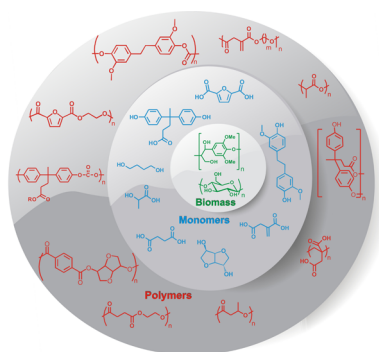


Alternative Monomers Based on Lignocellulose and Their Use for Polymer Production

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1. INTRODUCTION

Polymeric materials play a key role in modern industry. Owing to outstanding and very versatile properties of polymers, they have rather quickly occupied the great niche of commodities. World plastic production is continuously growing from 1.7 Mton/year in 1950 to 288 Mton/year in 2012. Fossil sources are still required for production of the major part of polymers, as only 5% of chemicals are currently produced from renewable feedstocks.¹ Nevertheless, the application of natural chemicals as feedstocks for the manufacture of polymers is steadily increasing. Different motivations induce such a high interest toward new biobased materials. First of all, the global depletion of petroleum resources and their uneven spread over the world stimulate the rational use of biomass as a renewable and ubiquitous resource. Additionally, overwhelming of dumps with nondegradable plastics causes serious ecological problems, stimulating the developments toward new biodegradable materials. Here we have to point at the distinction between the terms “biobased” and “biodegradable”. Biobased products are manufactured from renewable sources, but several examples of biobased and nonbiodegradable products, e.g., biopolyethylene, biopolyamide 11,² exist. It should be noted that each new material has to be tested for biodegradability before it can be claimed to be so. For example, linear polymers produced from itaconic acid are biodegradable, but cross-linking of the polymer chains slows down the biodegradation.³

This review focuses on the transformation of lignocellulose-derived platform chemicals into alternative monomers and their use as building blocks for novel polymeric materials. Taking into account the great diversity of biomass consisting of polysaccharides, aromatic compounds, triglycerides, proteins, etc., a great number of alternative monomers and novel polymers are potentially accessible. Herein we focus mainly on lignocellulose as feedstock, a natural material annually produced in significant amounts. The worldwide biomass production by land plants was estimated to be $(170\text{--}200) \times 10^9$ tons/year with ca. 70% representing plant cell walls.⁴ Lignocellulose does not compete with the food industry and is readily available as a part of various waste streams of, e.g., agriculture, forestry, and the paper industry. Therefore, lignocellulose is likely to be the main renewable source of carbon to substitute hydrocarbons in the future.

Lignocellulose itself is a composite of three polymers comprehending cellulose, hemicelluloses, and lignin. Cellulose and hemicelluloses are polysaccharides consisting of hexoses and pentoses, and lignin is a branched polymer of aromatic alcohols. Cellulose, hemicelluloses, and lignin dramatically differ in composition and/or reactivity. Therefore, a fractionation of lignocellulose before further processing is required. Efficient fractionation poses a challenge due to the very strong mutual interactions of the constituents forming the lignocellulosic composite. In general, fractionation considers successive selective solubilization of hemicelluloses and lignin leaving cellulose as solid residue. Fractionation processes often rely on a chemical treatment of lignocellulose sometimes associated with physical impact. Several reviews appeared covering potential fractionation processes comprehensively.^{5–9} Upon depolymerization and further transformation of cellulose, hemicellulose, and lignin, biomass-based platform chemicals become available offering the opportunity for tailored transformations toward promising alternative monomers for polymer production.¹⁰ Consequently, the workflow for a

production of novel polymers based on lignocellulose comprehends (1) the fractionation of lignocellulose into cellulose, hemicellulose, and lignin followed by (2) depolymerization into carbohydrates and aromatic monomers, (3) subsequent catalytic or thermal transformations into platform chemicals, (4) their further conversion to the desired alternative monomers, and (5) the final polymerization of these monomers. Just as for fractionation, several recent reviews discuss the depolymerization of lignocellulose and the synthesis of platform chemicals.^{11–14} This review focuses on the two latter steps discussing the most important alternative monomers accessible based on lignocellulose and their integration into potential polymers (Figure 1). It should be noted that this review does not consider the following aspects of polymer production:

- Drop-in technologies converting biomass into conventional monomers that can be directly used for well-established processes of polymer production, i.e., polyesters of terephthalic acid produced based on petrochemical terephthalic acid and biomass-based diols. In general, the properties of these polymers are well-known and do not depend on the source of the carbon feedstock.¹⁵
- Naturally synthesized modified biopolymers, specifically modified starches, which currently have a great share in the market of biopolymers. Comprehensive reviews on their properties can be found elsewhere.^{11,15–19}
- Thermochemical processes that degrade biomass to nonfunctional chemicals (i.e., syngas)^{11,20} prior to construction of polymers are omitted from this review, as they can be described in terms of conventional thermochemistry.
- Copolymers and blends as materials with improved properties are not in the focus of this review. Instead, this review covers homopolymers.¹⁵

Although we do not discuss here the aforementioned points, these directions of development receive great attention and exhibit commercial importance.

The transformation of lignocellulose into polymers is significantly hampered by its rigid structure. Theoretically, lignocellulose is a low-cost resource of monosaccharides and phenolic compounds. Practically, pretreatment and fractionation of lignocellulose, as well as depolymerization and downstream processes, still pose challenges. Nevertheless, intensive research in this area has already led to several new approaches toward a rational use of lignocellulose. A number of companies have announced the production of bulk chemicals based on lignocellulosic feedstocks. The great majority of commercially produced biobased polymers are currently utilizing hydrolyzed starch or molasses as source of glucose. We believe that advances in processing of lignocellulose will help in switching to this sustainable raw material in the near future.

The review consists of two main parts. Section 2 considers the syntheses of lignocellulose-based monomers starting from selected platform chemicals. Section 3 discusses the syntheses and properties of polymers produced from the discussed alternative monomers. The review includes wherever possible information on the production volumes of the chemicals manufactured on an industrial scale, based on press releases of the manufacturers and available academic literature. It is difficult to estimate the accuracy of these figures due to several reasons. First of all, the production volumes change during the time and a number of productions are planned to be started or enlarged in the near future. Additionally, companies often

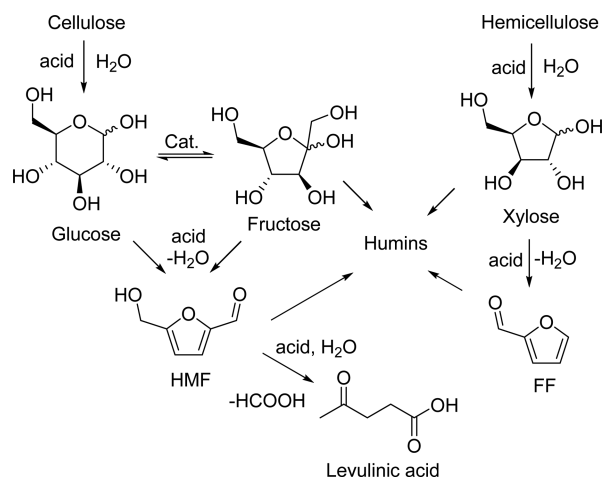
provide information in terms of the maximal capacity of a process but not the real current production volume of a product. Therefore, the given production volumes should be considered as estimations given to evaluate the order of magnitude of the products and to compare the market share of different monomers and polymeric materials.

2. MONOMERS BASED ON CELLULOSE, HEMICELLULOSE, AND LIGNIN

2.1. Furan-Based Monomers

The platform chemicals 5-hydroxymethylfurfural (HMF) and furfural (FF) present the starting point for the synthesis of furan-based monomers. Comprehensive information on their production and further chemical transformation is available in recent reviews.^{21,22} In short, the production of HMF and FF relies on an acid-catalyzed hydrolysis of cellulose and hemicellulose to the corresponding carbohydrate monomers glucose and xylose. Subsequent treatment of glucose and xylose under acidic conditions leads to their respective dehydration products HMF and FF (Scheme 1).

Scheme 1. Routes to HMF and Furfural (FF) from Cellulose and Hemicellulose



The synthesis of HMF and FF from carbohydrates has been known for a long time. Due to a relatively easy preparation by distillation, FF was already produced commercially in 1923.²³ For example, Durite Plastics Inc. started the manufacture of phenol–furfural resins for robust shaped plastic materials.²⁴ In 1949 du Pont started the production of adiponitrile via a multistep process starting from FF. Furan-based resins are also employed as binders in the foundry industry (furan–urea resins) and furfural/furfuryl alcohol modified phenolic resins are used as binders in the refractory and carbon industry. The current world production of FF is estimated at ca. 250 000 tons/year, demonstrating its importance. HMF production, in contrast, is much more problematic due to further transformation to levulinic acid and formic acid via a rehydration reaction.²⁵ This can be largely avoided by switching to nonaqueous solvents; however, since biomass fractionation processes mostly employ water, a large energy penalty has to be paid for the removal of water. These problems aside, HMF has received considerable attention as its oxidation product 2,5-furandicarboxylic acid (FDCA) constitutes a suitable replacement for terephthalic acid (TPA) and isophthalic acid.²⁶ The

market for TPA exceeds 50 000 ktons/year, demonstrating the large potential for the replacement by biomass-based HMF. TPA is mostly used in the large-scale synthesis of polyesters (e.g., poly(ethylene terephthalate) (PET)) and polyamides (e.g., poly(phthalamides), aramids), which are used in textiles and beverage containers. In theory the use of FDCA as a substitute for TPA together with biomass-based ethylene glycol allows the preparation of completely renewable polyesters, leading to a significant reduction of greenhouse gas emissions.²⁷ Other potential applications of FDCA include its use in the manufacture of polyureas²⁸ and polyester polyols.²⁹ As a result, new and improved routes as well as scale-up of processes for the production of HMF are actively being researched. In 2013, AVA Biochem BSL AG started the first industrial HMF production facility with a small capacity of 20 tons/year. Furthermore, Avantium is currently building a pilot plant for the production of FDCA with a capacity of 50 000 tons/year which is to come on stream in the coming years.

Besides this application, furanic monomers possess a large potential for the replacement of various fossil-based monomers. HMF and FF are furan-based molecules that contain formyl and/or hydroxymethyl groups. Via both catalytic and synthetic organic pathways these can be converted to a variety of different functional groups that are suitable for polymerization reactions (Scheme 2).³⁰ Excellent reviews on the large diversity of furanic monomers and their application in polymer chemistry have been published before by Gandini et al.^{31,32} Therein, the syntheses of monomers are only briefly discussed. Closer examination reveals that in many cases wasteful synthetic organic transformations using stoichiometric reagents were employed. However, the large scale preparation of biomass-based polymers imposes stringent demands on the routes of monomer preparation. These routes are preferably catalyzed by cheap catalysts using atom-efficient transformations with low waste production to enable low-cost products and environmentally friendly processes. In addition, it is particularly desirable to develop routes toward monomers that are currently employed, thus avoiding reoptimization of polymer preparation. Nevertheless, the unique chemical and structural properties of novel monomers may provide access to novel polymers with improved properties.

Catalytic oxidation, reduction,³³ and amination reactions provide access to a number of different furan-based monomers (Scheme 2). For example, catalytic reduction and hydrogenolysis of FF and HMF can give rise to a variety of cyclic and open chain diols suitable for use in polyesters. Reductive amination offers opportunities for the preparation of diamines, which are suitable for use in polyamides. Furthermore, FF also possesses a large potential for the preparation of bifunctional monomers via dimerization reactions. Therefore, the focus of this section will be mainly on the catalytic routes toward HMF and FF derived monomers.³⁴ In what follows, an overview concerning the more recent developments of the preparation and utilization of furan-based monomers will be discussed.

2.1.1. Oxidation of 5-Hydroxymethylfurfural. Owing to the great potential of FDCA, its preparation via the oxidation of HMF (and derivatives) has received considerable attention in recent years. To date a large number of catalyst systems and methods have been developed. The oxidation reaction of HMF to FDCA is in fact a series of oxidation steps, which depending on nature of the catalyst can follow a different course (Scheme 3). For example, initial oxidation of the aldehyde function yields 5-hydroxymethylfuran-2-carboxylic acid (HMFCa), whereas

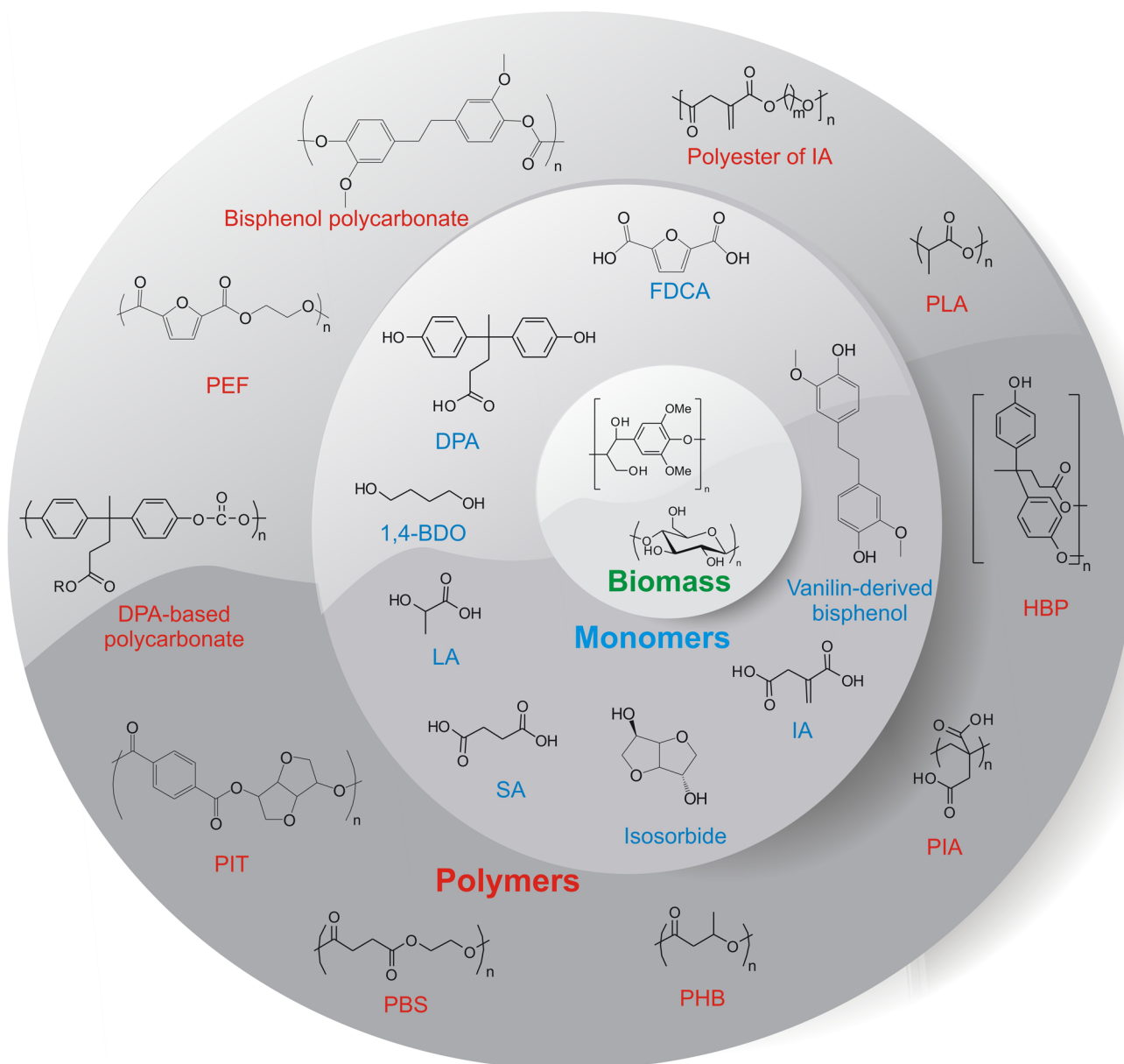
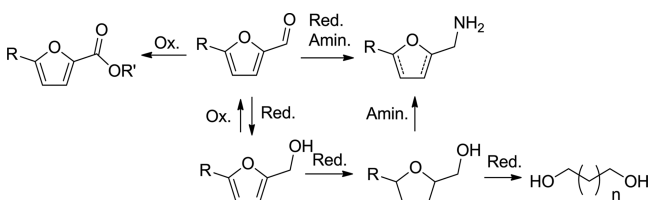


Figure 1. Production of biobased polymers. Abbreviations for the monomers: LA (lactic acid), IA (itaconic acid), SA (succinic acid), 1,4-BDO (1,4-butanediol), DPA (diphenolic acid), and FDCA (2,5-furandicarboxylic acid). Abbreviations for the polymers: PLA (poly(lactic acid)), HBP (hyperbranched polymer), PIA (poly(itaconic acid)), PHB (poly(3-hydroxybutyrate)), PBS (poly(butylene succinate)), PIT (poly(isosorbide terephthalate)), and PEF (poly(ethylene 2,5-furandicarboxylate)).

Scheme 2. Overview of Catalytic Functional Group Transformations of HMF/Furfural (FF) Leading to Polymer Intermediates

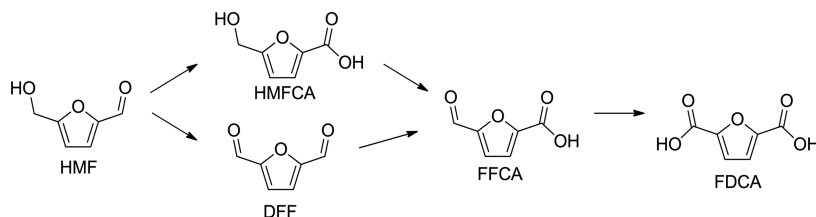


initial oxidation of the alcohol results in 2,5-diformylfuran (DFF). Further oxidation of these products will first result in 5-formylfuran-2-carboxylic acid (FFCA) and ultimately 2,5-furandicarboxylic acid (FDCA).

The reaction can be performed using homogeneous metal salts, using enzymes, using supported metal catalysts, and electrochemically. In what follows, a brief summary of the metal-catalyzed approaches will be given.

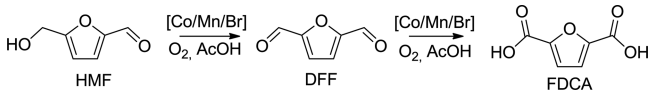
2.1.1.1. The Amoco Mid-Century Process. The oxidation of HMF to FDCA bears a similarity with the oxidation of xylenes to phthalic acids. These are commercially produced via the Amoco Mid-Century process, which employs a homogeneous catalyst system comprised of a mixture of Co/Mn/Br salts in acetic acid.³⁵ Applied to HMF, the selective preparation of DFF or FDCA is possible depending on the employed conditions (Scheme 4).

Using Co/Mn/Br/Zr, Partenheimer et al. reported a yield of 61% FDCA, after 3 h at 125 °C under 70 bar O₂. High purity FDCA precipitates from the reaction after cooling, leaving the catalyst in solution.^{36,37} Sanborn disclosed the use of Co/Mn/

Scheme 3. Oxidation of HMF to 2,5-Furandicarboxylic Acid (FDCA)^a

^aIntermediates: 5-hydroxymethylfuran-2-carboxylic acid (HMFCFA), 2,5-diformylfuran (DFF), and 5-formylfuran-2-carboxylic acid (FFCA).

Scheme 4. Oxidation of HMF into 2,5-furandicarboxylic acid (FDCA) via Amoco Mid-Century Process

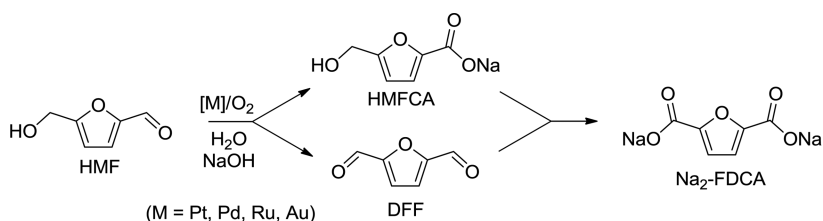


Br and Co/Ce/Br catalysts under similar conditions for the preparation of FDCA, and yields up to 56% were reported.³⁸ Saha et al. proposed a Co/Zn/Br catalyst with addition of trifluoroacetic acid to improve the reaction. After 3 h at 90 °C under 10 bar O₂, a yield of 60% FDCA was obtained.³⁹ Recent patent applications by Archer Daniels Midland Co.^{40,41} and Eastman Chemical Co.^{42,43} reveal that the preparation of FDCA via the Amoco process can be significantly improved by optimization of reaction conditions. Yields up to 89% were reported, constituting a significant improvement over earlier reports. Although the Amoco process utilizes relatively cheap metals and enables high productivity and facile product separation, the inherent instability of HMF under acidic conditions limits efficient conversion. Besides this, the radical autoxidation can lead to overoxidation to CO₂ and the use of organic solvents together with O₂ gas introduces the risk of a runaway reaction with extreme consequences. Hence, the development of a selective atom-efficient process which is performed in water using recoverable catalysts is preferred.⁴⁴ In this respect supported metal catalysts based on noble metals such as Pt, Au, Pd, and Ru have been studied most extensively.

2.1.1.2. Noble Metal Catalyzed Oxidation. Alternatively, noble metals can be applied as catalysts for the aerobic aqueous oxidation of HMF (Scheme 5). Leupold et al. disclosed the oxidation of aqueous HMF using Pt/C. The pH of the reaction mixture was kept at 7 by the addition of aqueous NaOH, and a yield of 98% of the disodium salt of FDCA (Na₂-FDCA) was reported.⁴⁵ Using Pt/Al₂O₃ leads to similar results.^{46,47} Lilga et al. studied the use of Pt/ZrO₂ in a continuous setup using feeds with different pHs and noticed decreased reaction rates and altered product selectivity when going to more acidic conditions.⁴⁸ Niu et al. proposed the use of reduced graphene oxide as support, and a yield of 85% was obtained at room

temperature and atmospheric pressure.⁴⁹ Siankevich et al. prepared unsupported, stabilized Pt nanoparticles, and over 95% yield was obtained after 24 h at 80 °C under 1 bar O₂.⁵⁰ Thus, it is clear that Pt alone is a suitable catalyst for this transformation. Studies by Gaset et al. and Ait Rass et al. also show that the addition of dopants such as Pb and Bi can enhance the reaction rate.^{51–54} A report by Kröger et al. using a Pt–Bi/C catalyst demonstrated the feasibility of performing the dehydration of fructose to HMF and subsequent oxidation to FDCA in a one-pot reaction. Nevertheless, only a moderate yield of 25% FDCA was obtained based on fructose.⁵⁵ The mechanisms of the Pt and Au catalyzed reactions were studied by Davis et al.^{56,57} By using ¹⁸O-labeled water and O₂, it was shown that the catalyst performs mainly dehydrogenation of the alcohol function and that the incorporated oxygen originates from water. Kinetic studies on the Au-catalyzed oxidation of HMF to FDCA revealed that HMFCFA is more readily obtained as an intermediate oxidation product, suggesting that oxidation of the carbonyl function is easier. However, in the case of ruthenium- and platinum-catalyzed reactions, both DFF and HMCA were present as intermediates, often in comparable amounts. This shows that the type of metal used as catalyst can have a large influence on the selectivity of the oxidation reaction.

As for the Pt-catalyzed reaction described above, the aqueous Au-catalyzed reaction is invariably conducted in the presence of (over)stoichiometric amounts of base. Several groups have studied the influence of reaction parameters such as temperature, pressure, and catalyst support (e.g., TiO₂, CeO₂, Ce/Bi/O, HT (hydrotalcite), MgO, etc.).^{58–64} Good to excellent yields of the metal salts of Na₂/K₂/Mg-FDCA (often denoted as FDCA) are achieved in nearly all cases. Dumesic et al. studied the conversion of glucose to HMF and subsequent oxidation to FDCA as a two-step cascade process. First, glucose was converted into HMF over a combination of solid Lewis and solid Brønsted acids. Thereafter HMF was recovered by extraction or evaporation of solvent and oxidized to FDCA with yields of 35–50% related to glucose.⁶⁵ The same principle was also demonstrated for fructose by Yi et al., who used Au/HT in combination with Na₂CO₃ as base.⁶⁶ A comparison of

Scheme 5. Noble Metal Catalyzed Aerobic Aqueous Oxidation of HMF To Produce the Disodium Salt of 2,5-Furandicarboxylic Acid (Na₂-FDCA)

the activities of supported Pt, Pd, and Au catalysts by Davis et al. showed that Au catalysts are typically more active than Pt and Pd. However, unlike Pt and Pd, further conversion of the intermediate HMFCFA does not occur readily using stoichiometric amounts of base.⁶⁷ Interestingly, several studies show that bimetallic Au/Pd catalysts exhibit enhanced activities and stability as compared to their monometallic counterparts.^{68–70} In fact, it has also been demonstrated that HMF can be converted to FDCA under neutral conditions using Au–Pd/CNT, albeit highly diluted solutions of the substrate were used.⁷¹ A positive effect of alloying Au with Cu has also been observed.⁷² However, it appears that this effect is dependent on the used support.⁷³

Pd-based catalysts have also been applied for the aqueous aerobic conversion of HMF to FDCA. Siyo et al. immobilized PVP-stabilized Pd nanoparticles onto various oxidic supports. The highest FDCA yield (>90%) was obtained for the ZrO₂ and La₂O₃ supported catalysts.⁷⁴ Studies by Lui et al.⁷⁵ and Zhang et al.⁷⁶ demonstrated the use of Pd supported on magnetic Fe₃O₄ and γ -Fe₂O₃ phases. In addition, the reaction can be catalyzed by a suspension of PVP-stabilized Pd nanoparticles leading to 90% FDCA yield.⁷⁷

Studies by Riisager et al. on CeO₂- and TiO₂-supported Ru(OH)_x showed that the reaction can also be conducted under base-free conditions, leading to 60% FDCA after 18 h at 140 °C.⁷⁸ Basic oxidic supports (e.g., HT, MgO, MgAl₂O₄) were tested, and in the case of MgAl₂O₄ only minor leaching of the support occurred.⁷⁹ The reaction was also studied in ionic liquids under base-free conditions. However, only a maximum yield of 48% FDCA could be obtained using Ru(OH)_x/La₂O₃.⁸⁰ Both the oxidation and hydrogenolysis of HMF were explored using 2 wt % Ru–K–OMS-2 (manganese oxide octahedral molecular sieves). High FDCA yields of 93.4 and 66 mol % were achieved in alkaline and base-free conditions, respectively.⁸¹

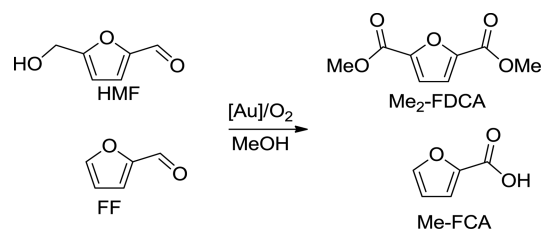
2.1.1.3. Base Metal Catalyzed Oxidation. Besides noble metal catalysts only a few reports have appeared that deal with the use of base metals. A polymeric Fe(III)/porphyrin catalyst was reported by Saha et al.⁸² The reaction was conducted at high dilution in water at 100 °C using 4–10 bar air and resulting in a maximum yield of 79% FDCA. The authors propose that the reaction proceeds via a radical reaction mechanism. A similar study deals with the use of Co(II)-*meso*-tetra(4-pyridyl)-porphyrin anchored to a Merrifield resin. A screening of oxidants showed that ^tBuOOH was most active and after 24 h at 100 °C an FDCA yield of 90.4% could be achieved.⁸³ Co(acac)₂ on silica was used for the dehydration of fructose and in situ oxidation to FDCA. A yield of 72% was reported based on fructose.⁸⁴ CoO supported on magnetic Fe₃O₄ was also tested in a one-pot, two-step protocol involving fructose dehydration by Fe₃O₄–SiO₂–SO₃H in DMSO (dimethyl sulfoxide) followed by oxidation. A maximum yield of 60% FDCA was obtained using ^tBuOOH as oxidant.⁸⁵

In spite of the significant advancements in activity and stability of supported metal catalysts, all of the aforementioned protocols suffer from serious drawbacks, which render potential processes uneconomical. Particularly the use of bases as cocatalysts for noble metals, which after neutralization lead to the formation of stoichiometric amounts of salts, is a serious problem. Protocols that achieve full conversion under neutral aqueous aerobic conditions are typically performed at very high dilution. This introduces a costly water separation step. Thus, ideally the reaction is carried out at high HMF concentrations

so that after the reaction mixture is cooled down high purity product precipitates, leaving the catalyst solution ready for recycle.⁸⁶

Contrary to the aqueous reactions, performing the reaction in methanolic solution negates the need for bases and the dimethyl ester of FDCA (Me₂-FDCA) is obtained directly (Scheme 6). Christensen et al. and Corma et al. have reported

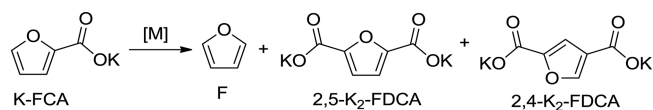
Scheme 6. Conversion of HMF and Furfural (FF) to the Dimethyl Ester of 2,5-Furandicarboxylic Acid (Me₂-FDCA) and the Methyl Ester of 2-Furancarboxylic Acid (Me-FCA) Respectively in Methanol Solution



the efficient conversion of HMF in methanol over supported Au catalysts.^{87,88} In a similar fashion FF has been converted to its ester (Me-FCA).^{89–92}

2.1.1.4. Henkel Reaction. Besides the oxidation of HMF, FDCA can also be produced from FCA via the Henkel reaction (Scheme 7).

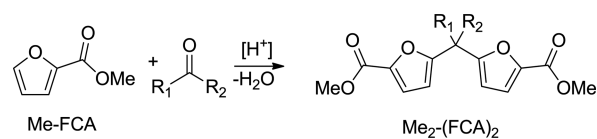
Scheme 7. Henkel Reaction of the Potassium Salt of 2-Furancarboxylic Acid (K-FCA) To Produce the Dipotassium Salt of 2,5-Furandicarboxylic Acid (2,5-K₂-FDCA) with Furan (F) and Dipotassium Salt of 2,4-Furandicarboxylic Acid (2,4-K₂-FDCA) as Side Products



In this reaction the potassium salt of FCA (K-FCA) is heated to above 250 °C in the presence of a Lewis acid catalyst (e.g., ZnCl₂) to enable a disproportionation of the carboxylate group. A mixture containing furan (F) and 2,5- and 2,4-K₂-FDCA is obtained with a high proportion of the 2,5-isomer.^{93,94}

2.1.1.5. Dimerization of 2-Furancarboxylic Acid. Next to FDCA, the methyl ester of FCA also possesses significant potential for use as a monomer in polyesters. It is known from the literature that Me-FCA can be dimerized via a condensation with aldehydes and ketones (Scheme 8). The resulting dimers bear a structural similarity with the bisphenol series and as such introduce novel properties to polyesters. The dimerization reaction is performed in concentrated H₂SO₄ at 0 °C and in the case of formaldehyde (R₁, R₂ = H) and acetaldehyde (R₁ =

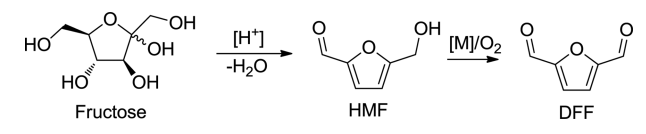
Scheme 8. Condensation of the Methyl Ester of 2-Furancarboxylic Acid (Me-FCA) with a Carbonyl Compound



H, $R_2 = \text{CH}_3$) good yields (80–84%) of the diesters are obtained.⁹⁵ For the dimerization with acetone ($R_1, R_2 = \text{CH}_3$), the temperature is increased to 60 °C and a moderate yield of 65% is obtained.⁹⁶

2.1.1.6. Selective Oxidation to 2,5-Diformylfuran. Besides the complete oxidation of HMF to FDCA, the selective oxidation of HMF to 2,5-diformylfuran (DFF) has also been extensively studied (Scheme 9). In addition, it is more soluble

Scheme 9. Dehydration of Fructose and Selective Oxidation of HMF to 2,5-Diformylfuran (DFF)



in organic media, thus facilitating the use of biphasic systems in which the dehydration of carbohydrates to HMF can be coupled via extraction to oxidation in organic media. As a result, many studies also focus on the one-pot conversion of carbohydrates to DFF.

A study by Nie et al. showed that of the noble metal catalysts particularly Ru exhibits the best selectivity for the dehydrogenation of the alcohol function of HMF. Using Ru/C in toluene, selectivities up to 96% are obtained at 110 °C under 20 bar O_2 . A comparison of supports showed that Ru/C exhibited better activities and selectivities than the respective oxide supported catalysts (e.g., Al_2O_3 , ZSM-5, TiO_2 , ZrO_2 , CeO_2 , MgO , and Mg_2AlO_x).⁹⁷ Nevertheless, a selectivity as high as 97% could also be demonstrated for Ru/ γ - Al_2O_3 in toluene at 130 °C under much lower O_2 pressure.⁹⁸ The reaction can also be performed in methyl isobutyl ketone (MIBK) and methyl *tert*-butyl ether (MTBE) (i.e., solvents used for the extraction of HMF from aqueous solution). Wang et al. proposed a trimetallic (Ru/Co/Ce) mixed oxide catalyst. After 12 h at 120 °C in MIBK, a yield of 82.6% DFF was obtained at 96.5% HMF conversion.⁹⁹ Under similar conditions, using Ru on silica spheres in MIBK, a DFF yield of 94% was obtained.¹⁰⁰

Using a novel Ru/CTF (CTF, covalent triazine framework) catalyst, Artz et al. studied the conversion of HMF to DFF in MTBE.¹⁰¹ After 3 h at 80 °C under 20 bar air, HMF was fully converted. The liquid phase contained only DFF; however, the yield did not exceed 75%. It was proposed that the missing DFF remained adsorbed on the porous network.

