

Rigid Biobased Building Blocks: Current Developments and Outlook

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ABSTRACT: In this perspectives paper we will look at the state-of-the-art in rigid renewable building blocks for biobased materials, with a focus on two types of carbohydrate-based difunctional monomers, i.e., isohexides and furan-2,5-dicarboxylic acid (FDCA).

KEYWORDS: Biobased building blocks, FDCA, isohexides, polymers

1 INTRODUCTION

The continuously increasing interest in biomass and biobased materials is fuelled by growing concerns about fossil feedstock depletion, as well as greenhouse gas emissions and global warming. Whereas most of the current focus is on using terrestrial vegetable biomass as alternative feedstock for energy carriers (e.g. transportation fuels) and chemicals production, aquatic biomass (e.g. micro- and macroalgae) is also being explored as a renewable feedstock source. A successful transition from a fossil-feedstock-based economy to a biobased economy can only be achieved sustainably if there is no competition with food and feed production, and negative effects of (indirect) land use change are prevented. Hence, biobased feed stocks should be limited to non-food crops and agro residues. Given the huge scale of current global industrial petrochemicals production, the choice of biobased feedstock is determined by availability if a significant impact is desired. Hence for terrestrial biomass these restrictions limit the potential sources to lignocellulose and residues (e.g. wood, grasses, straw, bagasse) and specific energy crops like rapeseed and jatropha. Lignocellulosic biomass on average contains 40–50% cellulose, 20–30% hemicellulose, 20–30% lignin, and varying amounts of proteins, fats and oils, and minerals [1,2]. Although lignin is a highly interesting potential source of aromatic chemicals like phenol, and expected to become abundantly available from lignocellulosic biorefineries, the economically viable production of resin-grade

(i.e. high purity) aromatic monomers from lignin is not likely in the short term [3]. Whereas in the case of lignin the challenges are mostly chemical and technological, the use of, e.g., terpenes as feedstock for the production of aromatics is severely hampered by the limited availability compared to the potential demand. Since carbohydrates (C6 and C5 sugars) are abundantly available they are the most likely candidates as feedstock for the production of bulk (platform) chemicals for materials production. Basically two approaches can be distinguished in the transition towards a biobased (i.e. carbohydrate based) economy; transformation of biomass feedstocks to existing (fossil based) chemicals, also known as drop-in, or transformation of biomass to “new” chemicals. Both approaches have their own merits. While the drop-in approach capitalizes on the use of existing expertise and capital, the major drawback is the energy penalty that has to be paid when transforming highly functionalized feedstock with a high oxidation state (carbohydrates, high oxygen content) into existing petrochemicals (low functionality hydrocarbons and aromatics). The “net” removal of water from carbohydrates requires (non-renewable) hydrogen and energy, and results in a low overall atom efficiency. On the other hand, the transformation of biomass into “new” chemicals will require the development of new expertise and technology all along the value chain (from monomer production to materials processing). The term “new” relates to the fact that the chemicals and materials of interest are not produced on a large scale (or even small scale), while for some of these chemicals the first scientific reports date back to the late nineteenth century. So although the lack of knowledge of these new biobased chemicals can be considered as detrimental, the prospect of developing new materials with new properties

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as well as intellectual property is a strong incentive for many to explore this strategy. Furthermore, transformation of carbohydrates into “new” building blocks like (tetrahydro) furans, lactic acid or succinic acid by selective defunctionalization follows the thermodynamically preferred pathway, resulting in a more energy efficient reduction of the number of functional groups, while retaining (part) of the unique structural characteristics of the biomass feedstock.

The resulting biobased building blocks often differ dramatically from their petro-based analogues (if those exist at all) on a variety of aspects including polarity, reactivity and chirality.

Regarding biobased materials, there is an increasing demand for biobased, sustainable performance materials, where the emphasis is on performance and endurance, as opposed to (bio)degradability. Hence (unsaturated) polyesters, polyamides, polyurethanes and epoxy resins have become the areas of interest for many in the field of biobased monomers. Whereas relatively flexible renewable building blocks (diacids, diols, polyols) are becoming increasingly industrially available (from carbohydrate or oleochemical sources), there is a growing need for rigid biobased monomers for the production of high performance, engineering polymers, with high glass transition (T_g 's) and melting temperatures (T_m 's) and excellent mechanical properties.

In their 2004 study for the US Department of Energy (DOE) called “Top Value Added Chemicals from Biomass”, Werpy *et al.* listed the top twelve biobased chemicals with a unique structure [4]. In their follow-up study from 2010 Bozell and Petersen revised this list based on the level of technological development and commercialization [5]. Nevertheless, in both studies only two types of biobased difunctional rigid building blocks were included: i.e. furan-2,5-dicarboxylic acid (2,5-FDA or FDCA) and 1,4:3,6-dianhydrosorbitol (isosorbide). Our focus in this paper will be from the perspective of these two classes of high interest rigid biobased building blocks, i.e., isohexides and FDCA.

