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# New (and Old) Monomers from Biorefineries to Make Polymer Chemistry More Sustainable

Majd Al-Naji, Helmut Schlaad, and Markus Antonietti\*

This opinion article describes recent approaches to use the “biorefinery” concept to lower the carbon footprint of typical mass polymers, by replacing parts of the fossil monomers with similar or even the same monomer made from regrowing dendritic biomass. Herein, the new and green catalytic synthetic routes are for lactic acid (LA), isosorbide (IS), 2,5-furandicarboxylic acid (FDCA), and *p*-xylene (*p*XL). Furthermore, the synthesis of two unconventional lignocellulosic biomass derivable monomers, i.e.,  $\alpha$ -methylene- $\gamma$ -valerolactone (MeGVL) and levoglucosenol (LG), are presented. All those have the potential to enter in a cost-effective way, also the mass market and thereby recover lost areas for polymer materials. The differences of catalytic unit operations of the biorefinery are also discussed and the challenges that must be addressed along the synthesis path of each monomers.

## 1. Introduction

Polymers from fossil monomers obviously have gotten a bad reputation. This is not related to the many benefits and cultural improvements polymers brought, but it is mostly due to human misbehavior in dealing with waste and how some people make money with it. We see megatons of plastic waste filling the oceans,<sup>[1]</sup> killing sea animals, or just washed unpleasantly on the shore. In simple words: something must change. On a smaller microscale, microplastic is released from consumer products or by abrasion of plastic and rubber parts, by washing coated textiles, etc, estimated to be around 200 megatons only in the Atlantic ocean.<sup>[2]</sup> Furthermore, how can we avoid fossil-based polymer and their ingredients and

additives such as bisphenol A, nonylphenols, methylparaben, or fluorinated polymers, as such? Sustainability is becoming a global imperative, and major scientific and political players are promoting the paradigm of “naturals” and “biorefinery” as a solution for the transition toward sustainable society. In this regard, biorefinery is refining/upgrading the renewable feedstocks (biomass, ideally nonedible lignocellulosic biomass) to yield commodity chemicals and possibly a biofuel by means of chemical and biological conversion technologies.<sup>[3–12]</sup>

In these regards, lignocellulosic biomass is most abundant, widely available in the form of wood or as rather inex-

pensive side products as bagasse or corn stover, easy to store, harvest and to transport. It is available in the 100 metric tonne per annum scale from forestry and agriculture, and there is no food-fuel competition.<sup>[13–17]</sup> Lignocellulosic biomass based on its origin can vary from one plant species to the others as well as from one part to the others in the same plant.<sup>[18]</sup>

The three major components of lignocellulosic biomass are cellulose (40–50%), hemicellulose (25–35%) and (3) lignin (15–20%), (Figure 1).<sup>[19,20]</sup> All three are valuable and can be used as a raw material base for the following monomers to generate. Paper industry is well aware how to separate the three components on the largest scales, and usually it starts with hydrolysis of the hemicellulose under mild aqueous conditions of acid or base pretreatment,<sup>[19–22]</sup> which then allows more easy separation of the lignin and the cellulose fibers (“paper pulp”). The hydrolysate contains D-xylose, L-arabinose, D-galactose, D-glucose and D-mannose. Lignin is a 3D, glassy polymer with an amorphous structure build up by oxidative radical polymerization of phenolic units, e.g., *p*-coumaryl, coniferyl and sinapyl alcohol. Up to now, the chemical structure of lignin is not really completely understood.<sup>[19–21]</sup> For simplicity, we will not discuss the possibilities for polymer science coming with the lignin fraction, as it is a separate subject worth an independent article. In this context, we only can point to the literature describing “lignin first biorefinery.”<sup>[23–31]</sup>

Carbohydrate based biomass contains, when compared to petroleum-based polymers, a greater fraction of oxygen (e.g., cellulose which is around C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, i.e., about 50 wt% is oxygen). This makes polysaccharides polar, and water as a medium will be optimum and effective solvent to run reactions. However, oil refinery catalysts are usually not made for to survive extreme aqueous media. Classical process engineering

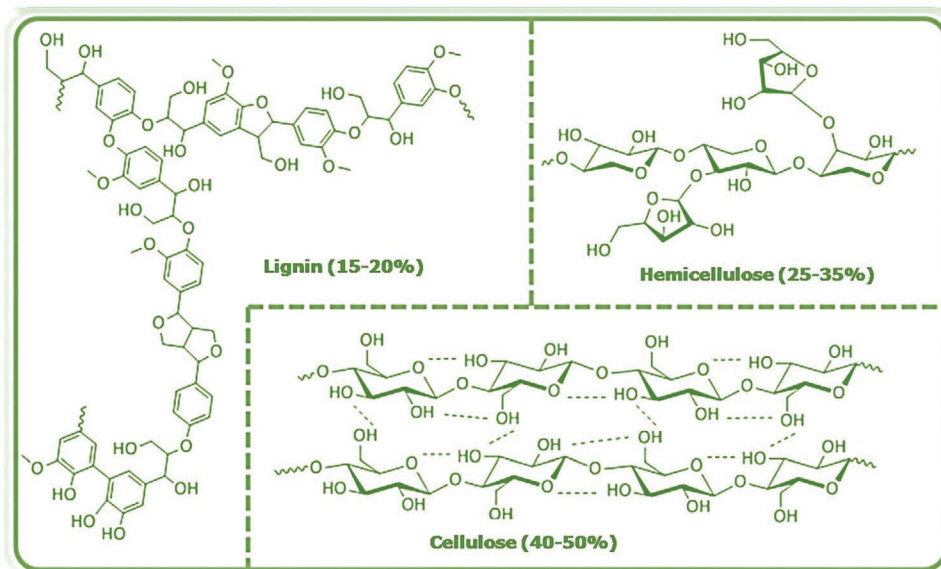
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**Figure 1.** Lignocellulosic biomass chemical composition and its structure.

