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Multicatalysis from renewable resources: a direct route to furan-based polyesters†

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Here we present a multicatalytic route to produce 2,5-bis(hydroxymethyl)furan and the corresponding (co)polymers from stable 2,5-furandicarboxylic acid. This approach combines the use of several commercial catalysts and in particular allows to quantitatively obtain two key furan intermediates, not contaminated by humins.

Renewable materials have recently gained much attention as an alternative to petroleum-based polymers.^{1–8} However, the main challenge is still to design efficient and selective transformations of abundant, renewable, low-cost raw materials into innovative polymeric products.^{9,10} Among the new bio-based polymers that have emerged over the past decade, furanic materials are of particular interest.^{11–15} The availability of monomer feedstocks from renewable resources has given these polymers an increasing prominence in the market. As such, 2-hydroxymethyl-5-furfuraldehyde, also known as 5-(hydroxymethyl)furfural (HMF), which is obtained by dehydrating hexoses from biomass, has been viewed as having great potential, as it can be used to synthesize many valuable products. HMF can be converted to various 2,5-disubstituted furans, including 2,5-bis(hydroxymethyl)furan (BHMF), which has a rigid symmetric structure, allowing to obtain polymers with higher glass transition temperatures and better mechanical properties.¹⁶ Surprisingly, the potential of BHMF is largely underestimated, although it can be used as a monomer for the synthesis of polyesters, polycarbonates or polyurethanes. BHMF can be obtained by a variety of synthetic routes, but selective hydrogenation of HMF is the most widely employed.^{17,18} However, HMF from renewable resources is often contaminated with highly coloured polymeric impurities called humins.¹⁹ Since the purity and especially the colour of

the monomer are important to obtain high quality colourless polymers (required for example by the packaging industry), the removal of humins from HMF production processes remains a problem. DuPont and ADM have recently developed effective processes to produce stable 2,5-furandicarboxylic acid (FDCA), that is virtually free of humins, from contaminated HMF.²⁰ Therefore, there is an interest in investigating the hydrogenation of 2,5-furandicarboxylic acid esters in order to produce BHMF that would be of high quality for polymer synthesis. This would complement the scope of reported furan-based polyesters, in particular those based on FDCA and on various aliphatic diols.¹¹

To synthesize BHMF-derived polyesters, we chose to use one-pot catalytic transformations, which have significant advantages over conventional multi-step syntheses, such as time and cost savings, reduced waste and energy consumption.^{21–23} These synthetic schemes, which proceed through two or more consecutive catalytic steps, can serve as a versatile method in polymerization reactions.^{24–28} However, the different catalytic systems used must be compatible with each other but also with the solvent, the substrate and the by-products of the reaction in order to achieve high activity and selectivity.^{29–32} Multicatalytic synthesis is therefore not only a useful methodology to follow for the production of (macro)molecules, but also a promising green approach for polymer synthesis.³³ In this regard, oligomeric furan-based diols are also interesting synthetic targets due to the reactivity of the hydroxyl end groups with different functional groups.³⁴ However, oligomeric diols are mainly synthesized industrially by depolymerization routes that are carried out under severe/drastring conditions (*e.g.*, high temperature and pressure).³⁵ Since furans are temperature sensitive, there is a real interest in developing alternative synthetic routes for the production of oligomeric furan diols. A multicatalytic approach can overcome these pitfalls with a combination of catalysts performing the desired reactions.

Herein we present a practical route to biobased furan-incorporating polyesters by way of a multicatalytic reaction using simple commercial catalysts. This process provides direct

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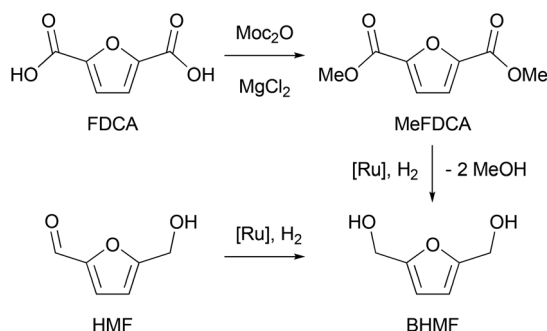
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access to BHMF and the corresponding copolymers in high yields.