A common strategy to facilitate easy catalyst separation is the use of magnetic nanoparticles. After the reaction, the catalyst can be immobilized by magnetic force, enabling removal of the solvent without an otherwise difficult filtration. This principle was demonstrated by Wang et al., who used Fe_3O_4 coated with SiO_2 as support for amine-anchored RuCl_3 . After 4 h of reaction at 120 °C and atmospheric pressure, a DFF yield of 86% was obtained at full HMF conversion.¹⁰²

Magnetic catalysts were also applied in the two-step conversion of fructose to DFF via HMF. The dehydration reaction was performed in DMSO with a catalyst composed of alkylsulfonic acid groups anchored to silica-coated Fe_3O_4 . A yield of 90% HMF was obtained after 2 h at 130 °C. After that, a catalyst composed of Ru immobilized on hydroxyapatite-coated γ - Fe_2O_3 was added. After 27 h a yield of 79% DFF was obtained based on fructose.¹⁰³

In a more holistic approach, Ebitani et al. studied the conversion of glucose to DFF. The reaction sequence entails

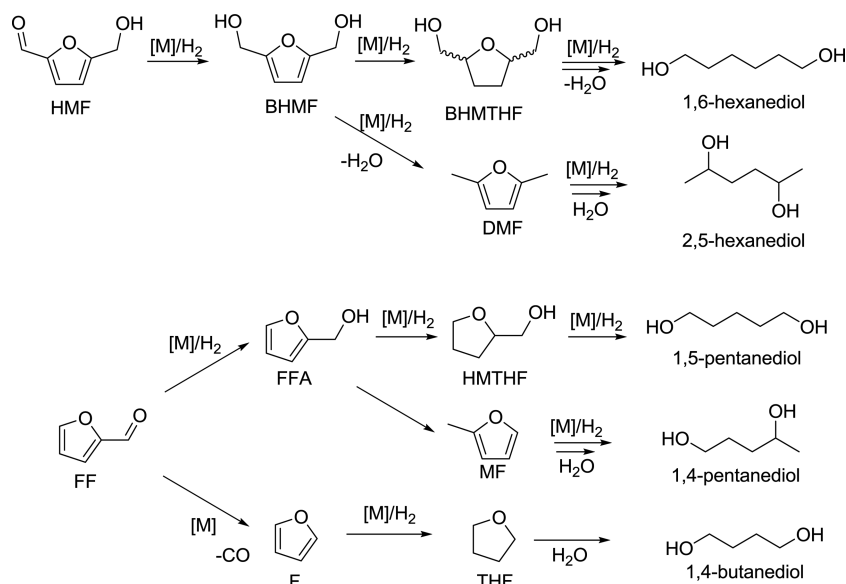
the initial conversion of glucose to fructose using basic hydroxalcalites. Up to 40% fructose was formed in DMFA (*N,N*-dimethylformamide), which is close to the equilibrium conversion. In turn the formed fructose was dehydrated with an Amberlyst catalyst giving 33% HMF based on glucose. Finally, a Ru/HT was employed and a final DFF yield of 20% was obtained after full consumption of HMF.¹⁰⁴ The same approach was also studied for the conversion of raffinose to DFF.¹⁰⁵

Vanadium-based catalysts have been shown to catalyze aerobic oxidation of alcohols to aldehydes and ketones. This and the relatively low cost of vanadium as compared to noble metals has spurred increased research concerning the use of vanadium based catalysts for the oxidation of HMF to DFF. In 1997, Moreau et al. reported full conversion of HMF in the presence of $\text{V}_2\text{O}_5/\text{TiO}_2$ in toluene and MIBK.¹⁰⁶ More recently, Riisager also studied the activity of 10 wt % $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5/\text{zeolite}$ catalysts and noted a high degree of leaching in all cases. Lowering the catalyst loading suppresses leaching; however, still the leached species contributed significantly to the overall conversion. Under optimized conditions (i.e., DMSO, 125 °C, 10 bar O_2) a yield of 84% DFF was obtained.¹⁰⁷ Antonyraj et al. prepared a $\text{V}_2\text{O}_5/\text{C}$ catalyst and obtained 95% conversion with 96% selectivity after 4 h at 100 °C.¹⁰⁸ To test for leaching, the catalyst was stirred under reaction conditions and subsequently the filtered solution was tested for further conversion of HMF. Approximately 9% DFF was obtained without further conversion after filtration, suggesting the heterogeneity of the catalyst. Nie et al. studied the influence of oxidic supports on the behavior and properties of VO_x monolayers. A correlation between reducibility of the support and catalyst activity was proposed and TiO_2 and ZrO_2 were identified as being the most active.¹⁰⁹

In addition to supported V_2O_5 catalysts, also ion-exchange immobilized VO^{2+} catalysts have been proposed. Le et al. tested the activity of VO^{2+} exchanged on sulfonated carbons and noted a high leaching stability but a poor DFF selectivity.¹¹⁰ Canós et al. coordinated $\text{VO}(\text{acac})_2$ on PVP (poly(vinylpyridine)) and SBA-15 functionalized with pyridine groups. Both catalysts exhibited excellent selectivity; however, the PVP-based catalyst was significantly more active giving 60–78% after 24 h as compared to 33% for SBA-15.¹¹¹

Grushin et al. studied the one-pot, two-step conversion of fructose to DFF in DMSO. Fructose was dehydrated using an ion-exchange resin at 80–110 °C to give 77% HMF. After this various vanadium-based salts were added for the oxidation. After 13–19 h at 150 °C, DFF yields of 25–45% were obtained based on fructose.¹¹²

Carlini et al. reported HMF oxidation to DFF in the presence of vanadyl phosphate as catalyst and DMFA as solvent.¹¹³ A study by Tao et al. details the use of MIL-101 (i.e., a Cr-based metal–organic framework) loaded with Pd and V for the one-pot, one-step conversion of fructose to DFF. The reaction was carried out for 10 h at 140 °C and a DFF yield of 34% was obtained.¹¹⁴ Aiming at the one-pot, one-step conversion of fructose to DFF, Xu et al. studied the use of Amberlyst-15 and $\text{VO}(\text{acac})_2/\text{poly}(\text{aniline})$ catalysts in a mixture of 4-chlorotoluene and DMSO. A maximum DFF yield of 70% was obtained after 14 h at 110 °C.¹¹⁵ Xiang et al. studied the possibility of the direct conversion of glucose to DFF using a combination of catalysts comprised of CrCl_3 and NaVO_3 in DMA (*N,N*-dimethylacetamide). In a two-step approach up to 55% DFF

Scheme 10. Overview of Products Obtainable via Reductive Transformation of HMF and Furfural (FF)^a

^aPossible heterocyclic products: 2,5-bis(hydroxymethyl)furan (BHMF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTfHf), 2,5-dimethylfuran (DMF), furfuryl alcohol (FFA), 2-(hydroxymethyl)tetrahydrofuran (HMTHf), 2-methylfuran (MF), furan (F), and tetrahydrofuran (THF).

was obtained. Nevertheless, performing the reaction in one step only led to a maximum yield of 18%.¹¹⁶

As discussed above, manganese oxide based catalysts can be used for the oxidation of HMF to FDCA; however, recent studies show that these catalysts can also be used for the selective synthesis of DFF. Yadav et al. proposed the use of an Ag loaded OMS-2 catalyst. A screening of solvents at 165 °C under 15 atm air showed that this catalyst exhibits good activity and selectivity in various solvents.^{117,118} Nie et al. tested a number of different nanostructured MnO₂-based catalysts in DMFA at 110 °C. All catalysts exhibited high selectivity for DFF although the productivity varied considerably. A relationship could be established between the productivity and the reducibility/oxidizability of the catalyst.¹¹⁹ Liu et al. also showed that Mn₃O₄ supported on Fe₃O₄ is a suitable catalyst for the selective oxidation of HMF. Up to 82% yield could be achieved in DMFA.¹²⁰

The use of Mn-based catalysts in the one-pot conversion of fructose to DFF was demonstrated by Yang et al. A catalyst combination of sulfated SBA on Fe₃O₄ and K-OMS-2 was used in a two-step approach. Fructose dehydration was performed in DMSO, and after 2 h at 110 °C a HMF yield of 81% was obtained. After that K-OMS-2 was added and the reaction was left for another 6 h to give a final DFF yield of 80%.¹²¹

Recently Riisager et al. reported a copper catalyzed oxidation of HMF. The aerobic oxidation reaction is performed using a combination of CuCl and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) in acetonitrile, and a DFF yield of 95% was reported after 24 h under 1 atm O₂.¹²²

Recent studies show that the oxidation of HMF to DFF can also be achieved without the use of a metal catalyst. Patent applications by Evonik and Roquette Frères describe the use of a catalyst system composed of HNO₃ and AA-TEMPO (4-acetamino-2,2,6,6-tetramethylpiperidine-1-oxyl) for the aerobic oxidation of HMF in acetic acid.^{123,124} Full conversion to DFF is reported after 3 h at 50 °C under 1 bar O₂. Aellig et al. used TEMPO immobilized on silica in a continuous setup under

similar conditions in 1,2-dichloroethane. Notably, optimization of the contact time for this flow system is crucial for obtaining DFF in good yields. At a contact time of 2 min, selectivity of DFF reached 98% at nearly full conversion of HMF, whereas an increase of the contact time to 8 min led to significant overoxidation to FDCA.¹²⁵ Karimi et al. immobilized TEMPO on silica-coated Fe₃O₄ to enable magnetic catalyst separation. Instead of nitric acid, *tert*-butylnitrite was used as cocatalyst and the reaction proceeded efficiently within 10 min at 50 °C.¹²⁶

2.1.2. Monomers Accessible via Reduction of 5-Hydroxymethylfurfural and Furfural. The reductive transformation of HMF and FF also offers interesting opportunities for the preparation of polymer intermediates. As shown in Scheme 10, hydrogenation of the aldehyde function of HMF yields 2,5-bis(hydroxymethyl)furan (BHMF) and subsequent hydrogenation of the ring results in 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTfHf). BHMTfHf, in turn, can be ring-opened leading to the formation of 1,2,6-hexanetriol, which under suitable conditions can be further converted to 1,6-hexanediol.¹²⁷ As such, a direct route is established with important intermediates for the production of caprolactam and nylon.¹²⁸ Depending on the employed catalyst, hydrogenolysis of the hydroxymethyl groups of BHMF can occur leading to the formation of 2,5-dimethylfuran (DMF). Ring-opening and subsequent hydrogenation of DMF can lead to 2,5-hexanediol.¹²⁹ In addition, DMF can be converted to *p*-xylene via diels-alder reaction with olefins.

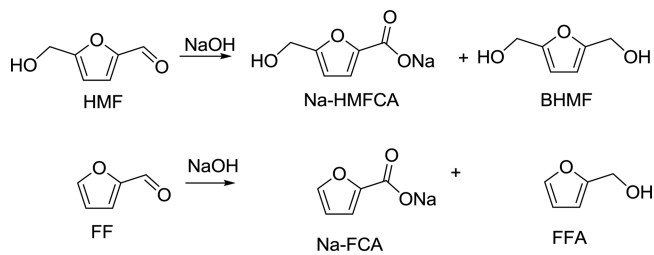
In the case of furfural (FF), selective hydrogenation of the aldehyde function results in the formation of furfuryl alcohol (FFA) which is already an important intermediate in the manufacturing of furan-type resins¹³⁰ such as various synthetic fibers and rubbers. It can also be used as environmentally benign solvent for pigments or phenolic resins and as a lubricant or dispersing agent. As shown in Scheme 10, further hydrogenation of the furan ring can result in 2-(hydroxymethyl)tetrahydrofuran (HMTHf). Ring opening of HMTHf can give rise to either 1,5-pentanediol or 1,2-pentanediol. This reaction has been studied in detail by

Tomishige et al., and mainly 1,5-pentanediol is obtained for Rh or Ir catalysts modified with ReO_x or MoO_x .^{131–137} Alternatively, hydrogenolysis of the alcohol function of FFA can also lead to 2-methylfuran (MF), which after ring opening may lead to 1,4-pentanediol. Besides this, decarbonylation of FF may result in the formation of furan (F)¹³⁸ which can be further converted to tetrahydrofuran (THF) and 1,4-butanediol.¹³⁹ Thus, HMF and FF are suitable intermediates for not only the preparation of “drop-in” diols such 1,6-hexanediol, 1,5-pentanediol, and 1,4-butanediol but also for novel furan-based diol structures. In what follows only the preparation of BHMF and BHMTFH and conversion of DMF to *p*-xylene will be discussed.

2.1.2.1. Preparation of 2,5-Bis(hydroxymethyl)furan. 2,5-Bis(hydroxymethyl)furan (BHMF) is often observed as an intermediate in the synthesis of other products such as DMF (a potential fuel additive), BHMTFH (vide infra), etc. Aiming at DMF, a screening of carbon supported catalysts (i.e., Pd, Ni, and Ru) by Saha et al. at 150 °C in THF shows that particularly Ru exhibits good selectivity to BHMF.¹⁴⁰ While studying the reductive etherification of HMF with ethanol to 2,5-bis-(ethoxymethyl)furan, Balakrishnan et al. showed that Sn-doped $\text{Pt}/\text{Al}_2\text{O}_3$ exhibits good selectivity for the selective hydrogenation of HMF under relatively mild conditions. A BHMF yield of 82% was obtained after 5 h at 60 °C under 14 bar H_2 .¹⁴¹ In a similar study Cao et al. reported up to 97% BHMF using Cu/SiO_2 .¹⁴² Chatterjee et al. proposed MCM-41 supported catalysts for the selective hydrogenation of HMF. A screening of MCM-41 supported metals (i.e., Ir, Rh, Pt, Pd, Au, and Ni) in water revealed that particularly Pt gives good conversion and selectivity. After 2 h at 35 °C under 8 bar H_2 up to 99% yield was obtained.¹⁴³ Chen et al. immobilized Ru clusters on nanosized mesoporous zirconium silica. After 4 h at room temperature, 98% conversion with 92% selectivity toward BHMF was obtained in water under 5 bar H_2 .¹⁴⁴ Aiming at the synthesis of 1-hydroxy-2,5-hexadione, Liu et al. studied the hydrogenation of HMF to BHMF using a commercial Pd/C catalyst. The reaction performed in THF/ H_2O at 80 °C under 100 bar H_2 gave 82% yield after 20 h.¹⁴⁵ Tomishige et al. reported the selective hydrogenation of unsaturated aldehydes in H_2O using an Ir– $\text{ReO}_x/\text{SiO}_2$ catalyst. The catalyst could be applied to a wide range of unsaturated ketones including FF and HMF. In the case of HMF, a BHMF yield of >99% was obtained after 6 h at 30 °C under 80 bar H_2 .¹⁴⁶ Cai et al. studied the conversion of (poly)saccharides to BHMF and BHMTFH in a one-pot approach using ILs (ionic liquids). The authors note that, under relatively mild conditions (50 °C, 60 bar), Ir/ TiO_2 exhibits good selectivity toward BHMF.¹⁴⁷ Ohyama et al. studied the use of Au catalysts for the conversion of HMF to BHMF. Gold subnano particles were deposited on a range of metal oxide supports. Of these Al_2O_3 showed the best selectivity. Up to 96% BHMF was obtained after 2 h at 120 °C under 65 bar H_2 .¹⁴⁸ Based on the above reports, it is evident that the selective hydrogenation of HMF to BHMF is possible using a variety of different metal catalysts. However, in many cases follow-up reactions occur necessitating strict reaction control. Alternatively, the hydrogenation can also be performed by hydrogen transfer catalysis over oxidic catalysts, the so-called Meerwein–Ponndorf–Verley reduction. When isopropyl alcohol is used as hydrogen donor, the respective isopropyl ethers are obtained.¹⁴⁹ However, when methanol is used over MgO , excellent yields of >99% of BHMF are obtained after 3 h at 160 °C.¹⁵⁰

Another interesting possibility for the preparation of BHMF is the base induced Cannizzaro reaction of HMF (Scheme 11).

Scheme 11. Cannizzaro Reaction of HMF and Furfural (FF) Yielding 2,5-Bis(hydroxymethyl)furan (BHMF) and Furfuryl Alcohol (FF) with Sodium Salts of 5-Hydroxymethylfuran-2-carboxylic (Na-HMFCA) and 2-Furancarboxylic Acids (Na-FCA) as Side Products, Respectively



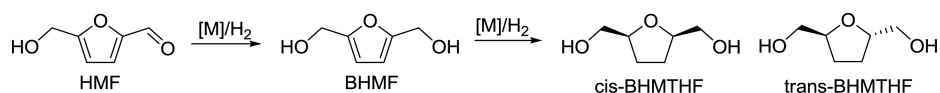
An equal amount HMFCA is produced alongside BHMF. Both products can potentially be applied as polymer intermediates. Subbiah et al. reported that the reaction proceeds with good selectivity in water at 0 °C. Optimization of reaction conditions led to a maximum yield of 86% BHMF after 18 h in the presence of 1.1 equivalents of base.¹⁵¹ The same reaction could also be applied to FF resulting in comparable yields. It has also been reported that the reaction can be performed successfully in ILs. Kang et al. could recycle the IL up to five times with consistently good yields.¹⁵²

2.1.2.2. Preparation of 2,5-Bis(hydroxymethyl)-tetrahydrofuran. Next to the selective hydrogenation of HMF to BHMF, its total hydrogenation to BHMTFH has also been studied (Scheme 12). Due to the relatively stable furan ring, typically harsher conditions are required (i.e., higher temperatures and pressures, compared to the reduction of the aldehyde group).

It is known from earlier literature that the reaction can be catalyzed by nickel catalysts (e.g., Raney nickel, Ni/kieselgur). When performed in Et_2O at 130–160 °C under 70–140 bar, up to 90% yield is obtained with a high proportion of the cis product.^{153–156} A recent study by Connolly et al. shows that the reaction can be performed in various solvents and that Raney Ni is both more active and selective than Pd/C.¹⁵⁷ Complete conversion of a highly concentrated mixture of HMF in ethanol was reported by Sanborn et al., who used zirconium promoted Ni/kieselgur at 200 °C under 103 bar H_2 .¹⁵⁸ Tomishige et al. studied the total hydrogenation of HMF and FF over bimetallic Ni-Pd/ SiO_2 catalysts. A maximum yield of 96% BHMTFH was reported for a catalyst with a Ni/Pd ratio of 7.¹⁵⁹ A recent report by Dumesic et al. shows that the reaction can also be efficiently catalyzed by Ru/ CeO_2 . Up to 91% yield was obtained after 12 h at 130 °C.¹⁶⁰ However, the cis/trans ratio was not reported.

2.1.2.3. Catalytic Pyrolysis of Furans to *p*-Xylene. *p*-Xylene is the precursor of terephthalate, which is an important monomer for PET production. Currently, *p*-xylene is produced by the methylation of toluene and benzene using a zeolite as catalyst. In 2011, Toste et al.¹⁶¹ reported the synthesis of *p*-xylene via a multistep process from 2,5-dimethylfuran (DMF) which is derived from 5-(hydroxymethyl)furfural (HMF) and acrolein which is produced from glycerol. Dauenhauer et al.¹⁶² developed a zeolite catalyzed transformation of ethylene and DMF to *p*-xylene. Good selectivity to *p*-xylene (75%) could be achieved in *n*-heptane with an H–Y zeolite at 300 °C. Under

Scheme 12. Hydrogenation of HMF to 2,5-Bis(hydroxymethyl)tetrahydrofuran (BHMTHF) via 2,5-Bis(hydroxymethyl)furan (BHMF)

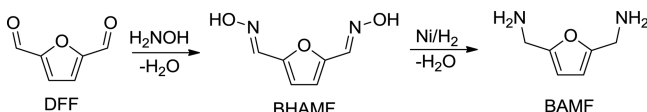


these conditions, the competing side reaction, ring-opening hydrolysis, could be effectively inhibited. In their further study, the selectivity to xylene could be improved to 90% by using an H-BEA zeolite catalyst.^{163,164} Beside the conversion of ethylene and DMF, *p*-xylene can also be produced from propene and methylfuran, which is derived from furfural. Huber et al.¹⁶⁵ demonstrated that a simple zeolite surface modification method allows increasing *p*-xylene selectivity from propene and methylfuran. Tetraethoxysilane was used to narrow the pore openings of ZSM-5 catalysts, which caused more space confinement and, thus, increased the para-selectivity from 32 to 96%. With the aim of arenes production, methylfuran and methanol can also be used as substrates but the selectivity to *p*-xylene is relatively lower.¹⁶⁶

2.1.3. Novel Furanic Monomers via Amination.

2.1.3.1. Production of 2,5-Bis(aminomethyl)furan. A patent application by Evonik discloses the preparation of DFF and its conversion to 2,5-bis(aminomethyl)furan (BAMF) (Scheme 13). Examples are given for the conversion of DFF to the bis-

Scheme 13. Preparation of 2,5-Bis(aminomethyl)furan (BAMF) via the Bis-oxime (BHAMF)



oxime (BHAMF) using hydroxylamine HCl. Subsequent hydrogenation in THF using Raney nickel at 50 °C leads to 95% yield of BAMF.¹²³

Co-workers from Rhodia have reported a homogeneous iridium-catalyzed reductive amination process for the preparation of functionalized furan derivatives (Scheme 14). The reported examples deal mainly with benzylamine as amine. An iridium catalyst {[CpIrX₂]₂ or [CpIr(NH₃)₃][X]₂ (X = halide)} was applied in the reaction.¹⁶⁷

Co-workers from BASF reported the use of ruthenium acridin based pincer complexes containing phosphine for the amination of alcohols. Examples are given for the amination of BHMF with ammonia to BAMF. Yields up to 96% are reported under relatively mild conditions. (140–150 °C, THF/*tert*-amyl alcohol, 6 equivalents of NH₃, 35–38 bar H₂, 18–21 h).¹⁶⁸ Under similar conditions, triphos ligands (tridentate and bidentate phosphine ligands) with ruthenium are less efficient and give incomplete conversion with the monoaminated product dominating the product spectrum.¹⁶⁹ The reductive amination of the monoamine using Raney Ni is also known from the patent literature.¹⁷⁰ Two very recent patent applications by Ma et al. report the efficient conversion of

DFF and BHMF to BAMF over a variety of metal catalysts supported on metal oxides.¹⁷¹ Starting from DFF, ammonia gas is first introduced and left to reaction to give the bis(imine). Subsequently, hydrogen is introduced for the reduction to the bis(amine). Examples are given for catalysts such as Ni/CaO, Cu/Fe₂O₃, and Ru/ZrO₂ among others in organic solvents, and in all cases high conversions and selectivities are claimed.

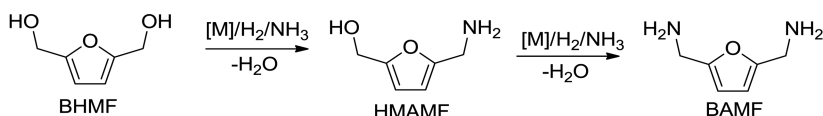
2.1.3.2. Dimerization of Furfurylamine. In a similar fashion as the dimerization of FCA (Scheme 8), the dimerization of furfurylamine (FFAM) has also been described (Scheme 15). A patent application by Still et al. details the conversion of FFAM to its formamide derivative before dimerization with acetaldehyde in concentrated HCl at –7 °C. After workup a yield of 65% is obtained based on FFAM.¹⁷² Studies by Lesimple et al. show that the reaction can also be performed with FFAM directly.¹⁷³ Yields between 85 and 95% of the hydrochloric acid salt of the dimer were reported for the reaction with acetone in concentrated HCl at 55 °C.¹⁷⁴

The conversion of the bis hydrochloride salt to the diisocyanate has also been shown to proceed efficiently. Yields between 70 and 76% are obtained after reaction with trichloromethylchloroformate.¹⁷⁵

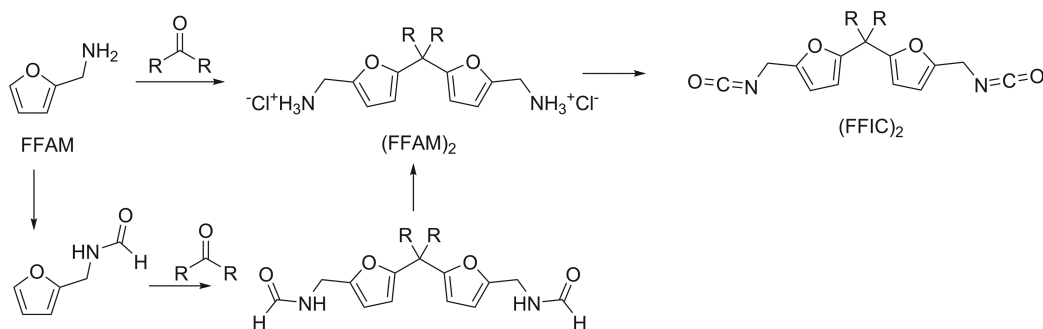
2.2. Levulinic Acid Platform

2.2.1. Levulinic Acid Production. Levulinic acid (LevA) is a keto-acid that is formed from C₆ carbohydrates under acidic conditions. LevA was highlighted as a high-potential platform molecule for synthesis of value-added chemicals as early as in 1956.¹⁷⁶ Formation of LevA was first observed by Mulder in 1840 when heating sucrose with mineral acids.¹⁷⁶ In the 1940s, it was shown that cellulosic substrates can be used for production of LevA.¹⁷⁶ Synthesis of LevA from polysaccharides is an acid-catalyzed multistep process that includes (i) hydrolysis of polysaccharides, (ii) formation of HMF as product of acidic dehydration, and (iii) rehydration of HMF to yield LevA and formic acid (Scheme 16). The process is associated with extensive formation of polymeric byproducts (humins) that decreases the carbon efficiency of LevA synthesis. Nevertheless, the manufacture of LevA based on lignocellulosic biomass in the so-called “Biofine process” was commercialized in the 1990s and reached a capacity of LevA production of 0.45 kt/year in 2005.¹⁷⁷ The start of the first commercial plant producing LevA with a capacity of 125 dry metric tons/day was planned by Biofine Technology LCC in the fourth quarter 2015.¹⁷⁸ The Biofine process is carried out continuously in two successive reactors catalyzed by 1–5 wt % mineral acid. The feedstock is supplied to a plug-flow reactor with a contact time of 13–25 s at 210–230 °C to accomplish hydrolysis and convert the carbohydrates into HMF. The effluent from the first reactor is supplied into a continuous

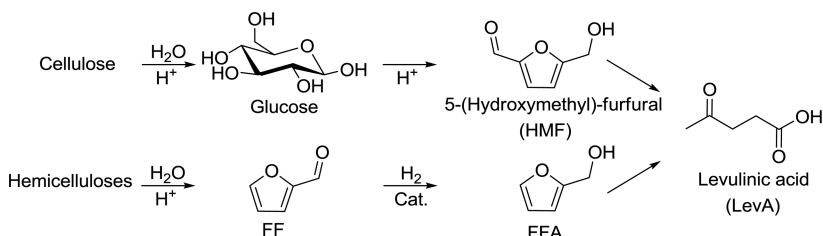
Scheme 14. Reductive Amination of 2,5-Bis(hydroxymethyl)furan (BHMF) To Produce 2,5-Bis(aminomethyl)furan (BAMF)



Scheme 15. Condensation of Furfurylamine (FFAM) with a Carbonyl Compound and Conversion to the Respective Diisocyanate ((FFIC)₂)



Scheme 16. Biomass-Based Routes toward Levulinic Acid (LevA) from Cellulose via HMF or from Hemicelluloses via Furfural (FF) and Furfuryl Alcohol (FFA)

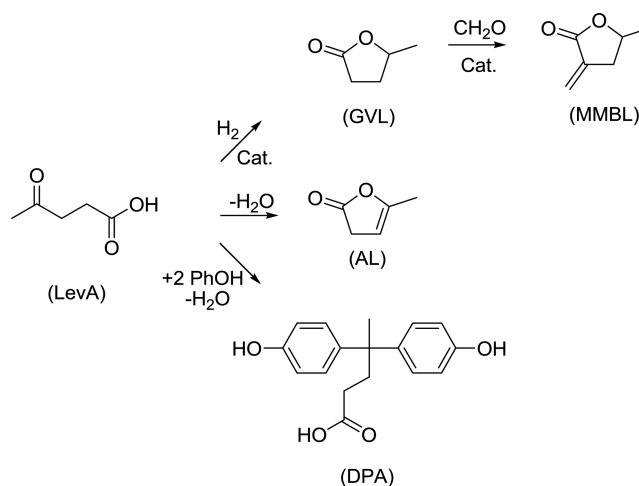


stirred-tank reactor operating at 195–215 °C for 15–30 min to convert HMF into LevA and formic acid. LevA is synthesized in the Biofine process with a nearly maximum productivity of the theoretical yield.¹⁷⁹ An alternative route for synthesis of LevA is the acid-catalyzed hydration of furfuryl alcohol (FFA) (Scheme 16). FFA is available as a product of furfural reduction.¹⁸⁰ Acid-catalyzed hydration of FFA is hindered by the low stability of the substrate in acidic medium due to resinification. Nevertheless, undesirable side processes can be suppressed by optimizing reaction conditions. For example, Gürbüz et al. conducted the extraction-assisted synthesis of LevA in a semibatch operation mode with 65% yield based on 10–20 wt % FFA.¹⁸⁰ A comprehensive overview on LevA production can be found in a recent review by Rackemann and Doherty.¹⁸¹

The most widely studied monomers derived from LevA are α -angelica lactone (AL), γ -methyl- α -methylene- γ -butyrolactone (MMBL) which is also called α -methylene- γ -valerolactone, and diphenolic acid (DPA) which is also referred to as 4,4-bis(4-hydroxyphenyl)valeric or 4,4-bis(4-hydroxyphenyl) pentanoic acid (Scheme 17). Other opportunities to involve LevA into the production of polymers comprehend its use as (i) substrate for synthesis of SA (section 2.4.2 of this review) or 1,4-BDO (section 2.4.3), (ii) feed for PHA production (section 3.4.2),¹⁸² and (iii) feedstock for the synthesis of diols applied for polyurethane production.¹⁸³

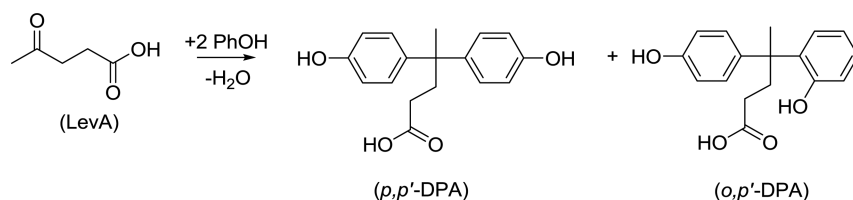
2.2.2. γ -Methyl- α -methylene- γ -butyrolactone and α -Angelica Lactone. γ -Methyl- α -methylene- γ -butyrolactone (MMBL) can be produced from LevA via a two-step process. The first step is a hydrogenation of LevA to γ -valerolactone (GVL). GVL can be produced in high yields by hydrogenation of LevA in the presence of ruthenium catalysts.^{184,185} The originally reported synthesis of MMBL included use of metallic sodium, being therefore hardly scalable.¹⁸⁶ More recently, Manzer et al. elaborated a continuous catalytic process for the synthesis of MMBL by condensation of GVL with formaldehyde. Alkali metals and alkaline earth metals supported on

Scheme 17. Synthesis of Monomers from Levulinic Acid (LevA): γ -Methyl- α -methylene- γ -butyrolactone (MMBL) via γ -Valerolactone (GVL); α -Angelica Lactone (AL); Diphenolic Acid (DPA)



SiO₂ were demonstrated to be efficient catalysts for the gas-phase process at 340 °C with a contact time of 1–6 s. The initial yield of MMBL reaches 60% but rapidly decreases as a result of catalyst blockage by high boiling byproducts. Nevertheless, the catalyst can be fully regenerated by heating under oxygen or nitrogen flow.¹⁸⁷ Manzer highlighted the difficulties connected to the high boiling points of reactants and product. Moreover, the handling of MMBL is challenging due to its rapid polymerization on standing.¹⁸⁷ Later on, Manzer and Hutchenson reported on a two-step cascade process for synthesis of MMBL from LevA, formaldehyde, and hydrogen. The reactions were carried out in supercritical or near-critical fluid phase using CO₂ as solvent. In the first reactor, a nearly quantitative synthesis of GVL takes place, and the effluent

Scheme 18. Synthesis of Diphenolic Acid by Condensation of Levulinic Acid (LevA) with Phenol Yielding *p,p'*-Diphenolic Acid (*p,p'*-DPA) and *o,p'*-Diphenolic Acid (*o,p'*-DPA)



serves as feed for the second step without purification of GVL. The yield of MMBL in the second reactor reaches 90%.¹⁸⁸

α -Angelica lactone (AL) is a monomer produced from LevA by dehydration in the presence of an acidic catalyst, e.g., acetic anhydride¹⁸⁹ or phosphoric acid.¹⁹⁰ Noncatalytic synthesis of AL is also possible by distillation of LevA under reduced pressure.^{190,191}

2.2.3. Diphenolic Acid. Diphenolic acid (DPA) is formed via the interaction of 1 mol of LevA with 2 mol of phenol in the presence of an acidic catalyst. Soluble acids such as H_2SO_4 ¹⁹² or HCl ^{193,194} efficiently catalyze the reaction. Moreover, solid catalysts were successfully tested for the discussed reaction, e.g., heteropoly acids partly substituted by cesium,¹⁹⁵ $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded on mesostructured silica materials,^{193,194,196} and sulfonated hyperbranched poly(arylene oxindole)s.^{197,198} Also Brønsted acidic ionic liquids exhibit catalytic activity.¹⁹⁹ Concentrated sulfuric acid catalyzes the reaction efficiently at room temperature,¹⁹² whereas solid acids require an elevated temperature of 100 °C or higher.^{193–198} A conversion of LevA up to 80% is reached after 8–24 h.^{193–198} The main side product of the transformation presents *o,p'*-DPA, while *p,p'*-DPA is the desirable product (Scheme 18). Under acidic reaction conditions, the byproduct is obtained in significant amounts: the ratio of *p,p'* to *o,p'* isomers varies from 1.1 to 3.6.^{193,194,196} Van de Vyver et al. have recently reported an increase of the *p,p'*-DPA selectivity by promoting the catalyst by thiol compounds. Thus, an acidic-thiol catalyst enables increasing the ratio of *p,p'* to *o,p'* isomers up to 19.5.¹⁹⁷ The selectivity improves due to the reaction of LevA with the thiol compounds leading to a bulky electrophilic intermediate that substitutes phenols preferentially at the para position.¹⁹⁸ Moreover, the addition of thiols increases the catalytic activity of acidic catalysts.¹⁹⁷ When using Brønsted acidic ionic liquids as catalysts, a mixture of a thiol-containing ionic liquid and an ionic liquid exhibiting a triflic anion proved to be the most efficient in terms of selectivity facilitating a ratio of *p,p'* to *o,p'* over 100.¹⁹⁹ Interestingly, Liu et al. reported that a decrease of the reaction temperature from 100 to 50 °C improves the selectivity toward *p,p'*-DPA in the presence of ionic liquids.¹⁹⁹

2.3. Isohexides and Derivatives

2.3.1. Isohexides: Properties and Applications. Isohexides are a group of three C_6 sugar-based diols, i.e., isomannide (1,4:3,6-dianhydro-D-mannitol), isosorbide (1,4:3,6-dianhydro-D-glucitol/-sorbitol), and isoidide (1,4:3,6-dianhydro-L-iditol). They are “V”-shaped molecules of two cis-fused tetrahydrofuran rings with an opening angle of approximately 120°. The two secondary hydroxyl groups substituted to the 2-C and 5-C positions exhibit *endo/endo* (isomannide), *exo/endo* (isosorbide), and *exo/exo* configurations (isoidide), respectively (Figure 2). All three isomers provide a high chemical stability of the rigid bicyclic structure

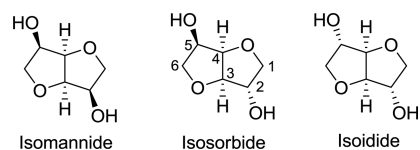


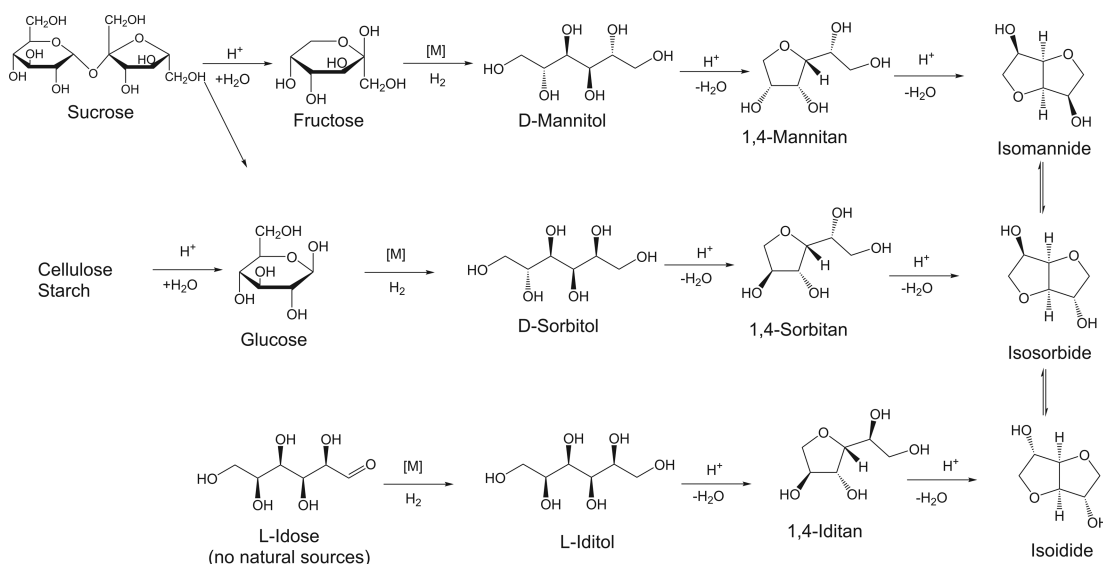
Figure 2. Three different isohexide isomers exhibiting different configurations of the 2-C and 5-C hydroxyl groups.