aims to avoid the technical problem caused by water through water elimination step by pyrolysis or even gasification at relatively high temperature (673–1073 K). The resulting “bio-oils” are rather hydrogen poor and chemically closer to coal than to fossil crude oil, and larger amounts of external and higher pressure up to 10 MPa are needed for further upgrading towards useful products.<sup>[19,32–34]</sup> A chemistry-oriented biorefinery must thereby reinvent chemical unit operations to be run in aqueous medium or at green solvent in liquid-phase and at elevated temperatures. Along the manuscript we will discuss that acid/base catalysis and hydrogenation/oxidation (this including combined unit operations as hydrogenolysis, isomerization, hydrodeoxygenation) alone can indeed move us through some relevant monomer space. Such reactions are conducted at relatively moderate reaction conditions of temperature (373–573 K) and pressure (2.0–5.0 MPa). This review aims to present an illustrative range of building blocks that derived from cellulosic biomass to allow economization of biodegradable polymers. As indeed practically all biodegradable polymers contain oxygen in the structure, this chemical/biological biorefinery has some advantages as compared to classical thermochemical approaches, i.e., pyrolysis, liquefaction and gasification, as useful oxygen functionality can be left in the structure of the final product. These possibilities are schematically summarized in **Figure 2**. There are earlier reviews available on the subject,<sup>[35]</sup> but recent progress indeed brought some of the target molecules close to the point where advances polymer science could take over and add to a more green polymer science, and this is how we set our focus.

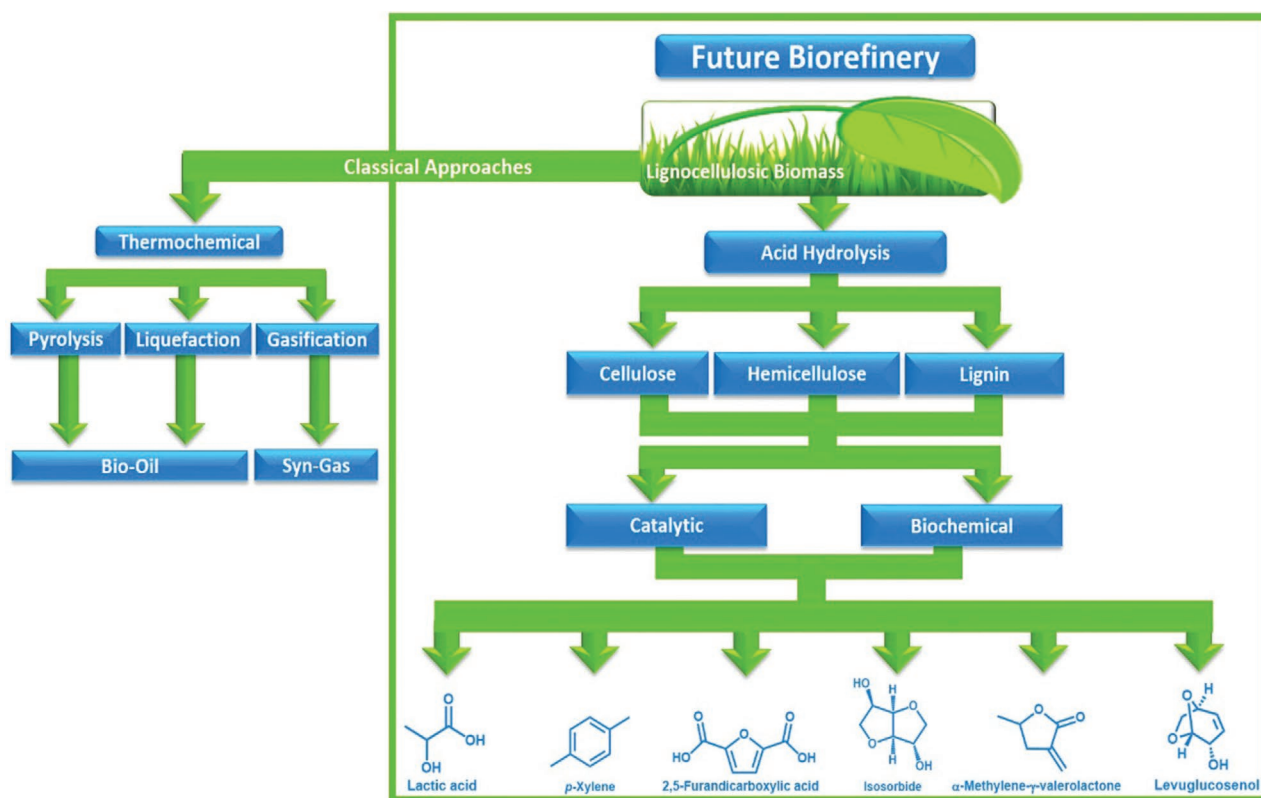
## 2. Lactic Acid from Glucose

Lactic acid (LA) or 2-hydroxypropanoic acid is a well-known monomer. The dehydration of LA into acrylic acid (AA) is attractive and an actual research topic, but the synthesis of di-lactide, which is used for the preparation of the biodegradable polylactic

acid (PLA), remains the most important application of LA.<sup>[36]</sup> Many reviews have recently been published summarizing the most recent advances in LA production and transformation.<sup>[8]</sup> LA generation is a model case to illustrate the tasks of biorefinery, shown in **Scheme 1**.

Two LA molecules have exactly the same composition as one hexose unit, and the transformation is accomplished in principle by a base-catalyzed retro-aldol C–C splitting, followed by a metal catalyzed hydride transfer, all in water as the only meaningful solvent for sugars (Scheme 1). This would make the reaction highly effective, fully atom efficient, and thereby green. In the ideal case, 1 g of glucose gives one gram of LA.