2 ISOHEXIDES

Isohexides, also known as 1,4:3,6-dianhydrohexitols, are rigid secondary diols based on C6-sugar alcohols. Depending on the hexose source used, three different isohexide isomers can be obtained by successive reduction of the aldose to the alditol, followed by acid catalyzed cyclodehydration to the isohexide. The three major isomers, i.e. isosorbide (1,4:3,6-dianhydrosorbitol), isoidide (1,4:3,6-dianhydroiditol) and isomannide (1,4:3,6-dianhydromannitol), are bicyclic structures composed of two cis-fused tetrahydrofuran rings with a 120° angle between the rings, which differ only by

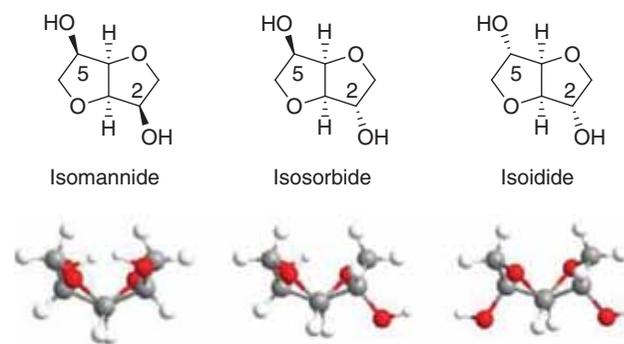


Figure 1 Chemical structure and spatial orientation of the three major isohexide isomers; spatial side-view along C3-C4 axis based on DFT calculations (B3LYP-TZV) [7].

the orientation of the hydroxyl groups at positions 2 and 5 [6]. Whereas two isomers are symmetrical with both hydroxyl groups in the endo (isomannide) or exo (isoidide) position, the third isomer (isosorbide) has a 2-exo, 5-endo configuration (Fig.1).

The position of the hydroxyl groups has significant influence on the reactivity, depending on the type of chemistry involved. Whereas the exo-hydroxyl group is less sterically hindered, the endo-hydroxyl group is more nucleophilic due to intramolecular hydrogen bonding. This difference in reactivity is an intrinsic feature in isosorbide chemistry.

Of the three mentioned isomers only isosorbide is produced on an industrial scale, which is mainly due to the limited accessibility of the precursors of the other two isomers. Isosorbide is produced from abundantly available glucose in two steps in high yields. Whereas currently starch is the major source of glucose, developments in lignocellulosic biorefineries will ultimately result in the production of glucose from non-food sources, thereby preventing competition with the food chain. Isomannide is prepared from mannitol, which is made by hydrogenation of fructose. Since fructose is less commonly available than glucose, the price of fructose is significantly higher. Sources of fructose are, e.g., sucrose or inulin, while enzymatic isomerization of glucose to fructose is also performed on an industrial scale. In contrast to sorbitol, the cyclodehydration of mannitol to isomannide is also less efficient [6]. The third isomer, isoidide, is even less accessible since the parent hexose, i.e. L-idose, is rarely found in nature and hence can only be prepared chemically. A recent patent application describing the synthesis of iditol in 5-steps via L-sorbose, starting from glucose, underlines the difficulty of obtaining this isomer [8]. On the other hand, according to the same authors, the cyclodehydration of iditol to isoidide is highly efficient. An alternative approach to obtaining isohexide isomers is the epimerization as described by Wright and

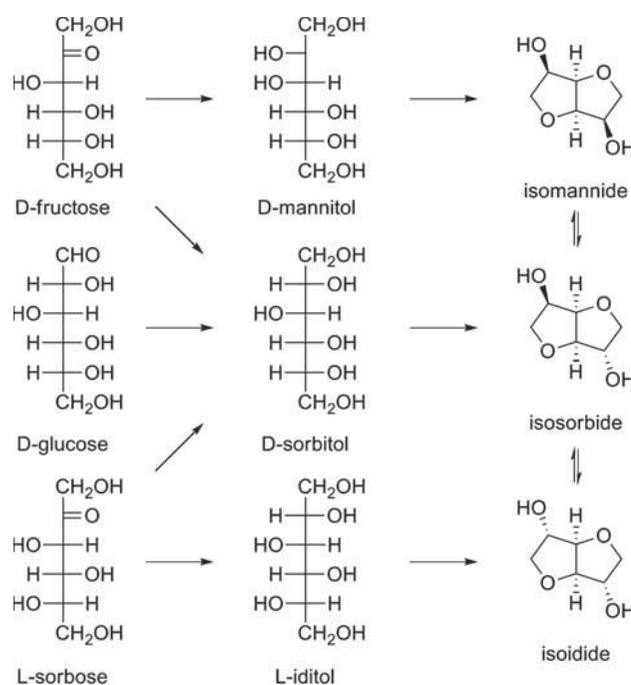


Figure 2 Schematic overview of synthetic routes to isohexides.