(cf. section 2.3.2), whereas reactivity of the two hydroxyl groups varies depending on their stereochemistry.

The most abundant and, thus, most prominent representative is isosorbide.^{200,201} According to SciFinder (April 14, 2015) there are 10 576 references on “isosorbide” while “isomannide” and “isoidide” are reported only 562 and 239 times, respectively. The production of isosorbide was first reported in a German patent filed from the company I.G. Farbenindustrie AG in 1927 entitled “Process for the production of valuable products from sorbitol”.²⁰² To that point, isosorbide and isomannide were mainly observed as byproducts upon the conversion of sugar alcohols with acids at elevated temperatures. These reports date back to the work of Bouchardat and Fauconnier in the late 19th century.^{203,204} Isoidide was first reported in 1945 by Fletcher et al., who found this compound by isomerization from either one of the other two isomers.^{205,206} Starting in the late 1920s and 1930s the synthesis of all three isomers from sugars as well as their further transformation by means of synthetic organic chemistry was investigated in detail. They regained enormous attention in the past three decades with the background of utilizing biomass as a renewable resource. Derivatives of isohexides are investigated for numerous application. For example, application of nitrates as pharmaceuticals, aliphatic esters and ethers as high boiling solvents and fuel additives, monosubstituted derivatives as surfactants with the isohexide being a sterically demanding polar headgroup, chiral auxiliaries or even ionic liquids and deep eutectic solvents have been reported.²⁰⁰ However, the main share of isohexide research appears to be devoted to their utilization as building blocks for polymers of all kinds due to their rigid structure in combination with two stereochemically well-defined functional groups.^{207–209} Thus, in sections 2.3.2 and 2.3.3 some light is shed on the development from synthetic to catalytic methods and the current status of the production of isohexides as well as their transformation into derivatives suitable for the production of biogenic polymers.

2.3.2. Production of Isohexides. Despite the research activities for more than a century, isohexides are still a niche product on the chemical market. Isomannide and isoidide, to the best of our knowledge, are produced only in small quantities mainly for research purposes. In contrast, isosorbide is already a step further down the road toward scale-up due to the abundance of its precursor sorbitol. The latter is so far mainly produced for food and the pharmaceutical industry by a

Scheme 19. Production Routes of the Isohexides from Their Naturally Abundant Resources (Isosorbide, Isomannide) or by Isomerization (Isoidide)



Ni-catalyzed hydrogenation of glucose that is derived by enzymatic cleavage of starch or sucrose. The overall capacity of sorbitol was 1.7 Mt in 2011 with an estimated growth rate of approximately 30% per year in this decade.²¹⁰ According to their own statements, the world's largest producer of isosorbide is the French company Roquette.²¹¹ They claim to have an annual production capacity of 20 000 t and sell a high purity grade isosorbide under the brand name POLYSORB P especially for application in biopolyesters. Comparable to the availability and production of sorbitol, mannitol can be obtained by hydrogenation of fructose, a less abundant but still well available compound in the sugar industry (Scheme 19). In the case of isoidide, alternative production routes, e.g., by isomerization, have to be developed since its precursors scarcely occur in nature.

2.3.2.1. Dehydration of Hexitols. Isohexides can be produced from all kinds of naturally abundant (poly)saccharides (Scheme 19). Isohexides can be directly synthesized from their corresponding C₆ sugar alcohols D-sorbitol, D-mannitol, and L-iditol, respectively, by an acid catalyzed 2-fold dehydration reaction. A high activity and selectivity toward the formation of isosorbide from sorbitol at low temperatures (160–180 °C) is observed especially when using strong mineral or organic Brønsted acids such as sulfuric acid or *p*-toluenesulfonic acid in aqueous solutions.²¹² Acids with a weaker acidity produce preferably sorbitans, the intermediate isomeric species or byproducts obtained by only 1-fold dehydration. Concerning this dehydration reaction, research activities in recent years were focused on the investigation and development of solid acid catalysts to enable continuous processing and catalyst separation and of course to avoid the necessity of neutralizing molecular acids in solution with the formation of significant amounts of salts as byproducts.

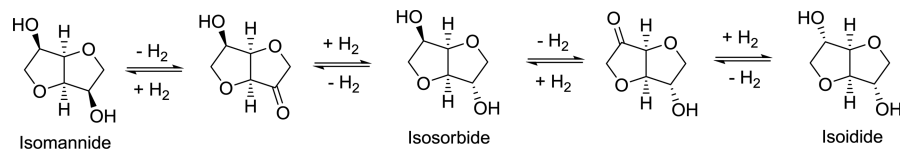
As applied in industrial acid-catalyzed gas phase reactions, zeolites are of great interest for this reaction. Among others especially H-beta zeolites with a high Si/Al ratio have recently attracted attention since high isosorbide yields of up to 76% at mild reaction temperatures of 127 °C can be obtained based on sorbitol.²¹³ The high activity is ascribed to the comparably high specific surface area of 590–670 m² g⁻¹ combined with a high

dispersion and good accessibility of the acid sites. The high selectivities are traced back to the rather hydrophobic surface of high Si/Al zeolites favoring the formation of less polar products from substrates of a higher polarity.

Another promising catalyst reported in recent years is sulfated zirconia, representing a quite strong acid.²¹⁴ In 2 h reaction time at 210 °C isosorbide yields of up to 61% at 100% conversion of sorbitol are obtained. Still, for this type of catalyst the stability in aqueous solution against sulfuric acid leaching due to hydrolysis has to be investigated in detail.

Besides inorganic solid acids also organic polymer-based acidic catalysts will most probably play a major role in future biorefineries. Such materials possess a high structural stability due to the covalent bonds of the polymer networks under the comparably mild reaction conditions in the liquid and often aqueous phases. Recently, Zhang et al. demonstrated the superior performance of a mesoporous polymeric acid in the dehydration of sorbitol.²¹⁵ At 140 °C for 10 h the sulfonated polymer gives full conversion and isosorbide yields of up to 88%. Catalytic activity of the mesoporous polymeric acid surpassed that of commercially available Amberlyst-15 and pure molecular acids such as sulfuric acid. The polymeric catalyst shows a turnover frequency (TOF) of 15.8 h⁻¹ and, thus, exceeds all other acids by a 2–5-fold higher TOF. Tailoring of the solid acidic catalyst and optimization of reaction conditions enable synthesis of selected dehydration products based on sorbitol. Xiu et al. reported high efficiency of a sulfonated polymer–silica–hybrid catalyst for the selective dehydration of sorbitol into 1,4-sorbitan.²¹⁶ In 4 h at 150 °C 1,4-sorbitan, the intermediate toward isosorbide, is obtained with a selectivity of 90% at full conversion of the substrate. Other catalytic systems are based, e.g., on solid heteropoly acids (HPA) such as silica-supported H₃PW₁₂O₄₀ reported by Sun et al.²¹⁷ Different oxidic supports were investigated. Silica appeared to be the ideally suited one since the HPA showed the highest acidity and the best performance in sorbitol dehydration with an isosorbide selectivity of 56% at 95% conversion at 250 °C. Recycling experiments proved the stability of the catalysts with the HPA maintaining the Keggin-type structure.

Scheme 20. Isomerization of the Three Isohexides by a Metal-Catalyzed De-/Rehydrogenation Mechanism



Alternative conversion routes for the dehydration reaction are based on ionic liquids (e.g., [TMPA][NTf₂]) as solvents with catalytic amounts of toluenesulfonic acid as reported by Kamimura et al.²¹⁸ Additionally, microwave irradiation was applied to heat the reaction mixture to a temperature of 180 °C with a significantly decreased reaction time of only 10 min. Under these conditions about 60% isolated yield of isosorbide can be obtained. Notably, the ionic liquid can be recovered by an extraction treatment with several successful recycling runs.

Yamaguchi et al. showed that the sorbitol dehydration is also possible using high temperature liquid water, thus avoiding the use of ionic liquids, organic solvents, or catalysts of any type.²¹⁹ The reaction can be carried out at 250–300 °C under hydrothermal conditions. Unfortunately, the main product typically found was 1,4-sorbitan, the intermediate toward the formation of isosorbide. The second dehydration step appeared to be significantly slower than the first one. Maximum yields of isosorbide of 57% could be obtained after 1 h at 317 °C.

As a further alternative, also Lewis instead of Brønsted acids can be used to catalyze the dehydration reaction. Rusu et al. reported the application of various metal phosphates under hydrothermal conditions at 180–250 °C in 70 wt % aqueous solutions as well as in pure molten sorbitol.²²⁰ Overall, full conversions of sorbitol with isosorbide yields of up to 70% have been achieved.

Reaction conditions to avoid the use of organic solvent or water were reported by Li et al.²²¹ They investigated the dehydration of sorbitol in reaction mixtures based on the substrate and zinc chloride hydrate. At reaction temperatures of 150–220 °C the salt hydrate is molten and able to dissolve sorbitol. The Lewis acid sites appear to be promising catalysts for the targeted dehydration reaction, and up to 85% yield of isosorbide is obtained.

2.3.2.2. Combined Hydrogenation and Dehydration Catalysis of Cellulose and Cellobiose. Besides the direct dehydration of the platform chemical sorbitol to isosorbide in recent years, the one-pot conversion of the most abundant renewable raw material cellulose gained increasing attention. It requires an acid catalyst for the hydrolysis and dehydration steps as well as a hydrogenation catalyst. Following up on the latter reaction system applying molten salt hydrates Li et al. investigated the combined hydrolysis and hydrogenation of cellobiose.²²² The latter is often used as a suitable disaccharide model system in which glucans are linked via β -1,4-glycosidic bonds that are comparable to cellulose. For the hydrogenation step in the sequential reaction, Ru/C was added as a solid hydrogenation catalyst. In a temperature range of 75–125 °C hydrolysis and hydrogenation occur in parallel with sorbitol yields of >95%. The hydrolysis appears to be the rate limiting reaction step. Typically, first the hydrolysis and subsequently the hydrogenation are broadly assumed as the standard reaction sequence in the scientific literature. A recent study showed that depending on the conditions also the hydrogenation of the terminal glucose unit can occur faster with a subsequent

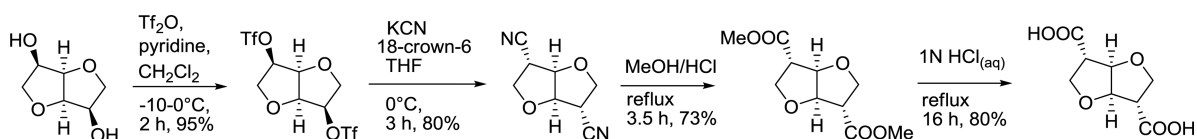
hydrolytic cleavage of the terminal sorbitol.²²³ In the case of cellobiose, the intermediate cellobitol was identified.

The molten zinc chloride hydrate reaction system was also investigated for the direct conversion of cellulose to isosorbide.²²⁴ The molten salt hydrate enables the full conversion of cellulose to glucose at 85 °C in 100 min, while the 2-fold dehydration reaction of sorbitol requires a higher temperature of 180 °C to obtain an isosorbide yield of 95% within 90 min. Despite the good performance of molten zinc chloride hydrate as reaction medium in terms of reactivity, the main issue is probably the separation of the final product. Therefore, the authors suggested the selective extraction of isosorbide using organic solvents such as xylene at elevated temperatures. Cooling the solvent down, isosorbide can be easily precipitated or transferred to an aqueous phase for further processing.

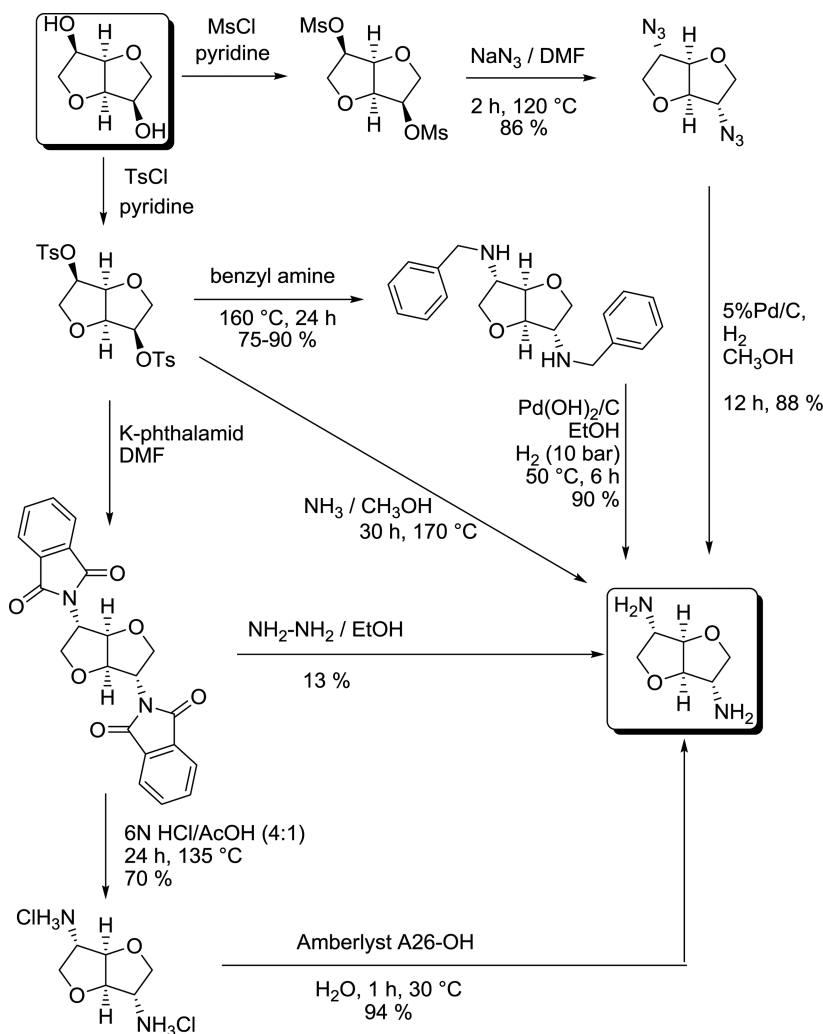
Another sequential process starting from cellulose was reported by Xi et al. using Ru supported on an acidic mesoporous niobium phosphate solid catalyst.²²⁵ Under optimized reaction conditions at temperatures of 230 °C isosorbide yields of up to 56% with regard to the cellulose as substrate were achieved. The remaining challenge in general is the solid interface of the nondissolved substrate cellulose with solid acid and hydrogenation catalysts due to the rather small contact area.²²⁶ Thus, either the cellulose has to be dissolved or alternatively Brønsted acids have to be used, providing free protons to enable a more efficient hydrolytic cleavage.

In this context, recent reports prove the feasibility of using combined solid hydrogenation and either soluble or nonsoluble Brønsted acid catalysts for the one-pot conversion of cellulose to sugar alcohols.^{227,228} Especially Op de Beek et al. demonstrated the optimized performance of combined commercially available Ru/C and silicotungstic acid for the selective production of isosorbide with a yield over 50% directly from cellulose.²²⁷ The versatility of this catalytic system was demonstrated on the one hand by successfully using microcrystalline cellulose as the model substrate with a lower reactivity due to the crystallinity as well as more application-related impure samples of cellulose pulps from organosolv fractionation. In a recent study by Yamaguchi et al. quite similar results were obtained by using Ru/C but in combination with the acidic ion-exchange resin Amberlyst 70 as a solid catalyst instead of dissolved heteropoly acids.²²⁹ The advantage is clearly the good separability of both solid catalysts in combination with the high activity. Overall, one major issue in the catalytic one-pot conversion of cellulose selectively to isosorbide via the multistep pathway is clearly the identification of catalysts that possess sufficient selectivity and of course stability in the respective liquid phase. Due to the polar substrate, intermediates, and the products quite polar solvents are required. Water appears to be a favored one for hydrothermal processing although the stability of many solid acid catalysts is questionable. For example, sulfonated polymers often undergo desulfonation at elevated temperature and release sulfuric acid as leaching molecularly active species. On

Scheme 21. Synthetic Strategy To Convert Isohexides (Shown Here: Isomannide) in a Four-Step Synthesis to the Dicarboxylic Acid Derivates under Inversion of the Configuration at Positions C2 and C5, Respectively



Scheme 22. Strategies for the Synthetic Production of Isohexide-Based Diamines



the other hand, solid inorganic acids often undergo structural changes under hydrothermal conditions and, thus, deactivate as well due to sintering.

2.3.2.3. Isomerization of Isohexides. Depending on the sterical differences of the three isomers' hydroxyl groups, significantly different polymer properties have been observed (cf. section 3.3). Especially isoidide enables the production of polymers with the highest molecular weights in direct comparison of all isomers due to its 2-fold *exo* configured hydroxyl groups with the least sterical hindrance. However, isoidide does not occur in nature while its precursors (*L*-idose or *L*-iditol, Scheme 19) are found only in negligible amounts. Thus, the most promising route for its production is by isomerization of either one of the other two isomers (Scheme 20). The reaction occurs under a hydrogen atmosphere using catalysts that are able to hydrogenate and dehydrogenate ketones and alcohols. The mechanism follows the initial

dehydrogenation of one of the two hydroxyl groups under formation of the respective ketone. The subsequent hydrogenation back to the alcohol can either result in the original configuration or undergo an inversion of the configuration. Also, a 2-fold dehydrogenation toward the diketone seems feasible. However, using this reaction route, none of the ketone intermediates has yet been identified in the literature. When the reaction is carried out in molten substrate or in aqueous solution, the three isomers are typically found in a ratio of 5–10% isomannide, 35–45% isosorbide, and 50–60% isoidide. This ratio, although not proven yet, appears to be the thermodynamic equilibrium that is independent of the applied hydrogenation catalysts.

This isomerization reaction has been reported for the first time in 1945/1946 by Fletcher and Goepf.^{230,231} They carried out the reaction in molten isosorbide as well as molten isomannide. Using Raney Ni as catalyst, at 250 atm of hydrogen

pressure and 200 °C, the reaction reached its apparent equilibrium after 2 h. Two decades later Wright and Brandner filed a patent and reported on the same reaction using silica ("kieselgur")-supported Ni as catalyst in an aqueous solution of isosorbide.^{232,233} They observed a similar equilibrium composition working at temperatures of 200–220 °C but at a significantly lower hydrogen pressure of 150 atm. The reaction was not further studied until recently Le Nôtre et al. reported the use of Ru/C as catalysts.^{234,235} It enabled milder reaction conditions with a reduced hydrogen pressure of only 40 bar at a temperature of 220 °C. Additionally, it shows a significantly improved stability in catalyst recycling compared to Ni/SiO₂ which appears to be not stable under the applied hydrothermal conditions.

2.3.3. Derivatives of Isohexides. Due to their two functional hydroxyl groups, the isohexides pose great potential for further functionalization. A huge number of stoichiometric as well as catalytic approaches have been reported to functionalize the hydroxyl groups by attaching differently functionalized organic residues via ether or ester bond formation.²⁰⁰ However, the direct replacement of the hydroxyl groups in positions 2 and 5 by alternative functional groups is of utmost importance since only then the advantage of the rigid isohexide backbone can be utilized compared to other aliphatic monomers with much higher flexibility. Thus, in the following synthetic and catalytic examples are discussed, focusing on the production of isohexide-based dicarboxylic acids, diamines, and diisocyanates.

2.3.3.1. Carboxylic Acid Derivatives of Isohexides. Rigid dicarboxylic acids, especially terephthalic acid, are of utmost importance for industrial scale polymer applications. Although isohexides show promising properties when applied as dicarboxylic acid monomers,²³⁶ there are only two reports so far that describe their production by a four-step synthetic procedure (Scheme 21).^{237,238} The critical step toward the dicarboxylic acids is the substitution with an additional carbon atom at each position. Therefore, the first step is the 2-fold protection of the hydroxyl groups with triflate leaving groups. Subsequently, they are substituted using potassium cyanide under formation of the isohexide dinitrile. In two further steps the nitrile groups are hydrolyzed under acidic conditions via the methyl ester to finally yield the dicarboxylic acid derivative. Compared with the substrate all substituted groups undergo inversion of the configuration. Thus, starting from isomannide the *exo/exo* configured dicarboxylic acid is easily accessible. However, the overall yield is approximately 45%. Considering the loss as well as the stoichiometric amounts of byproducts produced, the hazardous reagents, and the chlorinated solvents, a scale-up of this process on an industrial scale relevant for polymer production seems less feasible. So far, there are no reports on the catalytic production of the carboxylic acids from the pure isohexides by carbonylation of the hydroxyl groups although it might be a highly relevant alternative. The main challenge is probably the formation of byproducts due to the ether functionalities in the backbone that should also show a certain reactivity under the typically applied harsher reaction conditions for the carbonylation reaction.

2.3.3.2. Isohexide-Based Amines. The noncatalyzed synthetic production of isohexide-based diamines has been known since the 1940s. Similar to the dicarboxylic acid derivatives the functionalization involves two to three reaction steps starting with the insertion of a protection group, followed by the substitution with an amine or similar N-based derivative and

finally the transformation to the respective diamine (Scheme 22).

The first route proposed is based on the tosylated isohexide that is directly converted to the amine under harsh reaction conditions.²³⁹ In an autoclave the substrate is dissolved in ammonia-containing methanol and heated up under solvothermal conditions to 170 °C for 30 h to yield approximately 25% of the raw isohexide amines. Unfortunately, no yields of the final diamine product after distillation and crystallization are given.

A less suitable route for scale-up due to explosive reagents and intermediates was proposed in the 1980s. Initially, the mesitylated intermediate is formed which then is converted in good yields to the diazide undergoing an inversion of the configuration as well.²⁴⁰ In a final step the diazide can then be catalytically reduced using Pd/C and hydrogen in a methanolic solution to form the diamine in yields of up to 88%.²⁴¹

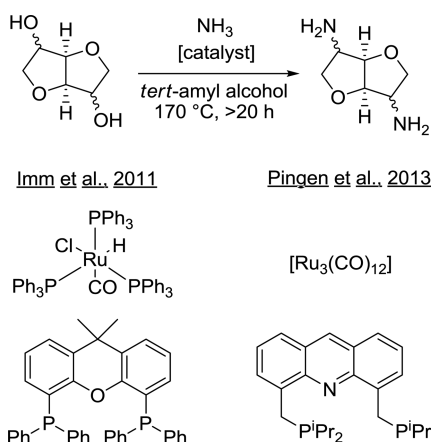
A less hazardous route starting from the ditosylated isohexide uses phthalamide for the functionalization.²⁴² The intermediate is then reduced using hydrazine in ethanolic solution. The disadvantage of that approach is on the one hand the high *E*-factor because the phthalamide auxiliary is of high molecular weight compared to the substrate and the other reagents and, thus, forms significant amounts of waste. On the other hand the reduction with hydrazine only results in diamine yields of up to 13%. Recently, a more efficient alternative was reported solving the issue of the low efficiency of the hydrazine reduction.²⁴³

Therefore, the phthalamide functionalized derivative is hydrolyzed using a mixture of hydrochloride and acetic acid at 135 °C for 24 h to cleave off the auxiliary under formation of the ammonium chloride salt formed by the diamine and hydrochloric acid. This intermediate is then in a final step with yields up to 94% converted to the diamine applying mild reaction conditions in an aqueous solution and the basic ion-exchange resin Amberlyst A26-OH.

Recently, the so far most efficient and appealing route was reported by Thiyagarajan et al.²⁴⁴ Also starting from the ditosylated isohexide, they functionalized the substrate with benzyl amine in good yields of 75–90%. In the second step the benzyl group is removed by catalytic hydrogenation, or rather hydrogenolysis, using carbon-supported Pd(OH)₂ as catalyst in ethanolic solution. At 10 bar hydrogen pressure and 50 °C for 6 h yields of 90% of the isohexide diamine can be achieved.

With the opportunities for the production of biogenic polymers based on rigid diamine building blocks, the need for more efficient routes toward the conversion of sugar alcohols to amines gained increasing attention in recent years.²⁴⁵ The industrial catalytic amination of alcohols with sufficient thermal properties is carried out typically at elevated temperatures of 350–500 °C with solid acid catalysts such as zeolites or alumina. For biogenic substrates and especially the isohexides, gas phase processing is not an option due to their low vapor pressure and high boiling temperature or even thermal decomposition. Thus, liquid phase processes in solvents that allow the dissolution of the polar substrates have to be developed. The catalytic one-pot amination of isohexides (Scheme 23) was first reported in 2011 by Imm et al.²⁴⁶ and a patent application was filed by Evonik.^{247,248} They applied molecular ruthenium catalysts in combination with additional xantphos-derived ligands in organic solvents such as *tert*-amyl alcohol. High yields of diamines of up to 96% were reported at full conversion at 170 °C. Soon after, comparable results based on isosorbide and isomannide were reported by Pinget et al.

Scheme 23. Catalytic Amination of Isohexides Using Different Molecular Ru Catalysts



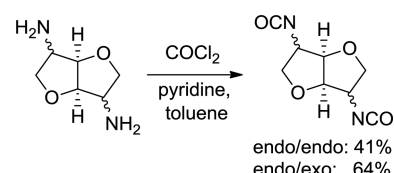
using a Ru-PNP-pincer catalyst.²⁴⁹ Other derivatives of the pincer catalyst in the amination of isohexides at a slightly higher reaction temperature of 200 °C were applied by BASF.²⁵⁰ All catalytic one-pot reactions have in common that, despite high yields of diamines, always a mixture of the three different configuration isomers occurs. This is an artifact of the assumed hydrogen auto transfer mechanism, also known as “borrowing hydrogen”.²⁵¹ It assumes that the catalyst initially dehydrogenates the alcohol to the ketone. The latter then reacts with ammonia to form the imine by condensation. In the final step, the imine is rehydrogenated to the amine using the “borrowed” hydrogen from the initial dehydrogenation step. Thus, during the last reaction step *exo* as well as *endo* configured hydroxyl groups can be formed.

Recently, it was proven that also solid catalysts such as Ru/C can be used in the amination of isohexides.²⁵² To maintain catalyst activity, a certain hydrogen pressure of at least 5 bar is necessary. Also, the solid catalyst allows water to be used as solvent since there are no stability or activity issues with the catalyst. The drawback using solid catalysts so far are the low yields of diamines that are achieved, apparently due to a reversible product inhibition since the diamines seem to adsorb preferentially on the active metal surface.

To avoid the complex reaction mechanism and the issues related to that, also the reductive amination of the isohexide diketones under similar conditions is feasible.²⁵³ However, so far the production of the pure diketone was reported only twice. Evonik developed a process using nitroxyl radicals, e.g., based on TEMPO (2,2,6,6-tetramethylpiperidinyloxy), for the stoichiometric oxidation reaction.²⁵⁴ Very recently, Gross et al. reported an enzyme catalyzed isohexide oxidation using TEMPO as oxidant and laccase as the biocatalyst.²⁵⁵ They obtained diketone yields of >99%. However, so far the experiments were carried out only on the milligram scale.

2.3.3.3. Isohexide-Based Isocyanates. Based on synthetically derived isohexide diamines, Bachmann et al. reported for the first time in 2001 the further conversion toward diisocyanates.²⁵⁶ Compared to diamines mainly for the polyamide market, the isocyanates are used in the production of polyurethanes which possess a significantly larger market share. The synthesis is based on a phosgenation reaction (Scheme 24) of the amine groups. Using dry phosgene (COCl₂) as reactant, the differences in reactivity of the differently configured amine groups were obvious. While the

Scheme 24. Synthesis of Isohexide Diisocyanates from the Respective Diamines



exo/exo configuration gave 80% isolated yield, the *endo/exo* as well as the *endo/endo* configured diamines gave isolated yields of the diisocyanates of 64 and 41%, respectively. To avoid the use of pure phosgene, the less hazardous diphosgene was applied as well. However, it is known that diphosgene gives high yields only in reactions with aromatic amines. Thus, maximum yields of 5% of isohexide-based diisocyanates were observed. Nevertheless, once the availability of isohexide diamines is improved and they are more established not only as a biogenic monomer but also as an intermediate for further processing, the production of the respective isohexide diisocyanates exhibits great potential toward industrial scale polyurethane markets with novel polymers of yet by far not fully explored novel properties.

2.4. Monomers Based on Biotechnological Routes

Biotechnological transformations of biomass feedstocks into building blocks for the production of polymers are currently the focus of numerous studies. Investigations in this direction are so effective that some processes have already been successfully commercialized. Furthermore, the capacity of biotechnological processes and the number of the manufacturers is gradually increasing. In most cases, the process of polymer synthesis consists of two steps. Enzymatic production of the desired monomers presents the first step, while the second step is a conventional polymerization process. The production of polyhydroxyalcanoic acids (PHA) differs from the general procedure, as in this case both the production of monomers and polymerization are conducted *in vivo*. Advances in this field of biocatalytic synthesis of monomers have recently been discussed in a number of reviews^{257–260} and used for estimations of the market growth.^{15,261} Therefore, details already covered recently are not included but we briefly summarize the biochemical routes toward the most important monomers. Additionally, we compare biotechnological routes with chemical pathways toward relevant monomers.