Traditionally, fermentation is the preferred option for the production of LA in industry. This approach relies on the use of glucose and bacteria and comes, when compared to classical chemical processes, with the drawback of a comparable low space-time productivity, the cost of separation, and massive aqueous side streams. Ideally, the direct chemical conversion of raw lignocellulosic substances could substantially simplify and increase the sustainability of LA production. For this reason, several groups have recently reported different approaches for the chemical synthesis of LA, which present clear economic advantages. Here, the alkaline hydrothermal treatment of cellulose has shown promising results. Splitting of simple carbohydrates into LA under basic conditions has been known for long time, but the ability of hydrothermal conditions to intensify the formation of LA has been just recently rediscovered.<sup>[36]</sup> A method was developed which uses Ni, Zn, and activated carbon in NaOH solutions (2.5 M) and converted cellulose into LA in only 5 min with a yield of 42% at 300 °C (6).<sup>[37]</sup> Alternatively, Ca(OH)<sub>2</sub> was used to generate LA from corn cobs in 45% yield at 300 °C.<sup>[38]</sup> Our group developed a competitive approach for the base catalyzed hydrothermal treatment of biomass based on the use of Ba(OH)<sub>2</sub>, using barium as a chelating cofactor.<sup>[23,36]</sup> The reaction involves the controlled depolymerization of the cellulosic portion of biomass, retro-Aldol-splitting to glyceraldehyde, followed by



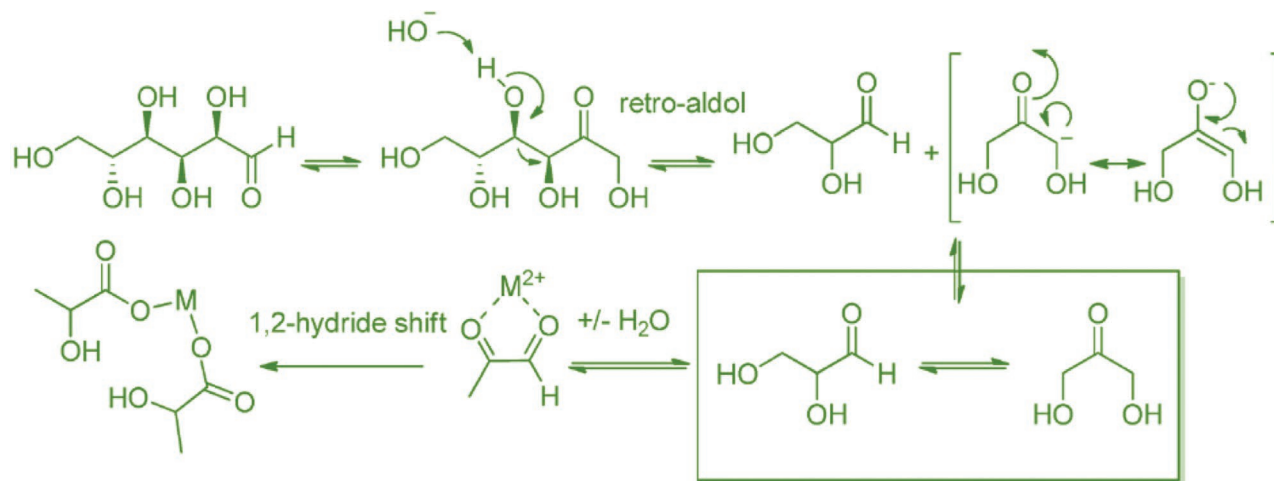
**Figure 2.** The classical and future routes for conversion of lignocellulosic biomass to new (and old) monomers.

a 1,2-hydride shift under the formation of barium lactate. The included lignin from wood can be easily recovered by simple filtration at the end of the reaction after precipitation as low molecular weight oligomers.

The group of Dong recently reported the preparation of LA from cellulose using lanthanide triflates, with europium triflate showing the best activity and a yield of  $\approx 63\%$ .<sup>[39]</sup> A second interesting report, which appeared almost simultaneously, described the efficient preparation of LA (68% yield) using Pb(II) ions at even milder temperatures (190 °C, 30 bar, N<sub>2</sub>, 4 h) starting from

cellulose.<sup>[40]</sup> For the last two approaches, we point to the necessity to remove heavy metals by distillation of the lactide.

For polymer science, it is important to mention that all the lactide made as such is racemic, contrary to fermentation. To make it more useful, one would have to apply stereo-selective ring-opening polymerization catalyst.<sup>[41–43]</sup> But even then, the enantiomerically pure polylactide is characterized by relatively limited thermal and mechanical properties (melting temperature at around 120–150 °C), as well as high water uptake. A possible option to move here forward are the double-helical



**Scheme 1.** The mechanism for formation of lactic acid (LA) from glucose via base hydrolysis.

stereocomplexes of poly(L-lactide) with poly(D-lactide), which has higher performance with substantially increased melting temperature of (>180 °C).<sup>[44]</sup> Here, we then could profit from the availability of both enantiomers from the chemical synthesis.

