized unsaturated γ-lactones, 3-(hydroxymethyl) furan-2(5H)-one (**3-HMFO**)[28] and β-hydroxy-MBL (**β-HMBL**)[28,29] (Scheme 3), leads to branched copolymers with very complex structures. Such complexity originates from different types of base-mediated mechanisms and mechanistic crossovers of Michael, oxa-Michael and proton transfer processes (*vide infra*). Withal, in the case of free-hydroxy monomers, furan-2(5H)-one (**FO**) (Scheme 3), the only vinyl-addition polymer was obtained through VAP. On the other hand, methyl-substituted derivatives of **FO**, 3-methyl- furan-2(5H)-one (**3-MFO**) and 5-methyl- furan-2(5H)-one (**5-MFO**) (Scheme 3) did not allow VAP under similar conditions leading to trimeric and dimeric structures, respectively.[28]

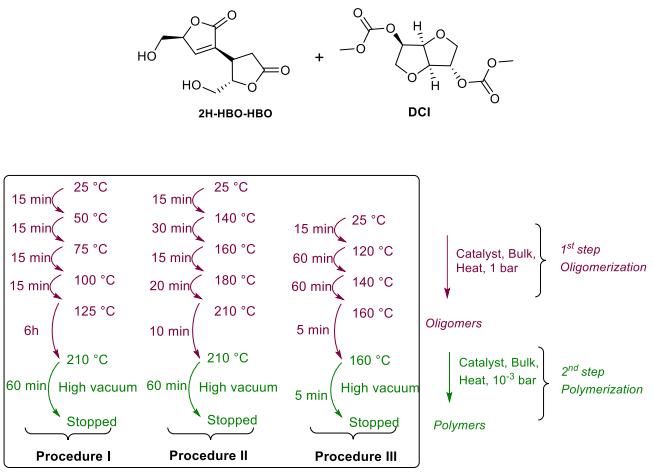
Herein, for the first time, the different pathways involved in the polymerization of a bicyclic bis(5-membered lactone)-containing molecule (**2H-HBO-HBO**), under basic conditions, were investigated. Furthermore, a comparative polymerization study on monocyclic (un-)saturated esters (**HBO** and **2H-HBO**) is also reported. This investigation provided valuable insight into the rarely reported polymerization of unsaturated γ-lactone monomers and it also led to new fully renewable hyperbranched materials with high potential production at an industrial scale.

Results and Discussion

Polycondensation attempts

Following our recent work on the preparation of polyesters *via* solvent-free polycondensation of **2H-HBO-HBO** with diacyl chlorides,[23] we decided to investigate the synthesis of polycarbonates by reacting **2H-HBO-HBO** with a dialkyl carbonate derivative of the bio-based platform chemical isosorbide,[30] namely di(methylcarbonate) isosorbide (**DCI**).

The polycondensation trials were performed in two steps according to three different procedures (I, II and III, Scheme 4). The first step was aimed at obtaining macromonomers (or oligomers) meanwhile the second step allows the condensation of the so-formed macromonomers/oligomers to achieve the wanted polycarbonates. Different transesterification metal-based catalysts (Cs_2CO_3, $Sc(OTf)_3$ $Ti(OBu)_4$) and an organocatalyst (triazabicyclodecene (TBD)) were used to promote the polymerization reaction.



Scheme 4. Two-step melt polycondensation trials of **2H-HBO-HBO** and **DCI** according to three different procedures (I, II and III)

Table 1. Polycondensation trials of **2H-HBO-HBO** with **DCI** or DMC

Entry	Procedure[a]	2H-HBO-HBO/ DCI/DMC	Catalyst[b]	Yield (%)[c]	*Main SEC distributions*[d]		T_g[e] (°C)	$T_{d5\%}$[f] (°C)
					$M_{n(SEC)}$ (kg.mol^{-1}) {*Đ*}	$M_{n(SEC)}$ (kg.mol^{-1}) {*Đ*}		
1	I	1.1/1/0	Cs_2CO_3	31	7.4 {1.8}	1.5 {1.0}	-19	161
2		1.1/1/0	$Sc(OTf)_3$	20	–	–	-18	169
3		1.1/1/0	$Ti(OBu)_4$	39	–	2.8 {1.7}	-16	159
4	II	1.1/1/0	Cs_2CO_3	27	–	3.0 {1.4}	–	293
5		1/1/0	Cs_2CO_3	35	–	3.9 {2.4}	–	287
6		1/1.1/0	Cs_2CO_3	41	23.2 {2.0}	3.8 {1.2}	–	241
7	III	1.1/1/0	Cs_2CO_3	53	63.9 {1.6}	3.4 {1.4}	-14	192
8		1.1/1/0	TBD	54	54.9 {1.5}	3.6 {1.5}	-14	160
9		0/1/0	Cs_2CO_3	62	5.3 {1.6}	1.1 {1.0}	91	221
10		0/1/10	Cs_2CO_3	42	5.3 {1.6}	1.0 {1.0}	–	109
11		1/0/5	Cs_2CO_3	40	57.5 {1.5}	2.0 {1.7}	90	216
12		1/0/10	Cs_2CO_3	42	41.7 {1.41}	2.0 {1.7}	92	220

[a] Polymerization procedures, including steps 1 and 2, are detailed in Scheme 4. [b] 1 mol% of the catalyst with respect to **2H-HBO-HBO**. [c] Isolated yield of the crude product, yield = (isolated mass/theoretical mass) *x* 100. [d] Determined in DMF (10 mM LiBr) at 50 °C. [e] Glass transition temperature determined by DSC, temperature ramp 10 °C/min. [f] TGA degradation temperatures at which 5% ($T_{d5\%}$) mass loss was observed under nitrogen.

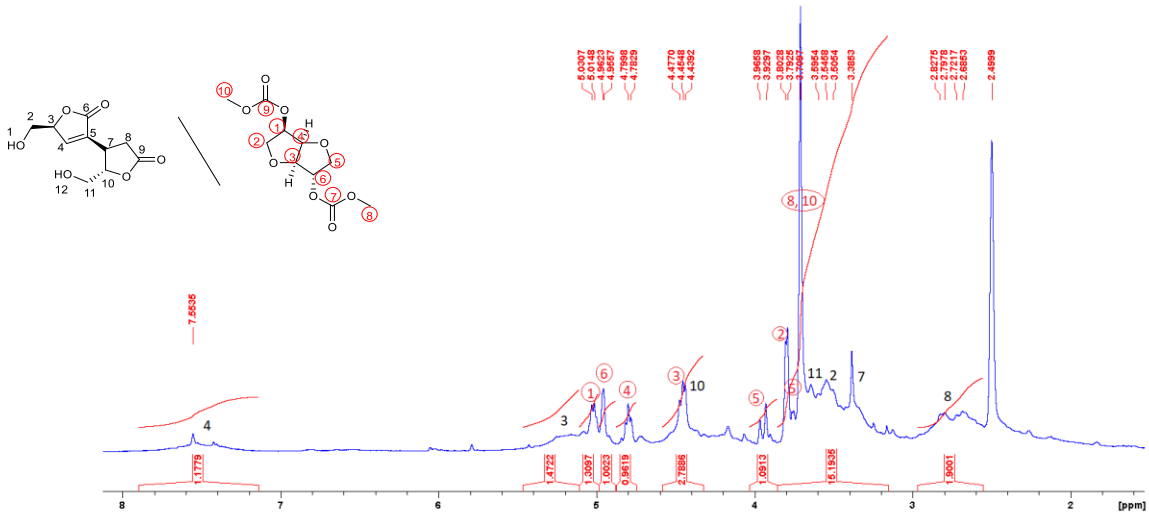


Figure 1. Typical ^{1}H NMR (DMSO-d_6) spectrum of a polymer obtained from the polymerization of **2H-HBO-HBO** in the presence of **DCI** (entry 7, Table 1).