Brandner, which involves catalytic interconversion of all three isomers in a hydrogen atmosphere [9,10].

Apart from various other applications such as pharmaceuticals, plasticizers and solvents, isohexides are also interesting building blocks for polymers. Due to their chirality and intrinsic rigidity isohexides have been explored for applications such as, e.g., liquid crystalline polymers (LCPs), powder coating resins, and engineering plastics. When incorporated into step growth polymers such as polyesters and polycarbonates, isohexides have two distinct effects. First and foremost the rigidity of the isohexides reduces chain mobility, resulting in an increase of the glass transition temperature (T_g) [11,12]. When applied to known polyesters, such as polyethylene terephthalate (PET), this can dramatically increase the application window of these materials. On the other hand, it is also observed that incorporation of high levels of isohexides into polyesters results in a reduction of crystallinity, and in the case of isosorbide into completely amorphous polymers [12]. This is believed to be caused by the formation of stereo-irregular polymers due to the asymmetry of isosorbide. The difference in reactivity of the two hydroxyl groups in isosorbide often results in problems encountered when attempting to make high molecular weight polyesters using melt polymerization. Molecular weight build-up of amorphous polymers under melt polymerization conditions is usually achieved by using high temperatures and extended reaction times. Such drastic conditions are

detrimental to isohexide stability, frequently resulting in severe coloration and molecular weight decrease. Since polyesters containing high levels of isosorbide are in most cases amorphous, high molecular weights are required in order to attain sufficient mechanical properties. Standard industrial practice to increase molecular weight by solid state polymerization (SSP) requires the polymer to be semicrystalline, which is not the case for isosorbide polyesters. Hence application of isosorbide in high molecular weight engineering plastics has not been successful yet. Of the other two isomers, isomannide has been shown to be rather ineffective for obtaining polyesters with industrially relevant properties due to low reactivity, and hence competition from unwanted side reactions (e.g. elimination and ring-opening). In contrast, isoidide, due to its symmetry, gives stereoregular polymers, resulting in semicrystalline materials, albeit at low degrees of crystallinity [12]. Also the higher reactivity of the two exo-hydroxyl groups generally results in significantly reduced color formation. Unfortunately, due to its limited availability the available data on isoidide polyesters are scarce compared to the commercially available isosorbide. Recently the group of Muñoz-Guerra published various papers on an alternative approach to rigid biobased building blocks, using cyclic acetals of aldaric acids and alditols, which also showed highly interesting thermal properties [13–19]. An in-depth discussion of this work, however, is beyond the scope of this paper.

Despite the broad industrial and academic interest only a limited number of review papers have been published on isohexides. An older review by Stoss *et al.* [6] deals with isohexides in a broad context, which was recently updated by Rose and Palkovits [20]. Kricheldorf gave a concise overview of the use of isohexides in polycondensates [21], while more recently Fenouillot *et al.* published a convenient review of the application of isohexides in polymer chemistry during the last two decades [12].

Overall it can be concluded that isohexides, and in particular isosorbide, are unique renewable rigid diols which are capable of dramatically altering polymer properties when incorporated into step-growth polymers. Whereas the beneficial effects of the intrinsic rigidity are obvious, and of high industrial importance, various other issues, like reduced reactivity, color formation and reduced crystallinity have so far hampered (large scale) industrial implementation. Here we will discuss three different strategies to overcome these drawbacks, with the aim of unlocking the full potential of isohexides in polymer chemistry.

The first strategy is based on using isoidide instead of isosorbide. Although literature on isoidide-containing polymers is scarce due to their limited availability, several authors have shown that isoidide has several

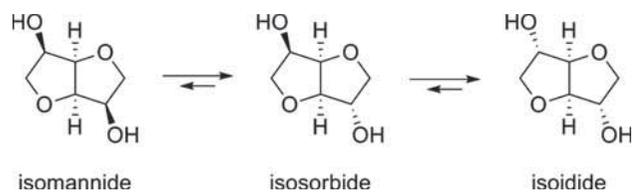


Figure 3 Catalytic epimerization of isohexides.

distinct advantages. The *exo* hydroxyl groups are more reactive than the *endo* hydroxyl groups in isosorbide and isomannide resulting in higher molecular weight polymers and significantly reduced color formation. Furthermore, because of the symmetry of isoidide, stereoregular polymers are obtained which increase the potential of crystallinity at high degrees of incorporation [22]. As mentioned previously, unfortunately isoidide is the least synthetically accessible isomer of the three isohexides. Roquette reported a multi-step procedure starting from D-glucose, via L-sorbose and L-iditol [8]. Despite its elegance, this method mainly suffers from the elaborate downstream processing required for separating L-iditol from the other hexitol isomers.