2.4.1. Lactic Acid. Lactic acid (LA) has been known since 1780 when Scheele isolated the compound from milk. The first factory for LA production was started in Littleton, MA, USA, in 1881.²⁶² A great increase in production of LA took place between 1998 and 2004 when PGLA-1 (USA), B&G (China), and Cargill Dow (USA) plants started up their production. PGLA-1 and B&G produced LA for food and industrial purposes, whereas a joint venture of Cargill and Dow (currently NatureWorks) started the synthesis of LA for polymer production with a capacity of 140 kt/year calculated on poly(lactic acid).^{261,263} Today the number of producers is gradually increasing and the market of LA is estimated to 300–400 kt per annum.¹ LA is produced biotechnologically by anaerobic fermentation of sugars. In the course of fermentation, the enzyme called lactate dehydrogenase converts pyruvic acid into LA. LA is optically active and exists in *L*- and *D*-forms. Advances in biotechnology enable production of optically pure LA in either *D*- or *L*-form, or a mixture of them. The content of

Table 1. Literature Data on Chemical Synthesis of Succinic Acid

entry	substrate	[substrate] ₀ ^a , wt %	oxidant	catalyst	time, h	T, °C	yield, %	ref
1	levulinic acid	<i>b</i>	O ₂	V ₂ O ₅	n.d. ^c	375	83	283
2	levulinic acid	12	HNO ₃	V ₂ O ₅	4	40	48 ^d	284
3	levulinic acid	0.6	O ₂	Ru/Fe ₃ O ₄ -SiO ₂	6	150	78	285
4	furfural	22	H ₂ O ₂	no	3	60	36	286
5	furfural	0.3	H ₂ O ₂	Amberlyst	24	80	74	288
6	two-step process:							287
	1. furfural → fumaric acid	12	NaClO ₃	V ₂ O ₅	17	95	46 ^d	
	2. fumaric acid → SA	30	H ₂ ^e	Pd/C	10	160		

^aAqueous solution of substrate. ^bGas phase. ^cNo data on contact time is available. ^dOverall isolated yield of SA. ^eReductant of fumaric acid.

D- and L-enantiomers significantly influences the physical properties of poly(lactic acid). The current manufacture of PLA utilizes LA with a chiral purity of over 98–99% of L-LA.²⁵⁸ Therefore, LA is mainly produced in the form of an optic isomer and only few producers manufacture racemic LA.²⁶³

The production of LA consists of four processing areas: (1) the fermentation of sugars to LA in the presence of a neutralizing agent to maintain a constant pH resulting in lactate salts; (2) acidification to convert these lactate salts to LA; (3) purification that includes separation of cells, nutrients, and residual sugars; (4) removal of water to achieve the required final product concentration, typically 60–70%.²⁶³ The overall yield of LA on carbon basis amounts to ca. 85–90% with 95% yield of the fermentation step and 5–10% losses upon product recovery.^{257,261} Neutralization of the broth (typically to pH 5.8–6.0) during fermentation is required as the reaction decelerates under acidic conditions. Ca(OH)₂ or CaCO₃ is conventionally applied for neutralization during fermentation to produce calcium lactate. On the purification step, the acidification with H₂SO₄ results in precipitation of calcium sulfate and LA remains in solution. This approach represents significant problems with waste disposal since 1 ton of gypsum per 1 ton of LA is produced.²⁶⁴ Improvement of the recovery technology of LA was proposed by means of electro dialysis, ion-exchange processes, ultrafiltration, nanofiltration, liquid-liquid extraction, crystallization, and distillation.^{258,261,263} Simultaneously, the development of a microorganism capable of fermentation under acidic conditions is under research.²⁶³ A microorganism that is able to produce LA at a final pH less than 4.0 has already been developed.²⁶⁵

The most significant cost contribution in the production of LA relates to the costs of the sugar feedstocks. Depending on the location, the sugar sources are either sucrose, or dextrose corn syrups, or starch hydrolysates.²⁶³ A great technological advantage originates from using cheap lignocellulosic hydrolysates as feedstocks. Hydrolysates of cellulose and hemicelluloses, but not lignin, are fermentable to LA. The application of lignocellulosic feedstocks requires significant optimization of the procedure. A special pretreatment is necessary to disrupt the lignin-carbohydrate complex and to destroy the crystalline structure of cellulose.²⁶⁶ Nevertheless, these obstacles have been overcome recently, as the company Cellulac from the United Kingdom has announced the start of a commercial continuous production of LA based on lignocellulosic wastes and deproteinized lactose whey with a capacity of 20 kt per annum. The start of commercialization is expected in 2014–2015. Future scale-up of the production to 100 kt/year in 2017–2018 has recently been announced.²⁶⁷

Alternatively to the biotechnological approach, solid and soluble catalysts for a carbohydrate-based synthesis of LA are

under active development.²⁶⁸ The catalytic activity of soluble bases for this reaction is already known for a long time.^{269,270} However, applying bases as catalysts for carbohydrate transformations is hampered by major drawbacks related to neutralization of the catalyst in the course of the reaction and low selectivity particularly in the case of high substrate concentrations. For instance, Ba(OH)₂ exhibits high efficiency under hydrothermal conditions affording 57% LA based on a 0.025 M solution of glucose, but when 1 M glucose solution is used, the yield of LA decreases to 30%.²⁷¹ Soluble and solid Lewis acids have recently been uncovered as efficient catalysts for the formation of LA and its esters.²⁶⁸ Catalysts containing Sn(IV) or Al(III) as active sites have been considered most frequently.²⁶⁸ The application of Sn-beta zeolites in methanol enables the synthesis of methyl lactate in 64% yield based on sucrose, whereas glucose or fructose yields 40% methyl lactate.²⁷² These lower yields for monosaccharide-based systems probably result from methylation of glucose or fructose as a competitive reaction.²⁶⁸ Cellulose as a substrate for LA is of the greatest interest from a commercial viewpoint. At the same time, cellulose is a highly resistant substrate requiring temperature higher than 180 °C for an efficient transformation. Nevertheless, recent publications report on the synthesis of LA from cellulosic feedstocks in yields of 40–60% in the presence of VOSO₄,²⁷³ Ca(OH)₂,²⁷⁴ Ba(OH)₂,²⁷¹ and Pb(II)²⁷⁵ as well as a mixture of Ni²⁺, Zn²⁺, NaOH, and activated carbon²⁷⁶ as catalysts, respectively. Cellulose,^{271,273,275,276} corn cobs²⁷⁴ or rye straw,²⁷¹ sugar bagasse,²⁷⁵ couch grass,²⁷⁵ and bran²⁷⁵ were used as substrates. Likewise, LA was obtained in yields of ca. 90% based on cellulose in the presence of ErCl₃²⁷⁷ and Er(OTf)₃.²⁷⁸ Being comparable with microbial catalysts in terms of activity, soluble and solid catalysts produce racemic LA, whereas biotechnological production can control the stereospecificity.

2.4.2. Succinic Acid. Succinic acid (SA) is regarded as one of the key intermediates for the production of biomass-based plastics. SA can be utilized as a monomer for the production of polyesters (specifically poly(butylensuccinate), PBS) and can be used as an intermediate for the synthesis of important monomers such as 1,4-butanediol or adipic acid.^{257,279} Similarly to LA, SA used to be of small interest for the naphtha-relying chemical industry. Therefore, the market of SA produced from fossil resources is only 15 kt per annum, whereas the total capacity of SA production is currently estimated to more than 170 kt per annum and gradually increases.²⁸⁰

SA for biomass-based plastics is currently produced biotechnologically utilizing the reductive part of the tricarboxylic acid (TCA) cycle.^{257–260,281} The fermentative production of SA is very carbon-efficient as the reaction of one molecule of glucose with two molecules of CO₂ yields two molecules of

succinic acid. However, fermentation is accompanied by the formation of formates and acetates increasing the costs of SA purification. Moreover, acidification of the broth during fermentation poses a challenge for the efficient production of SA. The traditional industrial production of organic acids relies on calcium titration (see, e.g., section 2.4.1), which is inevitably connected with gypsum formation as a byproduct. Therefore, a number of efforts were made recovering SA more economically. Process options including precipitation of SA, purification by ion-exchange processes, or electrodialysis were patented.²⁸¹ In fact, the expenses of downstream processing amount to 60–70% of the total production costs.²⁵⁸ Especially the production of SA under acidic conditions presents a promising approach that enables reducing recovery costs via recovery of the product by direct crystallization.²⁸² Additionally, intensive research focuses on replacing the currently used sugar feedstocks (sucrose, glucose, and fructose) by cheaper nonedible plant biomass.²⁸¹

The chemical production of SA has been reported as well, but received significantly less attention compared to biotechnological routes. Table 1 summarizes literature data on the chemical syntheses of SA. Levulinic acid^{283–285} or furfural^{286–288} can be converted into SA in 36–83% yield. Oxidants such as molecular oxygen,^{283,285} hydrogen peroxide,^{286,288} sodium chlorate,²⁸⁷ and nitric acid²⁸⁴ were suggested. Van Es et al. reported oxidation of levulinic acid by HNO₃ in the presence of V₂O₅ (Table 1, entry 2).²⁸⁴ Interestingly, the noncatalytic oxidation of levulinic acid with concentrated HNO₃ yields ca. 50% SA and up to 30% oxalic acid. Addition of V₂O₅ in catalytic amounts has nearly no influence on the yield of SA but catalyzes the conversion of oxalic acid into volatile byproducts. As a result, filtration of the reaction mixture and evaporation under vacuum affords pure SA.²⁸⁴ Furfural can be oxidized noncatalytically by H₂O₂ but the yield of SA is low owing to extensive formation of furanone, malic acid, and maleic acid as byproducts (Table 1, entry 4).²⁸⁶ The yield of SA can be improved by addition of Amberlyst as catalyst; moreover, the application of more diluted substrates and H₂O₂ probably increases the yield (Table 1, entry 5).²⁸⁸ A two-step conversion of furfural into SA was recently proposed by Tachibana.²⁸⁷ The process includes (1) oxidation of furfural by NaClO₃ in the presence of V₂O₅ as catalyst yielding 47% fumaric acid and (2) quantitative hydrogenation of fumaric acid into SA over Pd/C (Table 1, entry 6). The use of cheap and ecologically benign oxygen as oxidant is also efficient. The high-temperature process at 365–390 °C can be conducted over a V₂O₅ catalyst (Table 1, entry 1).²⁸³ Supported Ru nanoparticles enable decreasing the temperature to 150 °C when operating at an elevated oxygen pressure of 14 bar (Table 1, entry 3).²⁸⁵ Although chemical syntheses allow access to SA in good yields, the carbon efficiency is inferior compared to that of the fermentative processes due to the lack of naturally available C₄ substrates. The oxidative cleavage of C₅ substrates (levulinic acid or furfural) provides SA as a C₄ fragment and a C₁ compound that is most probably CO₂. Capture and valorization of CO₂ would improve the carbon efficiency of the chemical oxidation.

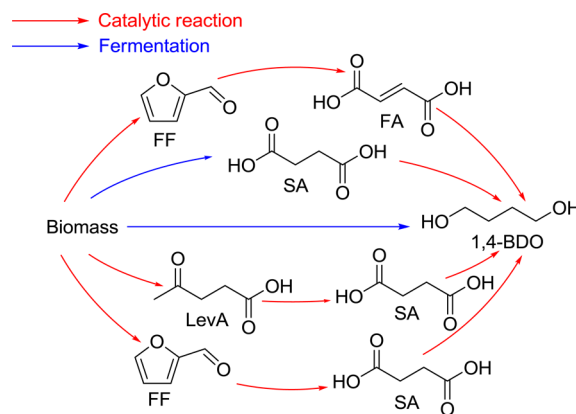
2.4.3. Diol Monomers. Diols are widely used in the polymer industry for the synthesis of polyesters and polyols. The efforts of biocatalytic investigations are currently focused on synthesis of four diols that are utilized or can potentially be used for the manufacture of biobased polymers, which are 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1,4-

butanediol (1,4-BDO), and 2,3-butanediol (2,3-BDO). 1,2-PDO and 1,4-BDO are produced today as bulk chemicals based on petroleum resources with volumes of 1500²⁸⁹ and 1300^{258,289} kt/year, respectively. The total market volume of 1,3-PDO is much less and is estimated to be 125 kt/year.¹ With a capacity of 90 kt per annum, the biobased production has already surpassed the naphtha-based manufacture of 1,3-PDO.¹

Microbial synthesis of 2,3-BDO was intensively investigated in the 1940s mainly considering 2,3-BDO as an intermediate for the production of 1,3-butadiene. The development was carried out up to the pilot plant stage.²⁹⁰ Due to the availability of cheap petroleum feedstocks in the 1950s, these studies have not been continued.²⁹⁰ Today, the interest in 2,3-BDO as a potential monomer and intermediate is revived. 2,3-BDO can be synthesized biotechnologically from a wide range of substrates. The advantages of the process are the possibility to reach a high concentration of 2,3-BDO of up to 150 g L⁻¹,²⁸⁹ a nearly quantitative yield of the product of up to 98%,^{289,291} and good productivity.^{289,291} To the best of our knowledge, no chemical biomass-based synthesis of 2,3-BDO has been proposed yet.

The production of 1,4-BDO from biomass has recently received a lot of attention. Different routes leading to 1,4-BDO are presented in Scheme 25.

Scheme 25. Proposed Routes for Biomass-Based Synthesis of 1,4-Butanediol (1,4-BDO)^a

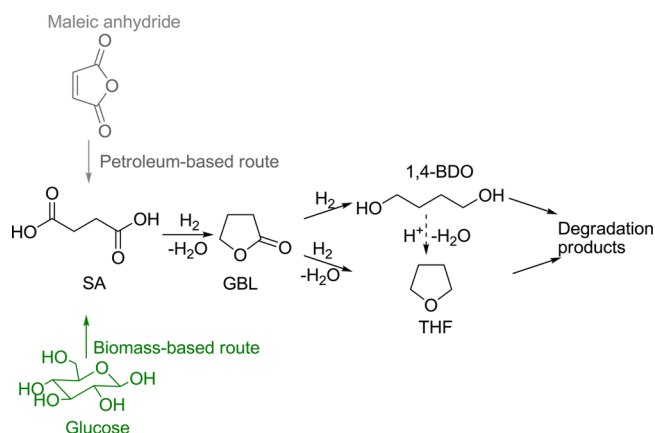


^aAbbreviations: FF (furfural), FA (fumaric acid), SA (succinic acid), and LevA (levulinic acid).

The biochemical production of 1,4-BDO based on glucose and sucrose has already been commercialized.^{1,258} The fermentation is conducted under batch operation mode, and the downstream processes include recovery of 1,4-BDO by liquid–liquid extraction.²⁹²

An alternative pathway toward 1,4-BDO relates to the synthesis of SA followed by reduction (Scheme 26). Section 2.4.2 summarizes the recent advances in the biotechnological and chemical syntheses of SA. Notably, the production of 1,4-BDO via fermentative synthesis of SA and successive hydrogenation is close to commercialization.¹ The high commercial interest in the hydrogenation led to extensive patent literature covering this field. Succinic anhydride, SA, and alkyl succinates are easily produced from maleates as intermediates in the hydrogenation toward 1,4-BDO (Scheme 26). Therefore, data concerning the hydrogenation of maleates can also be applied for the conversion of succinates. More recent literature considers direct transformations of alkyl

Scheme 26. Production of 1,4-Butanediol (1,4-BDO) via Hydrogenation of Succinic Acid (SA)^a



^aThe petroleum-based route relates to the chemical production of SA from maleic anhydride. The biomass-based route utilizes renewable feedstocks for synthesis of SA. Both routes have γ -butyrolactone (GBL) as intermediate and tetrahydrofuran (THF) as side product.

succinates,^{293–296} SA,^{297–300} or succinic anhydride.^{301,302} The hydrogenation can be carried out in vapor phase^{294,295,302} or in liquid phase using dioxane,^{293,301} water,^{298–300} methanol,²⁹⁶ and dioxane–water mixture²⁹⁷ as solvents. The hydrogenation of SA occurs stepwise via formation of γ -butyrolactone (GBL) that can be transformed either into 1,4-BDO or into THF (Scheme 26). The selectivity toward 1,4-BDO can be tuned by variation of the reaction conditions and tailoring of the catalyst. Formation of 1,4-BDO is thermodynamically limited;^{296,301} therefore, good yields of 1,4-BDO are achievable at optimal temperature, high pressure of H₂, and an excess of hydrogen over the organic substrate. High yields of 1,4-BDO^{293,294} of ca. 80% were reported for the hydrogenation at 170–180 °C and 170 bar H₂. Operation at higher temperature and lower pressure leads to preferable formation of THF.^{293,294} Copper-containing catalysts are very efficient for the synthesis of 1,4-BDO. Both bulk^{294,301,302} and supported^{296,301} catalysts were tested and a decrease of the copper surface area after reaction was reported for Cu/SiO₂.²⁹⁶ Promoting Cu with Zn significantly accelerates the first step of the reaction, i.e., the transformation of SA into GBL.^{301,302} More recently, also catalysts containing noble metals were investigated. In contrast to copper catalysts, monometallic Pd and Ru catalyze the formation of GBL as the final product.^{300,301} Bimetallic catalysts such as Pd–Re,^{293,298,299,301} Ru–Re,²⁹⁹ and Ru–Co²⁹⁷ were reported to be active for the production of 1,4-BDO in yields of up to 66%. Notably, the successive degradation of 1,4-BDO into *n*-butanol, *n*-propanol, and propionic acid was detected under reaction conditions.^{293,294,296,297,301} The synthesis of 1,4-BDO over the catalysts supported on Al₂O₃ or SiO₂ is accompanied by dehydration of 1,4-BDO into THF over acidic sites of the support.^{301,302}

Tachibana et al. reported the synthesis of 1,4-BDO starting from furfural via oxidation toward fumaric acid with successive reduction. The oxidation was accomplished with NaClO₃ over V₂O₅ as catalyst giving fumaric acid in 47% yield. The reduction of fumaric acid was performed over a Pd–Re/C catalyst yielding 63% 1,4-BDO. Notably, the reaction conditions for hydrogenation of fumaric acid are similar to those employed for hydrogenation of maleic anhydride or succinates: 160 °C, 130 bar H₂, and aqueous solution.²⁸⁷

Glucose and glycerol are typically considered as substrates for biotechnological synthesis of 1,2-PDO and 1,3-PDO. Due to the lower price of glucose compared to glycerol, this feedstock is used for industrial manufacture of 1,3-PDO. The transformation of glucose into 1,3-PDO includes two steps, namely the formation of glycerol from glucose and the further transformation of glycerol into 1,3-PDO. Industry utilizes the microorganism *Escherichia coli* genetically engineered by the expression of genes for glycerol production in 1,3-PDO strains.²⁶⁰ The production of 1,2- and 1,3-PDO based on glucose is not very carbon efficient as the products are more reduced compared to the substrate. Therefore, glucose is partly spent as a reductant forming lactates and CO₂ as by-products.^{289,291} Different ways to valorize these byproducts were suggested. For example, Zeng et al. successfully applied a mixed culture to convert byproducts simultaneously into methane, resulting in 1,3-PDO and methane as products.²⁸⁹

An alternative approach relates to the successive degradation of byproducts in a biogas reactor performed on the level of a pilot plant.²⁸⁹ After fermentation, the broth is filtered and is concentrated by evaporation, and 1,3-PDO is recovered by distillation.¹⁵ The yield of 1,3-PDO is ca. 50%.²⁸⁹ For the glucose- or glycerol-based production of 1,3-PDO, the costs of the feedstock represent up to 50% of the whole production costs. In order to reduce the costs, applying cheaper substrates such as raw glycerol or hemicellulose hydrolysate is studied.²⁸⁹ The fermentative synthesis delivers 1,2-PDO only in small yields of ca. 25%.²⁸⁹ Moreover, the fermentation produces very diluted solutions of 1,2-PDO with a maximum concentration of 2–9 g/L.²⁸⁹ These disadvantages hamper industrialization of the microbial process.

Chemocatalytic production of 1,2-PDO based on lignocellulose can be considered as an alternative to low-efficient microbial synthesis. Hydrogenolysis of cellulose or hemicelluloses results in a mixture of alcohols. In recent years, especially catalytic processes facilitating direct access to ethylene glycol as well as 1,2- and 1,3-PDO were intensively investigated. In the following, a brief overview of current developments is provided. Several reviews summarize the progress in this field, and the reader is referred to these references for a comprehensive literature overview.^{226,303–307}

The composition of the products can be tuned by changing the catalyst formulation and adjusting the reaction conditions. Thus, quite good selectivity toward ethylene glycol can be reached via a series of one-pot reactions, i.e., (1) hydrolysis of cellulose yielding glucose, (2) retro-aldol cleavage of glucose into three molecules of glycolaldehyde, and (3) hydrogenation of the latter.³⁰⁸ Since ethylene glycol is of great interest for the polymer industry, this transformation has recently received great attention. Hydrogenolysis of cellulose^{309–312} or even lignocellulose^{313,314} yields 38–73%^{309–314} ethylene glycol. The hydrogenolysis toward ethylene glycol is efficiently catalyzed by Ni–W₂C/AC,^{308,309,313,314} Raney Ni + H₂WO₄,³¹⁰ Ni/AC + La(OH)₃,³¹¹ and Ru/C + WO₃.³¹² More recent studies reported selective production of 1,2-PDO by hydrogenolysis of cellulosic biomass. Considering 1,2-PDO as the target product, the following series of transformations has to be accomplished: (1) hydrolysis of cellulose yielding glucose; (2) isomerization of glucose into fructose; (3) retro-aldol cleavage of fructose into C₃ fragments; (4) hydrogenation–dehydration of the latter yielding 1,2-PDO. This complex reaction cascade was efficiently performed in the presence of such catalysts as Ni–Cu/ZnO,³¹⁵ CuCr₂O₄/CuO,³¹⁶ Pd–WO_x/Al₂O₃,³¹⁷ Ru/C

+ $\text{WO}_3/\text{Al}_2\text{O}_3$ + C_{act} ³¹² and $\text{CuCr}_2\text{O}_4/\text{CuO}$ + $\text{Ca}(\text{OH})_2$.³¹⁸ Yields of 1,2-PDO equal 31–36%^{312,315,316} when using cellulose as substrate, and 53–61%^{317,318} based on glucose. Alternatively, use of inulin or fructose as substrates were suggested for synthesis of 1,2-PDO resulting in 40–62% yield.^{317,319} In addition to lignocellulosic substrates, catalytic hydrogenolysis of glycerol over supported metal catalysts can be used for the production of 1,2-PDO^{320–325} or 1,3-PDO.^{326–329} Additionally, hydrogenation of lactic acid³³⁰ and its derivatives, such as lactide³³¹ or ethyl lactate,^{332–334} enables 88–93% yields of 1,2-PDO. Co/SiO_2 ,^{332,334} Cu/SiO_2 ,^{330,332} $\text{Ru}(\text{II})$ complexes,³³¹ and $\text{Ru}-\text{B}/\text{Al}_2\text{O}_3$ ³³³ were reported to be efficient catalysts for the hydrogenation.

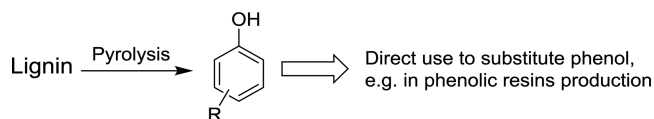
2.4.4. Itaconic Acid. Itaconic acid (IA) is a dicarboxylic acid containing a double bond (Figure 1). IA was first identified by Baup during pyrolytic distillation of citric acid in 1837. Other chemical techniques for synthesis of IA were proposed afterward, i.e., oxidation of isoprene or the method of Montecatini based on propargyl chloride, carbon monoxide, and water in the presence of nickel carbonyl as catalyst.³³⁵ Nevertheless, the fermentative synthesis of IA discovered in 1932 appeared to be most appropriate for commercialization. Since 1955, IA has been produced biotechnologically by means of fermentation of carbohydrates by fungi, specifically *Aspergillus terreus*.³³⁶ Most likely IA is formed via glycolysis and the tricarboxylic acid cycle as a product of enzymatic decarboxylation of citric acid.³³⁵ Mutagenesis of strains enabled production of IA with concentrations of up to 80 g L⁻¹.³³⁷ IA is produced using batch fermentation with suspended *A. terreus* on biomass,^{335,337} inoculated as spores on pretreated molasses.³³⁸ The operation time of fermentation is usually 7 days with a maximum productivity of IA of 1 g L⁻¹ h⁻¹.^{335,337} In recent years, several steps toward improved fermentation economics were undertaken. For example, optimized reactors and immobilized enzymes were investigated along with efforts focused on the elaboration of continuous operation and the application of cheaper substrates. The air lift reactor (ALR) appeared to be very promising for production of IA as it has much less energy demand than a stirred tank reactor (STR).³³⁹ Moreover, the ALR overcomes mechanical stirring which is beneficial because mechanical rotation can induce shear stress on fungi.³³⁷ However, immobilized *A. terreus* as well as application of continuous operation mode leads to a decrease of the IA concentration to 20–26 g L⁻¹ at maximum, which is inappropriately low for an industrial process.³³⁷ Good yields of IA rely on a good quality of the carbohydrate substrate as the productivity of IA is very sensitive to such components in the medium as Fe, Mn, Cu, Zn, P, and N.³³⁵ Utilizing crystalline carbohydrates is rather expensive. Instead, hydrolyzed starch and beet or sugar cane molasses as substrates were suggested. Prior to use, the molasses is treated by ion exchange or ferrocyanide.³³⁵ Traditionally, IA is recovered from the broth according to the following scheme: (1) removal of mycelium and solids by filtration; (2) evaporation of the solvent; (3) crystallization of IA at reduced temperature. If required, IA is decolorized by an activated carbon treatment. Additionally, several novel techniques for purification were suggested including ultrafiltration,³⁴⁰ reverse osmosis,³⁴¹ ion exchange,³⁴² and electro dialysis.³⁴³ Currently IA is produced with a capacity of ca. 80 kt per annum.³³⁷

2.5. Aromatic Monomers

2.5.1. From Biomass to Phenolic Monomers. Renewable phenolic compounds can be obtained from various biomass species and components, such as lignin, tannin, and extracts from cashew nut shell, palm oil, and coconut shell. Lochab et al.³⁴⁴ comprehensively reviewed the naturally occurring phenolic sources, the isolation process of desired phenol compounds, and the utilization of them for polymer production. In this section, we are mainly focused on the catalytic preparation of phenols from lignin and the chemical transformation of these phenols to novel monomers. At some points the potential to utilize lignin-derived monomers for the production of conventional monomers is highlighted, but the comprehensive discussion of these value chains is beyond the scope of this review.

2.5.1.1. Pyrolysis of Lignin to Phenolic Compounds. Pyrolysis is an effective way to degrade polymeric biomass materials into small molecules.³⁴⁵ Although the pyrolysis of lignin and lignocellulosics was carried out with the aim of biofuel production, this protocol can produce different phenols and arenes (Scheme 27).^{346,347} In principle, the phenols could

Scheme 27. Pyrolysis of Lignin Compounds to Phenols as Bridging Technology toward Conventional Monomers

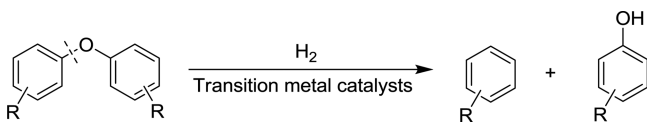


be directly used to replace fossil-based phenol synthesizing phenol–aldehyde resins. The drawback of the pyrolysis of lignin to monomers is the low content of the desired products in the mixture. It is difficult to isolate the pure chemicals from the mixture, which contains hundreds of compounds.³⁴⁵ Pyrolytic lignin is produced from lignin during the flash pyrolysis process. At high temperature natural lignin degrades into oligomers with lower molecular weight (ca. 1000 Da). These oligomers make up the main nonvolatile components of bio-oil and could be isolated from bio-oil.³⁴⁸ Sharma et al.³⁴⁹ reported the first catalytic pyrolysis of pyrolytic lignin in the presence of HZSM-5 with tetralin. They found that 30 wt % of the pyrolytic lignin could be converted to liquid products. Among them, the phenols content reached 6.9%. Fu et al.³⁵⁰ reported that the pyrolytic lignin could be transformed into aromatics with a reasonable carbon yield (40%) via catalytic or noncatalytic pyrolysis. In the absence of a catalyst, the main liquid products are phenols. The selectivities for cresol and phenol achieved 16 and 12%, respectively. Using ZSM-5 as catalyst, most phenols were deoxygenated, giving benzene and toluene with selectivities of 9 and 32%, respectively. The same group also described that the lignins obtained from pulping were not suitable for pyrolysis due to their high coke yield and sulfur contaminants. The pyrolysis of lignin in the presence of H_2 and an iron–silica catalyst in a fixed-bed reactor afforded a good selectivity for the hydrodeoxygenation of real lignin vapors to benzene, toluene, xylenes, phenol, cresols, and alkyl phenols. Compared to the noncatalytic pyrolysis, the selectivity for phenols could be enhanced from less than 20% to more than 60%.³⁵¹

2.5.1.2. Reductive Cleavage of Lignin to Phenolic Compounds. Reductive cleavage of lignin in the presence of hydrogen gas or a hydrogen donating solvent is another

effective method to depolymerize lignin, which is also applied for liquid fuel production. According to the investigation of the hydrogenation of model compounds, different phenols can be synthesized selectively. Bergman et al.³⁵² reported a ruthenium-catalyzed redox cleavage of the C–O bond of a lignin model compound delivering 4-acetylphenol with a yield of 99 mol % (Scheme 28). The reaction involved dehydrogenation of the

Scheme 28. Selective Cleavage of the Ether Bond of Lignin Model Compounds



substrate and reductive ether bond cleavage. Hartwig et al.³⁵³ demonstrated that the hydrogenation of diaryl ether in the presence of ligandless and carbene ligated nickel catalysts exhibited obvious differences in reactivity and selectivity. Using Ni(COD)₂ as catalyst, 97 mol % phenol could be obtained from 4-hydroxyl biphenyl ether. The in situ formed Ni nanoparticles were considered as active species. On the other hand, 4-hydroxyl biphenyl ether was mainly hydrogenated into hydroquinone and benzene in the presence of Ni(COD)₂ and a carbene ligand.³⁵⁴ The selective aryl ether bond cleavage also occurred over a heterogeneous Fe catalyst in situ generated from Fe(acac)₃.³⁵⁵

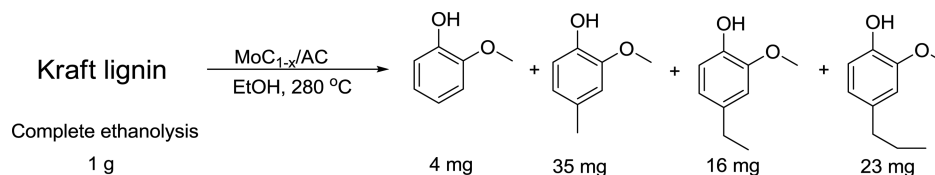
Compared to model compounds, the complex structure and poor solubility of natural lignin cause more difficulty for selective degradation to phenolic compounds. Recent studies revealed that transfer hydrogenation could favor the depolymerization of lignin into small molecules. Rinaldi et al.³⁵⁶ demonstrated the conversion of poplar wood lignin to several phenolic compounds in an *i*-PrOH/H₂O mixture with Raney Ni. In the process, *i*-PrOH acted as both solvent to extract lignin and hydrogen donor for reductive cleavage of the ether bonds. Similarly, valorization of native birch wood lignin into monomeric phenols over nickel-based catalysts in alcohols provided propylguaiaicol and propylsyringol with a total selectivity of >90% at a lignin conversion of about 50%. The presence of gaseous H₂ has no effect on lignin conversion, indicating that alcohols provide active hydrogen species.³⁵⁷ In the presence of nickel catalysts, lignosulfonate could also be hydrogenated into phenols.³⁵⁸ Weckhuysen et al.³⁵⁹ reported a two-step approach converting organosolv, kraft, and sugar cane bagasse lignin to monoaromatic compounds. The first step consists of lignin depolymerization in a liquid phase reforming (LPR) reaction over a 1 wt % Pt/ γ -Al₂O₃ catalyst at 225 °C in alkaline ethanol–water. GC analysis of the depolymerized lignin reaction mixture showed the formation of alkylated phenol, guaiaicol, and syringol-type products in 11, 9, and 5% yields from organosolv, kraft, and bagasse lignin, respectively. A complete ethanolysis of kraft lignin took place over an α -

MoC_{1-x}/AC catalyst in pure ethanol at 280 °C. As a result, 1 g of kraft lignin delivered 78 mg of substituted phenols (Scheme 29).³⁶⁰ Using Ni–W₂C/AC as catalyst, lignin in raw woody feedstock was converted selectively into monophenols with a yield of 46.5%.³⁶¹ Samec et al.³⁶² performed tandem organosolv transfer hydrogenolysis (TOH) of pine wood and birch wood with 23% yield of 2-ethoxy-4-(prop-1-enyl)phenol and 49% yield of 2,6-dimethoxy-4-(prop-1-enyl)phenol, respectively. These values corresponded to 92% of the theoretical maximum monomer yield. They also proposed a plausible mechanism of the selective production of the unsaturated phenols illustrated in Scheme 30.