The vast majority of the polymers obtained according to procedures I and II (Scheme 4) seemed to thermally degrade during the second step maybe as a result of the high temperature (entries 1-6, Table 1). This could be realized due to the too low solubility of the polymers obtained accompanied by a change in color from brownish to dark black at temperatures exceeding 200 °C. Nevertheless, size-exclusion chromatography (SEC) analyses of slightly soluble portions showed the formation of polymeric materials with observed molecular weight ($M_{n(SEC)}$) up to 23.2 kg.mol^{-1} and a dispersity (*Đ*) of 2.0 (entry 6, Table 1). To avoid the degradation of the polymer and to enhance its solubility, the second stage was then triggered at 160 °C instead of 210 °C and stopped after 5 min rather than 1 h (procedure III, entries 7 and 8, Table 1). In these conditions, the polymers obtained were fully soluble in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Interestingly, polymers with $M_{n(SEC)}$ up to 63.9 kg.mol^{-1} (*Đ* = 1.6) and 54.9 kg.mol^{-1} (*Đ* = 1.5) were obtained when Cs_2CO_3 and TBD were used, respectively (entries 7 and 8, Table 1). These materials showed good thermal stability; the temperatures at which 5% mass loss was observed ($T_{d5\%}$) were 192 °C (entry 7, Table 1) and 160 °C (entry 8, Table 1) and a negative T_g of -14 °C was noticed in both cases.

The polymeric structure of these materials was elucidated by careful interpretation of NMR spectra. In an example reported in Figure 1, it is evident the presence of signals related to both constituting monomers with proton integrations matching a nearly 1:1 ratio. ^{1}H and ^{13}C NMR show that H⑩ and H⑧ (~3.7 ppm) and C⑩ (55.0 ppm) and C⑧ (54.9 ppm) signals of **DCI** remained intact (Figure S4, Supporting Information-SI). Furthermore, ^{13}C NMR does not show any carbonyl signals that could be ascribed to a polycarbonate structure.

For comparison, the polymerization of **DCI** following procedure III was also attempted either alone or with 10 equiv. of dimethyl carbonate (DMC) (entries 9 and 10, Table 1). ^{1}H NMR of the corresponding polycondensation mixture shows a lower ratio of the H⑩ and H⑧ signals (Figure S8, SI). Furthermore, the ^{13}C spectrum displays three C=O signals at 153.5, 153.2 and 152.9 ppm with intensity ratios of 1:2:1 belonging to the *endo-endo*, *endo-exo* and *exo-endo*, and *exo-exo* connected carbonate groups (Figure S8, SI). This result is consistent with the observations reported by Chatti *et al.* on similar polymers, and was ascribed to the different reactivity of the *endo-* and *exo-*hydroxy groups that led to a random sequence.[31,32] Also in our case study, the stereocenters C⑥ and C① display different signals at 80.9 and 77.1 ppm, respectively, confirming the formation of a random sequence.

All these observations, in addition to ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC (Figures S5-S7, SI) led us to the conclusion that there was no condensation reaction between **2H-HBO-HBO** hydroxy groups and **DCI** carbonate moieties (Scheme

S1, SI), thus the polymeric materials formed have to be ascribed to another mechanism.

Furthermore, **DCI** did not show to act as a carboxymethylating or as a methylating[33] agent towards **2H-HBO-HBO**, regardless of the use of Cs_2CO_3 that is known as an efficient catalyst for the preparation of polycarbonates from isosorbide derivatives.[34] Nevertheless, we believe that **DCI** physically interacted with the so-formed polymer structure leading to the observed remarkable decrease in T_g to as less as -19 °C (Figure S20, SI). This hypothesis was later confirmed when **2H-HBO-HBO** polycondensation was attempted with 5 and 10 equiv. of DMC instead of **DCI** yielding to polymers with T_g of 90.3 and 92.2 °C respectively (Figures S26 and S27, SI), with no formation of polycarbonate structures (entries 11-12, Table 1). A similar difference in T_g values was also observed when the homopolymerization of **2H-HBO-HBO** was investigated in the absence of any other comonomer in the reaction medium (*vide infra*).

2H-HBO-HBO polymerization and trimerization of HBO-Bn

The tendency of **2H-HBO-HBO** to homopolymerize was confirmed by simply heating the monomer at 120 °C in bulk in a catalyst-free medium, as well as using Cs_2CO_3, TBD or $Ti(O^iPr)_4$. These experiments, summarized in Table 2, showed that an oligomer ($M_{n(SEC)}$ = 1.9 kg.mol^{-1}, $Đ$ = 1.2) (entry 13, Table 2) already formed without the aid of a catalyst, presumably through thermally-induced radical oligomerization (*vide infra*). Similarly, when $Ti(O^iPr)_4$ was employed as catalyst, an oligomers with an analogous SEC chromatogram was observed ($M_{n(SEC)}$ = 1.2 kg.mol^{-1}, $Đ$ = 1.2) (entry 16, Table 2). Interestingly, when a basic catalyst such as Cs_2CO_3 or TBD was involved (entries 14 and 15, Table 2), a quantitative conversion of the monomer was achieved in 1 h and three main mass distributions were observed by SEC analysis (Figure S17, SI). These regions corresponded to polymers with a large molecular weight difference, thus, their peaks were separated and $M_{n(SEC)}$ was estimated for each population. Such SEC multimodal profile was expected as **2H-HBO-HBO** is a bicyclic monomer with different functionalities. Nevertheless, the formation of polymers having $M_{n(SEC)}$ up to 809 kg.mol^{-1} ($Đ$ = 1.1) and 855 kg.mol^{-1} ($Đ$ = 1.1) was quite surprising (entries 14 and 15, Table 2). In addition, $M_{n(SEC)}$ values of 101 kg.mol^{-1} ($Đ$ = 1.8) and 108 kg.mol^{-1} ($Đ$ = 1.8) and a third short oligomers distribution of $M_{n(SEC)}$ = 1.3-1.7 kg.mol^{-1} ($Đ$ = 1.3-1.5) were observed. The very high molecular weight can be due to the polymer aggregation in solution (DMF) before SEC analysis.

In contrast to the results obtained in the presence of **DCI** (Table 1), the polymers exhibited a relatively high T_g (82 °C) (entry 15, Table 2); this value was found to be dependent on $M_{n(SEC)}$. For instance, a decrease of T_g to 25 and 27 °C was observed in the case of short oligomers (entries 13 and 16, Table 2). Regardless of the $M_{n(SEC)}$ values, the polymers showed good thermal stability with $T_{d5\%}$ in the range of 222-243 °C due to the formation of highly hyperbranched structures (*vide infra*).

In an attempt to elucidate the structure of the polymer formed, the polymerization mechanisms/pathways of **2H-HBO-HBO** were addressed. Furthermore, the polymerizations and possible reaction pathways of each constituting lactone ring, *i.e.* **2H-HBO** and **HBO**, in addition to **HBO-benzyl** (**HBO-Bn**)[35] (Scheme 6), were studied.

2H-HBO-HBO is a multifunctional monomer, thus its polymerization in the presence of a nucleophilic/basic catalyst can proceed according to two different pathways (Scheme 5):

- Pathway 1 (Scheme 5A) encompasses the deprotonation of one or both hydroxy group(s) of **2H-HBO-HBO** to form oxyanion(s);
- Pathway 2 (Scheme 5A) is related to the abstraction of the γ-proton to yield a carbanion.