A more convenient approach is based on the catalytic epimerization of more readily available isosorbide as reported by Wright and Brandner [9,10]. These authors subjected isosorbide to high temperatures (220–240°C) and high hydrogen pressure (100 bar at RT) in the presence of a nickel catalyst to obtain a mixture of all three isohexides containing 59% isoidide, 35% isosorbide and 6% isomannide. In order to improve the industrial applicability of this reaction we have recently developed an alternative procedure using a supported ruthenium catalyst [23]. By careful optimization of the reaction conditions it was possible to reduce the initial hydrogen pressure to 40 bar at RT, while still obtaining the desired equilibrium ratio after 2 h. Furthermore it was shown that the ruthenium catalyst was significantly more active than a nickel-based reference catalyst, even at a very low catalyst loading of 360 ppm ruthenium. A large-scale reaction, performed with a 50wt% aqueous isosorbide solution (200 g isosorbide) showed that scale-up is feasible, while high purity isoidide was obtained by fractional distillation of the equilibrium mixture. Furthermore it was shown that the undesired isomers (isosorbide and isomannide) could be reused as feedstock for a subsequent epimerization reaction, making this method highly atom efficient. Using this technology it should be possible to obtain isoidide via an efficient and industrially viable route, opening up new possibilities for its application in polymer chemistry.

A second strategy for increasing the reactivity of isohexides is the substitution of the relatively

unreactive secondary hydroxyl groups at the 2- and 5-positions with more reactive ones like amines or the corresponding isocyanates. This opens up possibilities for the production of, e.g., polyamides and polyurethanes. Thiem *et al.* were the first to describe the use of these isohexidediamines in the synthesis of polyurethanes and polyamides [24,25]. Recently, the use of high purity dideoxy-diaminoisoidide in the preparation of a series of fully biobased semicrystalline polyamides was reported [26,27]. Moreover, the increasing number of patent applications published on this subject is indicative of the industrial relevance of these biobased rigid diamines [28–30]. Nevertheless, scientific literature describing the synthesis of unsubstituted dideoxy-diamino isohexides is scarce. Most of the reported routes suffer from significant drawbacks, such as low overall yields of purified diamine (<15%) [6] or the use of highly explosive azide intermediates [31,32]. Since we required resin-grade dideoxy-diaminoisohexides for polymer synthesis we developed an improved stereospecific, yet stoichiometric route to dideoxy-diaminoisoidide, giving the desired diamine in 47% isolated yield and 99.9% purity [33]. Recently, the Beller group reported the elegant, highly efficient, direct catalytic conversion of isosorbide to dideoxy-diamino isohexides using ammonia [34,35]. Although a breakthrough from a green-chemistry point of view, this procedure also has drawbacks. Whereas high conversions are reported, unfortunately no isolated yields are given, nor the composition of the mixture of three dideoxy-diamino isohexides isomers obtained. Separation and purification of these isomers, required for application in high performance polymers, is non-trivial and can have detrimental effects on isolated yields. Hence we developed a semi-catalytic route starting from either isosorbide or isomannide, by subsequent transformation into the corresponding bistosylates, nucleophilic substitution by benzylamine and finally catalytic hydrogenolysis to obtain the pure stereoisomers (Fig.4) [36]. This three-step strategy gave the desired products dideoxy-diamino isoidide and dideoxy-diamino isosorbide with absolute stereo control in >80% overall isolated yield and high purity (>99% based on NMR and GC). Preliminary results on the scale-up of these reactions to kilogram scale show that this is feasible, giving access to sufficient amounts of resin-grade monomers to allow for polymer development.

The future challenge with regard to the development of isohexide-based diamines will be in developing an efficient, sustainable catalytic route with high regio-selectivity, as well as developing efficient separation technology in order to obtain the pure regioisomers. (Note: isomeric purity is only required for

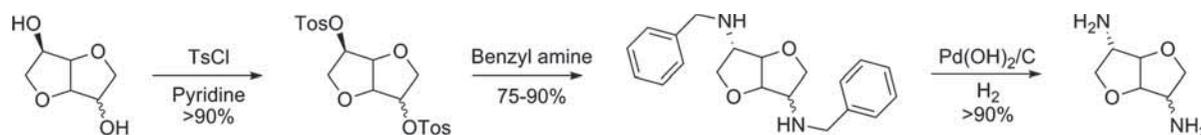


Figure 4 3-step stereospecific synthesis of dideoxy-diaminoisoidide and -isorbide.