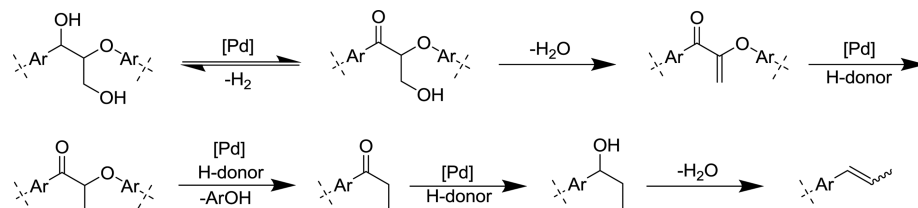
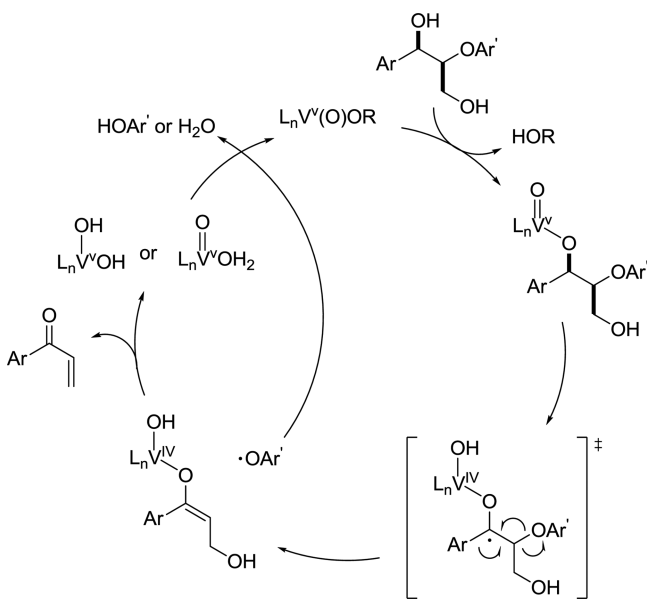
2.5.1.3. Oxidative Cleavage of Lignin to Phenolic Compounds. Oxidative cleavage of lignin is another effective way to produce phenolic compounds. To understand the cleavage of β -O-4 linkages of lignin, Toste et al.³⁶³ employed a dimeric model compound investigating the conversion in the presence of various homogeneous vanadium complexes. They found that tridentate Schiff base ligands containing vanadium complexes favor C–O bond cleavage over benzylic oxidation. The C–O bond cleavage reactions of dimeric lignin model compounds happen in a nonoxidative way, producing aryl enones as unprecedented degradation products. A possible one-electron mechanism was proposed (Scheme 31). Silks et al.³⁶⁴ reported reactivity studies of a ¹³C-labeled phenolic lignin model compound with catalysts **1** and **2** (Scheme 32). Vanadium catalyst **2** mediates a new type of reaction in which the C–C bond between the aryl ring and the adjacent alcohol group is broken to give 2,6-dimethoxybenzoquinone and an acrolein derivative. In contrast, catalyst **1** affords the C–O bond cleavage products 2-methoxyphenol and para-substituted 2,6-dimethoxyphenol, which were likely generated via the pathway reported by Toste et al.³⁶³

von Rohr et al.³⁶⁵ developed a polyoxometalate mediated oxidation of kraft lignin into functionalized phenols (Scheme 33). In their protocol, a radical scavenger was used to prevent lignin fragments from repolymerizing. Under optimized conditions, vanillin and methyl vanillate were obtained in a maximum yield of 5 wt % based on dry kraft lignin. Fu et al.³⁶⁶ employed H₃PMo₁₀V₂O₄₀ as catalyst to degrade five lignin species, i.e., pyrolytic lignin, hydrolytic lignin, alkali lignin, sodium lignosulfonate, and calcium lignosulfonate. Under optimized conditions, oxidative products with a yield of 65.21% were achieved from pyrolytic lignin. Using a mixture of cobalt acetate, manganese acetate, zirconium(IV) acetate, and hydrobromic acid as catalyst, ca. 10 wt % of substituted phenols (including hydroxybenzaldehyde, hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, and syringic acid) could be obtained from organosolv lignin.³⁶⁷ Bosmann et al.³⁶⁸ reported the oxidative depolymerization of beech lignin in ionic liquids, which enables the dissolution of a high amount of natural lignin. By adjusting the reaction conditions and catalyst loading, the selectivity of the process could be shifted from syringaldehyde as the predominant product to 2,6-dimethoxy-

Scheme 29. Complete Ethanolysis of Kraft Lignin to Phenols



Scheme 30. Proposed Pathway for Unsaturated Phenols Generation from Lignin

Scheme 31. Plausible Mechanism of Nonoxidative Cleavage of the β -O-4 Linkage of Dimeric Model Compounds

1,4-benzoquinone, which could be isolated as a pure substance in 11.5 wt % overall yield by a simple extraction/crystallization process.

Very recently, Stahl et al.³⁶⁹ described a method for the depolymerization of oxidized lignin under mild conditions in aqueous formic acid. In detail, aspen lignin was subjected to aerobic oxidation in the presence of 4-acetamido-TEMPO prior to the depolymerization.³⁷⁰ Then formic acid was added with sodium formate and reacted with the oxidized lignin at 110 °C for 24 h. As a result, over 60 wt % yield of low molecular mass aromatics were generated, including 52 wt % phenolic monomeric products (Figure 3) and 9 wt % dimers and

Scheme 33. Polyoxometalate Catalyzed Oxidation of Lignin to Vanillin

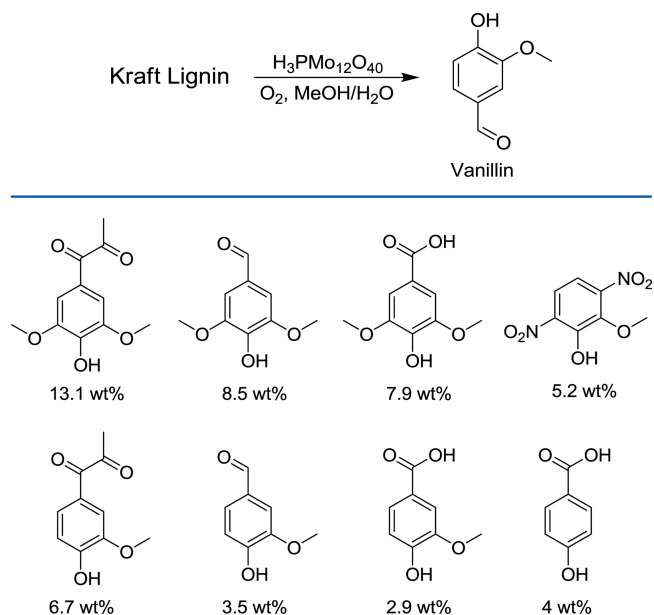
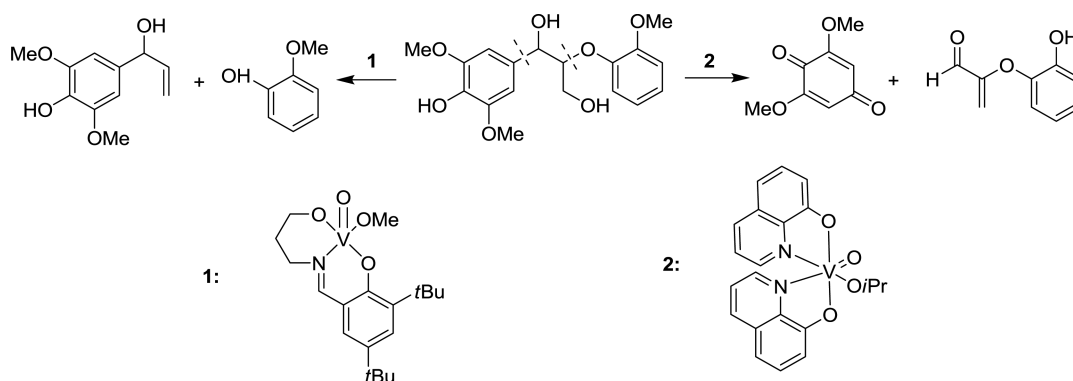


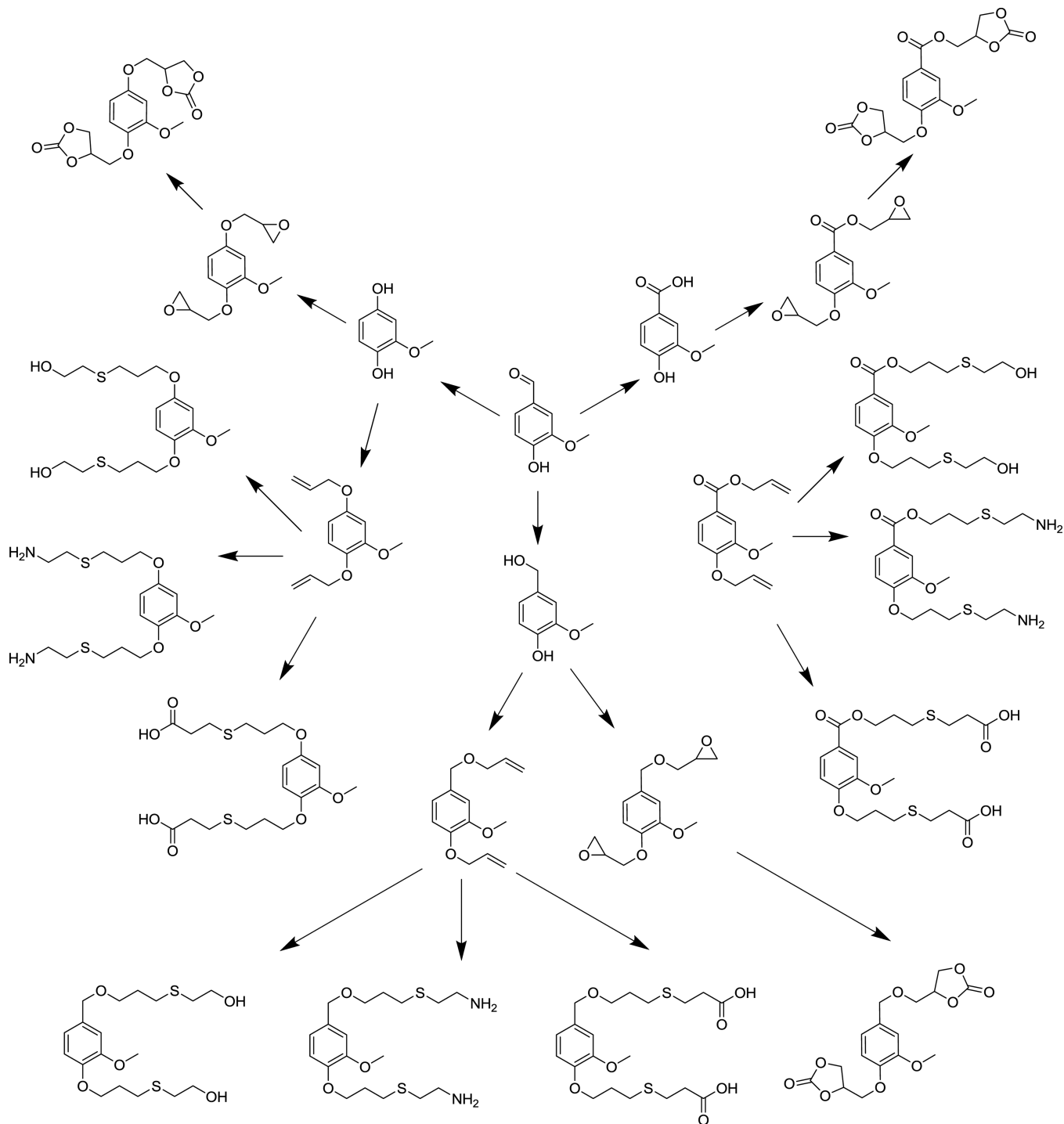
Figure 3. Phenolic products from the formic acid induced depolymerization of oxidized lignin.

trimers. Note that the formic acid was not consumed in the depolymerization process. Obviously, the reaction pathway differs from the hydrogenolysis mediated by metal catalysts. According to their mechanistic study, the oxidized α -carbonyl group played a crucial role in the following ether bond cleavage.

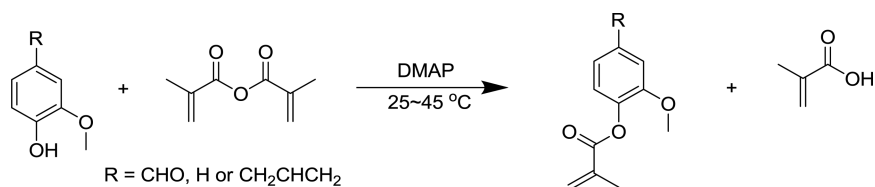
2.5.1.4. Conversion of Vanillin to Novel Monomers. Vanillin has been recognized as a representative lignin derived product because it is not only one of the major products from the oxidative lignin transformation but also possesses three

Scheme 32. Oxidative Cleavage of the β -O-4 Linkage and the C-C Bond of a Lignin Model Compound in the Presence of Different Vanadium Catalysts

Scheme 34. Some Vanillin-Derived Novel Monomers



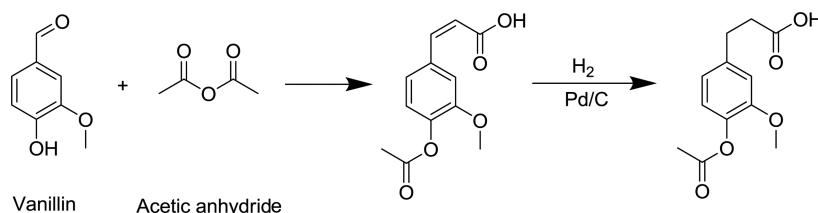
Scheme 35. Synthesis of Vanillin-Derived Methacrylic Ester



typical oxygenate functional groups, hydroxyl, methoxy, and formyl, on a benzene ring.^{37†} Although the yield of vanillin

from lignin is not adequate based on current studies, vanillin could still be considered as a targeted product from lignin in

Scheme 36. Synthesis of Acetyldihydroferulic Acid from Vanillin

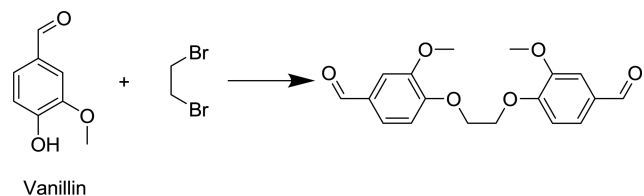


future works and it is also reasonable to utilize it as a lignin derived molecule for monomer synthesis. Recently, Caillol et al.³⁷² employed vanillin as a renewable building block to develop a platform of 22 biobased compounds for polymer chemistry. As shown in Scheme 34, vanillin-derived biobased monomers bearing epoxy, cyclic carbonates, allyl, amine, alcohol, and carboxylic acid moieties were synthesized. They can be used, among many others, in epoxy, polyester, polyurethane, and non-isocyanate polyurethane polymer synthesis.

Wool et al. developed the two-step, one-pot methacrylation of vanillin to produce a vinyl ester resin monomer to replace petroleum-based vinyl esters.³⁷³ They also converted guaiacol and eugenol to the corresponding vinyl esters by esterification with methacrylic anhydride and a catalytic amount of 4-dimethylaminopyridine (Scheme 35).

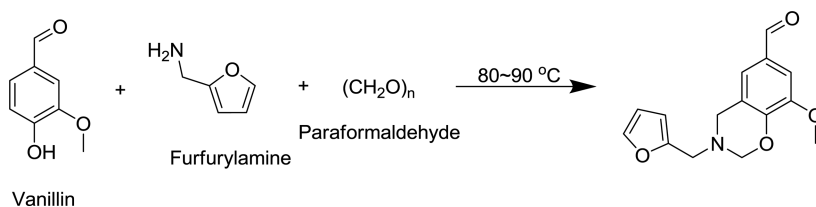
With the aim of replacing petroleum based terephthalate for poly(ethylene terephthalate) (PET) production, Miller et al.³⁷⁴ reported the synthesis of acetyldihydroferulic acid via a two-step process (Scheme 36). The first step is the Perkin reaction and esterification between vanillin and acetic anhydride providing acetylhydroferulic acid in a yield of 69%. The following hydrogenation in the presence of Pd@C yielded 85% acetyldihydroferulic acid. The authors also reported the production of novel dibenzaldehyde compounds from vanillin, 4-hydroxybenzaldehyde, syringaldehyde, and ethylvanillin with dibromoethane (Scheme 37). These monomers can copolymerize with tetraols, yielding polyacetal ethers with cyclic acetals.³⁷⁵

Scheme 37. Synthesis of Dibenzaldehyde Compounds from Vanillin



The novel vanillin-based benzoxazine monomer could also be synthesized via Mannich condensation reaction of vanillin,

Scheme 38. Synthesis of a Vanillin-Based Benzoxazine Monomer



furfurylamine, and paraformaldehyde applying a solvent-free method (Scheme 38).³⁷⁶

Harvey et al.³⁷⁷ demonstrated that a series of renewable bisphenols could be synthesized from creosol (2-methoxy-4-methylphenol) through stoichiometric condensation with short-chain aldehydes (Scheme 39). The starting material

Scheme 39. Renewable Bisphenol Production from Creosol



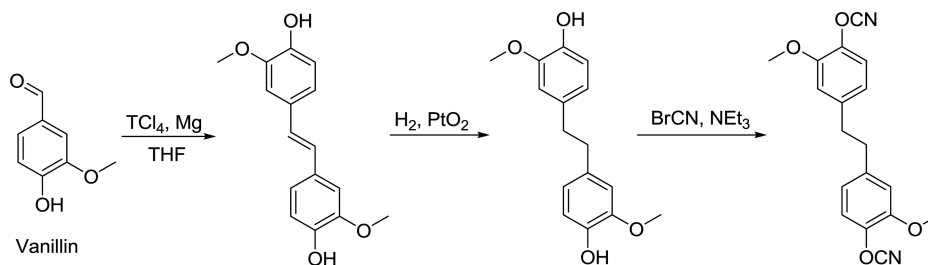
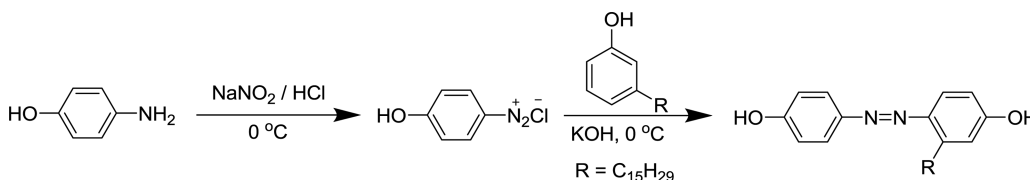
creosol can be readily produced from vanillin by hydrodeoxygenation in the presence of hydrogen gas and noble metal catalysts.^{371,378,379} It has also been shown that lignin-type phenols are suitable substrates for the Pd-catalyzed telomerization of 1,3-butadiene. The resulting octadienyl ethers are easily transformed via Claisen rearrangement to the ring alkylated products, providing opportunities for the preparation of phenolic rubbers via metathesis.³⁸⁰

Solely using vanillin as substrate, the bisphenol compounds could be produced through McMurry coupling in the presence of TiCl_4 and Mg. Consequently, a medium yield of the unsaturated bisphenol was obtained and the following Pt-catalyzed hydrogenation afforded 1,2-bis(4-hydroxy-3-methoxyphenyl)ethane which could be further converted into the dicyanate monomer (Scheme 40).³⁸¹

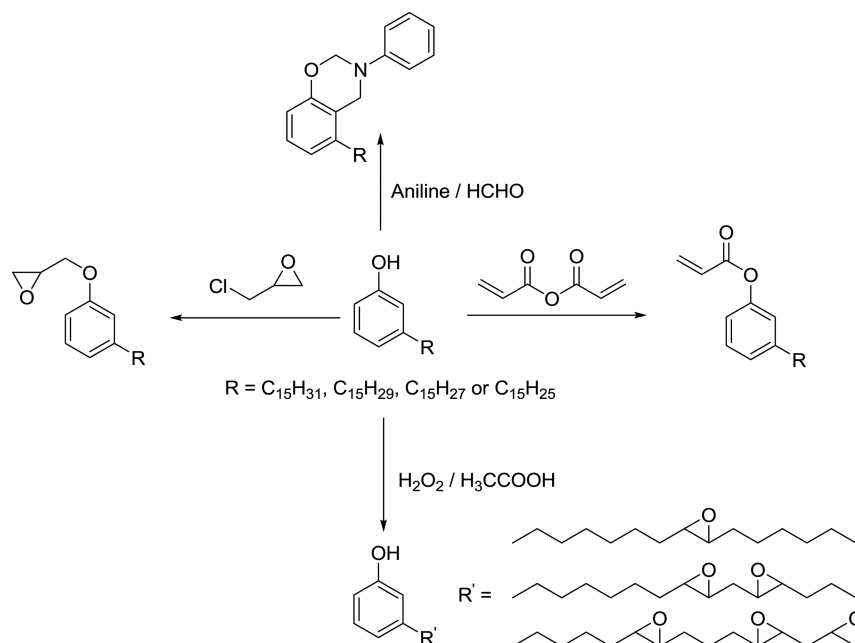
2.5.1.5. Conversion of Cardanol to Monomers. Cardanol, the major constituent of cashew nut shell liquid, is a kind of 3-alkyl substituted phenol. Typically, the heat-extracted cashew nut shell liquid contains approximately 52–60% cardanol. The unsaturated side chain and hydroxyl group enable a chemical modification of this compound to biomoners. Nando et al.³⁸² reported the synthesis of a bisphenol compound from cardanol and *p*-aminophenol (Scheme 41). The prepared bisphenol compound could be applied for thermoplastic polyurethane synthesis.

Similarly to vanillin, the hydroxyl group of cardanol can also be modified to generate monomers (Scheme 42). The cardanyl acrylate could be prepared from cardanol and acrylate

Scheme 40. Bisphenols and Dicyanate Production from Vanillin

Scheme 41. Synthesis of a Bisphenol Compound from Cardanol and *p*-Aminophenol

Scheme 42. Synthesis of Cardanyl Acrylate, Epoxy Resin, and Benzoxazine Monomer



anhydride. The compound could be used to produce a self-cross-linkable polymer owing to the C–C double bonds on the side chain of the cardanol moiety.³⁸³ Using cardanol, aniline, and paraformaldehyde as substrates, the cardanol derived benzoxazine monomer could be synthesized.³⁸⁴ The preparation of glycidyl ether of cardanol could be achieved by reacting epichlorohydrin and cardanol.³⁸⁵ Another way to introduce an epoxy group is epoxidation of the unsaturated side chain of cardanol with hydroperoxide and an organic acid.³⁸⁵

2.5.2. From Biomass to Arenes. **2.5.2.1. Arenes via Catalytic Pyrolysis.** As mentioned above, pyrolysis is an effective way to degrade lignin and other biomass components to small molecules. However, the broad product distribution causes difficulties in purification and utilization of these compounds. With this in mind, catalysts were introduced into the pyrolysis process with the aim of the selective production of useful chemicals, especially liquid fuels. Thus, zeolites were employed to deoxygenate substituted phenols^{349,350} and

furans^{385–391} and to maximize the yield of arenes. The arenes obtained from the pyrolysis of lignin could be used to produce various important monomers via the existing routes, which are currently applied in petrochemical industry, e.g., from toluene to TDI, from xylene to terephthalate, etc.

2.5.2.2. Reductive Cleavage of Lignin to Arenes. According to Rinaldi's work,³⁸⁶ pyrolytic lignin in bio-oil can be converted to arenes with high selectivity through Raney Ni catalyzed transfer hydrogenation utilizing 2-PrOH as solvent at 140 °C. Semiquantitative analysis by GC–GC–FID indicates that 71 wt % of the detected products are arenes, 26 wt % are alkanes, and 3 wt % are phenols. This is an effective and selective approach to lignin-based arenes. In the presence of $\alpha\text{-MoC}_{1-x}/\text{AC}$ and hot ethanol (280 °C), 1 g of kraft lignin can be converted to 74 mg of *m*-xylene and 22 mg of *p*-xylene.³⁶⁰ To produce styrene, alternative routes based on cinnamic acid through decarboxylation,^{392–399} decarbonylation,⁴⁰⁰ and olefin metathesis⁴⁰¹ were developed.

3. POLYMERS BASED ON BIOMASS-DERIVED MONOMERS

3.1. Polymerization of Furan Derivatives

Biomass-based furan derivatives introduced in section 2.1 offer several opportunities for the replacement of petrochemical-based monomers. Figure 4 lists the various HMF-derived

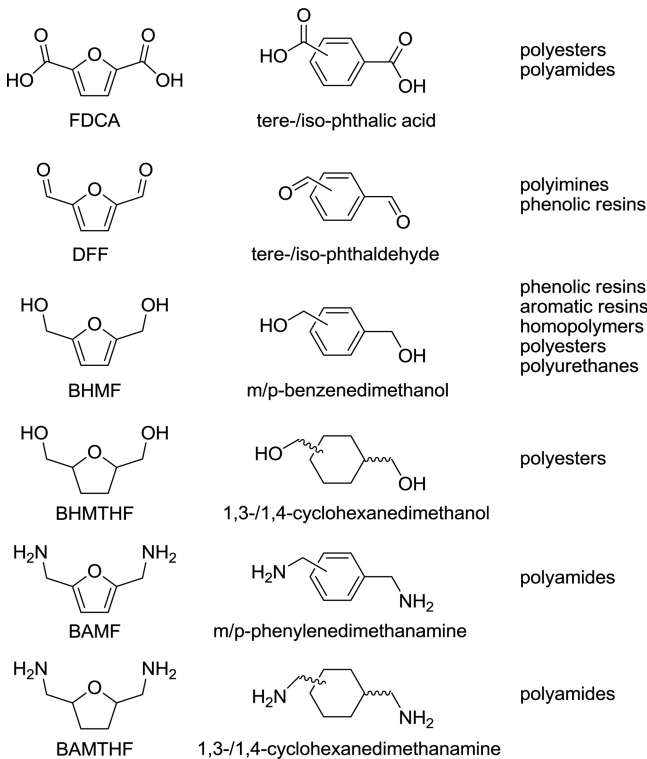


Figure 4. Furan-based monomers and petrochemical analogues with current applications: 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (BHMF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), 2,5-bis(aminomethyl)furan (BAMF), and 2,5-bis(aminomethyl)tetrahydrofuran (BAMTHF).

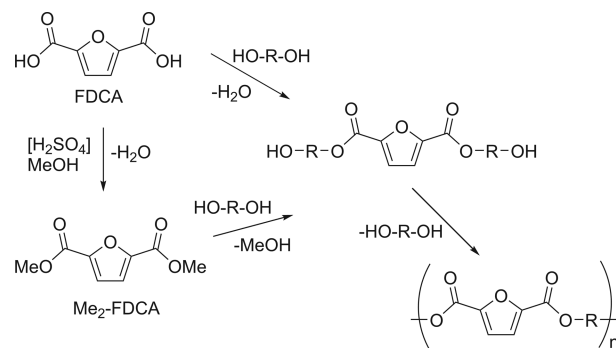
monomers together with their closest petrochemical analogues and the polymers produced based on these monomers. The literature concerning the use of these compounds in polymer chemistry is vast and will not be discussed or referenced here comprehensively as it is beyond the scope of this review. As discussed above, FDCA is already widely regarded as a suitable replacement of terephthalic or isophthalic acid. In line with this it seems reasonable to assume that DFF, BHMF, and BAMF are suitable replacements for tere-/isophthalaldehyde, *m*-/*p*-benzenedimethanol, and *m*-/*p*-benzenemethanamide, respectively. Nevertheless, the furan ring is comparatively more reactive and less stable than the benzene ring. For FDCA and DFF the mesomeric effect of the substituents improves stability, but for BHMTHF and BAMF this is not the case. Hence, it can be expected that the use of melt polymerization and thermal processing for these monomers and polymers is less feasible. This is much less the case for the THF derivatives BHMTHF and BAMTHF. However, for these monomers the enantiomeric purity is a decisive factor for applicability, as it is known that stereoregular polymers often possess better physical properties. As discussed above, current methods provide a mixture of isomers with typically a high proportion of the cis

isomer. In what follows a brief overview of the polymers based on HMF derivatives is given.

3.1.1. Polymers Based on 2,5-Furandicarboxylic Acid.

The literature concerning the polymerization of FDCA deals mainly with the synthesis of various polyesters (Scheme 43).

Scheme 43. Polymerization of 2,5-Furandicarboxylic Acid (FDCA) and Its Dimethyl Ester with Glycols



Besides this, FDCA is also applied for the preparation of poly(amides).³⁸⁷ Particularly the preparation, material properties, and applications of poly(ethylenefuranoate) (PEF) and poly(butylenefuranoate) (PBF) are studied most intensively. The literature on furanoate containing polymers and their properties has increased exponentially in recent years, warranting its own separate review. Hence, only a selection of the most recent literature with a focus on polymer preparation will be discussed here.

The application of polymeric furanoate esters in beverage containers and textiles imposes high demands on the quality of the polymer in terms of physical appearance, processability, mechanical strength, thermal and chemical stability, etc. A series of papers by Burgess et al. demonstrates that various properties of PEF are in fact superior to its petrochemical counterpart PET. PEF exhibits better mechanical properties, reduced gas permeability, a higher glass transition temperature, and slower chain mobility.³⁸⁸ In particular, the decreased likelihood of aromatic ring flip in the polymer leads to better barrier properties such as decreased O₂ and CO₂ permeability;^{389–391} however, due to the increased polarity of the furan ring water sorption capacity is increased.^{402,403}

Apart from the choice of diol, the properties of the polymer are mainly influenced by its length. Hence numerous studies focus on the optimization of polymer synthesis methods and benchmarking of the resulting properties. Current methods are focused on the use of either FDCA (i.e., direct polycondensation) or its methyl ester Me₂-FDCA (i.e., transesterification). In most cases the reactions are performed in a melt (i.e., solvent-free), which is subjected to different conditions in a number of stages.

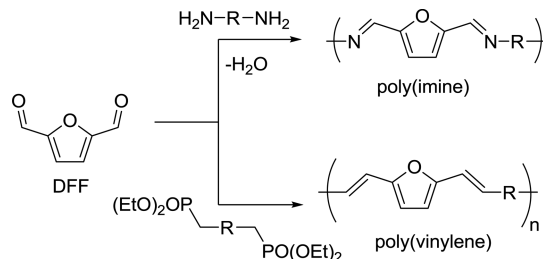
Both the direct polycondensation of FDCA and transesterification of Me₂-FDCA have been studied using a series of linear aliphatic glycols (e.g., EG,^{392–395} 1,3-PDO,³⁹⁶ 1,4-BDO,^{397,398} 1,6-hexanediol,³⁹⁹ and 1,8-octanediol⁴⁰⁰). A study by Belgacem et al. concerning a comparison between direct polycondensation and transesterification of PEF and PBF suggests that the direct polycondensation leads to increased amounts of polymer with desirable properties.⁴⁰¹ Besides linear diols also cyclic (e.g., cyclobutanediol,⁴⁰⁴ 1,4-bis(hydroxymethyl)cyclohexane,⁴⁰⁵ 2,2,4,4-tetramethylcyclobuta-

nediol)⁴⁰⁶ and other symmetric diols (e.g., 2,3-butanediol)⁴⁰⁷ are currently being investigated. The (trans)esterification reaction is typically performed in the presence of a Lewis acid catalyst, such as Sb_2O_3 , $\text{Ca}(\text{OAc})_2$, $\text{Zn}(\text{OAc})_2$, or titanium(IV) alkoxides (e.g., ^iPrO , ^tBuO). The melt, which at first contains excess diol, is heated to 160–190 °C to generate the diester of the diol with expulsion of water or methanol. Subsequently the temperature of the melt is further increased to 200–240 °C and all volatiles (i.e., excess diol) are removed under reduced pressure, at which point the polymer is being formed. Additional increases in polymer length can be achieved via solid-state postcondensation methods. For example, van Es et al. showed that annealing the solid polymer for 16 h at 150 °C leads to a dramatic increase of molecular weight.⁴⁰⁸ Also a patent application by Evian discloses the use of a tumble drier heated at 145–200 °C to double the molecular weight of the synthesized polymer.⁴⁰⁹

3.1.2. Polymers Based on 2,5-Diformylfuran (DFF)

The application of dialdehydes in polymer chemistry is relatively limited as compared to diols and dicarboxylic acids. Like FF, DFF can be used as an ingredient for the preparation of phenolic resins.^{410,411} One interesting application of DFF is its use in the synthesis of linear poly(imines) (Scheme 44).

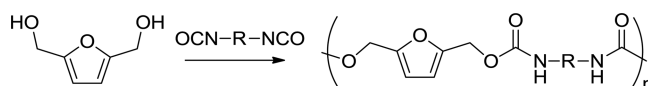
Scheme 44. Conversion of 2,5-Diformylfuran (DFF) to Poly(imines) and Poly(vinylene)



When the diamine is aromatic, conjugated polymers with interesting optical and electronic properties may be obtained.^{412–415} The same reactivity has also been employed for the synthesis of porous N-containing polymers^{416–418} and a urea type resin.⁴¹⁹ A reductive homocoupling reaction of DFF has also been studied; however, the resulting poly(vinylene) is too insoluble to generate polymers with sufficient length.⁴²⁰ By using the Horner–Wadsworth–Emmons reaction (i.e., coupling of phosphonate esters with aldehydes) with bifunctional aromatic linker molecules that contain solubilizing groups, increased molecular weights can be obtained. As with the poly(imines), the resulting poly(vinylene)s possess suitable electronic properties for use in organic thin film transistors.^{421,422}

3.1.3. Polymers Based on 2,5-Bis(hydroxymethyl)furan (BHMF). Early applications of BHMF include its use as a homopolymer in formulations for poly(isocyanurate) foam⁴²³ and furan resin-based binding compositions for glass fibers.⁴²⁴ Patent applications by The Quaker Oats Co. describe the use of BHMF and its homopolymers as ingredients in polyurethane foams (Scheme 45).^{425,426} The preparation of various furan-based linear polyurethanes was also studied in detail by Gandini et al.^{427–429} Besides this, its application as a comonomer in poly(acrylonitrile)⁴³⁰ and polyethers⁴³¹ has also been described.