Monomer formation sequence

To carry out a one-pot procedure, it is necessary to have a monomer synthesis process that can produce BHMF with a high yield and selectivity. We chose to start from FDCA, first forming its dimethyl ester (MeFDCA), then reducing it by hydrogenation, which avoids salt formation. As the first step, we thus studied the esterification of FDCA using dimethyl dicarbonate (Moc₂O) as a coupling agent (Scheme 1). On the basis of the mechanism proposed by Bartoli,³⁶ we assumed that the presence of a Lewis acid (MgCl₂) can cause a double addition of FDCA to the dicarbonate, affording a carboxylic anhydride and an alcohol. Then, the resulting symmetrical anhydride can react with the *in situ* released methanol from Moc₂O. Thus, reaction conditions were identified, leading to complete, selective conversion of FDCA into MeFDCA in THF (Table S2†). The reaction also proceeds efficiently in the more environmentally friendly MeTHF,³⁷ though with longer reaction times due to FDCA solubility issues.

Then, we investigated the next step of our multicatalytic sequence: the hydrogenation of 2,5-furandicarboxylic acid dimethyl ester (MeFDCA) in the presence of a molecular catalyst. Production of BHMF from HMF is a proven route with both homogeneous and heterogeneous catalytic processes.¹⁷ However, the above-mentioned issues with HMF intrinsic stability and storage motivate the search for alternative pathways. Along these lines, FDCA, and its ester derivatives could be efficiently harnessed as starting materials for polyester synthesis, especially when bearing in mind their use in implemented commercial solutions (Dupont-ADM process). Significant progress with the reduction of esters using hydrogenation³⁸ motivated us to probe this route when looking for efficient entry into the production of BHMF. Interestingly, the dimethylester MeFDCA has been very scarcely used as a substrate. More specifically, the single report was from Beller and coworkers, who reported unselective reduction, with a manganese pincer catalyst.³⁹ In spite of extended reaction time and use of a robust catalyst, the conversion of the aromatic diester into a mixture of the targeted diol and the monoreduced



Scheme 1 Catalytic access to BHMF from FDCA or HMF.

derivative evidenced that reduction of such a substrate may prove challenging. In the view of the breakthroughs in the field stemming from use of non-innocent pincer ligands, we probed two archetypical commercially available systems, namely Ru-PNP from Takasago⁴⁰ and Ru-SNS (Gusev catalyst)⁴¹ given their unique robustness and versatility, as well as their recognized potential in the hydrogenation of esters (Fig. 1).⁴² The latter is most particularly interesting when aiming at developing large scale processes, as it relies on a phosphine-free pincer ligand scaffold. Such an air-stable compound is thus easier and cheaper to produce and handle compared to phosphine-derived systems.

Representative results are summarized on Table 1. Under moderately demanding conditions (100 °C, 50 bar H₂) and in the presence of excess alkoxide, full conversion of 100 equivalents of diester is achieved within 2 hours in toluene. In the case of the PNP systems, the selectivity towards diol remains moderate, with marginal influence from either phosphine substituent (Ph vs. *i*Pr) or pre-catalyst coordination sphere (BH₄ vs. Cl) (Table 1, entries 1–3). The Gusev catalyst displayed superior performances, which could even be improved by raising H₂ pressure up to 80 bar (Table 1, entries 4 and 5). In the search for a less harmful solvent,³⁷ we probed anisole and 2-methyltetrahydrofuran (MeTHF) as solvent for the hydrogenation step (Table 1, entries 6 and 7). Rewardingly, use of MeTHF resulted in improved selectivity, as full conversion and quasi-total selectivity were achieved under a 50 bar H₂ pressure. Lowering the reaction temperature does only marginally impact selectivity, contrary to use of a shorter reaction time (Table 1, entries