### 3. *p*-Xylene from 2,5-Dimethylfuran

Until today, *p*-xylene (*p*XL) is produced by petrorefinery. *p*XL is considered to be one of the most important premonomers (platform chemicals preceding monomers) in polymer industry, but is complicated to separate from its *o*- and *m*-isomers. In 2015, around 37 million metric tons of fossil-based *p*XL were used, mostly for the production of poly(ethylene terephthalate) (PET) and other polyester fibers via terephthalic acid (from oxidation of *p*XL).<sup>[45–48]</sup> Certainly, this numbers showed that there is a great potential for the isomer-pure synthesis of *p*XL as a premonomer from renewable resources. In this context, there are reported studies for the synthesis of *p*XL from biomass-derived 2,5-dimethylfuran (DMF),<sup>[49]</sup> which involves a Diels-Alder cycloaddition of ethylene to form the intermediate 1,4 dimethyl-7-oxabicyclo[2.2.1] hept-2-ene, followed by a dehydration step to *p*XL using different types of zeolites as a catalyst.<sup>[45–48,50–52]</sup> For this reaction usually batch systems are used, combined with high reaction temperature (523–623 K), high ethylene pressure (5.0–7.0 MPa) and long reaction times (24–48 h).<sup>[53]</sup> All that looks less appealing in terms of green chemistry. Williams et al.<sup>[53]</sup> have reported a 75% yield of *p*XL as a result of cycloaddition of ethylene to DMF using H-Y zeolite at 573 K. Moreover, diverse side products from a competitive reaction on H-Y zeolite were found under the reported reaction conditions, i.e., 2,5-hexanedione, *p*XL alkylation products and polycondensates of 2,5-hexanedione.<sup>[53,54]</sup> H-Beta zeolite with a Si/Al ratio of 12.5 possessed higher selectivity to *p*XL with respect to H-FAU and H-ZSM-5 at 523 K and 6.2 MPa of ethylene.<sup>[53,55]</sup> This high performance of H-Beta is attributed to its resistance to deactivation and its ability to selectively catalyze the dehydration of the Diels-Alder cycloaddition intermediates to *p*XL. Phosphorus modification of Beta zeolite led to an increase in *p*XL yield from 75% to 97% using 523 K and 6.2 MPa of ethylene in batch system.<sup>[56]</sup> Similarly, Zr-, Sn-, and Ti-Beta zeolites with Lewis acid sites were found to be highly active and selective for the conversion of DMF to *p*XL in the presence of ethylene (6.2 MPa) at 523 K.<sup>[54,57]</sup> Of these, Zr-Beta exhibited the highest catalyst performance (DMF conversion = 99% and *p*XL selectivity = 90%).<sup>[57]</sup> Also, heteropolyacids and sulfonic acids supported on SiO<sub>2</sub> showed a high DMF conversion (94%) and *p*XL selectivity (85%), here due to enhanced Brønsted acid sites.<sup>[58,59]</sup> Differently, several trails were applied for synthesis of aromatics by Diels-Alder cycloaddition using furans and ethanol (as an in situ ethylene source) over zeolite as a catalysts in a batch system.<sup>[58–60]</sup> However, this approach requires high reaction temperatures to dehydrate ethanol to ethylene and led to high amount of by-products.

An alternative route for the sustainable production of aromatics from furanics was proposed by replacing the ethylene with different dienophiles such as acrylic acid or maleic anhydride.<sup>[48,61–63]</sup> In this greener and safer route, the reaction can be performed in liquid phase at lower reaction temperature

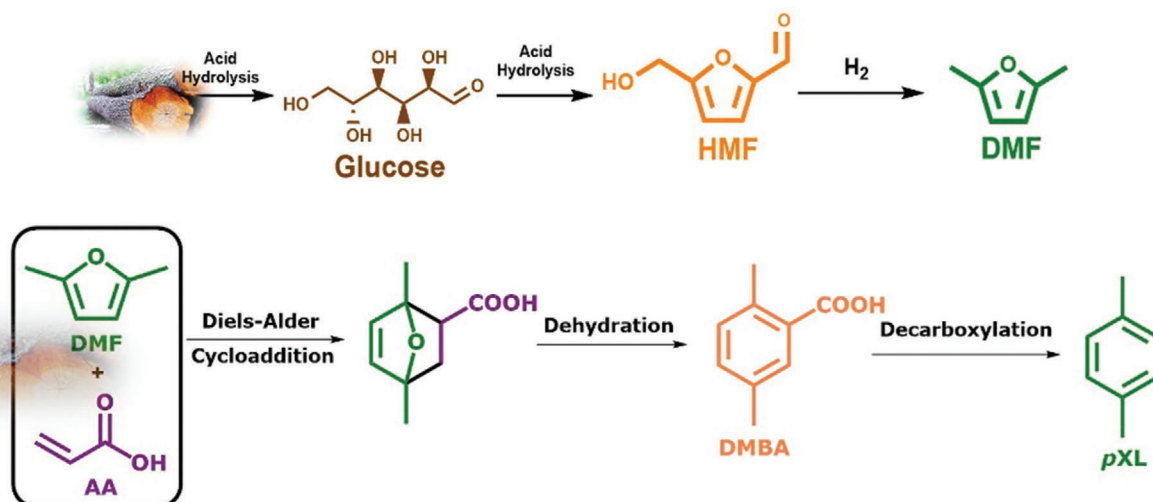
(423–473 K) and without external gas pressure. Furthermore, competing reactions that lead to the wide range of byproducts are suppressed, and the selectivity toward the targeted aromatics is increased. However, the synthesis of *p*XL utilizing this route was rarely described, as it comes with an additional elimination step to be handled best at an in situ cascade. As a move in this direction, the two steps batch synthesis of *p*XL from DMF and acrylic acid (AA) catalyzed by scandium(III) triflate (Sc(OTf)<sub>3</sub>) in ionic liquids under mild reaction conditions was reported.<sup>[62]</sup> It was found that 48% of *p*XL and 22% of 2,5-dimethylbenzoic acid (DMBA) are formed in the first step. The consecutive second step includes a decarboxylation of the *p*XL and DMBA mixture which improves the yield of *p*XL to 57%.<sup>[43]</sup> Similarly, the reaction between DMF and AA at room temperature was performed by using acidic ionic liquid ([Bmim]H<sub>2</sub>SO<sub>4</sub>) in a batch system. We recently reported on a three-reaction waterfall cascade reaction for *p*XL synthesis with high yield (83%) in continuous flow mode (**Scheme 2**). From a polymer perspective, the easy-to-separate side product, 2,5-dimethylbenzoic acid (13%), is even more interesting for substituted polyesters. This cascade reaction includes a Diels-Alder cycloaddition of DMF to AA, the dehydration to form the phenyl-ring, and a final decarboxylation to *p*-xylene and was successfully performed in a continuous flow system over Beta zeolite. All utilized reagents, i.e., DMF and AA, in this approach are derived from the cellulosic fraction. DMF is a standard platform chemical obtained from lignocellulosic biomass by dehydration to 5-hydroxymethylfurfural, which then is hydrodeoxygenated to DMF.<sup>[64]</sup> In parallel, AA can be obtained via catalytic dehydration step of LA as described in the second section of this manuscript. Alternatively, AA can be obtained by reacting bio-based glycerol and formic acid to allyl alcohol followed by catalytic oxidation step to acrylic acid.