Scheme 45. 2,5-Bis(hydroxymethyl)furan (BHMF) Based Polyurethane



An early study by Moore et al. describes the attempted melt transesterification of $\text{Me}_2\text{-FDCA}$, BHMF, $\text{Me}_2\text{-THFDCA}$, and BHMTHF in various combinations (Figure 5).⁴³² The authors note that in all cases blackening of the melt occurred. Also the THF-based monomers showed degradation, which was attributed to oxidation. When esterification was performed with the respective acid chloride derivatives under basic conditions, white polymers could be obtained only in the case of BHMTHF. A recent patent application by Pepsico Inc. claims the preparation of various biomass-based polyesters. Therein the melt polymerization of BHMF with adipic acid is described to proceed between 190 and 240 °C in the presence of Sb_2O_3 , yielding 62% polyester.^{401,433}

A series of papers by Yoshie et al. deals with the esterification of BHMF with succinic acid. Also here the esterification is performed under basic conditions.^{434–437} A self-healing property is imparted on the material by the addition of a bismaleimide cross-linker which undergoes reversible Diels–Alder adduct formation with the furan rings.

A paper by Loos et al. demonstrates the use of lipases for the transesterification polymerization of BHMF with a series of diacids ranging from succinic and dodecanedioic acid (Scheme 46).⁴³⁸ Molecular weights between 1600 and 2400 were obtained with dispersions between 1.12 and 1.22.

3.1.4. Polymers Based on 2,5-Bis(aminomethyl)furan (BAMF)

Gandini et al. have studied the polymerization of 2,5-bis(aminomethyl)furan and 2,5-bis(carboxyl chloride)furan for the preparation of furan-containing polyamides (Scheme 47). The acid chloride derivatives could be successfully polymerized using various aniline based linker molecules. However, polymerization of 2,5-bis(carboxyl chloride)furan with BAMF gives polymeric products with low molecular weights and yields not exceeding 60%. This was explained by the high reactivity of CH_2 groups attached to the furan ring of aminomethylfuran giving rise to side reactions.⁴³⁹

A patent application by BASF discloses the use of BAMF as a hardener for epoxy resins. The epoxy mixture containing BAMF is intended for application in water resistant floor coatings.⁴⁴⁰ Co-workers from Rhodia also reported the use of HMF derived amines as curing agents in epoxy resins. Examples are given for 2,5-bis(aminomethyl)tetrahydrofuran, which is prepared in a multistep procedure involving hydrogenation of HMF (Raney Ni), methansulfonation, azidation, and hydrogenation (Pd/C).⁴⁴¹ Rhodia reported the use of 2,5-bis(isocyanate)furan/tetrahydrofuran in combination with polyacid anhydrides for the preparation of polyimides.⁴⁴² As described above, the bisaminomethyl is prepared via a multistep procedure starting from the bis(hydroxymethyl). Also, Evonic disclosed a patent for the use of bis(aminomethyl)furan/tetrahydrofuran as a hardener and substitute for benzyl alcohol in epoxide resins.⁴⁴³

Rodia also claims the preparation of polyamides of BAMF. BAMF is first converted to the carboxylic ammonium salts by stoichiometric mixing with diacids. The resulting aqueous solution is converted to polyamides by melt polycondensation. In a similar fashion polyamides of 2,5-bis(aminomethyl)-

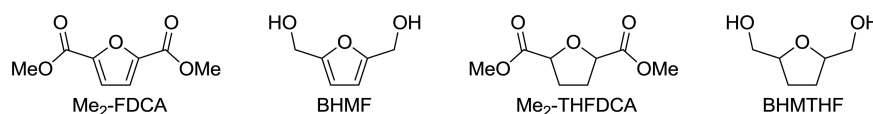
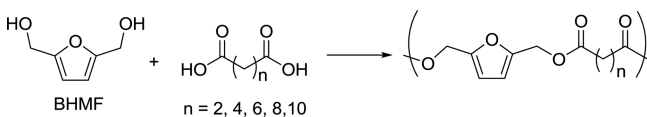


Figure 5. Biomass-based diesters and diols used for melt polymerization: dimethyl 2,5-furandicarboxylate ($\text{Me}_2\text{-FDCA}$), 2,5-bis(hydroxymethyl)furan (BHMF), dimethyl 2,5-tetrahydrofurandicarboxylate ($\text{Me}_2\text{-THFDCA}$), and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF).

Scheme 46. Esterification of 2,5-Bis(hydroxymethyl)furan (BHMF) with Aliphatic Diacids



tetrahydrofuran (BAMTHF) are also claimed.⁴⁴⁴ Other applications of BAMF include its use in epoxide resins,⁴⁴⁵ polyurethane elastomers,⁴⁴⁶ and polymeric Schiff bases.⁴¹⁵

3.1.5. Polymerization of FCA Dimers. Early studies by Gandini et al. demonstrated that the dimers of FCA can be successfully applied as monomers in the transesterification reaction with EG, 1,3-PDO, and 1,4-BDO (Scheme 48).⁴⁴⁷ Thus, the dimer is highly stable and can be employed in melt polymerization. The corresponding diacid chloride has also been prepared and applied for the polymerization with bisphenol type diols⁴⁴⁸ and diamines.^{449–452} Conversion of the ester with hydrazine yields the corresponding hydrazide which has been applied for the synthesis of novel poly(hydrazides)⁴⁵³ and polysemiacylcarbazines.⁴⁵⁴

Also more recently FCA dimers have been used in the synthesis of various copolymers, for example, in block copoly(esters) with PET,⁴⁵⁵ random copolymers with TPA by melt condensation,^{456,457} copolymers with sulfonated isophthalic acids,^{458,459} and copolymers with hexamethylene diamine and ethylene glycol.⁴⁶⁰

3.1.6. Polymerization of Furfurylamine Dimers. The most studied application of the furfuryl amine dimer is its conversion to the diisocyanate and subsequent conversion to polyurethanes (Scheme 49). In addition, it has been shown that this monomer can be employed for the preparation of poly(imides) by reaction with aromatic anhydrides (e.g., pyromellitic dianhydride)⁴⁶¹ and polyureas by reaction with diisocyanates.⁴⁶² As with BAMF discussed above, conversion to poly(imines) is also feasible.⁴⁶³

Cawse et al. studied the preparation of polyurethanes using the diisocyanate of the furfurylamine dimers as a substitute for bis(4-isocyanatophenyl)methane (MDI). The authors note that these monomers are relatively stable and behave as benzylic-type compounds with properties in between those of aromatic and aliphatic isocyanates.^{464–466} The properties of the resulting polymers were comparable to those of the petrochemical analogues.

Gandini et al. studied the preparation of “all-furanic” polyurethanes using bis-furan isocyanates with various furan-based diols.^{427,429,467} It was shown that the polymer properties

of these combinations are diverse enough to allow tuning the material for the intended application.

3.2. Polymerization of Levulinic Acid Derivatives

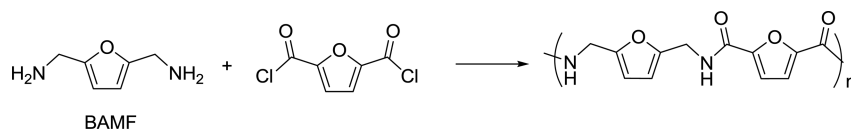
3.2.1. Poly- γ -methyl- α -methylene- γ -butyrolactone.

Poly- γ -methyl- α -methylene- γ -butyrolactone (PMMBL) is very easily obtained via vinyl polymerization of MMBL that occurs even spontaneously at room temperature.¹⁸⁷ Today, MMBL is often considered as a biomass-based structural analogue of methyl methacrylate (MMA) (Scheme 50). MMBL can be polymerized easier than MMA due to the high energy of the exocyclic double bond of MMBL resulting from the ring strain and the fixed *s-cis* conformation.⁴⁶⁸ Additionally, the high reactivity of MMBL in radical polymerization can be explained by efficient stabilization of active radical species by resonance in the nearly planar five-membered lactone ring.⁴⁶⁸

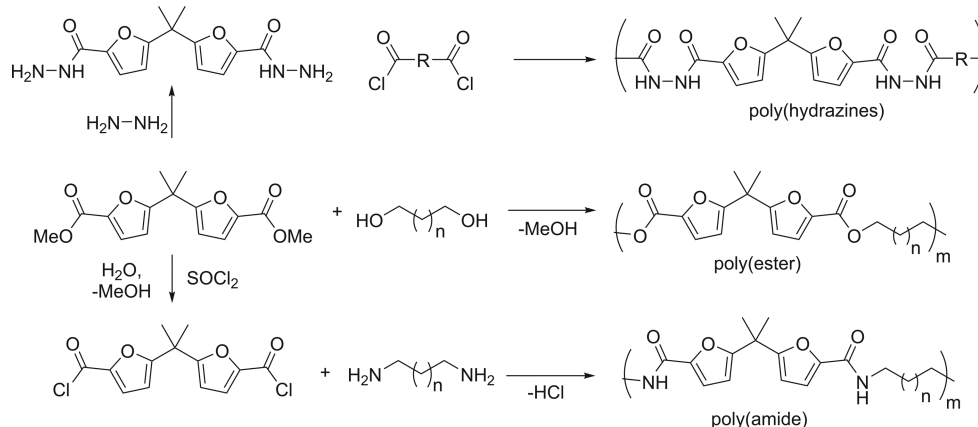
Early investigations reported a synthesis of PMMBL via free-radical emulsion polymerization as well as radical, anionic, and group-transfer polymerizations.^{469,470} A disadvantage of such approaches relates to incomplete conversion of MMBL even after long reaction times.⁴⁶⁹ More recent research uncovered a number of active catalysts for the polymerization. The group of Chen made a significant contribution to the development of a suitable catalytic polymerization: they reported the catalytic activity of ambiphilic silicon propagators (nucleophilic silyl ketene acetal initiating moiety and the electrophilic silylium catalyst),⁴⁷¹ metallocene⁴⁶⁸ and nonmetallocene⁴⁷² complexes, half-sandwich dialkyl rare earth metal (REM) complexes,^{473,474} and an organic phosphazene superbases.⁴⁷⁵ Frustrated Lewis pairs and Lewis acidic–basic adducts exhibit activity for the polymerization via formation of zwitterionic species.^{476,477} Interestingly, frustrated Lewis pairs composed of alane ($\text{Al}(\text{C}_6\text{F}_5)_3$) as a Lewis acid and phosphines or N-heterocyclic carbenes as a Lewis base are very efficient catalysts for the polymerization of MMBL.⁴⁷⁶ Surprisingly, the frustrated Lewis pairs containing the most widely used borane ($\text{B}(\text{C}_6\text{F}_5)_3$) are catalytically inactive, but the conventional Lewis acid–Lewis base adduct ($\text{Ph}_3\text{P}\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$) is very efficient for polymerization.⁴⁷⁷ This effect was described by Xu and Chen and explained in terms of B site acidity, P site basicity, steric crowding around P, and the strength of the P–B association in solution. The compromise of these properties determines the high catalytic activity of $\text{Ph}_3\text{P}\rightarrow\text{B}(\text{C}_6\text{F}_5)_3$.⁴⁷⁷

The newly uncovered catalysts enable a very rapid complete polymerization lasting 10 min or less at room temperature.^{468,471,473–476} Polymers with a molecular mass of ca. 50 kg mol⁻¹ are formed.^{468,471,473,474,476} Prolonging the reaction time increases the molar mass up to ca. 500 kg mol⁻¹.⁴⁷¹

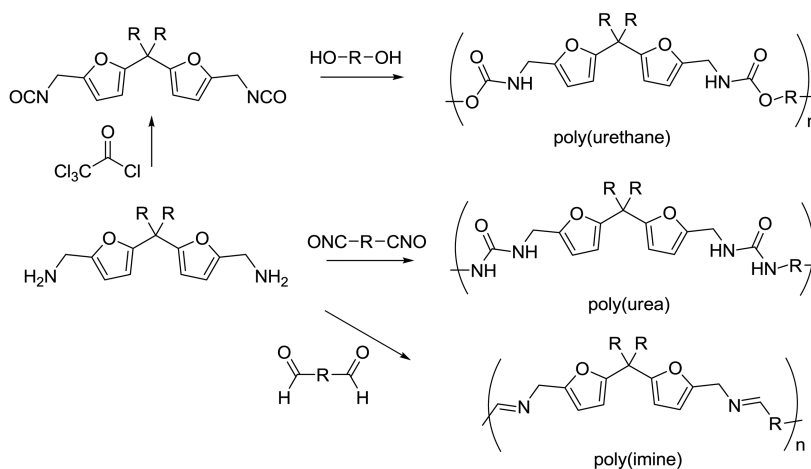
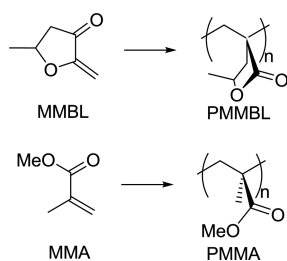
Scheme 47. Polymerization of 2,5-Bis(hydroxymethyl)furan (BAMF) with 2,5-Bis(carboxylchloride)furan



Scheme 48. Polyester and Polyamides Derived from 2-Furancarboxylic Acid (FCA) Dimers



Scheme 49. Polyurethanes, Polyureas, and Poly(imines) Derived from Furfurylamine Dimers

Scheme 50. Structural Similarity of Poly(γ -methyl- α -methylene- γ -butyrolactone) (PMMBL) and Poly(methyl methacrylate) (PMMA)

PMMBL with narrow^{468,471,473,476} or broad^{472–476} molar weight distributions can be obtained.

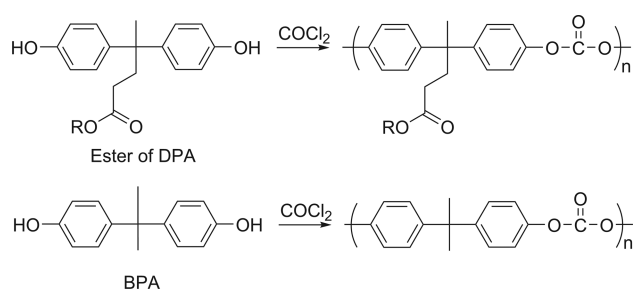
The thermal properties of atactic PMMBL are superior to those of atactic PMMA. Thus, the glass transition temperature (T_g) of PMMBL is 225 °C, which is ca. 120 °C higher than that of PMMA.^{468,471} Decomposition of PMMBL occurs in a narrow temperature window ($T_{ini} = 365$ °C, $T_{end} = 441$ °C); likewise the decomposition of PMMA ($T_{ini} = 340$ °C, $T_{end} = 390$ °C).^{468,471} The good thermal properties of PMMBL can be explained by the conformational rigidity resulting from the cyclic structure of the MMBL monomer.⁴⁷¹ Notably, copolymers^{468,471,478} and blends⁴⁷⁸ of MMBL were also successfully synthesized. Importantly, all homopolymers of MMBL synthesized to date are atactic and amor-

phous,^{471,472,474,476,479} although a number of attempts to control the stereochemistry were undertaken. For instance, the polymerization was started from the optically pure (*R*)-MMBL⁴⁶⁹ or a chiral single-site metallocenium catalyst was used.^{473,479} The small size of the monomer and the high reactivity of the exocyclic double bond are the major reasons for extreme difficulties controlling the tacticity of PMMBL.⁴⁷⁹ Notably, syntheses of isotactic PMMA⁴⁷⁹ and β -PMMBL^{474,479} (β -methyl- α -methylene- γ -butyrolactone is an isomer of MMBL) were reported, but polymerization of MMBL under the same reaction conditions yields amorphous polymers.^{474,479}

The properties of isotactic PMMBL are expected to be superior to those of the atactic polymer. However, very little is currently known about the influence of stereochemistry on the properties. For example, radical polymerizations started either from (*R*)-MMBL or from (*RS*)-MMBL resulting in both cases in atactic polymers with comparable thermal stability. However, the polymers derived from the (*R*)-MMBL monomer are less soluble in organic solvents than materials obtained based on racemic monomers. This finding was explained by the high content of mm triads in the polymer based on (*R*)-MMBL, whereas the material synthesized from (*RS*)-MMBL contains predominantly mr and rr triads.⁴⁶⁹

3.2.2. Polymers Based on Diphenolic Acid. Polymers based on diphenolic acid (DPA) can be rather versatile. The structure of DPA resembles the structure of bisphenol A (BPA) (Scheme 51), which is a petroleum-derived monomer of

Scheme 51. Synthesis of Polycarbonates Based on Esters of Diphenolic Acid (DPA) or Bisphenol A (BPA)

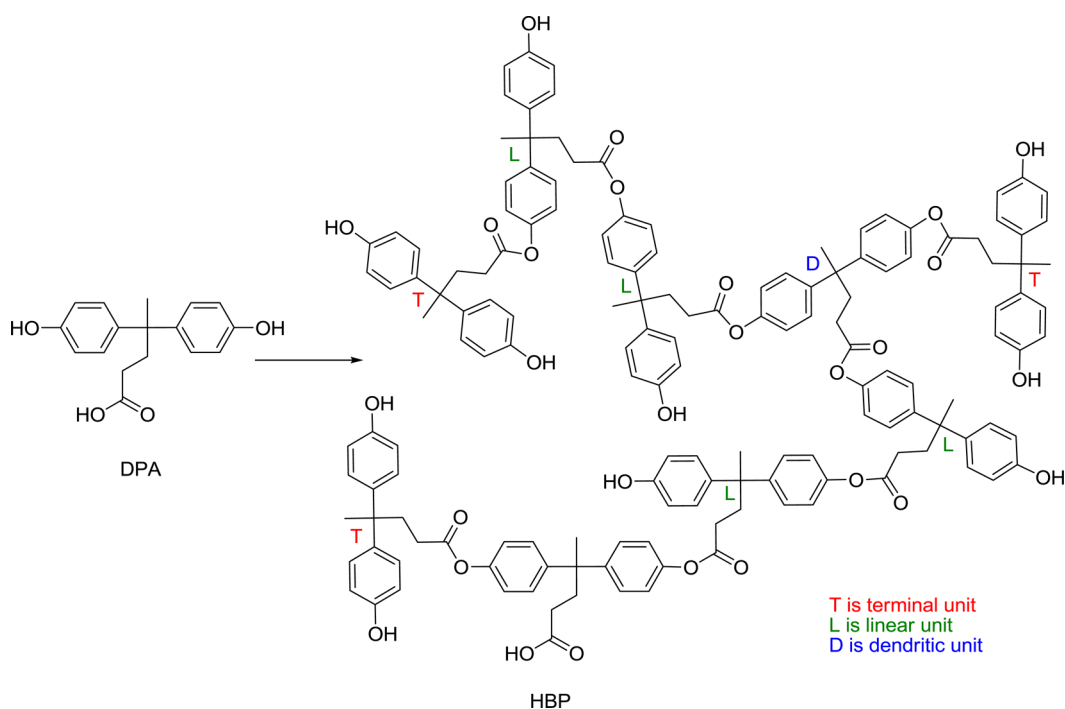


polycarbonates. Due to the very high demand of polycarbonates, great attention is paid to elaborating technologies to displace BPA by DPA.¹⁷⁹ Syntheses of polycarbonates based on DPA and phosgene have been published.^{480–483} Moreover, copolymers and blends based on DPA, BPA, and phosgene were synthesized.⁴⁸¹ Prior to polymerization, the carboxyl group of DPA is protected by esterification to avoid branching and obtain a linear polymer.⁴⁸¹ The polycarbonates can be prepared by interfacial polymerization using phosgene in gaseous phase and the DPA ester in pyridine solution.⁴⁸¹ Alternatively, phase-transfer catalysis in aqueous–organic medium is suitable for polymerization. The catalyst transfers the monomers in the form of an ionic pair from the aqueous medium into the organic phase where polymerization occurs.⁴⁸⁰ Moore and Tannahill comparatively studied the properties of polycarbonates based on DPA and BPA and found out that the polymers exhibit nearly the same molecular mass of 40 kg mol⁻¹ and a similar polydispersity index.⁴⁸¹ Conventional BPA-based polycarbonates have very high T_g 's of ca. 150 °C due to the very stiff backbone and minimal molecular rotation. Polycarbonate obtained from DPA demonstrated a lower T_g of 108 °C and a decomposition temperature of 330 °C. Polymers synthesized from DPA are soluble in organic solvents

and could be cast to form clear, flexible films.⁴⁸¹ Polycarbonates based on esters of DPA can be transformed into polycarbonates containing unprotected carboxyl side groups, e.g., by acidic hydrolysis or thermolysis.⁴⁸³ The polycarbonate acid has a T_g of 148 °C that is higher than that of the ester-containing polymers. It was explained by hydrogen bonding of carboxylic groups which retards chain motion.⁴⁸³ The polycarbonate acid can be dissolved in dilute aqueous NaOH and exhibits properties of a polyelectrolyte. Upon addition of Zn²⁺ or Al³⁺, polycarbonate acid undergoes strong cross-linking.⁴⁸³

An alternative application of DPA as monomer is the preparation of hyperbranched polymers (HBPs, Scheme 52). HBPs are highly branched macromolecules with three-dimensional dendritic architecture.⁴⁸⁴ A DPA molecule has one carboxylic and two hydroxylic groups which enables its intermolecular condensation into an AB₂ type HBP shown in Scheme 52. HBPs resemble dendrimers, but the latter are synthesized via multistep syntheses, yielding highly defined structures with little, if any, defects.⁴⁸⁵ In contrast, HBPs are available in a one-pot synthesis, i.e., can be easily produced in large scale.^{485,486} The properties of HBPs differ from that of linear analogues; e.g., HBPs are highly soluble in organic solvents⁴⁸⁷ and exhibit different intrinsic and melt viscosities.⁴⁸⁵ Polymerization of DPA is conducted via melt condensation under reduced pressure in the presence of a catalyst.^{485,487} The process is carried out in a temperature-programmed mode increasing the temperature stepwise from 120 to 210–225 °C.^{485,487} HBP with a M_w of 47–128 kg mol⁻¹ is formed in high yield, often higher than 75%.^{485,487} The polymerization is catalyzed by compounds containing transition metals, e.g., Co(OAc)₂,^{485,487} Ti(OBu)₄,⁴⁸⁵ and Bu₂Sn(OAc)₂.⁴⁸⁵ DPA can be used as a monomer for HBP synthesis without an activation or transformation of the acid group to the ester.⁴⁸⁸ Nevertheless, when using as substrates for polymerization the methyl, ethyl, and phenyl derivatives produced by esterification of DPA, polymers with different molecular weights form.⁴⁸⁵ The choice

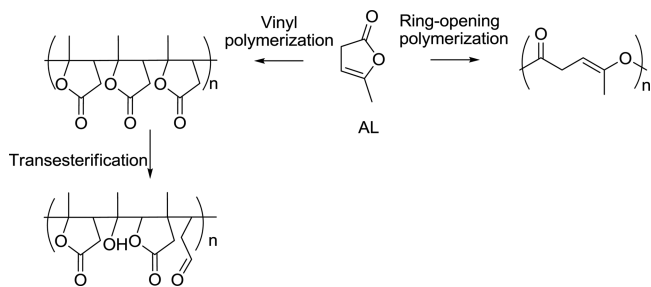
Scheme 52. Polymerization of Diphenolic Acid (DPA) into Hyperbranched Polymer (HBP)



of catalyst also enables variations of the molecular mass of the HBP.⁴⁸⁵ Importantly, intramolecular cyclization of DPA does not occur during polymerization.⁴⁸⁵ The HBP obtained from DPA is amorphous with a T_g of 100–110 °C.⁴⁸⁸ An important characteristic of HBPs is the degree of branching (DB). The DB is calculated according to the formula $DB = (D + T)/(D + L + T)$, where D , T , and L are the fractions of dendritic, terminal, or linearly incorporated monomers. DPA is a monomer of AB_2 type and can form a maximum of three bonds with adjacent units. As illustrated in Scheme 52, a terminal unit is attached to only one unit, a linear unit is connected to two units, and a dendritic unit is bonded to three adjacent units. Assuming the complete conversion (complete reaction of all carboxyl groups) and equal reactivity of all hydroxyl groups, the maximum DB achievable from a statistical point of view is 50%.⁴⁸⁹ As the functionalities of DPA are relatively far apart from each other, neither electronic nor steric effects influence the polymerization. Therefore, the experimentally obtained DB of DPA-based HBP is ca. 50% not depending on molecular mass, the polydispersity index, and the preparation technique of HBP.^{487,488} The portfolio of the DPA-based HBPs with different properties can be broadened further⁴⁸⁸ when, e.g., using polyols as core molecules⁴⁸⁶ or postpolymerization modification phenolic “end groups” of HBP.⁴⁹⁰ HBPs have numerous potential applications ranging from drug delivery to coating.^{484,491}

3.2.3. Polymers of α -Angelica Lactone. α -Angelica lactone (AL) can be polymerized via two pathways shown in Scheme 53. The first possibility concerns a vinyl polymer-

Scheme 53. Vinyl and Ring-Opening Polymerization of α -Angelica Lactone (AL)



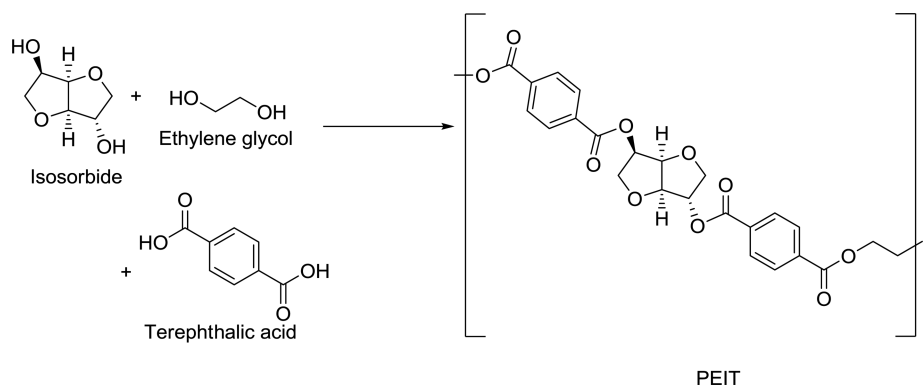
ization, and the second route is a ring-opening polymerization yielding polyesters. Notably, both pathways are hampered

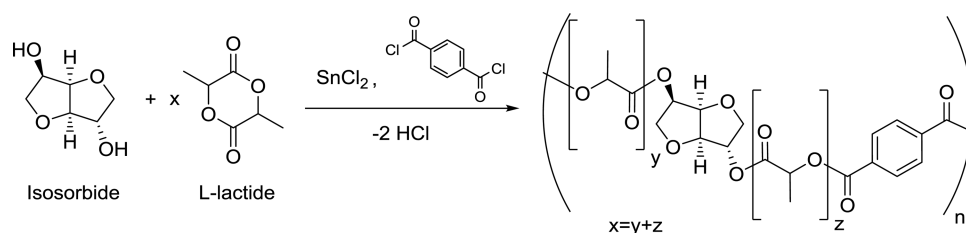
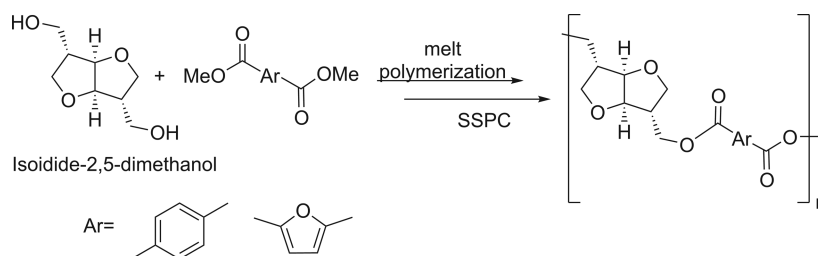
owing to the stability of AL. Hence, terminal substituents attached to the double bond limit the reactivity of AL for vinyl polymerization.¹⁸⁹ Moreover, five-member lactones have a small ring strain energy, which usually prevents the formation of high molecular weight polymers via ring-opening polymerization. Nevertheless, the presence of an endocyclic double bond increases the strain energy of AL, improving its reactivity.⁴⁹²

The vinyl polymerization of AL was described for the first time as long ago as 1939.¹⁸⁹ The polymerization was not feasible under conventional conditions of radical polymerizations, e.g., in the presence of peroxides.^{189,493} The best polymerization result was obtained in the presence of a Lewis acid, specifically a boron fluoride–ester complex.^{189,493} The product of polymerization was obtained in the form of a tacky dark red solid with a molecular weight of 800–900 corresponding rather to an oligomer than to a polymer.^{189,493} The compound was soluble in acetone, dioxane, and alcohols and insoluble in water, diethyl ether, benzene, and paraffins.⁴⁹³ The oligomer slowly dissolves in a solution of NaOH due to opening of the lactone rings.¹⁸⁹ Marvel and Levesque concluded on the “head to tail” structure of the AL oligomer synthesized in the presence of the boron fluoride–ester complex.¹⁸⁹ Notably, the utilized Lewis acid also catalyzes transesterification resulting in some free carboxyl and carbonyl groups (Scheme 53).

Reports on successful ring-opening polymerization of AL have recently been published to yield poly(4-hydroxypent-3-enoic acid) (Scheme 53). Sodium isopropylate was found to be an efficient catalyst resulting in a polymer with a molecular mass of $19.5 \pm 1.8 \text{ kg mol}^{-1}$ for polymerization at 60–65 °C for 40–60 min. Thus, produced polymers contain 68–80% units with a C=C double bond. The remaining 20–32% of the polymer was assumed to be polymerized via the vinyl-type route.⁴⁹³ Alternatively, the ring-opening polymerization of AL can be accomplished using stannous octoate as initiator and toluene as solvent at 130 °C for 30 h. Under such conditions the polyester with a M_n of 29 kg mol^{-1} and a polydispersity index of 1.25 is accessible.⁴⁹² Due to the presence of a double bond, polyesters of AL are not very stable. They degrade when exposed to daylight, undergo quick decomposition under acidic or basic conditions, and slowly decay in neutral medium.⁴⁹² However, the highly reactive double bonds present in poly(4-hydroxypent-3-enoic acid) can be potentially modified, opening a new route toward tailored biomass-based polymers.⁴⁹²

Scheme 54. Synthesis of Poly(ethylene-co-isosorbide terephthalate) (PEIT) Starting from Isosorbide, Terephthalic Acid, and Ethylene Glycol



Scheme 55. Synthesis of Copolyesters from Isosorbide, L-Lactide, and Terephthaloyl Chloride As Reported by Kricheldorf and Weidner⁵⁰⁴Scheme 56. Synthesis of Copolyesters Based on Isoidide-2,5-dimethanol and Terephthalic or 2,5-Furan Dicarboxylic Acid^{505a}

^aSSPC denotes solid-state postcondensation.

3.3. Polymers Based on Isohexides

Already in the 1990s two reviews on the early work concerning isohexide based polymers were published.^{494,495} In 2010 Fenouillot et al. published a comprehensive review.⁴⁹⁶ The aim of this work is to summarize recent results in this field. Furthermore, we will focus mainly on polymers which are produced directly from isohexides or after a functionalization at the isohexide backbone.

3.3.1. Application of Isohexides in Polyesters. Polyesters based on isohexides can generally be divided into two groups: isohexides as the diol monomer and as the dicarboxylic acid monomer. For the latter the isohexides have to be converted into their carboxylic acid derivatives as described above in section 2.3.3.1.

Very promising polymers based on isohexides as the diol monomer are polyterephthalates. They were described already in the 1980s by Thiem and Lüders.^{497,498} Since then these compounds found great interest, especially with isosorbide as a monomer. This is due to the excellent thermal properties of the polymers which can be obtained by the polymerization of terephthalic acid with isohexides instead of ethylene glycol. Depending on the synthesis, glass transition temperatures between 150 and 200 °C can be achieved which is well above the T_g of conventional poly(ethylene terephthalate) (PET) with ca. 70 °C.⁴⁹⁶ Thus, bottles made of poly(isosorbide terephthalate) (PIT) tolerate hot fillings in contrast to conventional PET bottles. However, lower molecular weights are obtained with isosorbide and also the amount of unreacted terephthalic acid groups remaining in PIT is higher than in PET. Therefore, research also concentrates on copolymers based on different ratios of isohexides with other dialcohols. One example is poly(ethylene-*co*-isosorbide terephthalate) (PEIT), which is displayed in Scheme 54. Storbeck et al. showed that the glass transition temperature is linearly increasing with the content of isosorbide in the copolymer and, thus, the properties of the material can be tailored.⁴⁹⁹

Unfortunately, with increasing amount of isosorbide also the coloring of the material increases due to thermooxidative

reactions, but the color of the polymer is important depending on the application. This challenge was addressed by Bersot et al., who increased the efficiency of the PEIT synthesis by using bimetallic catalyst systems containing antimony oxides and a metal salt based on lithium, aluminum, or magnesium.⁵⁰⁰ The use of these catalysts enables also a decrease in the synthesis temperature from 270 to 260 °C which leads to a polymer less yellow in color.

Quintana et al. investigated poly(ethylene terephthalate) terpolyesters containing different ratios of isosorbide and 1,4-cyclohexanedimethanol.^{501,502} Again the incorporation of isosorbide enhances the glass transition temperature while the incorporation of 1,4-cyclohexanedimethanol has no influence on T_g . However, with increasing substitution of ethylene units, the crystallinity of the polymer decreases as DSC measurements revealed. Below a content of 90% ethylene units, the polymer changes from semicrystalline to amorphous.⁵⁰¹

In 2014 Gioia et al. reported a strategy to synthesize polyester from recycled PET containing isosorbide and succinic acid.⁵⁰³ At first PET is depolymerized with isosorbide to oligomers which subsequently undergo a polycondensation with succinic acid. The authors identified tin based catalysts as the best concerning the combination of catalytic activity and color. Furthermore, if the right ratios of isosorbide and succinic acid are chosen, the resulting polymers have well-suited properties (T_g and end-group composition) for powder coating applications.

Kricheldorf and Weidner described copolyesters based on isosorbide, L-lactide, and terephthalic acid.⁵⁰⁴ In a one-pot reaction, the ring-opening polymerization of isosorbide and L-lactide and the polycondensation with terephthaloyl chloride are combined using SnCl_2 as a catalyst for both steps (Scheme 55). High glass transition temperatures of up to 181 °C are obtained, and they correlate almost linearly with the isosorbide fraction. If the incorporation of isosorbide moieties is below 30%, the glass transition temperature falls below 100 °C.