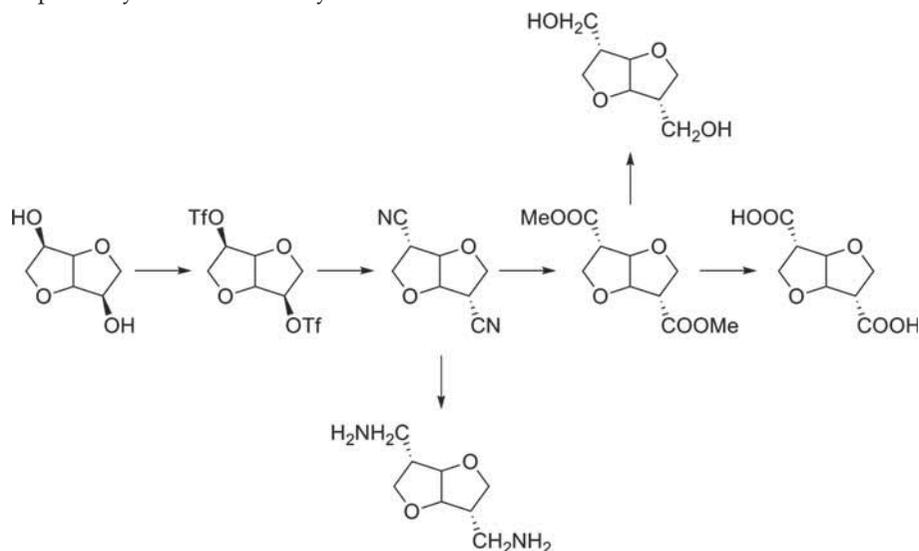


Figure 5 Synthetic route towards novel family of 2,5-(1-carbon extended)isohexides.

obtaining semicrystalline or high MW polymers, for amorphous polymers isomeric mixtures could already be effective.)

Jasinska *et al.* recently showed that high purity dideoxy-diamino isoidide can be efficiently incorporated into polyamides by a combination of bulk melt polycondensation followed by solid-state polymerization (SSP) giving colorless products with satisfactory molecular weights (>18 000 g/mol) [26]. The successful incorporation of both dideoxy-diamino isoidide and isosorbide into polyamide 4-10 and 4-13 furthermore showed that the reactivity of these monomers is sufficient to allow for high degrees of incorporation. Furthermore these authors showed that incorporation of diamino isohexides has significant effects on the type and degree of crystallinity [27]. Apart from the application of the free diamines as building blocks for polyamides, the corresponding (blocked) isocyanates are also of interest for the synthesis of biobased polyurethanes and polyureas [37]. Nevertheless, these results show that more work has to be performed on novel, mild polymerization methods in order to cope with the lower thermal stability of the diaminoisohexides compared to fully aliphatic diamines. Furthermore, more insight is required into the material properties of these polyamides and polyurethanes in application areas like coatings and fibers.

The third strategy to enhance the reactivity of isohexides is based on chain extension at C2 and C5 of

the isohexide skeleton. When isosorbide is reacted with ethylene oxide, bis(2-hydroxyethyl isosorbide) is obtained [38]. This derivative has two primary hydroxyl groups, which makes it significantly more reactive. Unfortunately, the increased distance between the functional groups and the bicyclic skeleton, as well as the flexible ether linkage, has detrimental effects on the rigidity and hence on the T_g of the polymers based on these monomers. Based on these results we concluded that chain extension should be limited to 1 carbon atom in order to retain rigidity. This hypothesis was tested by the development of a novel family of 1-carbon-extended isoidide derivatives, as reported by Wu *et al.* [39,40]. Although far from industrially viable, the synthetic route as depicted in Figure 5 allows for the stereo- and regiocontrolled synthesis of these new monomers, and hence the evaluation of the (basic) properties of the polymers based upon them. Activation of isomannide by reaction with triflic anhydride, followed by cyanation, yields the *exo-exo* configured dinitrile, which serves as a platform chemical for the synthesis of the corresponding diamine, diacid and diol.

The diacid, when incorporated into polyesters, indeed showed a significant increase in reactivity compared to the parent isohexide diols under melt polymerization conditions: polyesters with M_n 10,000 could be obtained at temperatures as low as 130°C [11]. In contrast to expectations, in the case of the isoidide

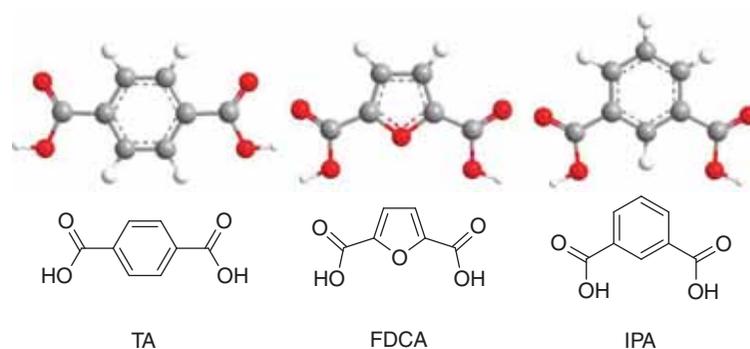


Figure 6 Structural comparison between terephthalic acid (TA), furan-2,5-dicarboxylic acid (FDCA), and isophthalic acid (IPA); top-view based on DFT calculations (B3LYP-TZV) [7].

diacid, the 1-carbon extension resulted in a significant decrease in T_g of the ensuing polyesters compared to incorporation of the parent isohexide. However, when compared to the fully flexible C6 analogue adipic acid, incorporation of isoididediacid resulted in an increase in T_g of approx. 50–70°C.