### 4. 2,5-Furandicarboxylic Acid from 5-Hydroxymethylfurfural

There can be no opinion article on green chemistry monomers without addressing 2,5-furandicarboxylic acid (FDCA). Bio-derived FDCA is indeed the second option for terephthalic acid replacement in heavy duty plastic bottles. FDCA is the oxidation product of HMF (**Scheme 3**). Also, the HMF production from lignocellulosic biomass is shown at Scheme 3. The conversion of HMF to FDCA was performed using nano-Au to MnO<sub>2</sub> to heteropolyacid catalysis, but as a biomonomer also by microbial oxidation.<sup>[8,32,65–75]</sup>

FDCA has practically “left” the hands of academic science and has received meanwhile both marketing and public reception so that the technology readiness level of this approach is the highest of all the discussed processes. DuPont, Corbion, and Synvina, a joint venture of BASF and Avantium, have created model plants where sugars are first dehydrated to HMF, then oxidized chemically or microbially to the wanted FDCA.<sup>[35,66–75]</sup> In 2020, a 5 kilotons per annum plant is under construction in Delfzijl, this securing enough production capacity for practical explorations.<sup>[76]</sup>

FDCA is not only a biobased replacement of terephthalic acid, but comes with improved properties and new chemical



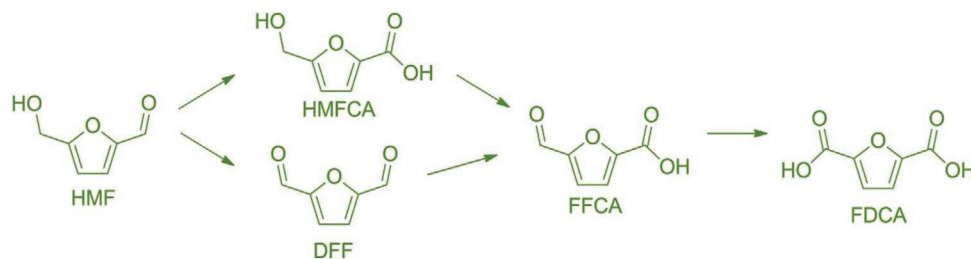
**Scheme 2.** Proposed pathway for the production of p-xylene (pXL) from lignocellulosic biomass. Primarily, glucose converted to DMF via acid hydrolysis, followed by hydroxydeoxygenation of HMF (top). Finally, DMF converted to pXL via three-in-one reaction namely Diels-Alder cycloaddition, dehydration and decarboxylation (bottom).

options. Furan polymers like polyethylene furanoate (PEF) have for instance a significantly higher oxygen and CO<sub>2</sub> barrier, thus allowing better food and drink preservation, and shelf life can in principle be doubled. There are excellent reviews on FDCA based polymers also beyond the commercially available PEF, including unusual high temperature engineering plastics,<sup>[68]</sup> and even process analyses and eco balances are reported.<sup>[69]</sup> This is why we can point the reader to this primary work.

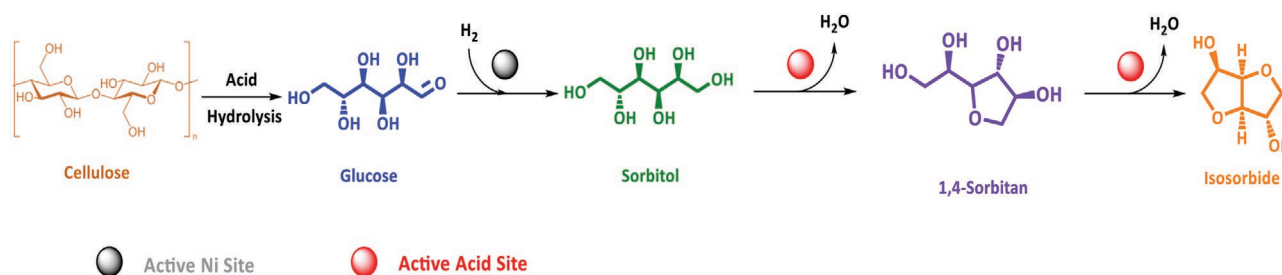
## 5. Isosorbide from Sorbitol

All monosaccharides, here glucose as a model case, can be selectively hydrogenated to sorbitol, and this is already done on largest scale (currently 9000 tons per year, but rapidly increasing because of its use as a “sugar-free” sweetener).<sup>[12,77,78]</sup> Sorbitol is one of the top “12” promising biorefinery molecules according to the US department of energy,<sup>[79]</sup> and in the present context of polymer science it can be further converted to a high value bio-based building blocks, namely 1,4-sorbitan and IS (Scheme 4).<sup>[65,80–83]</sup> Also isosorbide (IS) earned its importance from its exponentially growing market (expected to be 324.6 million US \$ at the end of 2020),<sup>[84]</sup> as it is involved in the synthesis of wide range of green and sustainable final products, such as polymers.<sup>[85–92]</sup> For instance, DURABIO<sup>[93]</sup> and

PLANEXT<sup>[94]</sup> are commercialized IS based polycarbonates with improved properties even when compared to reference transparent thermoplasts, e.g., both poly(methyl methacrylate) and bisphenol-A polycarbonate.<sup>[95]</sup> As packaging for hot-beverages, IS can be copolycondensed into polyethylene terephthalate (PET) or polyesters of FDCA.<sup>[87,96]</sup> Industrially, IS is produced with a yield of 77% by homogenous dehydration of sorbitol using H<sub>2</sub>SO<sub>4</sub> at 403 K.<sup>[97–99]</sup> In general, this process offers moderately high IS yield but it is neither economically efficient nor sustainable, because of aqueous waste. Several trials for IS production from sorbitol using solid acid catalysts, i.e., zeolites, mixed oxides and resins, were reported, too.<sup>[81,100–112]</sup> These trials use a molten bulk phase in small quantities (the solid phase consists of sorbitol and catalyst). Of these catalysts, Beta zeolite showed the highest catalytic performance (sorbitol conversion = 100% and IS yield = 76%).<sup>[113]</sup> Also, a catalyst-free sorbitol dehydration to IS in compressed water (590 K) under 10 MPa CO<sub>2</sub> was reported,<sup>[114]</sup> and a yield of IS of 57% was obtained.<sup>[114]</sup> Sels group showed that IS (>60%) can be straightforwardly produced from cellulose in a tandem reaction using two different catalysts (heteropolyacids for the dehydration reaction and Ru@carbon for the hydrogenation reaction) at 503 K and under 5 MPa of H<sub>2</sub>.<sup>[115]</sup> Similarly, the direct complete conversion of aqueous glucose solution to IS (yield = 79%) was reported using Ru/Dowex at 463 K after 24 h in batch system.<sup>[84]</sup>