Wu et al. reported very recently the synthesis of polyterephthalates based on a 1C-extended isoidide monomer: isoidide-2,5-dimethanol (IIDM) (Scheme 56).⁵⁰⁵ The melt

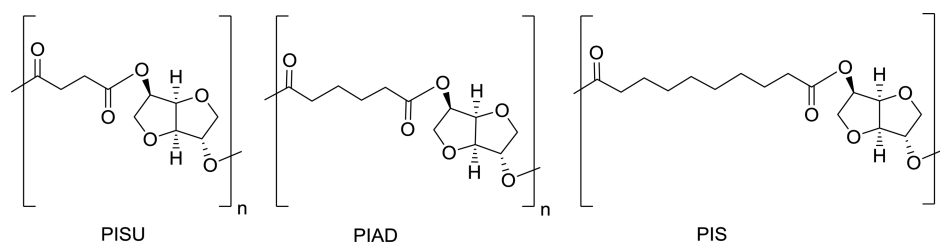


Figure 6. Structures of poly(isosorbide succinate) (PISU), poly(isosorbide adipate) (PIAD), and poly(isosorbide sebacate) (PIS).

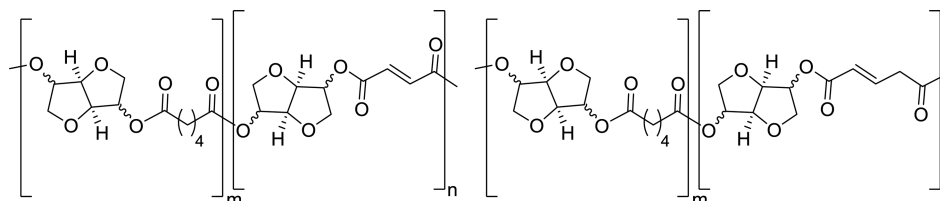


Figure 7. Structures of copolyesters from isohexides, adipic acid, and fumarate (left) or *trans*-glutaconate acid (right) as examples for copolyesters containing unsaturated acids.

polymerization of this compound with terephthalic acid yields a weight-average molecular weight of 3900 g mol^{-1} . However, if this prepolymer is used for solid-state postcondensation (SSPC), the molecular weight can be increased to $17\,700 \text{ g mol}^{-1}$. The glass transition temperature of this polymer is lower than that for the poly(isohexide terephthalates) but with $105 \text{ }^\circ\text{C}$ it is still higher than that for PET.

Further information on polyterephthalates based on isohexides can be taken from the review of Muñoz-Guerra et al.⁵⁰⁶

Additionally, the 1C-extended isoidide monomer reported by Wu et al. was polymerized with the biogenic FDCA (section 2.1.1).⁵⁰⁵ The reaction route is displayed in Scheme S6. Compared to the analogously obtained terephthalates, the molecular weight after melt polymerization is with $15\,200 \text{ g mol}^{-1}$ almost 4 times higher and can again be significantly increased by SSPC up to $60\,600 \text{ g mol}^{-1}$. However, the glass transition temperature for this polyester is with $94 \text{ }^\circ\text{C}$ lower than that for the corresponding polyterephthalate.

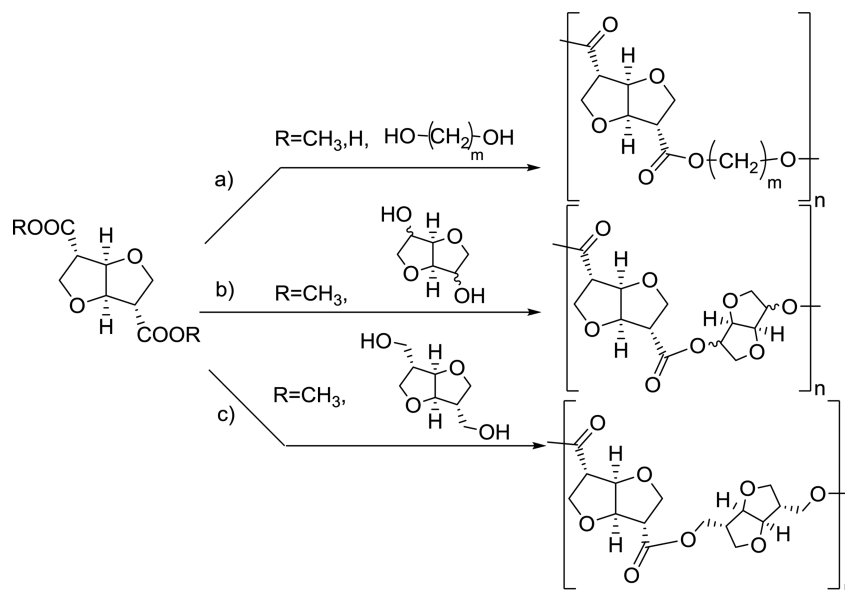
Polyesters based on isohexides and 1,4-cyclohexane dicarboxylic acids (CHDA) have been reported by Garaleh et al. in 2010.⁵⁰⁷ They tested various methods such as transesterification with the CHDA methyl ester, esterification of the free CHDA, and a reaction with neat CHDA dichloride or in different solvents. The most promising with isosorbide was the latter approach using dry dichloromethane as solvent and pyridine as the catalyst. The reaction proceeds at very mild conditions ($20 \text{ }^\circ\text{C}$) for 24 h. The same reaction conditions have been applied to isomannide and isoidide. However, for isoidide dioxane was chosen as the solvent. In all cases yields of over 96% were obtained. All synthesized polyesters exhibit high glass transition temperatures above $100 \text{ }^\circ\text{C}$ and even above $140 \text{ }^\circ\text{C}$ when the \bar{M}_n is higher than $10\,000 \text{ g mol}^{-1}$. Furthermore, the authors investigated copolyester of isosorbide with CHDA and succinic acid as well as a succinic acid homopolymer. However, through incorporation of succinic acid units T_g decreased and was as low as $77 \text{ }^\circ\text{C}$ for the homopolymer.

Poly(isosorbide succinate) (PISU) can also be prepared via a solvent free esterification at $180 \text{ }^\circ\text{C}$ over 24 h with titanium tetraisopropoxide as catalyst.⁵⁰⁸ The glass transition temperature of $73 \text{ }^\circ\text{C}$ is comparable to that of PET. Park et al. used the identical reaction conditions also to prepare poly(isosorbide

adipate) (PIAD) and poly(isosorbide sebacate) (PIS) starting from adipic acid and sebacic acid.⁵⁰⁸ Figure 6 displays the structure of all three polymers. Interestingly, the number-average molecular weights increase from PISU (2889 g mol^{-1}) over PIAD (8764 g mol^{-1}) to PIS ($19\,218 \text{ g mol}^{-1}$), while the glass transition temperature decreases in the same order: 73 , 35 , and $6 \text{ }^\circ\text{C}$, respectively. The authors investigated also the biodegradability of these polymers. PIAD has the highest degradability in comparison to PISU and PIS. After a 2 month in vitro degradation test, the residual weight percentages were 32.5, 82.0, and 93.5, respectively.

Copolyesters based on sebacic acid containing isosorbide and 1,10-decanediol were reported by Wei et al. very recently.⁵⁰⁹ In a two-step melt polycondensation poly(decamethylene sebacate-*co*-isosorbide sebacate) was obtained. Again an increasing isosorbide ratio causes an increasing glass transition temperature while the number-average molecular weight decreases. The incorporated isosorbide moiety decreases gradually the crystallinity. However, the crystal structure remains the same. Furthermore, with increasing isosorbide content the crystallization rate decreases, but the crystallization mechanism does not change.

Catalani and co-workers were the first to report polyesters based on isosorbide synthesized via enzymatic catalysis.⁵¹⁰ The authors used an immobilized lipase B from *Candida antarctica* (Novozym 435) as a catalyst in bulk and azeotropic polymerization of isosorbide and mainly different diethyl esters like diethyl adipate, diethyl glutarate, and diethyl suberate. Bulk polymerization led to low molecular weight polymers ($\bar{M}_w = 3800 \text{ g mol}^{-1}$), while the azeotropic polymerization with the right solvent mixture (cyclohexane:benzene) facilitated access to polyesters with weight-average molecular weights over $40\,000 \text{ g mol}^{-1}$. Furthermore, it was shown that the yield and molecular weight are higher when the diethyl acid ester is used as starting material in comparison to a longer or shorter ester or even the free acid. More recently the same group reported the enzymatic catalyzed incorporation of unsaturated acid units in homo- and copolyesters based on isosorbide and isomannide.⁵¹¹ They applied the same reaction conditions and enzyme as in their previous paper. The diacid compounds for the polycondensation were among others diethyl fumarate and diethyl *trans*-glutaconate diesters (Figure 7). The homopo-

Scheme 57. Synthesis of Polyesters Based on IIDCA (R = H) and IIDMC (R = CH₃)

lyesters of the isohexides with these unsaturated acids show much lower molecular weights than the poly(isohexide adipates) or the copolyesters containing unsaturated acid and adipic acid units. Interestingly, the unsaturated homo- and copolyesters based on isosorbide exhibit higher molecular weights than the polymers based on isomannide.

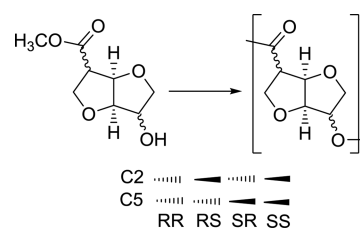
Also the synthesis of linear and cyclic ester oligomers based on isohexides and succinic acid can be catalyzed by immobilized *C. antarctica* lipase B.⁵¹² Esterification takes place in a solvent mixture (toluene:*tert*-butanol) at 65 °C over 24 h. The authors identified the temperature and the initial concentration of the substrate as the most important factors concerning the reaction yield. Furthermore, an enantioselectivity with regard to the substrate structure of the immobilized enzyme was observed. The conversion of isomannide was the highest and decreased for isosorbide and isoidide (isomannide > isosorbide >> isoidide). These experimental results were supported by substrate-imprinted docking analysis.

As mentioned above, isohexides can also be the carboxylic acid monomer in polyesters once they are converted to their carboxylic acid derivatives. In 2012 Wu et al. described the melt polymerization of isoidide dicarboxylic acid (IIDCA) and its dimethyl ester (IIDMC) with linear α,ω -diols (Scheme 57a).⁵¹³ DSC and wide-angle X-ray analysis showed that the obtained polymers are semicrystalline and according to NMR measurements the *exo-exo* configuration of the isoidide skeleton was preserved after polymerization. Comparing the polyesters based on IIDCA with polymers based on adipic acid with the same linear diol, the glass transition temperature is increased by 50–70 °C. However, the absolute glass transition temperatures are very low (–20 to 20 °C) in comparison to other polyesters where the isoidide structure is incorporated.

Fully isohexide-based polymers can be obtained via polymerization of IIDCA with the three isohexides as diol monomers (Scheme 57b).⁵¹⁴ The resulting polymers are amorphous with higher glass transition temperatures of 30, 73, and 85 °C for isomannide, isosorbide, and isoidide as the diol, respectively. Furthermore, changing the diol monomer to IIDM (Scheme 57c), still fully isohexide-based semicrystalline polyesters are obtained with an even higher molecular weight ($\bar{M}_{w, \text{IIDM}} =$

10 400 g mol^{–1} and $\bar{M}_{w, \text{II}} = 3600$ g mol^{–1}). However, the glass transition temperature is approximately 40 °C lower than when isoidide is used as the diol monomer. In general, the integration of isoidide is more effective to enhance the rigidity of the polymer than IIDCA or IIDM.

In contrast to the above-described AA–BB type polyesters (one monomer holds the functional group A and the other B), Thiagarajan et al. reported AB type polyesters (both functional groups A and B are present in the same monomer) based on isohexide hydroxyl esters (Scheme 58).⁵¹⁵ The authors stated

Scheme 58. AB-Type Polyesters Based on Isohexides As Reported by Thiagarajan et al.⁵¹⁵

that the configuration of the carboxyl group has only minor influences on the reactivity while the configuration of the hydroxyl group plays a major role. Only the RR and RS monomers (hydroxyl group in *exo*-position) form low molecular weight homopolymers with average molecular weights of 2500 and 2700 g mol^{–1}, respectively, while the SS and SR monomers (hydroxyl group in *endo*-position) form only oligomers. Thus, similar to the polyesters based on isohexides as diol monomers, the *endo*-configured hydroxyl group diminishes the reactivity and the stability. The homopolymers obtained from the RR and RS monomers are highly crystalline with high melting points considerably higher than those of their AA–BB analogues. However, their glass transition temperatures of homopolymers are significantly lower with 20 and 15 °C, respectively. Copolyesters based on the monomers RR:SR and RR:SS have higher molecular weights which are comparable to their AA–BB analogues, and also the glass transition temperature is enhanced.

3.3.2. Isohexides in Polyamide Synthesis. Already in the early 1990s Thiem et al. described polyamides based on isohexides by interfacial polycondensation with dicarboxylic acid dichlorides.⁵¹⁶ Interestingly, isoidide and isosorbide yield polyamides with relatively high molecular weights when reacted with isophthaloyl chloride while high molecular weight polyamides cannot be synthesized using isomannide.

Jasinska et al. developed semicrystalline polyamides using diamineisoidide (DAII) or diaminoisorbide (DAIS) with sebacic or brassylic acid (Figure 8) as well as copolyamides by

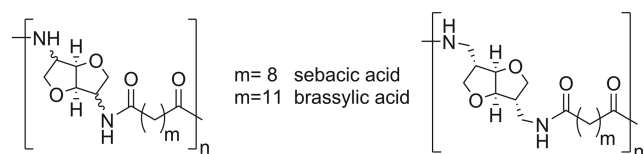


Figure 8. Polyamide based isohexides (left) or isoidide-2,5-dimethyleneamine (IIDMA) (right).

adding 1,4-diaminobutane (DAB).^{517–519} For the melt polycondensation a salt of the diaminoisohexide and the acid was formed in an ethanol–water mixture. The molecular weights of the obtained polyamides could be increased by a subsequent solid state polymerization, and number-average molecular weights over 18 000 g mol⁻¹ could be achieved. Yet, with increasing amount of isohexide moieties in the polymer the molecular weights decrease. For a comparison the authors also tested interfacial polymerization. However, the number-average molecular weights with this method are significantly lower.⁵¹⁷ Interestingly, increasing the diaminoisohexide fraction causes decreasing melting points for the polyamides. If polymers based on different acids are compared, the melting points and the molecular weights are higher when sebacic acid is used. Furthermore, the authors investigated the structure of the obtained (co)polyamides in more detail.^{518,519} The incorporated diaminoisohexide moieties have an effect on the hydrogen bond density as well as the chain conformation. This influence is more pronounced for DAII.

Very recently amorphous (co)polyamides based on DAII, DAB, and pimelic acid were reported by van Velthoven et al.⁵²⁰ Analogously to the findings in polyester synthesis based on isohexides, the integration of DAII adds rigidity to the polyamide and, thus, the glass transition temperature increases with the amount of DAII up to 103 °C for the homopolymer. At the same time the crystallinity of the material as well as the molecular weight decreases. In general, the number-average molecular weights are quite low with 1000–2000 g mol⁻¹.

In 2012 Wu et al. reported semicrystalline polyamides based on isoidide-2,5-dimethyleneamine (IIDMA) and sebacic or brassylic acid (Figure 8) as well as copolyamides through

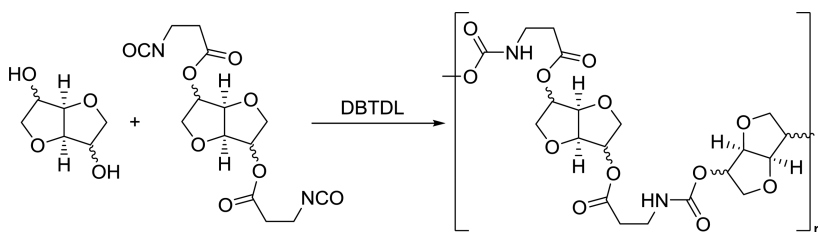
including 1,6-hexamethylene diamine.⁵²¹ The synthesis procedure is similar to that described above: a melt polymerization of the primarily formed nylon salt of the 1C-extended isoidide-based monomer IIDMA and the acid. The molecular weights could be enhanced by SSPC and number-average molecular weights of up to 49 000 g mol⁻¹ could be obtained. Also for these polyamides applies the higher the content of the rigid isohexide-based monomer the higher the glass transition temperature. However, the melting point is again decreasing in the same direction.

3.3.3. Isohexides in Polyurethanes. Polyurethanes based on isohexides can be synthesized starting from their diamine compounds as it was described by Thiem and Lüders already in 1986.⁵²² Yet, conveniently they serve more often as the diol monomer. In one recent example the isohexide is not only the diol monomer but also its backbone is found in the isocyanate (Scheme 59).⁵²³ The polymerization was catalyzed by a prominent catalyst for the synthesis of polyurethanes: dibutyltin dilaurate (DBTDL). The authors compared isosorbide and isomannide in this polymerization reaction. In many cases isoidide and isosorbide yield polymers with higher molecular weights. Strikingly, in this case the polyurethanes with the isomannide structure have higher molecular weights, glass transition temperatures, and decomposition temperatures, and exhibit a higher crystallinity compared to their isosorbide analogues. Furthermore, also their appearance is quite different. While the isosorbide based polyurethane is a fluffy, light brown powder, the isomannide based polyurethane is an opaque, white solid.

Biocompatible and biodegradable polyurethanes were described by Knowles, Gong, and co-workers.^{524,525} In an uncatalyzed one-shot bulk polymerization, polyurethanes based on isosorbide, hexamethylene diisocyanate (HDI), and poly-(caprolactonediol) (PCL-diol) or poly(tetramethylene glycol) (PTMG) were synthesized (Figure 9). The polymers containing PTMG are thermoplastic polyurethanes with excellent stress–strain properties. The obtained polyurethanes have high molecular weights of over 100 000 g mol⁻¹, but, with increasing isosorbide content the molecular weight decreases. Additionally, with increasing isosorbide content the glass transition temperature and the surface energy increase, while the water contact angle decreases. Concerning biodegradability, the polyurethanes with a high isosorbide fraction show an initial rapid weight loss in degradability studies. Thus, a high isosorbide ratio seems beneficial for enhanced biodegradability.

In 2012, He et al. presented another approach to biodegradable polyurethane membranes.⁵²⁶ In a two-step synthesis with DBTDL as catalyst polyurethanes containing isosorbide, L-lysine ethyl ester diisocyanate (LDI), and again PCL-diols as chain extender are obtained. First, the PCL-diols are polymerized with LDI before isosorbide is added to the

Scheme 59. Synthesis of Isohexide-Based Polyurethanes As Reported by Zenner et al.⁵²³ Catalyzed by Dibutyltin Dilaurate (DBTDL)



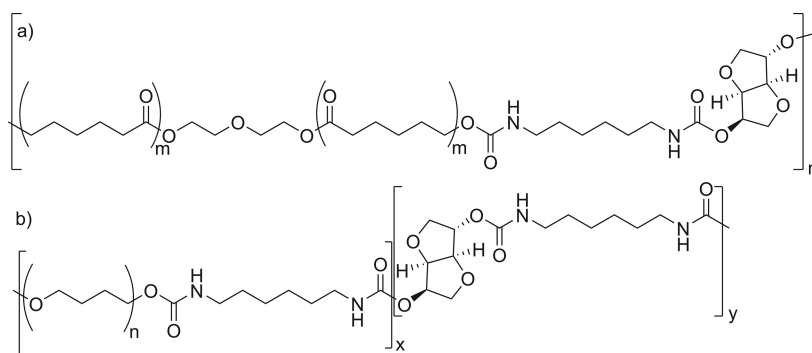
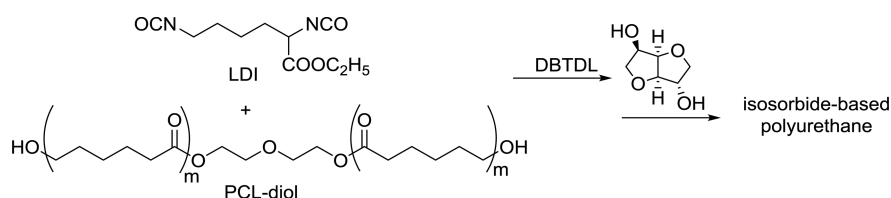
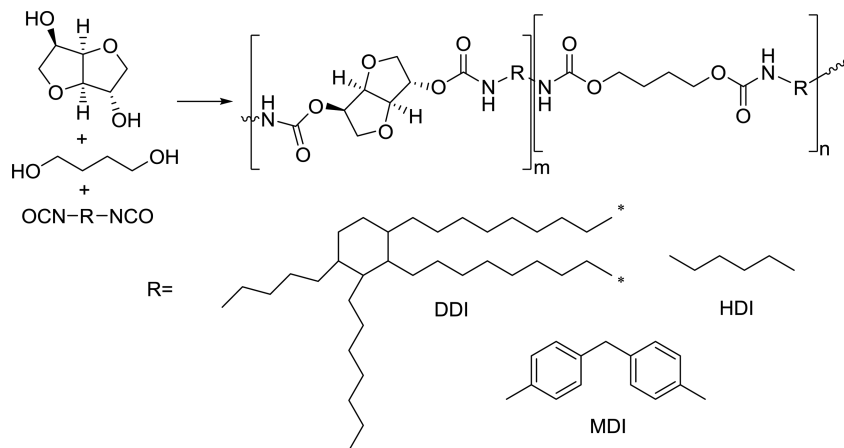


Figure 9. General structures of polyurethanes based on isosorbide, hexamethylene diisocyanate (HDI), and poly(caprolactonediol) (PCL-diol) (a) or poly(tetramethylene glycol) (PTMG) (b).

Scheme 60. Reaction Route toward the Isosorbide-Based Polyurethane Based on *L*-Lysine Ethyl Ester Diisocyanate (LDI) and Poly(caprolactonediol) (PCL-diol) in the Presence of Dibutyltin Dilaurate (DBTDL) as Catalyst Described by He et al.⁵²⁶



Scheme 61. Synthesis of Polyurethanes from Isosorbide, 1,4-Butanediol, and Different Isocyanates: 2-Heptyl-3,4-bis(9-isocyanatononyl)-1-pentyl-cyclohexane (DDI), Hexamethylene Diisocyanate (HDI), or Methylene bis(phenyl isocyanate) (MDI)^a



^aThe asterisk (*) marks the position of the isocyanate groups in DDI.

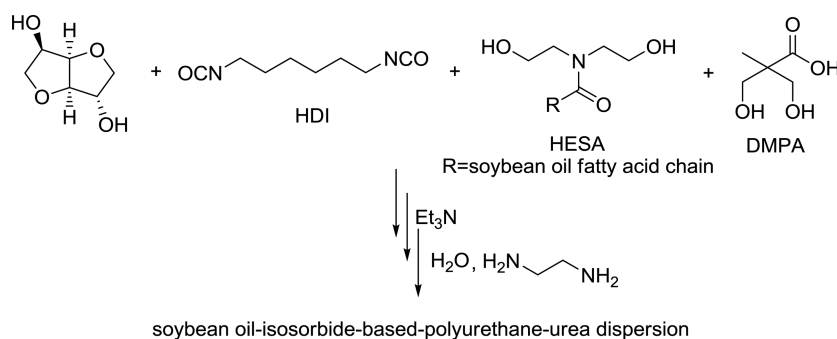
reaction (Scheme 60). Moreover, amino groups were introduced on the surface of the polyurethane membranes via an amination with 1,4-propanediamine. Onto this polycationic substratum type I collagen and chondroitin sulfate were then alternately deposited.

Charlon et al. and Marín et al. explored isosorbide based polyurethanes using 1,4-BDO as a second diol.^{527,528} In the work of Charlon et al. the diisocyanate monomer was a chemically modified dimer fatty acid, 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentyl-cyclohexane (DDI), which led in an one-step bulk reaction catalyzed by DBTDL to thermoplastic polyurethanes (Scheme 61).⁵²⁷ The polymers show a segregation of the hard segments (isosorbide) and the soft segments (1,4-BDO) with separate isosorbide and 1,4-BDO domains. The molecular weights of the thermoplastic polyurethanes are rather high with up to 31 800 g mol⁻¹. However,

the molecular weight decreases with increasing isosorbide content, which is attributed to the lesser reactivity of isosorbide in comparison to 1,4-BDO. Furthermore, a high fraction of isosorbide seems disadvantageous for good mechanical performance.

The linear polyurethanes synthesized by Marín et al. contain HDI and methylene bis(phenyl isocyanate) (MDI) as diisocyanate monomer (Scheme 61), and besides isosorbide also a diisosorbide diurethane was tested.⁵²⁸ The authors discovered similar trends as for the thermoplastic polyurethanes, and there was almost no difference whether the isohexide moiety was introduced as isosorbide or as diisosorbide diurethane. Additionally, the *exo*-configured hydroxyl group has a lesser reactivity. Thus, it was found to be the major chain end group.

Scheme 62. Synthesis of Soybean Oil-Isosorbide-Based-Polyurethane-Urea Dispersion from Isosorbide, Hexamethylene Diisocyanate (HDI), a Soybean Oil Based Amide (HESA) and Dimethylol Propionic Acid (DMPA)



Azizi et al. presented isosorbide based polyurethanes for a very specialized application.⁵²⁹ They synthesized microcapsules with polyurethane as wall material for encapsulating perfume in cosmetotextile applications. In an interfacial polycondensation using DBTDL as a catalyst, the polyurethanes were synthesized using isosorbide and MDI.

Varkey et al. investigated the optical and thermal properties of polyurethanes containing isosorbide, toluene diisocyanate, and chromophores based on linear diamines and ϵ -caprolactone.⁵³⁰ The obtained amorphous polymers showed higher glass transition temperatures and initial decomposition temperatures with increasing isosorbide content. Furthermore, also the specific rotation increases with a higher fraction of the chiral compound isosorbide. Additionally, the authors studied the nonlinear optical properties of the isosorbide-based polyurethanes and stated that their efficiency is comparable to the standard and can therefore be used in nonlinear optical applications.

Waterborne syntheses for isosorbide-based polyurethanes were reported by Xia et al.⁵³¹ as well as Li et al.⁵³² Polyurethanes containing besides isosorbide and HDI also dimethylol propionic acid (DMPA) and a soybean oil based amide (HESA) (Scheme 62) showed with increasing isohexide content not only an increase of the glass transition temperature but also better mechanical properties.⁵³¹ The Young's modulus increased from 2.3 to 63 MPa and the ultimate tensile strength increased from 0.7 to 8.2 MPa for a fraction of 0 or 20% isosorbide, respectively. However, there is a slight decrease of the thermal stability.

The study of NCO-terminated polyurethane building blocks based on isosorbide, LDI, DDI, and DMPA showed that the configuration of the hydroxyl group of the isohexide compound (*endo* vs *exo*) and the position of the isocyanide group (α vs ϵ) have a slight influence on the reactivity but in general do not hinder the formation of the polyurethane prepolymers.¹⁶⁴

Poly(ester urethane)s based on L-lactide, terephthaloyl chloride, diisocyanates, and isosorbide have been reported by Kricheldorf et al. in 2014.⁵³³ In section 3.3.1, we already mentioned polyesters based on the same compounds simply without the diisocyanates described by the same working group.⁵⁰⁴ The synthesis for the poly(ester urethane)s is quite similar. First, the bulk oligomerization of L-lactide and isosorbide takes place. Afterward the OH-terminated oligoesters undergo in situ polycondensation and polyaddition with terephthaloyl chloride and a diisocyanate simultaneously. SnCl₂ proved to be an appropriate catalyst for all three reactions. The tested isocyanates were 4,4'-diisocyanatodiphenylmethane and 2,4-diisocyanatotoluene. Comparing the polyesters⁵⁰⁴ with the

poly(ester urethane)s,⁵³³ the latter have a reduced thermal stability due to the formation of hydrogen bonds. However, it also improves the solubility in polar nucleophilic solvents.

3.3.4. Polymers Based on Hydroxyl Group Modified Isohexide Monomers. As already mentioned in the beginning of section 3.3, we focused mainly on polymers based on isohexides as monomers directly or after a functionalization at the isohexide backbone. However, a lot of work has also been done concerning OH-group modified monomers in order to introduce an isohexide backbone into a polymer. Here we only want to briefly summarize two quite recent publications.

Rajput et al. reported polyacetals based on isohexide-diacetals (Figure 10).⁵³⁴ In an acid catalyzed acetal metathesis

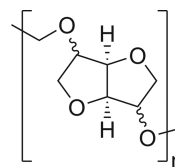


Figure 10. General polymer structure based on isohexide diacetals.

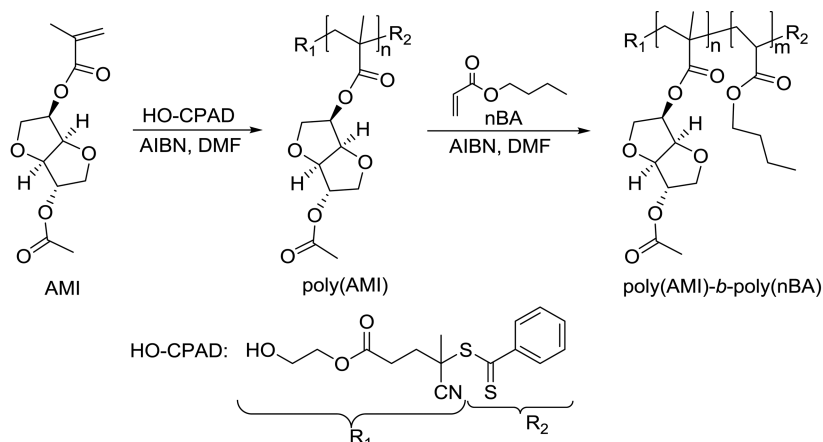
polymerization, polymers with number-average molecular weights of 3200–27 600 g mol⁻¹ were obtained. The molecular weights are the lowest for isomannide and the highest for isosorbide. However, with 65.5 °C the highest glass transition temperature was observed for a polyacetal based on isomannide. The melting temperatures are higher than for their linear C₅–C₆-polyacetal analogues.

Isosorbide-based polymethacrylates were reported by Gallagher et al. very recently.⁵³⁵ Therefore, acetylated methacrylic isosorbide (AMI) was used as a monomer in a free radical polymerization reaction (Scheme 63). Poly(AMI) has a high glass transition temperature of 130 °C and also a high number-average molecular weight of 88.9 kg mol⁻¹. Furthermore, the authors reported block copolymers based on AMI and *n*-butyl acrylate (nBA). First, a reversible addition–fragmentation chain transfer (RAFT) polymerization with 4-cyano-4-(phenylcarbonothioylthio)pentanoate (HO-CPAD) as chain transfer agent has been performed. Subsequently the chain extension was accomplished using nBA. The block copolymers possess two well-separated glass transition temperatures at about –45 and +120 °C. Thus, the poly(AMI) and poly(nBA) domains are most likely microphase separated.