It is also possible, in addition to the two previous basic activation pathways, that the initiation step is triggered by a nucleophilic attack of the base on the conjugated double bond. However, Chen *et al.* proved that the activation and initiation steps of the polymerization of **FO** and **MFO**s (Scheme 3) occurred mainly through basic activation.[28]

Table 2. Solvent-less homopolymerization of **HBO**-based monomers

Entry	Monomer	t (h)[a]	Catalyst[b]	Yield (%)[c]	*E* factor [d]	*Main SEC distribution*[e]		T_g[f] (°C)	$T_{d5\%}$[g] (°C)
						$M_{n(SEC)}$ (kg.mol^{-1}) {$Đ$}	$M_{n(SEC)}$ (kg.mol^{-1}) {$Đ$}		
13	**2H-HBO-HBO**	1	–	45	1.22	–	1.9 {1.2}	25	243
14	**2H-HBO-HBO**	1	Cs_2CO_3	98	0.03	101 {1.8} 809 {1.1}	1.3 {1.3}	60	229
15	**2H-HBO-HBO**	1	TBD	92	0.09	108 {1.8} 855 {1.1}	1.7 {1.5}	82	222
16	**2H-HBO-HBO**	1	$Ti(O^iPr)_4$	37	1.74	–	1.2 {1.2}	27	244
17	**2H-HBO**	6	–	0	–	–	–	–	–
18	**2H-HBO**	6	Cs_2CO_3	0	–	–	–	–	–
19	**2H-HBO**	6	TBD	0	–	–	–	–	–
20	**HBO**	96	–	49	1.04	14.9 {1.6}	0.8 {1.5}	45	141
21	**HBO**	3	Cs_2CO_3	99	0.03	48.0 {2.5} 853 {1.1}	2.5 {1.5}	86	170
22	**HBO**	3	TBD	95	0.07	44.3 {2.7} 865 {1.0}	1.8 {1.5}	80	161
23	**HBO-Bn**	6	–	0		–	–	–	–
24	**HBO-Bn**	6	Cs_2CO_3	85[h]	0.2	–	0.8 {1.1}	6	206

[a] Time required for viscosity to stop the stirring; except for entries 17, 20-22. [b] 1 mol% of the catalyst with respect to monomer used. [c] Isolated yield of the crude product, yield = (isolated mass/theoretical mass) *x* 100. [d] *E* factor = [m(monomer) + m(catalyst) - m(polymer)]/m(polymer); knowing that entries 13-24 are solvent-less reactions [e] Determined in DMF (10 mM LiBr) at 50 °C. [f] Glass transition temperature determined by DSC, temperature ramp 10 °C/min. [g] TGA degradation temperature at which 5% ($T_{d5\%}$) mass loss was observed under nitrogen. [h] No polymers formation was observed, and the reported yield is the conversion of the trimer formed, T(**HBO-Bn**), calculated from ^{1}H NMR.

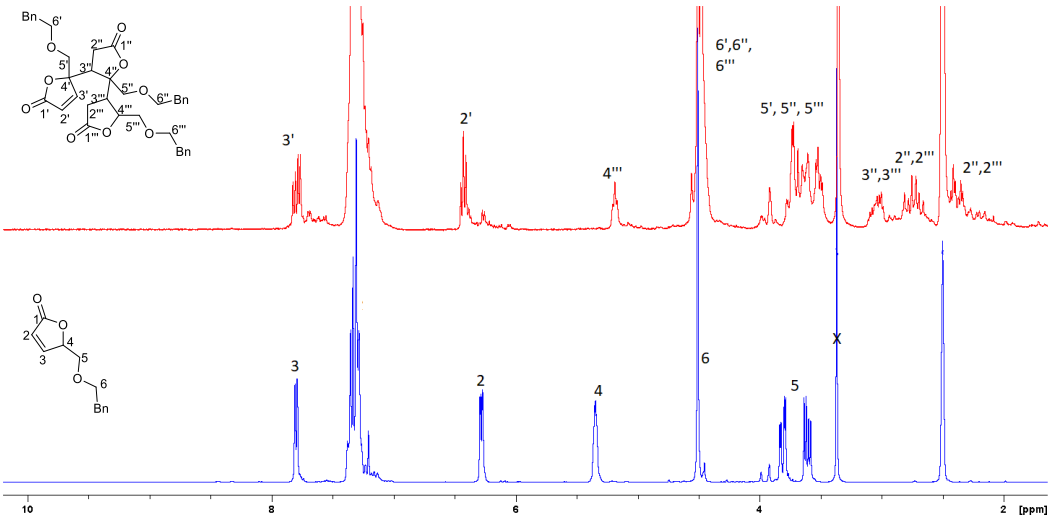
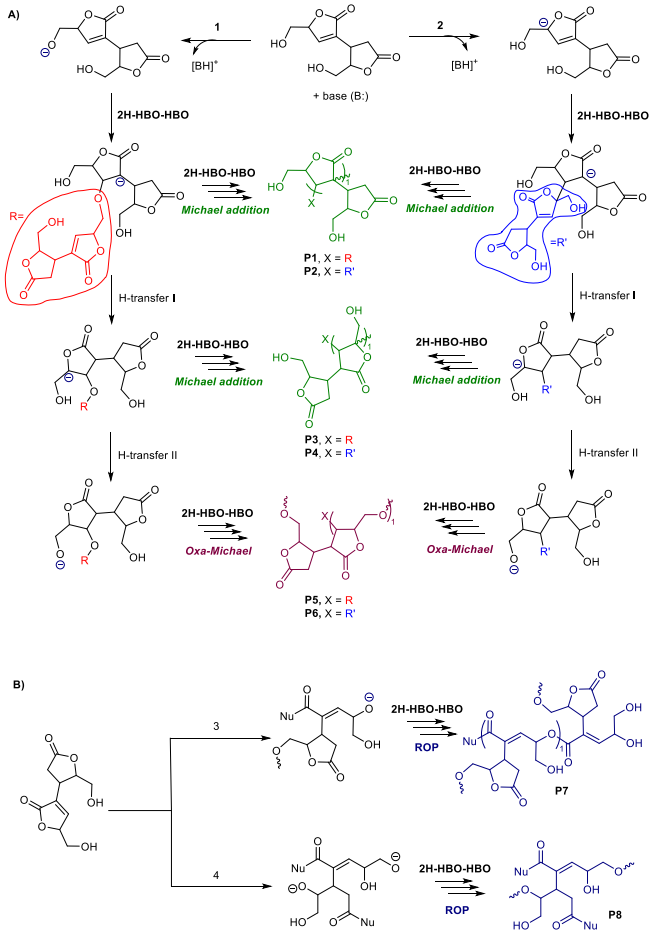


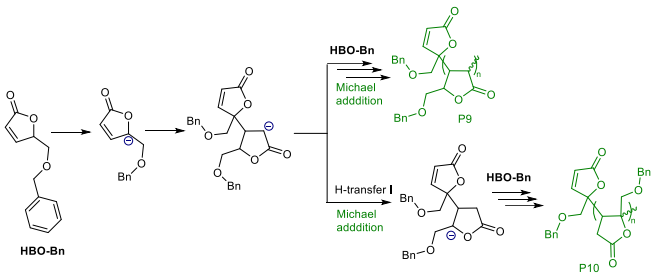
Figure 2. Overlay of ^{1}H NMR (DMSO-d_6) spectra of **HBO-Bn** (below, blue) and T(**HBO-Bn**) (above, red, entry 24, Table 2)



Scheme 5. Proposed mechanistic pathways involved in the base-promoted polymerization of **2H-HBO-HBO**

In pathways 1 and 2, the initiating and propagating species could only involve oxyanions *via* oxa-Michael addition/proton transfer alternating sequences to form poly(ether lactone) (P5 and P6). On the other hand, Michael addition to another **2H-HBO-HBO** molecule can also occur through the nucleophilic carbanion, to produce rigid vinyl polymer structures (P1-P4) via VAP.