**Scheme 3.** The synthesis pathway of 2,5-furandicarboxylic acid (FDCA) via oxidation of 5-hydroxymethylfurfural (HMF) to 5-hydroxymethyl-2-furancarboxylic acid (HMFA) or 2,5-diformylfuran (DFF) and subsequently to 5-formyl-2-furancarboxylic acid (FFCA).



**Scheme 4.** The synthesis route of isosorbide (IS) from cellulosic biomass by acid hydrolysis of cellulose to glucose, followed by hydrogenation of glucose to sorbitol over 35Ni/NDC, then sorbitol dehydration to 1,4-sorbitan and finally to IS over Beta zeolite.

Our group developed an efficient prototype scale production of IS from aqueous solution of sorbitol at 503 K using Beta zeolite (Scheme 4). Furthermore, we also report on the integrated process to IS starting from aqueous glucose solution in dual tubular reactors. This process includes as a first step aqueous-phase glucose hydrogenation to sorbitol over 35 wt% Ni catalyst supported nitrogen-doped carbon, followed by dehydration of the formed sorbitol to 1,4-sorbitan and subsequently to IS over Beta zeolite (Scheme 4), all without intermediate isolation and/or purification and in one flow.

In both processes, IS was obtained with high yield ( $\approx 80\%$ ), the remainder being 1,4-sorbitan, which could be looped back to the second tube reactor for continued dehydration. The calculated apparent activation energies suggested that the first dehydration step of sorbitol to 1,4-sorbitan is very fast, while the removal of the second water molecule to form IS is the rate determining step. The major problem here still is that classical zeolites optimized by oil industry show low stability in polar media under the given conditions. Therefore, the existence of new and stable acidic heterogeneous catalysts under hydrothermal conditions is of a great interest. The present of such a catalyst would allow IS production to be much cheaper than the current process that uses  $\text{H}_2\text{SO}_4$  as homogeneous catalyst and creates a lot of acidic wastewater.

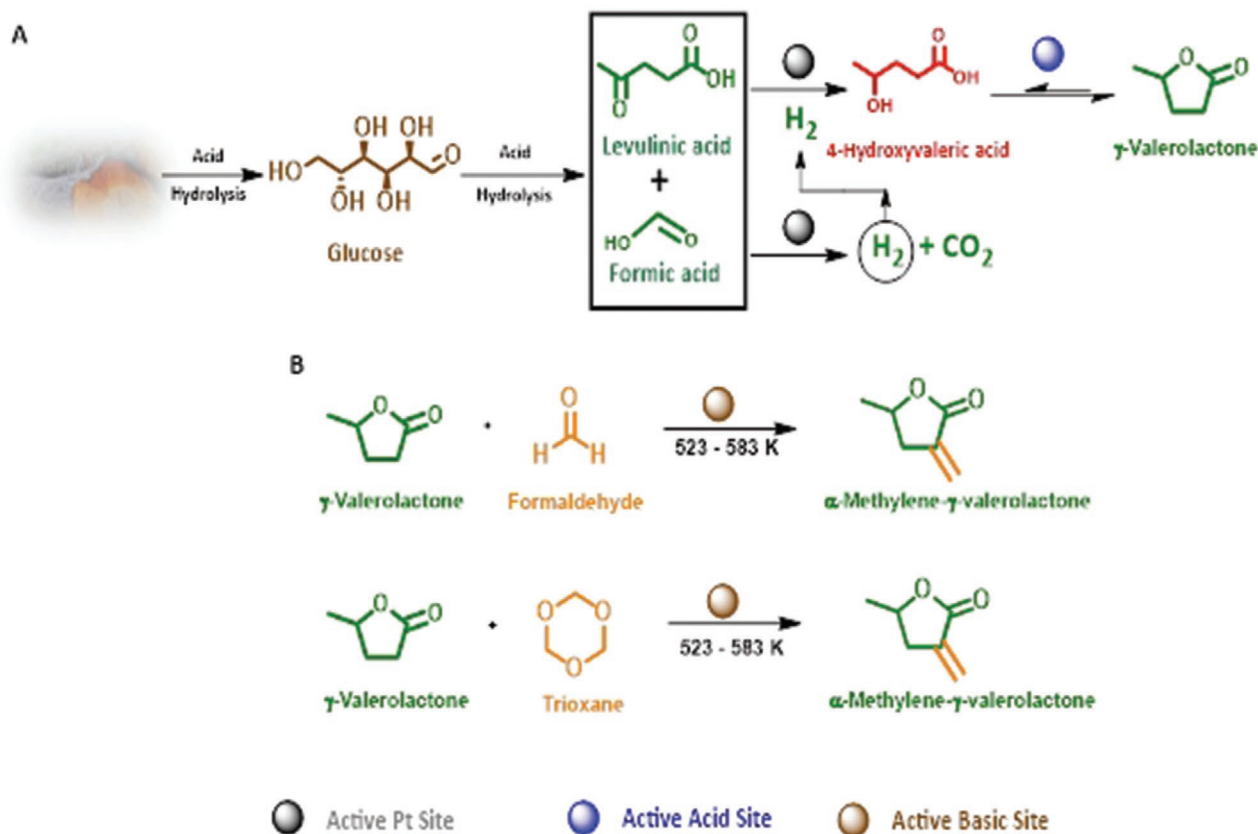
## 6. $\alpha$ -Methylene- $\gamma$ -Valerolactone from $\gamma$ -Valerolactone