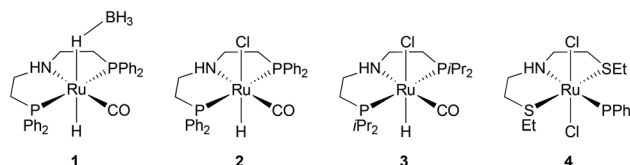


Fig. 1 Ester hydrogenation precatalysts used for this study.

Table 1 Ru-Catalysed hydrogenation of MeFDCA^a

Entry	[Ru]	Temperature (°C)	P(H ₂) (bar)	Time (h)	Solvent	Sel. ^b (%)
1 ^c	1	100	50	2	PhMe	42
2	2	100	50	2	PhMe	54
3	3	100	50	2	PhMe	39
4	4	100	50	2	PhMe	83
5	4	100	80	2	PhMe	96
6	4	100	50	2	PhOMe	80
7	4	100	50	2	MeTHF	99
8	4	80	50	2	MeTHF	96
9	4	80	50	1	MeTHF	88
10 ^d	4	100	50	2	MeTHF	99

^a Unless otherwise noted, the reaction was carried out on MeFDCA (0.81 mmol, 100 eq.) with catalyst (1 eq.) and KO^tBu (10 eq.) in solvent (2.5 mL) in a 25 mL Parr reactor. Conversion of MeFDCA, determined by ¹H NMR, is quantitative for each entry. ^b Selectivity towards BHMF, determined by ¹H NMR. ^c No base additive. ^d 5 mol% KO^tBu.

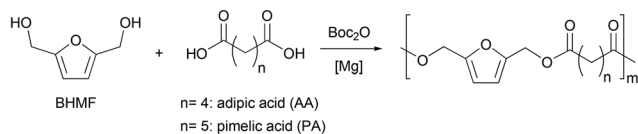
8 and 9). Finally, use of a lesser amount of alkoxide base (5% vs. 10%) resulted in comparable results from our best conditions (entry 10 vs. entry 7). The effectiveness of the bench-top stable SNS system in achieving full and selective conversion of MeFDCA into BHMF demonstrates its applicative potential, as previously underlined.⁴³ Under these conditions, no reduction of the aromatic furanic system was observed.⁴⁴ Thus, using our multicatalytic methodology, the combination of MgCl₂ and Gusev's catalyst provides BHMF from 2,5-furandicarboxylic acid with excellent selectivity. As a side note, we checked that HMF can also be reduced into BHMF with full conversion and selectivity using identical reaction conditions than with MeFDCA (as in entry 10 from Table 1).

Polymer formation step

With an efficient and quantitative synthesis of BHMF in hand, we then explored the step-growth polymerisation of the resulting mixture using a dicarboxylic acid as a comonomer. Industrially, polyesters are mainly produced by reacting a diester (*i.e.*, an activated acid function) with a diol. This reaction in equilibrium requires the energy-intensive use of high temperatures, which favors certain secondary reactions. In particular, etherification reactions can take place, especially in the case of BHMF, where the OH groups are very reactive, and can dehydrate to form BHMF ethers.¹⁶ In order to conduct our polymerization under mild conditions, we therefore investigated the use of di-*tert*-butyl dicarbonate (Boc₂O) as a coupling agent for the reaction of BHMF with different dicarboxylic acids (Scheme 2). Indeed, as already observed in the first step of the sequence, the reaction of carboxylic acids in the presence of dialkyl dicarbonates and a Lewis acid catalyst allows the formation of anhydrides.^{45–47} These intermediates can

then react with the *in situ* released methanol in the case of Moc₂O or with an alcohol more nucleophilic than *t*BuOH that is formed when using Boc₂O.⁴⁸