Considering the steric hindrance of the propagating carbanions, P1-P4 are less likely to occur, although they can potentially exist as very short oligomers (trimer). This was inferred by looking at the polymerization experiments of the hydroxy-deprived **HBO-Bn** (entries 23 and 24, Table 2). Noticeably, in this case, there is only one possible proton abstraction in **HBO-Bn** at the γ-position leading finally to either P9 or P10 (Scheme 6).



Scheme 6. Proposed mechanism for the base-promoted **HBO-Bn** polymerization.

When **HBO-Bn** was heated in the absence of a catalyst (entry 23, Table 2), no reaction was observed. However, as soon as a catalyst comes into play (*e.g.* Cs_2CO_3, entry 24, Table 2), a new trimer, T(**HBO-Bn**) formed through Michael addition as evident by the ^{1}H-NMR spectrum of the reaction mixture (Figure 2). The two newly formed saturated rings can be monitored by the presence of H2'', H3'', H2''' and H3''' in the region of 3.03-2.33 ppm. The formation of T(**HBO-Bn**) was probably due to Michael addition of the γ-carbanion (generated by proton transfer) rather than the α-carbanion. This can be verified by the integration of γ-proton which is found close to 1 (Figure 2). The SEC analysis showed the formation of a new molecule of 0.8 kg.mol^{-1} (*Đ* = 1.1).

The trimer showed a soft structure with elastic and easily deformable texture at room temperature (Figure S1, SI) due to the low T_g (6 °C). In addition, a remarkable thermostability with $T_{d5\%}$ = 220 °C was measured.

Overall, the polymerization attempts of **HBO-Bn** demonstrated that a free hydroxy group is indeed necessary for the polymerization to proceed, mainly through an oxo-Michael addition mechanism. Nonetheless, during the **2H-HBO-HBO** polymerization, we cannot exclude the formation of some new trimeric molecules (or even slightly bigger) through Michael addition.

Besides, one or both 5-membered cyclic lactone(s) of **2H-HBO-HBO** can be ring-opened to form polyester main-chain structures *via* anionic ring-opening polymerization (pathways 3 and 4, P7 and P8, Scheme 5B). To check the potentiality of P7 and P8 to form, we investigated the polymerization ability of each constituting lactone (*i.e*. **2H-HBO** and **HBO**) under the same conditions.

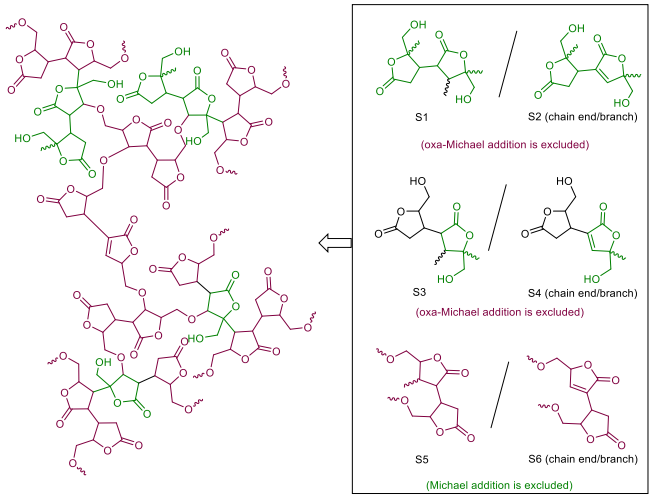
All trials to polymerize **2H-HBO** at 120 °C using Cs_2CO_3 or TBD failed (Figure S11, SI). These results highlight the necessity of having an endocyclic reactive C=C - as in the case of **HBO** (*vide infra*) - for the polymerization to occur. Furthermore, in accordance with the previously investigated polymerization of **FO**, **3-MFO**, **5-MFO** and **3-HMFO**,[28] no evidence of ROP process could be observed in the case of **2H-HBO-HBO**, and **HBO** (*vide infra*).

A series of 1D and 2D NMR experiments were also performed to better understand the complex hyperbranched/crosslinked structures that originated from the polymerization of **2H-HBO-HBO**. Unfortunately, no valuable information could be collected by the 2D NMR. Considering the 1D NMR spectra, the first most prominent peaks are those related to the endocyclic C=C at 7.55-7.40 ppm (^{1}H NMR) and 150.8-149.9 and 135.3-132.7 ppm (^{13}C NMR) (Figure S9, SI). Indeed, the fact that the double bond remained intact during the polymerization was quite surprising. However, Chen *et al*. reported the same behavior in the case of base-activated polymerization of hydroxy-containing **3-HMFO**[28] and **β-HMBL**[28,29] monomers. This was justified by proton transfer processes that keep the C=C intact. Furthermore, the oxo-Michael addition product can undergo dehydration to give back the C=C.[29] The multiplicity of the peaks observed in both cases is due to “at least” six different substructural units (S1-S6: repetitive units, chain ends and branches, Scheme 7) that could be present in the polymer structure. Besides, dehydration can also occur within the polymer backbone leading to shorter unsaturated structures.[29] Such shorter oligomers were identified by SEC analysis (*vide supra*).

Due to the presence of different structural units (S1-S6, Scheme 7), several carbonyl groups signals are present in the 176.0-170.6 ppm region. The formation of quaternary carbons resulted from the Michael addition of the carbanion at γ-position (green colored lactones of S1-S4, Scheme 7) can be noticed at 96.0-95.9 ppm. The appearance of carbon signals at 103.0-99.9 ppm was ascribed to the double bond migration to the saturated ring of **2H-HBO-HBO**. The presence of polyether linkage, due to the oxa-Michael addition of the deprotonated hydroxy groups (S5 and S6), was confirmed in i) ^{1}H NMR through the formation of new signals in the region of 3.6-3.1 ppm and disappearance of OH peak at 4.7 ppm, and ii) ^{13}C NMR by the appearance of new peaks at 72.1-68.9 ppm.

Finally, ^{13}C NMR analysis showed the indubitable formation of new saturated lactone units at 37.4-32.6 ppm due to the Michael addition on the endocyclic C=C.

In consideration of all the above-discussed observations, we concluded that the poly(**2H-HBO-HBO**) structure incorporates not only vinyl and ether linkages, but also **2H-HBO** and **HBO** rings leading to a complex hyperbranched/crosslinked copolymeric structure of poly(vinyl-ether lactone).