$\gamma$ -valerolactone (GVL) is one of the obvious candidates as a sustainable monomer. An application of strong acids to sugar or straw in water gives in high yield of levulinic acid and formic acid (Scheme 5). Transfer hydrogenation of levulinic acid using formic acid as a hydrogen source results on the formation of 4-hydroxyvaleric acid, which immediately undergoes to ring-closure into the GVL.<sup>[116–119]</sup> This reaction in modern hydrogenation catalysts occurs in practically complete yields to GVL,<sup>[120]</sup> which can be converted to wide range of compounds such as pentenoic acid, valeric acid, 2-methyltetrahydrofuran, 1,4-pentandiol and  $\alpha$ -methylene- $\gamma$ -valerolactone (MeGVL) that can be upgraded to a fine chemicals and sustainable polymers. Of these monomers, MeGVL is a type of methacrylic monomer with high similarity to methyl methacrylate (MMA) in its structure and properties.<sup>[121–123]</sup> This similarity gives MeGVL potential for an ecofriendly production of poly(MeGVL), with the option to substitute even high glass transition fossil thermoplastics,

such as polymethacrylimide. As MeGVL is one of most promising monomers from GVL, companies as GFBiochemicals mark it as a future product for their development plan in monomer synthesis.<sup>[124]</sup> However, the synthesis of MeGVL from GVL was rarely described and has some complexity. Already in 1953, Allied Chemical & Dye Corporation had patented the non-catalytic synthesis of MeGVL using GVL and ethyl formate in absolute ethanol in the presence of granulated sodium sand.<sup>[125]</sup> Tanaka et al.<sup>[126]</sup> reported on a noncatalytic two step approach for MeGVL synthesis using ethyl formate and paraformaldehyde and tetrahydrofuran or dimethylsulfoxide as solvents. The vapor-phase GVL conversion toward MeGVL over different rare earth elements supported on  $\text{SiO}_2$  was also investigated.<sup>[125]</sup> The results presented by Manzer.<sup>[122]</sup> reported only the value of GVL conversion without mentioning the yield and selectivity to MeGVL over different catalysts and reaction temperatures. All reported studies focus on the utilization of basic catalyst to facilitate the nucleophilic attack of formaldehyde on  $\alpha$ -position of GVL. To our interpretation, the low yield of MeGVL in all available studies is due to the presence of  $\text{H}_2\text{O}$  in the formaldehyde source which inhibit the " $\alpha$ -methylenation" reaction. Furthermore, the high polymerizability of MeGVL lead to undesired uncontrolled deposit formation.

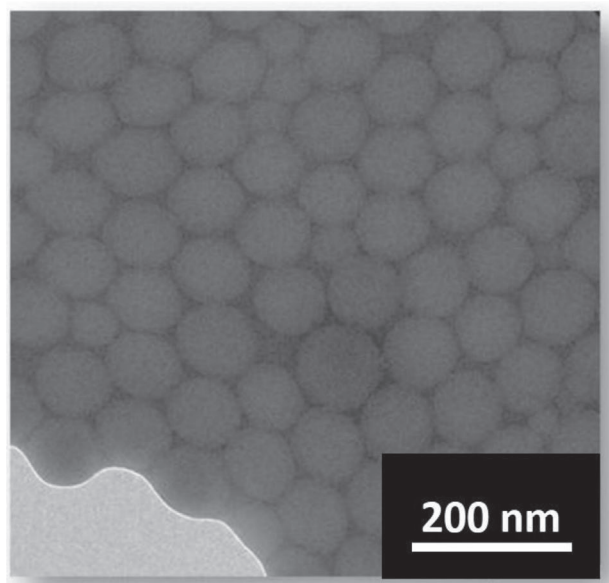
Recently, our group developed a new route for higher yield MeGVL synthesis based on utilization of trioxane (Tx) as an anhydrous formaldehyde source which catalytically depolymerizes at 483–503 K to formaldehyde (3 molecules).<sup>[125]</sup> The anhydrous formaldehyde source is advantageous for efficient synthesis of MeGVL from GVL (Scheme 5). In this process, using 5.0 wt.% Cs and introducing mesopores to a microporous Beta zeolite, the MeGVL yield improved from 33% to 52%. This is due to enhanced accessibility, mild basicity and acid-less functionality of the prepared catalyst. Furthermore, we have successfully synthesized poly(MeGVL) with molecular weight of ( $\approx 10^5$  g mol<sup>-1</sup>) via heterophase radical polymerization. Also, scanning electron microscopy (SEM) image showed that the synthesized polymer exhibited homogenous spherical morphology with size of 70–80 nm of each sphere (Figure 3). The resulting poly(MeGVL) showed chemically equivalent properties with respect to petrochemically based acrylates.<sup>[121]</sup> To our opinion, further progress for this monomer is only restricted by primary yields and thereby the availability of more effective heterogeneous base catalysts, which survive the partly rather aggressive conditions. We already discussed that making polymers more green or degradable is more and more coupled to the availability of a new generation of catalysts, surviving water,





**Scheme 5.** A) The synthesis pathway of GVL from lignocellulosic-derived levulinic acid and formic acid over bifunctional catalyst. B) Traditional pathway for the synthesis of MeGVL from GVL in the presence of FA from formalin or paraformaldehyde over basic catalyst (top), the new tandem route uses trioxane as the formaldehyde source (bottom).