To evaluate the feasibility of the overall process, we conducted preliminary experiments with the magnesium catalyst able to perform the first step with a [catalyst]/[BHMF] ratio of 1:100 (Table 2, entry 1). We first tested the copolymerization of BHMF with adipic acid. The choice of adipic acid is justified by the fact that copolymers formed from this diacid should have a higher degradability than other furan derivatives, as shown by the Bikiaris group for adipate-based copolymers.⁴⁹ By reacting one equivalent of adipic acid and BHMF with di-*tert*-butyl dicarbonate and a suitable catalyst, it is indeed possible to obtain quantitatively the corresponding polymer. More precisely, the mild Lewis acid MgCl₂ selectively catalyses the formation of the polyester within 115 hours at 30 °C (Table 2, entry 1). As expected, the reactivity of the catalytic system is improved by increasing the reaction temperature to 60 °C which allows to reach a complete conversion in 20 h (Table 2, entry 2). We then thought that the poor solubility of MgCl₂ made it difficult to control the polymerization properly. Therefore, we decided to investigate the reactivity of a well-defined magnesium chloride derivative, namely the sterically demanding amido (TMP)MgCl·LiCl (TMP = 2,2,6,6-tetramethylpiperidyl) for the polycondensation step.⁵⁰ Although several bimetallic combinations are known for organic applications,^{51–54} magnesiate complexes, such as (TMP)MgCl·LiCl, have been scarcely reported for polyester synthesis.⁵⁵ However, the presence of the halide salt in (TMP)MgCl·LiCl is argued to increase the solubility and the polarity of the magnesium complex,⁵⁶ therefore enhancing its reactivity thanks to increased basicity compared to the lithium chloride free compound.⁵⁷ In our case, (TMP)MgCl·LiCl should therefore readily deprotonate the acid to a carboxylate that would make it more reactive for nucleophilic attack on the dicarbonate. Gratifyingly, polyesterification of adipic acid by BHMF is efficiently carried out in the presence of (TMP)MgCl·LiCl to give a polymer with a *M_w* value of 16000 (Table 2, entry 3). Again, by increasing the reaction temperature to 80 °C with either MgCl₂ or (TMP)MgCl·LiCl, we were able to obtain copolymers more rapidly, albeit with lower

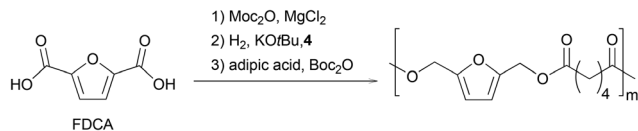


Scheme 2 Copolymerisation of BHMF and linear aliphatic diacids.

Table 2 Synthesis of aliphatic polyesters^a

Entry	Catalyst	Temperature (°C)	Time (h)	Conv. BHMF ^b (%)	<i>M</i> ₂ ^c	<i>M</i> _n ^{expd} (g mol ⁻¹)	<i>M</i> _w ^{expd} (g mol ⁻¹)	<i>D</i> ^d	<i>T</i> _g ^e (°C)	<i>T</i> _m ^e (°C)
1	MgCl ₂	30	115	94	AA	2970	11 950	4.0		
2	MgCl ₂	60	20	100	AA	3890	9600	2.5		
3	(TMP)MgCl·LiCl	60	24	100	AA	6410	16 080	2.5	-9	47
4	MgCl ₂	80	15	100	AA	1820	4520	2.5		
5	(TMP)MgCl·LiCl	80	15	100	AA	6240	11 940	1.9		
6	MgCl ₂	60	17	100	PA	2800	6640	2.4		
7 ^f	MgCl ₂	60	30	100	PA	4150	10 230	2.5		
8 ^f	(TMP)MgCl·LiCl	60	22	100	PA	4340	10 320	2.3	-23	42

^a Conditions: BHMF (100 eq.), *M*₂ (100 eq.), catalyst (1 eq.), Boc₂O (220 eq.), MeTHF ([*M*₂] = 1.2 M). ^b Determined by ¹H NMR spectroscopy. ^c Conversion of *M*₂ is quantitative for each entry. ^d Determined by size-exclusion chromatography (SEC-RI) at 35 °C. ^e Determined by differential scanning calorimetry (DSC; second scan). ^f Reaction was initiated with 100 eq. of Boc₂O until complete consumption of PA, then an additional 100 eq. of Boc₂O was added.