Scheme 7. Possible hyperbranched structure of poly(**2H-HBO-HBO**) and the corresponding possible repetitive units/chains ends/branches that can exist

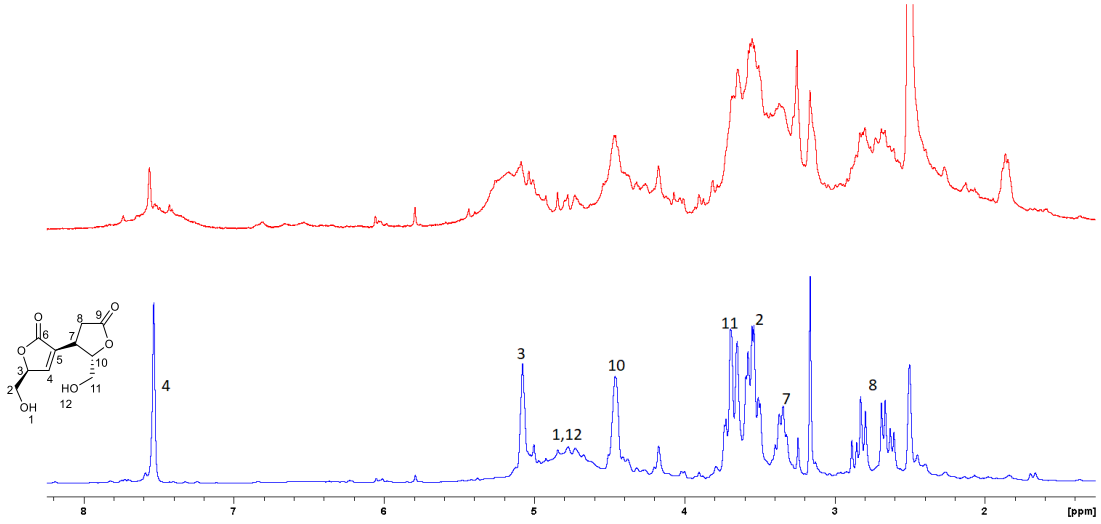


Figure 3. Overlay of ^{1}H NMR (DMSO-d_6) spectra of **2H-HBO-HBO** (below, blue) and the polymer produced by TBD (above, red, entry 15)

Polymerization of HBO

The polymerization of the monocyclic and less sterically hindered **HBO** was then tested in the presence of Cs_2CO_3, (entry 21, Table 2) or employing organo-catalyst TBD (entry 22, Table 2). Both experiments led to the quantitative formation of polymers in 3 h (*E* factor = 0.03 and 0.07, respectively). However, when the reaction was performed without any catalyst (entry 20, Table 2), 96 h were necessary to achieve a good conversion (49%, *E* factor = 1.04).

Before describing the structural details and mechanistic pathways leading to the polymer from this highly valuable monomer, it is worth mentioning its behavior in water. Interestingly, the texture of poly(**HBO**) was completely altered when stirred in water at room temperature for few hours (duration depends on the quantity). The poly(**HBO**) directly recovered from the polymerization showed a very rigid and tough texture which made it difficult to be ground manually. However, as soon as the water was added, the outer layers of this dark orange polymer material turned gradually into a fine and fluffy yellow powder. This can be due to the breakage of physical interactions (*e.g.* hydrogen bonds) upon the addition of water. Noticeably, there was no weight loss and no evident change in T_g and $M_{n(SEC)}$ for the water-treated polymer.

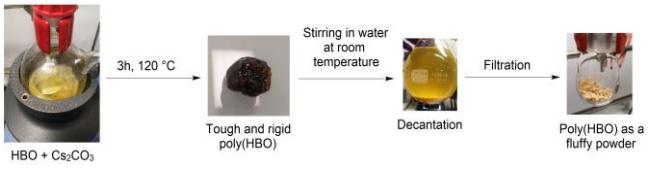


Figure 4. Polymerization of **HBO** and transformation of poly(**HBO**) texture from rigid dark orange solid to yellow fluffy powder

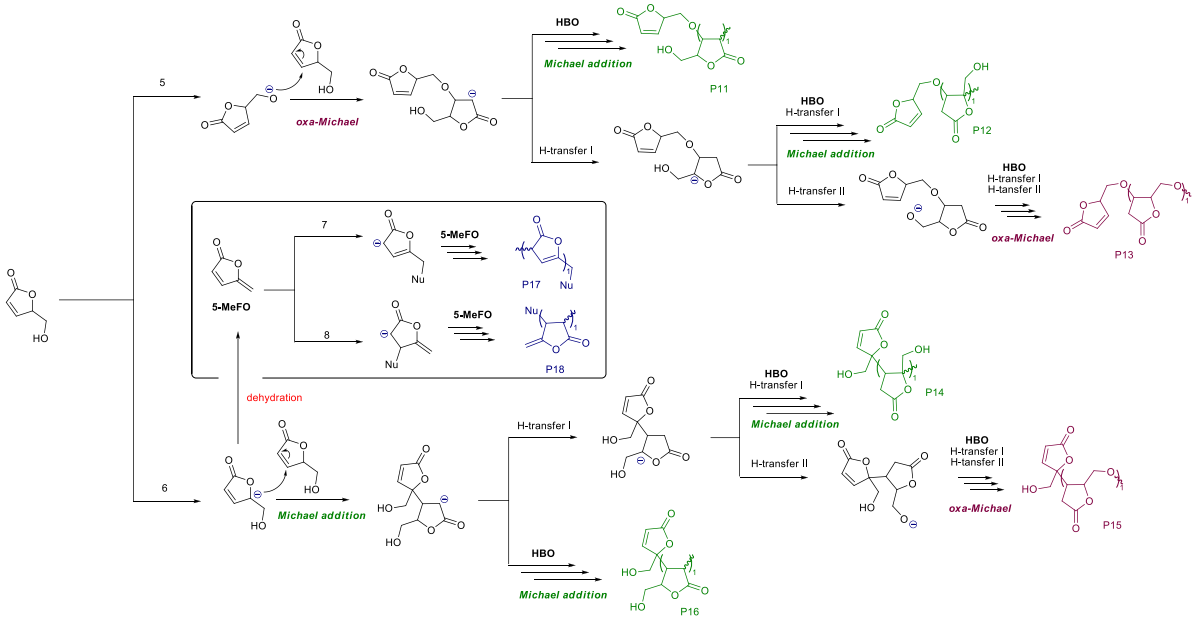
As in the case of **2H-HBO-HBO**, SEC analyses show a multimodal profile with three main distributions. All our trials to remove the short oligomers through polymer fractionation/precipitation were unsuccessful. For example, DMF was used to solubilize the polymers and different non-solvents, including methanol, ethanol and THF, were adopted to isolate only the long-chain polymers. Nonetheless, this led also to the precipitation of the short-chain oligomers as proven by SEC. The values of T_g lie in the range of 45-86 °C depending on the catalyst presence and the $M_{n(SEC)}$ of the polymer. For instance, in the absence of catalyst, the $M_{n(SEC)}$ is equal to 14.9 kg.mol^{-1} which corresponds to a T_g of 45 °C (entry 20, Table 2). However, when Cs_2CO_3 or TBD was employed (entries 21 and 22, Table 2), an increase of T_g to 86 °C and 80 °C, respectively, was observed due to the formation of longer polymer chains with more hyperbranched structure ($M_{n(SEC)}$ = 44.3-48.0 kg.mol^{-1}). Interestingly, a population of polymers having 853-865 kg.mol^{-1} appeared also in the latter two cases. Regardless of the $M_{n(SEC)}$ value, the polymers showed good thermal stability with $T_{d5\%}$ in the range of 141-170 °C.

Considering the **HBO** trifunctional structure, its polymerization pathways using a nucleophilic/basic catalyst were expected to be rather complicated. Based on the aforementioned mechanisms of the polymerization of **2H-HBO-HBO** and trimerization of **HBO-Bn**, the following main two observations can be made: *i*) although it cannot be completely excluded, ROP of **HBO** would be quite difficult due to the low ring strain, *ii*) hydroxy group is crucial for the propagation step to proceed. According to these considerations, Scheme 8 depicts some of the multiple competing pathways that can occur through Michael addition, oxa-Michael addition and proton transfer processes.

The main difference between **HBO** and **2H-HBO-HBO** is that the former is less sterically hindered (no substituent at α-position) which may favor more Michael addition reactions using the α-carbanion produced from pathways 5 and 6. Nevertheless, it seems from the polymerization attempts of **HBO-Bn** that long polymers were less likely to occur on the α-position, and that hydroxy-mediated proton transfer was necessary to increase the polymer molecular weight through oxa-Michael addition.