The synthesis of a series of fully isohexide-based polyesters showed that a combination of the isoididediacid with either isosorbide or isoidide resulted in low MW polyesters (M_n 2,500) with T_g 's ranging from 70–80°C [41]. When the parent isoidide was substituted by the 1-carbon extended idide diol, the T_g decreased to 45°C, yet molecular weight increased by a factor of 2, underlining the increased reactivity. Even more interesting was the observation that polyesters containing the extended idide diol were semicrystalline at even up to 100% incorporation of the isohexidediol. In the case of semiaromatic polyesters this made it possible to use solid-state polymerization (SSP) as a mild method to increase molecular weight (by a factor of 5, to M_n 30,000) [41]. When compared to the polyester of terephthalic acid and isoidide, the analogous polyester containing the extended ididediol showed a dramatic drop in T_g of approx. 100°C (209°C vs 105°C) [42,43]. However, the new polyester is a semicrystalline polymer which allowed for SSP, resulting in an increase in M_n by a (nonoptimized) factor of 3.

Given the current laborious stoichiometric synthetic route it is obvious that the 2,5-(1-carbon extended)isohexides described here are still at an academic stage of development. Nevertheless it was shown that especially in the case of the extended diol, highly interesting and industrially relevant polymer properties can be obtained. Future work in this area will need to focus on further exploration of the effects of incorporating these monomers in condensation polymers, as well as developing more sustainable, catalytic and industrially viable routes to 1-carbon extended isohexides.

3 FURAN DICARBOXYLIC ACID

Furan derivatives have been investigated as potentially renewable building blocks for polymers for over a century. Initially, thermosetting resins based on furfural or furfuryl alcohol found use in a range of applications [44]. Although currently not yet commercially available on a large scale, furan-2,5-dicarboxylic acid (2,5-FDA or FDCA; Fig.6) is probably one of the most interesting furan-based monomers (based on the properties of the monomer as well as FDCA-based polymers). In the aforementioned DOE study by Werpy *et al.* FDCA was rated as number 2 in their top 12 value-added chemicals from biomass [4]. The report states that FDCA “has a large potential as a replacement for terephthalic acid, a widely used component in various polyesters, such as PET and PBT.” Their conclusion was that: “The utility of FDCA as a PET/PBT analogue offers an important opportunity to address a high volume, high value chemical market. To achieve this opportunity, R&D to develop selective oxidation and dehydration technology will need to be carried out. However, the return on investment might have applicability of interest to an important segment of the chemical industry.” Although FDCA is advocated by various sources as the ultimate biobased alternative to terephthalic acid (TA), there are significant differences between these two molecules [7]. Although both FDCA and TA are aromatic molecules, the large differences in delocalization energy (22 kcal versus 36 kcal/mol for furan and benzene respectively) give the furan nucleus a significant diene character, which is, e.g., expressed by the Diels-Alder reactivity of furan [45,46]. Hence, the aromatic ring of FDCA can be expected to be more reactive than in TA, especially under high temperature polymerization conditions. Another relevant parameter for polymers is the angle between the carboxylic acid groups which determines the degree of

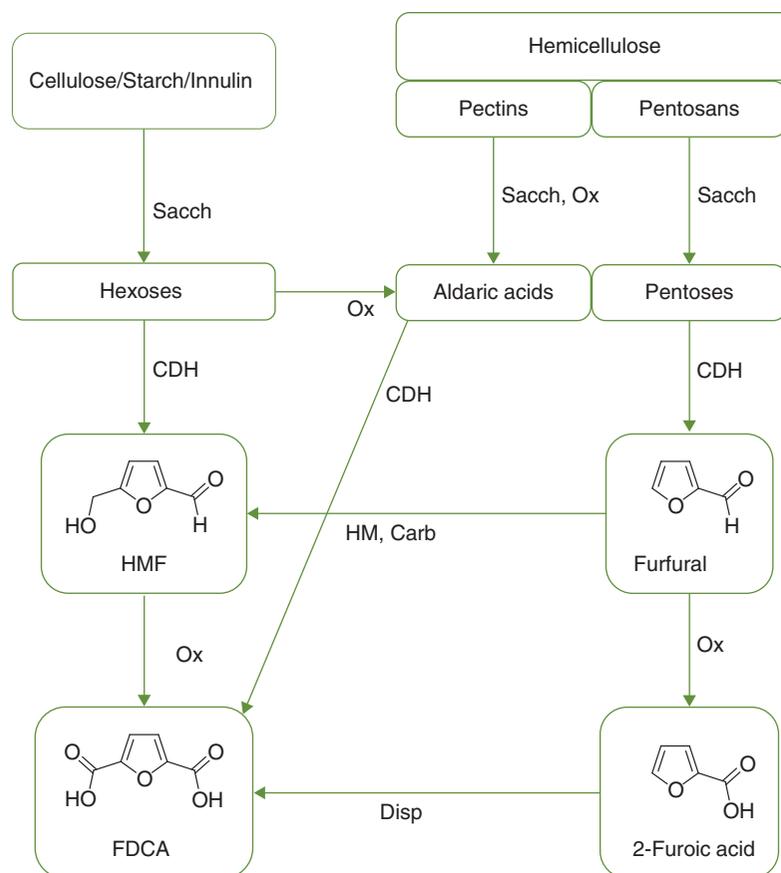


Figure 7 Schematic overview of pathways from polysaccharides to FDCA: Sacch = saccharification, CDH = cyclodehydration, Ox = oxidation, HM = hydroxymethylation, Carb = carbonylation/carboxylation, Disp = disproportionation.