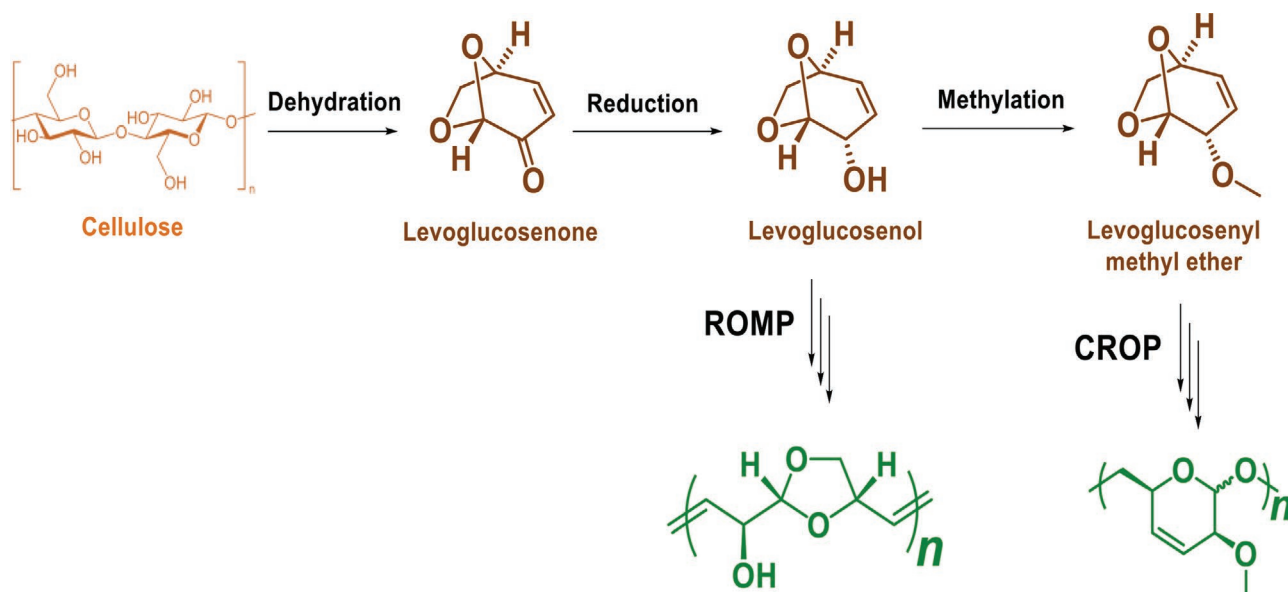
acids, and in general biomass derived functionalities, which was not necessary for the optimization of oil-based processes.



**Figure 3.** Scanning electron microscope image of the synthesized latex of poly(MeGVL).

## 7. Levoglucosenol from Levoglucosenone

Levoglucosenone is an unsaturated bicyclic acetal, which is obtained by controlled acid-catalyzed pyrolysis of (waste) cellulose. Nowadays, it is produced in industrial quantities (50 tons per year) by the Circa Group Ltd., Australia, and the derivative dihydrolevoglucosenone (Cyrene) has been launched as an environmentally friendly solvent to replace dipolar aprotic solvents like *N*-methyl-2-pyrrolidone. Levoglucosenone itself cannot be polymerized, so far, but can be easily converted into polymerizable levoglucosenol (LG) and levoglucosenyl alkyl ethers (Scheme 6). These chiral monomers contain double bonds as well as acetal units, which are eligible to either ring-opening metathesis polymerization (ROMP)<sup>[127]</sup> or cationic ring-opening polymerization (CROP),<sup>[128]</sup> to yield polyacetals with different microstructures. The polyacetal produced by ROMP is amorphous with a glass transition temperature of about 100 °C, i.e., similar to polystyrene, while that produced by CROP is semicrystalline with a melting temperature of ≈120 °C. The polymers can be further modified by hydrogenation and thiol-ene addition as well as by cross-linking and are degradable in acidic environment. A most appealing aspect of this approach is the possibility to generate a platform of new sugar-based monomers from levoglucosenone, which can be polymerized by different methods, to produce a huge variety of new reactive functional and degradable polymers.



**Scheme 6.** Bicyclic acetal monomers produced from levoglucosenone (from cellulose) for ring-opening metathesis polymerization (ROMP) or cationic ring-opening polymerization (CROP).

## 8. Conclusion

The idea to use monomers made from regrowing natural products is as old as civilization as such, and it gains further impetus in the current public crisis of polymer science related to the “three big global problems of polymer industry”: marine plastic waste, microplastic, and leakage of endocrine disruptive components into our food chain. Old, but also new monomers come up, and the costs of such monomers turn into a major issue, as most of the current green syntheses cannot compete with optimized classical fossil products. There are indeed hundreds of “little” problems to be solved to make degradable polymers cost- and performance-competitive with its fossil-derived counterparts, but we also see the fair chance to tackle them. In this context, “biorefinery”, i.e., the generation of such chemicals from regrowing resources, via green processes and utilizing only sustainable (new) catalysts is a mandatory step to achieve a sustainable and biodegradable polymer. To illustrate, lactic acid or isosorbide are well-elaborated monomers, but recent progress in hydrothermal water chemistry allows us to expect availability on a cost level even below petrorefining.

It is this availability of such monomers which will bring also challenges and opportunities to polymer science. A chemically synthesized lactide is chirally mixed, maybe racemic, and it needs stereoregular ring opening polymerization catalysts to turn this “disadvantage” into a potential materials benefit, as we had observed it with the role model of fossil it-polypropylenes.

Solutions and offers of nature for polymers and monomers are rich, and their processing is water based. Nature uses both biodegradation, but for more robust, long standing parts also bioinertness, if not even self-repair and healing (“trees”). Lignin for instance is difficult to degrade microbially, but lignin is mostly up-cycled after the first “usage cycle” to humic matter, and the leftovers then contribute to soil fertility and food security.<sup>[129]</sup>

Better understanding and addressing of such processes into man-made polymers are the next step to come for polymer science: be unconditioned reliable under operation conditions, but turn into something useful (at worst inert) once your usage has ended is the new mission. All that could start with the right monomers and intelligence in product design.

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## Conflict of Interest

The authors declare no conflict of interest.

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biodegradable polymers, biorefineries, carbohydrate-based monomers, green polymers, lignocellulosic biomass

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