Once again, ^{1}H NMR (Figure 5) and ^{13}C NMR (Figure S12, SI) show that some endocyclic double bonds are retained in the polymer structure as previously discussed. However, in the case

of poly(**HBO**), broader alkene signals are accompanied with several peaks at 7.8-4.4 ppm and 6.4-6.2 ppm in the ^{1}H NMR spectrum and at 160.9-154.6 ppm 124.1-119.9 ppm in the ^{13}C NMR spectrum. Besides, more than 20 carbonyl signals are visible in ^{13}C NMR in the region of 177.6-170.9 ppm indicating the presence of at least 20 structural units or/and a mixture of connected polymers to form a highly hyperbranched poly(vinyl-ether lactone).



Scheme 8. Possible mechanistic scenarios of the polymerization of **HBO**

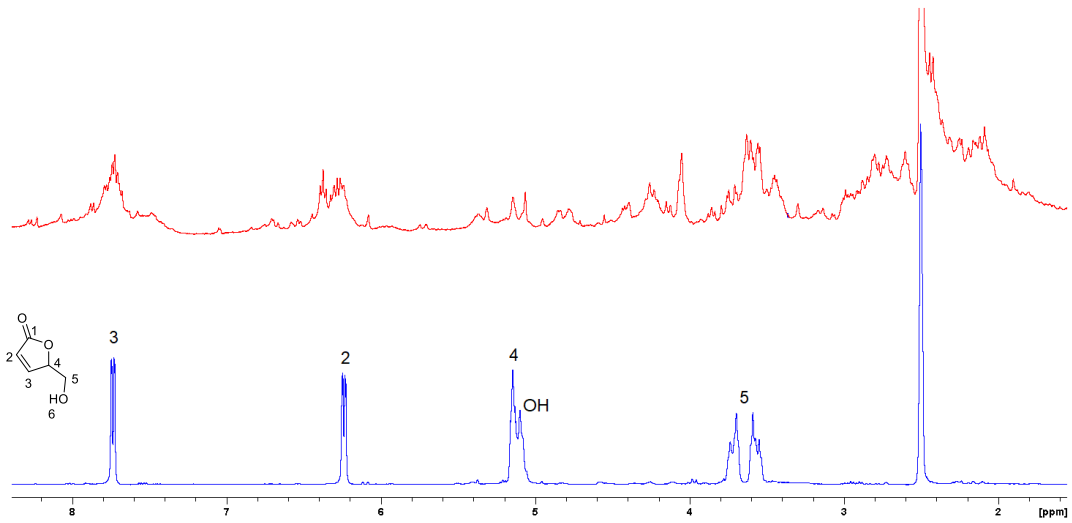


Figure 5. Overlay of ^{1}H NMR (DMSO-d_6) spectra of **HBO** (below, blue) and the polymer produced by TBD (above, red, entry 22)

Some proposed polymeric structures are shown in Figure S12 (P11-P16, SI) along with the estimated chemical shifts attribution of the corresponding protons and carbons. Interestingly, the formation of saturated lactone structures due to the Michael and oxo-Michael represented in both pathways, 5 and 6, is obvious by ^{1}H NMR (3.0-2.6 ppm and 2.4-2.0 ppm) and ^{13}C NMR (38.0-20.0 ppm). On the other hand, the dehydration of **HBO** under basic conditions can also occur to yield 5-methylene-2(5H)-furanone (**5-MeFO**) (pathways 7 and 8, Scheme 8). The presence of traces of **5-MeFO** can be detected by ^{1}H NMR and ^{13}C NMR (Figure S12, SI). Nonetheless, our attempts to polymerize **5-MeFO** - under similar conditions - all failed due to the high instability of this molecule, especially in basic conditions. Thus, no clear evidence of the formation of P17 or P18 was observed.

Conclusion

In this work, we investigated for the first time the homopolymerization of the newly reported bicyclic diol, **2H-HBO-HBO**, obtained through a sustainable two-step process from **LGO** (dimerization followed by Baeyer-Villiger oxidation). Interestingly, heating **2H-HBO-HBO** at 120 °C in the presence of a basic metal catalyst (Cs_2CO_3) or organo-catalyst (TBD) led to a quantitative monomer conversion in < 1 h into a new 100% renewable hyperbranched polymer. Such polymer formation was proven to take place so fast which prevents any polycondensation between the hydroxy groups of **2H-HBO-HBO** and the di(methylcarbonate isosorbide (**DCI**). Despite the different polycondensation procedures attempted, our trials to prepare polycarbonate were unsuccessful. Nonetheless, the T_g of poly(**2H-HBO-HBO**) could be readily tuned by using **DCI**, where a remarkable decrease from 82 °C to -19 °C upon its addition was measured.

We also investigated **HBO** as a promising monomer to directly produce (without any modification) biorenewable functional polymer materials with *E* factor as less as 0.03 kg of waste/kg of poly(**HBO**). Although the polymer structure is very complex to elucidate, due to the different possible mechanism pathways that can simultaneously occur in basic condition, poly(**HBO**) is of great interest as: *i*) the constituting monomer is readily accessible at the multikilo-scale from the commercially available **LGO** (ton/year scale), *ii*) the catalyst, *i.e.* Cs_2CO_3, is commercial and of low cost (~ 0.6 €/g), *iii*) the polymerization process is quite easy and is convenient to be adopted at an industrial scale. Very interestingly, we found out that poly(**HBO**) can be transformed in water from a very rigid polymer to a fluffy yellowish powder. SEC and DSC analyses showed that such a change in texture had no influence on the $M_{n(SEC)}$ and T_g of the polymer after treatment.

To understand the polymerization mechanism, we attempted the homopolymerization of **2H-HBO** and **HBO-Bn** under similar conditions. The **2H-HBO** trials showed that the endocyclic double bond is crucial for the polymerization to occur. Furthermore, **HBO-Bn** polymerization experiments showed that a free hydroxy group is necessary for the propagation to proceed. Interestingly, in the case of **HBO-Bn**, a new trimer T(**HBO-Bn**) was obtained when **HBO-Bn** was heated at 120°C in the presence of Cs_2CO_3.

Finally, by careful interpretation of NMR spectra, and putting all experimental pieces together, we can conclude that poly(**HBO**), as well as poly(**2H-HBO-HBO**), have probably a poly(vinyl-ether lactone) complex copolymeric structure. Such hyperbranched/crosslinked materials could be obtained through Michael addition, oxa-Michael addition and proton transfer processes.

Experimental Section

Chemical and reagents. All manipulations with air-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, on a high-vacuum line. Levoglucosenone was graciously provided by Circa group. Potassium carbonate 99% (Acros), cesium carbonate 99.5% (Acros), hydrogen peroxide 30% (Fischer). Isosorbide, palladium on carbon (10%), aqueous hydrochloric acid (36% w/w), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (98%), benzyl 2,2,2-trichloroacetimidate (99%) and dimethyl carbonate (99%) were purchased from Sigma-Aldrich. HPLC grade solvents (dimethylformamide, ethyl acetate, methanol, dichloromethane and cyclohexane) were purchased from Thermofisher Scientific and used as received. Ultra-pure laboratory-grade water was obtained from MilliQ,18.2 megaOhms. TLC analyses were performed on an aluminum strip coated with Silica Gel 60 F254 from Merck, revealed under UV-light (254 nm) then in presence of potassium permanganate staining solution. All chemicals and reagents were used as received without purification.

Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy. ^{1}H NMR spectra were recorded on a Bruker Fourier 300 MHz (DMSO-d_6 residual signal at 2.5 ppm). ^{13}C NMR spectra were recorded at 75 MHz (DMSO-d_6 residual signal at 39.52 ppm).