linearity of the monomer. In TA this angle is 180° , giving highly linear, rigid, and often easily crystallizable polymers. In FDCA this angle is significantly smaller ranging from 129.4° (X-ray diffraction) to 133.6° (DFT) [39], and hence closer to the value of 120° found for isophthalic acid (IPA), as is illustrated in Figure 6. This difference in angles will have profound effects on, e.g., crystallization kinetics, crystal structure, and degree of crystallinity [47–49].

FDCA can be obtained from two major classes of biobased feedstocks; i.e. C5 sugar based and C6 sugar based (Fig. 7) [50]. C5 sugars (pentoses) are obtained from hemicellulose containing agricultural residues such as corn cobs, oat hulls, or bagasse, giving furfural (furan-2-carbaldehyde) as primary intermediate. Hydroxymethylation or carbonylation can be used to introduce a carbon functionality at the 5-position [51]. Subsequent oxidation will yield FDCA. Another approach is based on the Henkel reaction which involves a disproportionation of salts of 2-furoic acid [52–54].

C6 sugars (hexoses), mainly D-glucose and D-fructose, are readily available by hydrolysis of polysaccharides such as starch, cellulose or

inulin respectively, and can be directly transformed into 5-hydroxymethylfurfural (HMF) by cyclodehydration (Fig. 7) [55–57]. Oxidation of HMF in turn will yield FDCA. In spite of its versatility as a platform molecule, HMF is currently not produced on an industrial scale, although various companies have announced plans for short term commercial production of FDCA, which are thought to involve HMF (and derivatives) as intermediate. Another C6 sugar route is based on the use of aldaric acids, which can be converted to FDCA by cyclodehydration [58]. Aldaric acids can be obtained by oxidation of hexoses or alduronic acids (a major constituent of pectins).

Despite increasing efforts, both from academia and industry, in the development of synthetic routes towards FDCA, several challenges remain. Production of HMF, either directly from D-glucose, or via D-fructose is a major topic in biobased chemistry. Whereas the production of crude HMF does not pose a problem with regard to conversion of the starting hexoses, selectivity towards HMF and efficient down-stream processing are still lacking. The formation of unwanted by-products like levulinic acid (in the presence of water) and humins (resulting

from acid catalysis) especially decrease selectivity and can result in high DSP costs in order to purify the HMF for the consecutive oxidation step. Increasing selectivity by using environmentally disputed catalysts like chromium or the use of expensive solvents like ionic liquids also pose a challenge to DSP and, although highly interesting from a scientific point of view, are not likely to become part of an eventual large scale industrial process [59]. Another approach is taken by the Avantium company whose current pilot scale process involves the preparation of more stable HMF ethers (e.g. methoxymethylfurfural), which are subsequently oxidized to FDCA [60–63].

The pectin-based route currently suffers from two distinct drawbacks; i.e. the relatively low yield of the cyclodehydration step [58], and the lower feedstock availability of pectins versus glucose/fructose polysaccharides. The first issue is the subject of ongoing investigations, while the second could eventually be overcome by developments in the conversion of hexoses to aldaric acids. A major benefit of the pectin route is that it allows for the synthesis of high purity FDCA, which is essential for polymer synthesis [64]. The alternative hemicellulose route via already industrially produced furfural also faces several challenges. While furfural is already commercially produced on an industrial scale, the selectivities and yields of the processes require significant improvements in order to reduce costs [65]. Furthermore, reports on the catalytic functionalization of the 5-position of furfural (or 2-furoic acid) have so far been very scarce in both scientific and patent literature. Another largely overlooked route based on a Henkel type disproportionation reaction is an interesting alternative given the coproduction of FDCA and furan [52–54].

A general challenge for routes towards FDCA is the required purity of the monomer. Resin grade FDCA (>99.9% purity) should have a quality comparable to purified terephthalic acid (PTA) if high molecular weight polymers, such as polyesters, are the main application areas. Alternatively, the first large scale industrial application of FDCA could be in markets where purity is less restrictive, such as unsaturated polyester resins and plasticizers [66–68]. Therefore it is difficult to “pick a winner” amongst all the different routes currently pursued.