Scheme 3 Sequence from FDCA to furan-based polyesters.

masses (Table 2, entries 4 and 5). For the copolymerization of BHMF with pimelic acid, non-sequential addition of Boc_2O did not lead to a high molar mass polymer with MgCl_2 as a catalyst (Table 2, entry 6). Therefore, we attempted a sequential addition (*i.e.*, of two portions of 100 eq. of Boc_2O , the second one being added upon complete diacid conversion) to avoid decomposition of the dicarbonate involved. Under these conditions, MgCl_2 was able to convert both substrates within 30 h while allowing for an increase in molar mass (Table 2, entry 7). For $(\text{TMP})\text{MgCl}\cdot\text{LiCl}$, the same reactivity was observed (Table 2, entry 8). It should be noted that the copolymer obtained from adipic acid and BHMF has a T_g of $-9\text{ }^\circ\text{C}$ (Table 2, entry 3), while the copolymer of pimelic acid and BHMF has a glass transition of $-23\text{ }^\circ\text{C}$, due to the more flexible nature of the pimelate backbone (Table 2, entry 8). In agreement with literature data, the two copolymers have very close melting temperatures ($47\text{ }^\circ\text{C}$ vs. $42\text{ }^\circ\text{C}$).¹⁶ Furthermore, in order to gather qualitative mechanistic information, *in situ* IR follow-up of the copolymerization of BHMF and PA was performed in THF at $40\text{ }^\circ\text{C}$ in the presence of MgCl_2 . It showed in a first stage the consumption of the acid with transient formation of pimelic anhydride. Then, the anhydride species reacted with the di-alcohol monomer, resulting in polyester formation (Fig. S17†).

Finally, we focused on the one-pot process (Scheme 3). We hypothesized that the Lewis acidity of the magnesium complex involved in the first step would be sufficient to catalyze the final polymerization reaction. Therefore, an esterification was performed with 100 eq. of furandicarboxylic acid in MeTHF. After complete conversion of FDCA with MgCl_2 as catalyst, the solvent was removed *in vacuo*, Gusev catalyst and KOtBu were added in MeTHF. After 2 hours at $100\text{ }^\circ\text{C}$ under 50 bar H_2 pressure, the volatiles were removed under vacuum and the polymerization was conducted at $60\text{ }^\circ\text{C}$ in the presence of adipic acid and Boc_2O . Polymers with a M_w of 2400 g mol^{-1} and a dispersity of 1.8 were obtained.

Even if the full one-pot sequence did not deliver at this stage a polymer with characteristics up to those obtained *via* dedicated synthesis, adjustment of the third catalytic system should improve the outcome of the process in terms of copolymer molecular weight.

Conclusions

A new multicatalytic synthetic route to produce 2,5-bis(hydroxymethyl)furan and the corresponding (co)polymers has been developed from stable FDCA. This approach makes it possible to directly obtain bio-based materials in the form of copolymers, without needing to isolate and purify intermediates. Our

future efforts are oriented towards further study of the reaction mechanism, as well as development of catalytic systems that exhibit higher reactivities for the whole process.

Author contributions

L. G., N. N. and P. N. performed the experiments. L. G., N. N., P. N., R. M. G. and C. M. T. analysed the data. A. M., R. M. G. and C. M. T. wrote the paper. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts of interest to declare.

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