Size exclusion chromatography (SEC) was performed at 50 °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 (5 µm MIXED-D 300 x 7.5 mm) using 10 mM Lithium Bromide in HPLC grade dimethylformamide as the mobile phase at a flow rate of 1.0 mL/min. Calibration was performed with poly(methyl methacrylate) standards from Agilent Technologies.

Thermogravimetric Analysis (TGA) was measured with a TGA Q500 (TA Instruments). Typically, ~2 mg of each sample was equilibrated at 50 °C for 30 min and was flushed with highly pure nitrogen gas. All the experiments were performed with a heating rate of 10 °C/min up to 600 °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) was performed with a DSC Q20 (TA Instruments). Typically, ~8 mg sample was placed in a sealed pan, flushed with highly pure nitrogen gas and passed through a heat-cool-heat cycle at 10 °C/min in a temperature range of -50 °C to 100 °C (or 170 °C when needed). Three heat/cool cycles were done for each sample where the last two cycles were dedicated to analyzing the heat flow of the sample after being cooled in controlled conditions. The T_g values recorded herein are those obtained from the third cycle.

Synthesis of monomers

*Baeyer-Villiger oxidation of **LGO** into **HBO**.* 1 kg of **LGO** (7.93 mol) was cooled down with an ice bath followed by dropwise addition of 0.81 L of 30% aq. H_2O_2 solution (9.78 M, 7.92 mol) under nitrogen over 3.5 hours. After completion of the addition, the reaction was warmed to 50 °C and stirred for an extra 20 hours. The presence of H_2O_2 was evaluated with peroxide strips and, if any, the residual H_2O_2 was quenched using sodium sulfite. The reaction mixture was then concentrated in vacuo and the residue was distilled of (150 °C/ 0.7-0.9 mbar) to provide **HBO** as a clear oil that readily crystallized (71% yield). All analytical data were in agreement with the ones reported in the literature.[5]

*Palladium-catalyzed hydrogenation of **HBO** into **2H-HBO**.* 250 mg of 10% Pd/C (10% w/w) was added to a solution of 1.4 g **HBO** (12.30 mmol) in 15 mL of ethyl acetate (0.80 M) at room temperature. The stirred suspension was degassed 3 times and placed under nitrogen. The suspension was then hydrogenated at room temperature until TLC showed complete consumption of starting material. The crude mixture was filtered over a pad of Celite® and the filtrate was concentrated to dryness to yield quantitatively pure **2H-HBO**. All analytical data were in agreement with the ones reported in the literature.[5]

*Synthesis of benzyl ether of **HBO** (**HBO-Bn**).* 0.84 g of **HBO** (7.38 mmol) was dissolved in 5 ml of CH_2Cl_2 and 3 mL of cyclohexane under N_2, then 1.35 mL of benzyl 2,2,2-trichloroacetimidate (8.05 mmol) and triflic acid (0.74 mmol in 1 mL CH_2Cl_2) were added. The reaction was left stirring for 4 h then the medium was diluted with 20 mL of CH_2Cl_2. The resulting

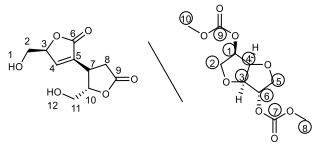
solution was washed with 3 x 20 mL of HCl (2 M), 20 mL of water then 20 mL of brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was then purified by flash chromatography using cyclohexane/AcOEt (1:1) to give **HBO-Bn** as a yellow oil (52%). All analytical data were in agreement with the ones reported in the literature.[35]

*Synthesis of **2H-HBO-HBO***. 7.77 g of **LGO** (61.50 mmol) was solubilized in 6.6 mL of methanol and 135 mg of K_2CO_3 (0.90 mmol) was added. The solution was stirred at room temperature until the precipitate hindered the stirring. The reaction was filtered to obtain **LGO**-Cyrene™ as an orange solid (99%) that could be engaged in the next step without further purification. To 4.5 g of **LGO**-Cyrene™ (19.74 mmol) was added 4.44 mL of 30% aq. H_2O_2 (43.50 mmol). The system was stirred at 45 °C until full consumption of the starting material. The medium was concentrated, then the crude product was purified by flash chromatography Acetate/Methanol (100/0 to 90/10) to give a colorless oil that was readily crystallized (60% yield). All analytical data were in agreement with the ones reported in the literature.[23]

*Synthesis of **DCI***. In a 250 mL double-necked bottom round flask equipped with a Dena-Stark trap and condenser, 5 g of isosorbide (34.21 mmol) was reacted with 90 mL of dimethyl carbonate (1.07 mol) in presence of 0.95 g of K_2CO_3 as a base (6.80 mmol), at 90 °C for 6 h. After cooling, the reaction crude was filtered and concentrated in vacuo to achieve **DCI** in quantitative yield. A pure sample of **DCI** was obtained *via* column chromatography using DCM/MeOH (99/4). All analytical data were in agreement with the ones reported in the literature.[36]

Polymerizations

*Polycondensation trials of **2H-HBO-HBO** and **DCI**.* Three procedures (I-III) were attempted by a two-step melt polycondensation method (Scheme 4). A typical experiment of procedure III (entry 7, Table 1) was performed as follows. Under N_2 atmosphere, 500 mg of **2H-HBO-HBO** (2.20 mmol), 522 mg of **DCI** (2.00 mol), and 7.1 mg of Cs_2CO_3 (1 mol% based on **2H-HBO-HBO**) were added into a round-bottom flask connected to a vacuum line, equipped with a condensate trap. The reaction mixture was heated from room temperature to 120 °C at a heating rate of about 32 °C/5 min and stirred continuously for 1 h. The temperature was then increased to 140 °C and maintained for 1 h to completely distill the methanol (if any) and unreacted monomers. The temperature was again increased by 20 °C to attain 160 °C and then only left stirring for 5 min. A high vacuum (10^{-3} bar) was then applied at 160 °C for 5 min (the time required for the viscosity to completely stop the stirring). The samples were used for characterization without purification.



^{1}H NMR (DMSO-d_6) δ (ppm): 7.55 (H4), 5.21 (H3), 5.02 (H①), 4.96 (H⑥), 4.79 (H④), 4.47 (H③), 4.43 (H10), 3.94 (H⑤), 3.80 (H②), 3.79 (H⑤'), 3.70 (H⑧ and H⑩), 3.59 (H11), 3.54 (H2), 3.38 (H7), 2.81 (H8), 2.67 (H8').

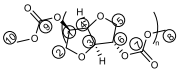
^{13}C NMR (DMSO-d_6) δ (ppm): 175.6 (C6), 171.8 (C9), 154.6 (C⑨), 154.3 (C⑦), 149.0 (C4), 85.3 (C③), 84.0-82.7 (C10 and C3), 80.7 (C④), 80.6 (C⑥), 76.7 (C①), 72.3 (C⑤), 70.3 (C②), 62.8 (C2), 61.7 (C11), 55.0 (C⑩), 54.9 (C⑧), 33.4 (C7), 32.7 (C8).

*Polycondensation trials of **2H-HBO-HBO** and DMC.* A typical experiment (entry 12, Table 1) was performed as follows. Under N_2 atmosphere, 500 mg of **2H-HBO-HBO** (2.20 mmol), 1.8 mL DMC (21.9 mmol), and 7.1 mg of Cs_2CO_3 (1 mol% based on **2H-HBO-HBO**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure (procedure III) as described in the previous paragraph for the polycondensation attempt of **2H-HBO-HBO** and **DCI**, except that DMC was used instead of **DCI**.

^{1}H NMR (DMSO-d_6) δ (ppm): 7.52 (H4), 5.16 (H3), 4.43 (H10), 3.63 (H11), 3.54 (H2), 3.38 (H7), 2.81 (H8), 2.68 (H8').