With regard to potential applications of FDCA, polymers and especially thermoplastic polyesters are the major focus. Whereas reports on polyesters containing FDCA date back to the late 1940s and 1950s, with the first scientific paper by Hachihama *et al.* [69] in 1958, very little, if any, polymer properties were reported that are relevant to evaluating their commercial potential. Also, the prolific work by the groups of Moore [58] and Gandini [70] in the 70s

and 80s mainly focused on polymer preparation. The recently increased interest in FDCA has, however, led to a small surge in reports on improved polyester synthesis as well as property analyses.

Gandini and coworkers reported on the synthesis and molecular and thermal analysis of poly(ethylene furan-2,5-dicarboxylate), or PEF, as well as the 1,3-propanediol analogue PPF [47,71,72], while Grosshardt *et al.* reported on FDCA polyesters based on long chain diols, including their mechanical properties [73]. Also, recently Ma *et al.* investigated copolymers of FDCA with ethylene glycol and 1,4-butanediol. Unfortunately, no mechanical analysis of the various block co-polyesters was performed [74]. Jiang *et al.* reported the direct esterification of FDCA with a range of diols from ethylene glycol up to 1,8-octanediol [75]. The polymers obtained by the latter authors were brown to yellow products, depending on the maximum polymerization temperature. When compared to other literature reports the reported molecular weight (M_n) value of 105,000 for PEF appears to be overestimated, especially since only direct melt polymerization of the free diacid was performed. A very recent paper by Ma *et al.* describes the synthesis of poly(butylene 2,5-furandicarboxylate) (PBF), including a detailed DSC and XRD study into its crystallization behavior [76]. Unfortunately also in this case no mechanical data are given. Gruter *et al.* evaluated different types of catalysts for the polycondensation of FDCA or its dimethyl ester with ethylene glycol and 1,4-butanediol. They concluded that the dimethyl ester of FDCA allows for higher reaction rates and improved color [63]. In addition, a patent by the same authors describes the synthesis of high molecular weight PEF by solid-state polymerization (SSP) [77]. Also, recently Dam *et al.* reported some application properties of PEF, such as gas barrier properties and mechanical properties after recycling [78]. Gas barrier properties of PEF appear to be superior to those of PET: 2 times better for water, >2 times better for CO_2 , and >6 times better for O_2 . According to these authors this may allow for new packaging applications that are currently unattainable for PET, such as for beer, wine, vegetable oils, etc. De Jong *et al.* also reported the use of SSP to increase the MW of PEF and PPF [79]. Their study included more industrially relevant issues like recyclability, gas permeability and bulk density. As one of the latest additions to the state of FDCA polyester reports, Knoop *et al.* reported on the bench scale synthesis of PEF, PPF, and PBF by consecutive melt polymerization and solid-state polymerization [64]. Both crystallization behavior and mechanical properties are reported for high MW PEF (M_n 83,000) obtained via SSP.

So far, academic as well as industrial research has shown that FDCA-based polyesters have interesting

properties, and are in many ways comparable to terephthalic-acid-based polyesters. Nevertheless, despite the growing knowledge base on FDCA polyester (i.e. PEF) properties, there is still a considerable need for more insight into properties and behavior in order to identify potential areas of application, such as packaging, fibers, coatings, etc. Furthermore, industrial processing of FDCA polyesters by, e.g., extrusion, injection molding, fiber spinning etc., will need to be developed in order to become viable production processes for polyester products. Last but not least, the transition from a petrochemical-based material to a biobased material should not only be economically feasible, but also ecologically sustainable. In this respect, a recent paper by Eerhart *et al.* on the energy and greenhouse gas (GHG) balance of the production of polyethylene furanoate (PEF) shows that in principal PEF can be produced sustainably [80].

In contrast to the steadily increasing stream of papers and patents on FDCA in polyesters, reports on the application of this building block in polyamides are scarce. In the 1960s–70s several papers described aliphatic and alicyclic polyamides based on FDCA [81,83]. Whereas melt polycondensation of the alkyl-diammonium salts gave unsatisfactory results due to significant decarboxylation, interfacial polycondensation appeared effective [82]. More than a decade later, Gandini and coworkers published various papers on aramid-type FDCA polyamides as well as all-furanic polyamides [84–86]. These authors concluded that the former type of polymers had higher molecular weights and better thermal stability than the latter [84]. The FDCA aramid analogue (i.e. the polyamide with 1,4-phenylenediamine) displayed lyotropic liquid-crystalline behavior, which could allow for solution spinning (comparable to commercial aramid processes) [84,86]. Since then only Grosshardt *et al.* have reported on FDCA polyamides [73]. Melt polymerization with aliphatic diamines (C6–C12) gave only low to moderate molecular weight polyamides. In contrast to previous reports [81,82], all polyamides were completely amorphous. Given the increasing interest in industrial high strength fibers (e.g. aramids, ultra-high-molecular-weight polyethylene), it is also more than likely that in the area of polyamide research FDCA will become a topic of interest once again in the near future.

4 CONCLUSION

Overall it can be concluded that, if the aforementioned challenges and hurdles are successfully addressed, polymers based on rigid renewable building blocks like isohexides and FDCA have a bright future.

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