^{13}C NMR (DMSO-d_6) δ (ppm): 175.5 (C6), 171.9 (C9), 149.0 (C4), 83.8-82.7 (C10 and C3), 61.6 (C2 and C11), 33.4 (C7), 32.7 (C8).

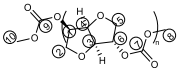
*Polycondensation trials of **DCI** and DMC.* A typical experiment (entry 10, Table 1) was performed as follows. Under N_2 atmosphere, 500 mg of **DCI** (1.90 mmol), 1.6 mL **LGO** (19.00 mmol), and 6.2 mg of Cs_2CO_3 (1 mol% based on **DCI**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure (procedure III) as described previously for the polycondensation attempt of **2H-HBO-HBO** and **DCI**.



^{1}H NMR (DMSO-d_6) δ (ppm): 5.04 (H①), 4.98 (H⑥), 4.83 (H④), 4.45 (H③), 3.97 (H⑤), 3.81 (H②), 3.75 (H⑤').

^{13}C NMR (DMSO-d_6) δ (ppm): 153.5, 153.2 and 152.9 ppm with intensity ratios of 1:2:1 (three C=O signals, *endo-endo*, *endo-exo*, *exo-endo*, and *exo-exo*), 85.2 (C③), 81.1 (C④), 80.8 (C⑥), 77.3, 76.9 and 76.7 (C①), 72.3 (C⑤), 70.4 (C②), 55.0 (C⑩), 54.9 (C⑧).

*Homopolymerization of **DCI**.* A typical experiment (entry 9, Table 1) was performed as follows. Under N_2 atmosphere, 500 mg of **DCI** (1.90 mmol) and 6.2 mg of Cs_2CO_3 (1 mol% based on **DCI**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure (procedure III) as described previously for the polycondensation attempt of **2H-HBO-HBO** and **DCI**.



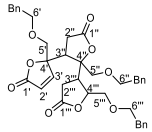
^{1}H NMR (DMSO-d_6) δ (ppm): 5.04 (H①), 4.98 (H⑥), 4.83 (H④), 4.45 (H③), 3.97 (H⑤), 3.81 (H②), 3.75 (H⑤').

^{13}C NMR (DMSO-d_6) δ (ppm): 153.5, 153.2 and 152.9 ppm with intensity ratios of 1:2:1 (three C=O signals, *endo-endo*, *endo-exo*, *exo-endo*, and *exo-exo*), 85.2 (C③), 81.1 (C④), 80.8 (C⑥), 77.3, 76.9 and 76.7 (C①), 72.3 (C⑤), 70.4 (C②), 55.0 (C⑩), 54.9 (C⑧).

*Homopolymerization of **HBO**.* A typical experiment (entry 21, Table 2) was performed as follows. Under N_2 atmosphere, 1.0 g of **HBO** (8.70 mmol) and 29.0 mg of Cs_2CO_3 (1 mol% based on **HBO**) were added into a round-bottom flask. The reaction mixture was heated from room temperature to 120 °C at a heating rate of about 32 °C/5 min. The temperature was then maintained at 120 °C and the reaction stirred continuously for 3 h until viscosity stopped the stirring. The samples were used for characterization without purification.

As a result of the very complex structure of poly(**HBO**), the interpretation of ^{1}H and ^{13}C NMR (DMSO-d_6) is provided in Figure S12 in the Supporting Information.

*Trimerization of **HBO-Bn**.* A typical experiment (entry 24, Table 2) was performed as follows. Under N_2 atmosphere, 0.50 g of **HBO-Bn** (2.40 mmol) and 8 mg of Cs_2CO_3 (1 mol% based on **HBO-Bn**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure as described previously for the homopolymerization of **HBO** (except that trimerization duration was 6h).



^{1}H NMR (DMSO-d_6) δ (ppm): 7.78 (1H, H3'), 7.30 (15H, Bn), 6.42 (1H, H2'), 5.18 (1H, H4'''), 7.78 (1H, H3'), 4.48 (6H, H6', H6'', H6'''), 3.72 (2H, H5'), 3.65 (2H, H5''), 3.50 (2H, H5'''), 3.02 (2H, H3'' and H3'''), 2.75-2.33 (4H, H2'' and H2''').

^{13}C NMR (DMSO-d_6) δ (ppm): 175.4 (C1'), 175.3 (C1''), 171.6 (C1'''), 156.4-156.0 (C3'), 137.9-137.6 (OCH2C_{Bn}), 128.3-126.4 (Bn), 123.6 (C2'), 90.3 (C4''), 89.9 (C4'), 78.1 (C4'''), 72.7 (C6'), 72.4 (C6''), 72.3 (C6'''), 71.2 (5'), 70.9 (5''), 70.6 (5'''), 29.5 (C3''), 29.4 (3''').

*Homopolymerization trial of **2H-HBO**.* A typical experiment (entry 18, Table 2) was performed as follows. Under N_2 atmosphere, 0.50 g of **2H-HBO** (4.30 mmol) and 14 mg of Cs_2CO_3 (1 mol% based on **2H-HBO**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure as described previously for the homopolymerization of **HBO**. The reaction was left to stir for 6h. ^{1}H and ^{13}C NMR of an aliquot of the obtained solution were performed. No polymer was recovered.

*Homopolymerization of **2H-HBO-HBO**.* A typical experiment (entry 14, Table 2) was performed as follows. Under N_2 atmosphere, 0.50 g of **2H-HBO-HBO** (2.20 mmol) and 7.1 mg of Cs_2CO_3 (1 mol% based on **2H-HBO-HBO**) were added into a round-bottom flask. The reaction has then proceeded following a similar procedure as described previously for the homopolymerization of **HBO** (except that only 1 h was needed for the viscosity to stop the stirring).

As a result of the very complex structure of poly(**2H-HBO-HBO**), the interpretation of ^{1}H and ^{13}C NMR (DMSO-d_6) is provided in Figure S9 in the Supporting Information.

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Conflicts of interest

There are no conflicts to declare.

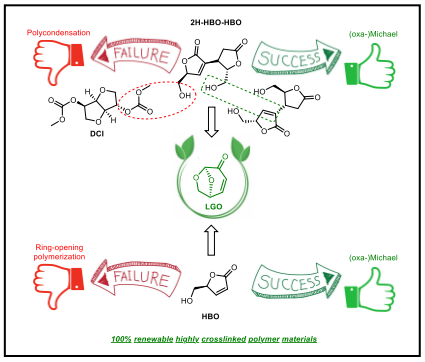
Author Contributions

S.F., F.Aricò and F.Allais conceived the research. S.F. and F.Allais led and managed the research. S.F. performed the polymerizations, studied the mechanisms and wrote the article. A.L.F. performed the synthesis of HBO-Bn and 2H-HBO. L.M. performed the synthesis of 2H-HBO-HBO. M.A. performed the synthesis of DCI. A.A.M.P. performed the synthesis of HBO and 5-MeFO. A.G. observed the formation of yellowish powder of poly(HBO) upon water treatment. A.L.F., L.M., M.A., A.G., F.Aricò and F.Allais reviewed the results. F.Aricò and F.Allais reviewed and approved the article. All authors have approved the final version of the manuscript.

Keywords: Levoglucosenone • HBO • green polymerization • renewable polymers • hyperbranched materials

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Entry for the Table of Contents



The environmentally benign polymerization of **HBO** and **2H-HBO-HBO**, which are readily accessible from cellulose byproducts, leads to the formation of 100% renewable poly(vinyl-ether lactone) copolymer structures. The easiness of preparation of these **HBO**-based polymers, their low-cost production process, as well as their interesting and tunable thermal properties, make them a suitable bio-choice to substitute petrochemical-derived commodity polymers.