3.4. Polymers Produced Using Biotechnological Processes

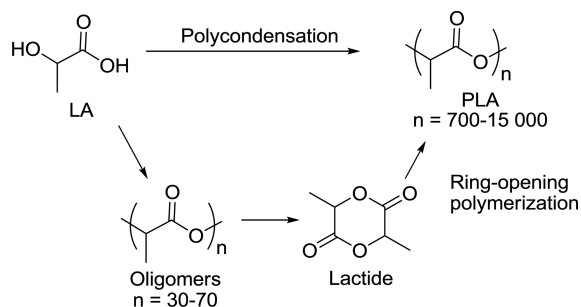
3.4.1. Poly(lactic acid). Poly(lactic acid) (PLA) was first synthesized over 150 years ago, but its instability under humid

Scheme 63. Synthesis of an Isosorbide-Based Block Copolymer Poly(AMI)-*b*-poly(nBA) Based on Acetylated Methacrylic Isosorbide (AMI)



conditions retarded the introduction into the market. In the 1960s the usefulness of PLA in medical application became apparent. After intensive research in 1980–1990s, Cargill developed a continuous process for the production of high purity lactide based on reactive distillation.^{261,536} Since then the capacity of the PLA production has gradually increased. For example, the market of PLA increased from 30 kt per annum in 2002²⁶¹ to the current volume of 300–400 kt/year.^{1,537} Scheme 64 presents two existing procedures of PLA synthesis, namely

Scheme 64. Synthesis of Poly(lactic acid) (PLA)

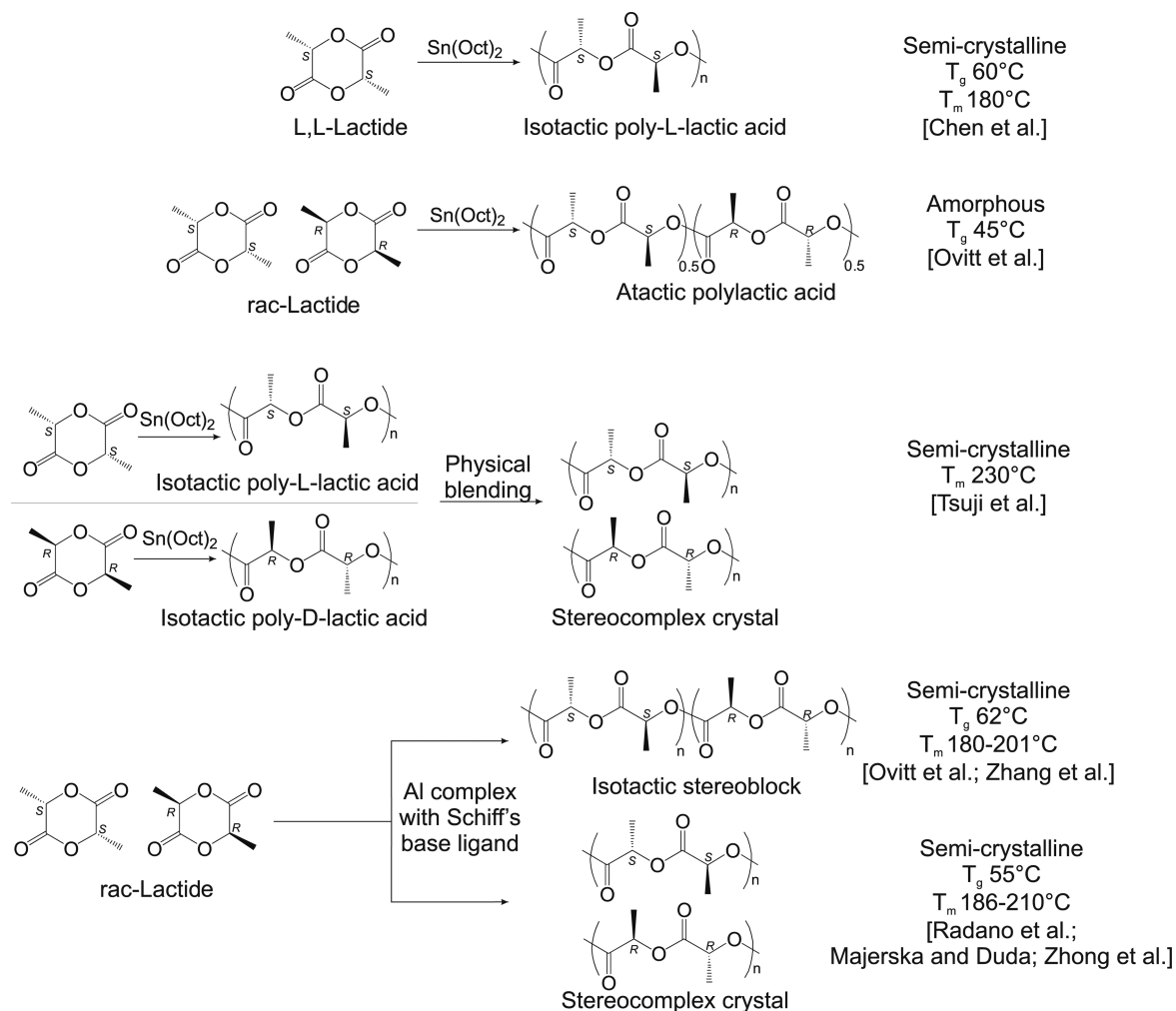


direct polycondensation and ring-opening polymerization of lactides. Both processes rely on a substrate of very high purity strongly relying on purification of crude LA as a crucial operation step. Direct polycondensation is an organic solvent-based process under azeotropic removal of water by distillation. The removal of water at a high degree of polymerization is challenging due to the very slow diffusion of moisture out of the highly viscous polymer.²⁵⁸ Importantly, the presence of water is detrimental as it decreases the molecular weight of PLA. Therefore, only a few companies use the direct polycondensation process for production of PLA.²⁵⁸ Most manufacturers of PLA employ ring-opening polymerization catalyzed by organometallic catalysts.^{538–540} First, LA is oligomerized at high temperature and reduced pressure to remove water. Later on, the catalytic depolymerization of these oligomers under low pressure yields lactide. Vacuum distillation or crystallization is used to remove the residual LA from lactide. Finally, the polymer is produced via catalytic ring-opening polymerization of lactide in the melt (Scheme 64).

PLA is currently utilized as a packaging thermoplastic for food packing and is suggested as a commodity plastic for

general packaging applications. Materials based on PLA and its copolymers have extensive applications in the biomedical field such as drug delivery capsules, suture and bone fixation material as well as tissue engineering, etc.^{540,541} Moreover, PLA has a wide range of possible applications and a very high potential to replace hydrocarbon-based polymers owing to similar properties.⁵⁴² Poly(L-LA) and poly(D-LA) are semicrystalline in nature. The molecular weight of PLA varies from 100 to 300 kg mol^{-1} , which is similar to that of a conventional polymer such as poly(ethylene terephthalate) (170–350 kg mol^{-1}). Well-known for polymers, a higher molecular weight of PLA results in an increase of the strength owing to a decrease in the relative motion of the chains as they become longer. PLA exhibits good transparency, glossy appearance, high rigidity, and biodegradability.

The stereochemistry of lactide is of great importance for the physical and mechanical properties of the resulting PLA. Scheme 65 illustrates the thermal properties of PLAs depending on optical purity and the catalyst. The first investigations on the catalytic polymerization of lactides demonstrated that optically pure L-LA or D-LA yields polymers with much better properties than those of materials produced based on racemic LA. Conventionally, the polymer-grade L-LA contains less than 1–2% D-LA. Polymerization of L-LA gives rise to an isotactic crystalline polymer with a melting point (T_m) of ca. 180 °C and a T_g of ca. 60 °C. When heated above T_g , the wares made of PLA change their shape and even degrade under high moisture conditions.²⁵⁸ The optical purity of L-LA is very important for the synthesis of high-quality PLA, because even traces of D-LA lead to inhibition of crystallization as well as a decrease of T_g and T_m values.⁵³⁹ The polymerization of lactides is carried out commonly in the presence of a tin octoate catalyst ($\text{Sn}(\text{Oct})_2$) but the activity of more than 100 different catalyst for this reaction was reported in the literature.^{539,549} Polymerization of racemic LA leads to the formation of an amorphous polymer with low T_g of 45 °C and poor mechanical properties. Tsuji et al. reported on the remarkable thermal stability of a 1:1 physical blend of poly-L-LA and poly-D-LA. The melting point of the blend is as high as 230 °C, which is 50 °C higher than that of the individual forms⁵⁵⁰ due to assembly of isotactic crystalline polymers into a stereocomplex crystal.⁵⁵⁰ The first reported synthetic approaches suggested separate polymerization of L-lactides and D-lactides prior to blending,⁵⁵⁰ but direct synthesis of the stereocomplex crystal from racemic LA would be more

Scheme 65. Thermal Properties of PLA (Poly-LA) Depending on Optical Purity and the Catalyst for Polymerization^a

^aSn(Oct)₂ refers to tin octoate catalyst. The scheme summarizes data published by Chen et al.,²⁵⁸ Ovitt et al.,⁵⁴³ Tsuji et al.,⁵⁴⁴ Zhang et al.,⁵⁴⁵ Radano et al.,⁵⁴⁶ Majerska and Duda,⁵⁴⁷ and Zhong et al.⁵⁴⁸

advantageous. The pioneering study by Spassky et al. demonstrated the preferable synthesis of isotactic polymers starting from the racemic lactides catalyzed by Al complexes with chiral Schiff's base ligands as catalysts.⁵⁵¹ Optimization of the catalyst^{543,545–548} enabled synthesis of PLA based on racemic lactide with as good thermal properties as the optically pure polymer. The reason for improved thermal stability relates to the preferential formation of isotactic polymers that finally form either isotactic stereoblocks^{543,545} or stereocomplex crystals^{546–548} (Scheme 65). The newly discovered class of catalysts for polymerization enables the use of racemic LA; i.e., LA synthesized either by fermentation or by heterogeneous catalysis can be potentially utilized as a monomer. An alternative approach toward application of racemic LA for polymerization includes its enantiomeric resolution prior to polymerization. Advances in the enantiomeric separation of LA have very recently been reviewed by Dusselier et al.²⁶⁸

3.4.2. Polyhydroxyalkanoates. Polyhydroxyalkanoates (PHA) are the most well-known family of polymers synthesized directly inside cells. Traditionally the biotechnological synthesis of polymers implies a fermentative production of monomers with successive chemical polymerization. The production of PHA does not require an intermediate isolation of the

monomers: The polymers are accumulated in the cytoplasm under growth limiting conditions in the presence of a carbon source.^{258–261,542,552,553} Poly(3-hydroxybutyrate) (PHB) was the first representative of PHA uncovered in 1926 (Figure 11).

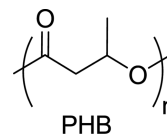


Figure 11. Poly(3-hydroxybutyrate) (PHB).

This polymer received the most attention, although PHA containing more than 150 different monomers have been synthesized since then, mainly on the laboratory scale.²⁵⁸ Depending on the type of bacteria and synthesis conditions, PHA monomers can contain carbon chain lengths ranging from 3 to 14. In some cases the monomer structure contains functionalities such as halogens, benzene, unsaturated bonds, epoxides, and cyclic groups.⁵⁵³ Obviously, the great variation potential of the monomer structure results in diverse properties of PHA. In vivo synthesis provides different types of PHA

polymers, i.e., homopolymers, copolymers, and block copolymers.^{258,259,542}

The production of PHA includes three steps, namely, (1) fermentation, (2) isolation, and (3) purification.²⁶¹ The vessel for fermentation is filled with a mineral medium and inoculated with seed ferment (containing the microbe or bacteria).²⁶¹ PHA can be produced by a great number of bacteria, i.e., by over 30% of soil-inhabiting bacteria as well as bacteria in activated sludge, in high seas, and in extreme environments.²⁵⁸ The fermentation usually lasts 38–48 h.²⁶¹ During the fermentation, the carbon source is fed to the vessel at various rates. Theoretically, a broad variety of carbon feedstocks can be used, including cellulose hydrolysates, municipal solid wastes, lactose from whey, and wastes from biodiesel production.^{261,542} Practically, high-value substrates such as sucrose, vegetable oils, and fatty acids are used in order to reach sufficiently high rates of fermentation.²⁶¹ Isolation of PHA is accomplished by extraction with the successive addition of an antisolvent and recovery of the polymers by solid–liquid separation. The PHA are further purified by washing with different solvents.²⁶¹

Despite the very attractive properties of PHA, these polymers have not entered the bulk market yet owing to high production costs.²⁶¹ PHA are currently produced by a number of companies with a total capacity of ca. 50 kt per annum.²⁶⁰ Currently PHA and their copolymers are predominantly used as biodegradable plastics for food packing.^{542,553} Being biocompatible and nontoxic, PHA have a number of biomedical applications.^{542,553} PHA can be utilized in the chemical industry as sources of valuable optically pure acids available via hydrolysis of PHA.⁵⁵³ Moreover, after use as bioplastics, a transformation of PHA into biofuels via successive hydrolysis and esterification has been suggested.⁵⁵³

PHA are semicrystalline polymers with molar masses of 200–3000 kg mol⁻¹, T_m 's of 60–177 °C, and T_g 's of –50 to 4 °C.⁵⁵² PHB is the most produced polymer of the PHA family. It exhibits very good thermoplastic properties ($T_m = 180$ °C), and articles made of PHB retain their shape in the temperature range from –30 to 120 °C. Unlike most biobased polymers, PHB is water-insoluble and relatively resistant to water degradation.²⁶¹ Some applications of PHB are restrained by the high stiffness and brittleness of the polymer,²⁶¹ as well as by a narrow processing temperature range, the tendency to “creep”, and slow crystallization.⁵⁴² However, the properties of PHB can be improved when copolymerized with other monomers, e.g., 3-hydroxyvaleric or 3-hydroxyhexanoic acid.²⁶¹

3.4.3. Poly(butylene succinate). Poly(butylene succinate) (PBS) is a biodegradable polyester consisting of SA and 1,4-BDO as building blocks. Bulk production of PBS based on biobased SA and petrochemical-based 1,4-BDO started at the beginning of the 2000s.²⁶¹ Before that PBS was manufactured relying exclusively on fossil feedstocks. Due to the development of 1,4-BDO synthesis from renewable feedstocks, the manufacturers recently announced the shift toward a fully biomass-based production of PBS.¹ The current production volume of PBS is ca. 40 kt per annum.¹

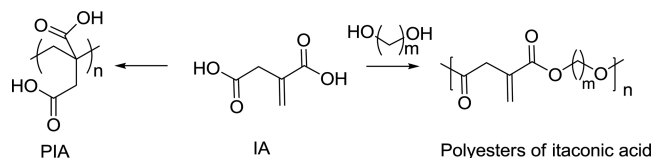
Owing to excellent mechanical properties of PBS and its blends, this polymer is very likely to substitute some conventional polymers such as polypropylene (PP) or poly(ethylene terephthalate) (PET).^{542,554} PBS is a semicrystalline polymer with a T_g of –32 °C and a T_m of 115 °C.^{258,554} Currently PBS-based materials are utilized as barrier films, for packaging, as dishware, and as drug encapsulation systems.⁵⁴²

Moreover, PBS is used as a component of blends or copolymers.^{1,542,554}

Synthesis of PBS is possible via transesterification or direct condensation of SA with 1,4-BDO.^{258,554} The transesterification of dimethylsuccinate with 1,4-BDO is conducted under an inert atmosphere at 150–190 °C in the presence of catalysts. Such compounds as tetra-*n*-butyl-titanate, tetra-isopropyl-titanate, SnCl₄, distannoxane, lanthanide triflates, and *p*-TSA were reported to be efficient catalysts for transesterification. Using dimethylsuccinate and 1,4-BDO in stoichiometric amounts is of great importance to obtaining a polymer with high molecular mass. This is crucial for application, as PBS with a M_w lower than 100 kg mol⁻¹ is brittle.⁵⁵⁴ Owing to the higher volatility of 1,4-BDO, a 10% excess of this component over SA is usually used. When the transesterification occurs and methanol is removed, the polycondensation is conducted under vacuum at 200–240 °C. A direct condensation of SA with 1,4-BDO is also possible via melt polymerization or from solution. PBS has good processability; i.e., it can be easily converted to end products by conventional melt technology.^{15,261} However, the viscosity of linear PBS and its copolymers decreases rapidly when the processing temperature is 20 °C higher than the melting point due to weak intermolecular interactions, making film blowing difficult. This problem can be solved either by chain extension using chain-extending agents or by cross-linking of PBS.⁵⁵⁴

3.4.4. Poly(itaconic acid). Poly(itaconic acid) (PIA) is a polymer synthesized by vinyl polymerization of IA. As IA contains a double bond and two carboxylic groups, either vinyl polymerization or formation of polyesters is possible (Scheme 66). The former type of polymerization is studied in more

Scheme 66. Polymerization Routes of Itaconic Acid (IA): Vinyl Polymerization into Poly(itaconic acid) (PIA) and Formation of Polyesters



detail, and significantly less is known about utilization of IA as a monomer unit of polyesters. Vinyl homopolymerization of IA is challenging as it fails under traditional polymerization conditions, e.g., in the presence of potassium persulfate or in alkaline solution.⁵⁵⁵ Marvel and Shepherd reported the synthesis of PIA by polymerization in 0.5 M HCl initiated by potassium persulfate, but the yield of the polymer is only 35% after 68 h at 50 °C.⁵⁵⁵ Later on, the two-step synthesis of PIA was suggested via (1) radical polymerization of dialkyl itaconates⁵⁵⁶ or β -monoalkyl itaconates⁵⁵⁷ and (2) successive hydrolysis of the polymers to yield PIA. This approach helps increase the yield of PIA to 86% because alkyl itaconates can be polymerized much easier compared to IA. Additionally, polyalkyl itaconates are readily hydrolyzed in the presence of acids or bases.⁵⁵⁷ More recently, the synthesis of PIA was successfully and rapidly completed via radical polymerization after full⁵⁵⁸ or partial^{559,560} neutralization of IA. Quantitative yields of PIA are obtained as a result of rapid polymerization of neutralized IA within 1–2.5 h. Depending on the polymerization conditions, the molar mass of PIA varies from 1 to 20 kg mol⁻¹.^{558–560} PIA is soluble in water and methanol and

insoluble in many organic solvents including ethanol. PIA recovered by freeze-drying contains water of hydration in molar amounts nearly equal to the amounts of IA monomers. Drying of hydrated PIA under reduced pressure leads to the formation of anhydrides.^{293,557} For a long time PIA as an alkaline salt or in sulfonated form has been used as component of cleansing agents and shampoos. From the 1990s the application field of PIA and copolymers of IA was enlarged to the medical field, specifically for drug delivery purposes.⁵⁶¹ Notably, not only IA but also its derivatives are actively used for synthesis of polymers. For instance, easily polymerizable alkyl itaconates are used as plastics, adhesives, elastomers, and coatings. The copolymers of IA with unsaturated compounds, e.g., acrylic acid, aconitic acid, and butadiene, have been known for a long time.²⁹³ Many copolymers of IA find application for the production of synthetic fibers, coatings, adhesives, thickeners, and binders.³³⁹ For example, IA in small concentrations of 1–5% is utilized as a comonomer of rubberlike resins. IA can also be used for synthesis of biobased epoxy resins.^{562,563} Another promising application of IA relates to the production of glass-ionomer dental cement that contains a copolymer of IA with acrylic acid.⁵⁶¹

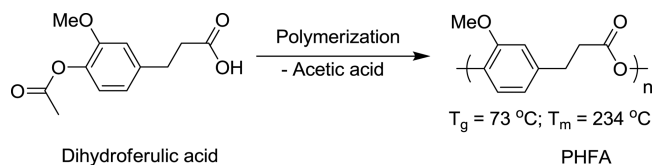
Polyesters based on IA (Scheme 66) received much less attention compared to PIA. Poly(ethylene itaconate) can be synthesized by bulk condensation of IA or dimethylitaconate with ethylene glycol under moderate vacuum (40–50 mmHg) at 100–120 °C in the presence of catalytic amounts of *p*-toluenesulfonic acid.⁵⁶⁴ The obtained polymer is insoluble in water, benzene, and hydrocarbons but soluble in polar organic solvents such as acetone, chloroform, and THF. The molar mass of poly(ethylene itaconate) is ca. 1.2 kg mol⁻¹. Importantly, the lateral double bond is very reactive and hyper-cross-linking is observed when the conversion of the monomer exceeds 85%. When kept at room temperature in solution or as solid, poly(ethylene itaconate) readily undergoes cross-linking after 24 or 48 h without addition of any initiator of polymerization.⁵⁶⁴ Similar results were obtained when polymerizing itaconic anhydride with 1,2-epoxybutane in the presence of Mg(OEt)₂,⁵⁶⁵ Al(O^{*i*}Pr)₃,⁵⁶⁵ bis-(nonafluorobutanesulfonyl) imide,⁵⁶⁶ and Sc(OTf)₃⁵⁶⁶ as catalysts. However, in this case the polymerization was accompanied by isomerization of itaconate to cytraconate. This method enables the synthesis of polymers with a molar mass *M_n* of up to 50 kg mol⁻¹.⁵⁶⁵ The capability of IA-containing polyesters to undergo cross-linking enables tailoring the polymers by introducing some IA as copolymer. For example, IA in amounts of less than 10% was copolymerized with PBS,³ poly(propylene carbonate),⁵⁶⁷ and a polyester containing maleate and 3-methyl-1,5-pentanediol units.⁵⁶⁶ In all cases cross-linked polymers were successfully synthesized even at a low concentration of IA. Interestingly, Tang et al. first copolymerized a polyester containing IA, maleate, and 3-methyl-1,5-pentanediol and then conducted a selective photo-cross-linking of the exotype double bonds of itaconates, whereas the double bonds of maleate stayed intact.⁵⁶⁶

3.5. Polymers Based on Bioaromatic Monomers

Organosolv lignin, kraft lignin, and liginosulfonate are abundant wastes from the pulp industry. The application of them is of great economical interests and environmental advantages. Several reviews reported the direct application of lignins in composite materials.^{568–571} This section will mainly focus on the synthesis of polymers from lignin monomers.

3.5.1. Polyesters Based on Vanillin Monomers. As mentioned in section 2.5.1.4, a two-step conversion of vanillin could produce dihydroferulic acid, which contains a carboxylic group and a acetyl protected hydroxyl group. The bifunctional molecule can be used to replace both glycol and terephthalate for PET production. Efficient polymerization of dihydroferulic acid was accomplished in the melt (200–220 °C) with Sb₂O₃ or Zn(OAc)₂ as catalyst (Scheme 67).³⁷⁴ Dynamic vacuum was

Scheme 67. Polymerization of Dihydroferulic Acid into Poly(dihydroferulic acid) (PHFA) as a Renewable Substitute for PET



applied to remove acetic acid as the byproduct of this condensation polymerization. As a result, polymeric products with *M_n* from 630 to 17 800 Da were obtained. The *T_m* for a typical sample is measured as 234 °C, and its *T_g* is measured as 73 °C. These values are comparable to those of PET (*T_g* = 67 °C; *T_m* = 265 °C).

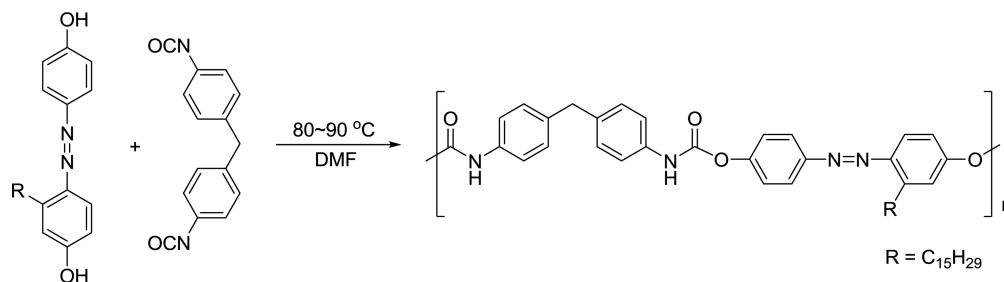
3.5.2. Application of Diphenolic Monomers in Polyurethanes. The cardanol derived diphenolic compound is able to react with MDI to produce polyurethane (PU) with a high intrinsic viscosity of 1.85 dL/g (Scheme 68). The PU material was stable under UV radiation and also exhibited good thermal stability below 290 °C.³⁸²

3.5.3. Polycarbonates Based on Vanillin Monomers. Based on bisphenol obtained from vanillin, a polycarbonate was synthesized through transesterification of it with diphenyl carbonate (Scheme 69). This reaction gave a resin with a *M_n* of 3588 Da as determined by GPC, and a polydispersity of 1.9. The material exhibited a *T_g* of 86 °C, lower than that of conventionally prepared bisphenol polycarbonate (120 °C).³⁸¹

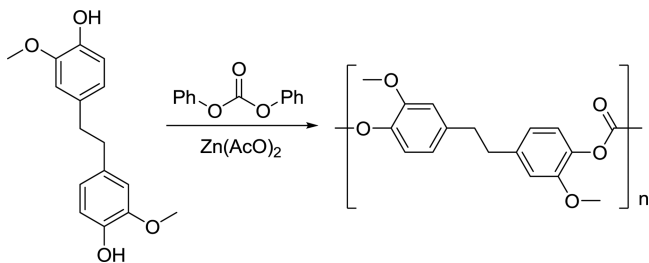
3.5.4. Polyacrylates. Using vanillin derived methylacrylate as substitute of styrene, various polymeric materials could be prepared. Although methyl acrylated vanillin is solid at room temperature,³⁷³ a low viscous resin could be prepared via adding glycidyl methyl acrylate to the mixture of methyl acrylated vanillin and methyl acrylate (Scheme 70).⁵⁷² The latter is the byproduct of methyl acrylated vanillin, and it could be transformed by glycidyl methyl acrylate to form cross-linked glycerol dimethyl acrylate. Resin curing generated a hard, transparent thermoset that possessed a broad glass transition, *T_g* = 155 °C, and *E'*(at 25 °C) = 3.6 GPa. Thermogravimetric analysis revealed a two-stage thermal decomposition profile with a *T_{max}* = 426 °C and *T_{50%}* = 405 °C.⁵⁷² Methyl acrylated vanillin could also be applied in RAFT polymerizations with lauryl methacrylate. The resulting materials exhibited *T_g* values near and above 100 °C and degradation temperature values of at least 300 °C. Interestingly, small-angle X-ray scattering and transmission electron microscopy studies showed that the extension of the vanillin-based polymers with lauryl methacrylate yielded block polymers with self-assembled bcc nanospheres.^{573,574}

Similarly, methyl acrylated cardanol is able to afford a linear polymer by solution polymerization of the monomer in toluene using 0.8% azobis(isobutyronitrile) as initiator. Upon removal of the solvent, the polymer undergoes cross-linking on

Scheme 68. Application of the Cardanol Derived Diphenolic Compound in Polyurethane (PU) Synthesis



Scheme 69. Polycarbonate from Vanillin Derived Bisphenol

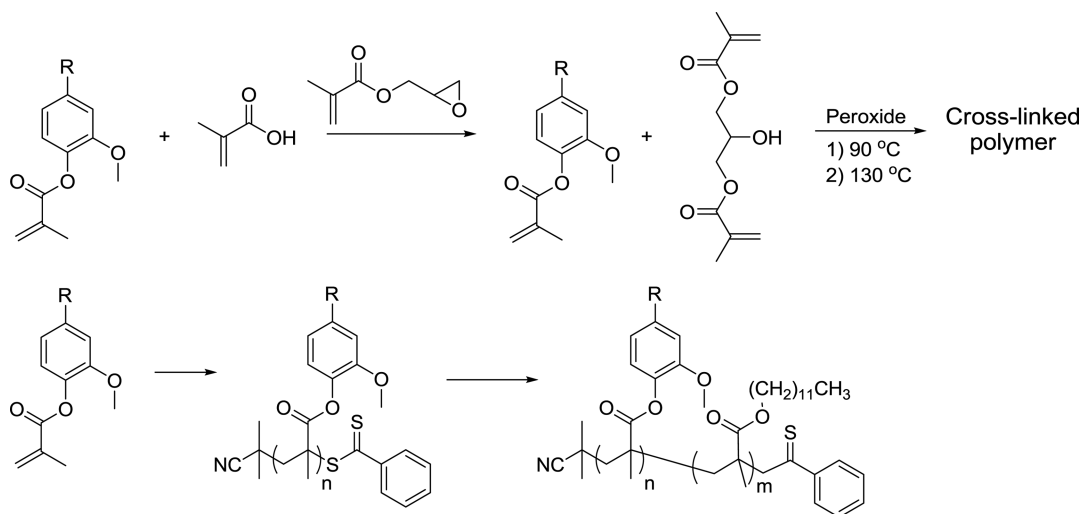


exposure to air (or UV light) to give an insoluble transparent film. However, in bulk and suspension polymerization the polymer undergoes in situ cross-linking in the absence of any cross-linking agent.³⁸³

3.5.5. Polyethers. Spirocyclic polyether was synthesized by the condensation of pentaerythritol with vanillin derived dialdehyde (Scheme 71). The M_n of the as-prepared material is 10 600 Da and T_g and $T_{95\%}$ are 129 and 308 °C, respectively. In this way, another seven cyclic polyethers with T_g ranging from 68 to 129 °C were prepared from lignin-related dialdehydes and tetraols.³⁷⁵

3.5.6. Epoxy Resins. The curing of vanillin based epoxy resins using isophorone diamine as hardener provided a solid material with a T_g of 117 °C, indicating the epoxy resin is promising to replace the reprotoxic bisphenol A epoxy resin.³⁷² Similarly, the cardanol based epoxy resin was cured by aromatic polyamine and the composites based on this material were applied as anticorrosive paints.³⁸⁵

Scheme 70. Polymer from Methylacrylated Vanillin



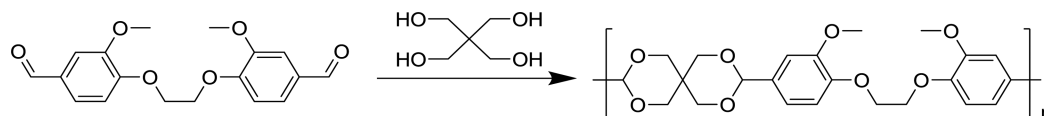
3.5.7. Benzoxazine Resins. Polybenzoxazines are a relatively new class of high performance polymers. The benzoxazine synthesized from vanillin, furfuryl amine, and formaldehyde could be polymerized at 179–232 °C according to the DSC scan. The T_g of the vanillin derived polybenzoxazine is 270 °C, much higher than that of conventional polybenzoxazine materials. A single-step decomposition was also observed at high temperature (320–650 °C) due to degradation of the Mannich base.³⁷⁶ Using cardanol based benzoxazine and epoxy as substrate, a series of composite materials could be obtained after thermal curing. The materials displayed a two-stage degradation pattern and were found to be stable up to 300 °C by thermogravimetric analysis. A lower char yield at 650 °C compared to pure homopolymers was also observed due to a less-ordered structure formed upon copolymerization.³⁸⁴

3.5.8. Polycyanurate. The (bis)cyanate ester prepared from vanillin was amenable to thermal cure under modest conditions (Scheme 72). A DSC study showed that the monomer started to be cured below 200 °C to yield a thermoset material with a T_g of 202 °C, which indicated the material was comparable to some of the highest-performing petroleum-derived epoxy resins.³⁸¹

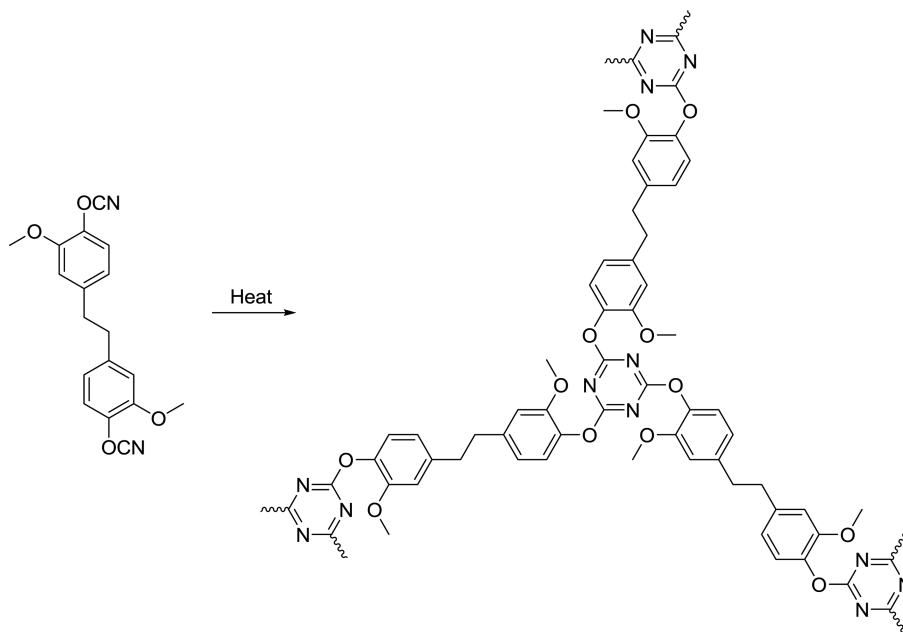
4. CONCLUDING REMARKS

In recent years, the valorization of lignocellulose as feedstock for the production of platform chemicals has found tremendous attention. At the same time, the further transformation of these platform chemicals into alternative monomers has been an area of growing research interest. Nevertheless, one has to point out

Scheme 71. Synthesis of Spirocyclic Polyether from Vanillin Derived Dialdehyde



Scheme 72. Thermal Cyclotrimerization of Bis(cyanate) Ester into Polycyanurate



that several of the monomers discussed in this review have already been synthesized by means of organic synthesis several decades ago. However, the renewed interest in lignocellulose-based monomers entailed the design of green catalytic synthesis protocols to access these monomers. A further advance of suitable catalytic processes enabling an efficient monomer production presents certainly a key requirement for a cost-competitive and sustainable large-scale production of these compounds. Furthermore, most platform chemicals still lack commercial production processes hampering the implementation of value chains based on these platform chemicals and their market entry. Nevertheless, several of the presented alternative monomers have proven a high potential for application in polymer production. They allow not only substitution of conventional petrochemical monomers but also facilitate an improved material performance. In this regard, tailored polymers based on renewable building blocks become accessible.

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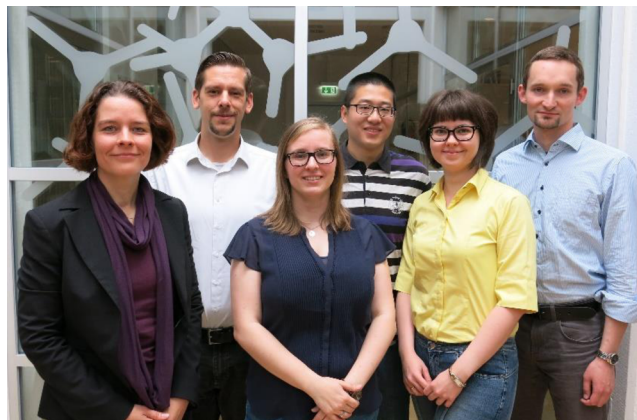
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

Biography



Regina Palkovits (left) is Full Professor for Heterogeneous Catalysis and Chemical Technology at RWTH Aachen University. She graduated in chemical engineering from Technical University Dortmund in 2003 and carried out her Ph.D. under the supervision of Prof. Ferdi Schüth at the Max-Planck-Institut für Kohlenforschung from 2003 to 2006. Afterward, she joined the group of Prof. Bert Weckhuysen at Utrecht University as a postdoctoral fellow. In 2008, she returned as a group leader to the Max-Planck-Institut für Kohlenforschung, and since 2010 she has been Professor at RWTH Aachen University.

Peter J. C. Hausoul (second from left) was born in The Netherlands in 1981. He studied chemistry at Utrecht University and obtained his M.Sc. degree with a focus on organometallic chemistry and homogeneous catalysis in 2008. He obtained his Ph.D. degree in 2013 at the same university in the inorganic chemistry and catalysis

group under the supervision of Prof. Bert Weckhuysen. In 2012 he joined the group of Prof. Dr. R. Palkovits, where he is currently employed as group leader, supervising both academic research and projects with industrial partners. His research interests concern the development of supported single site catalysts as well as fundamental and applied research on catalytic biomass conversion.

Rebecca Pfützenreuter (third from left) is a doctoral student at the Chair of Heterogeneous Catalysis and Chemical Technology at RWTH Aachen University. She joined the Palkovits group in 2012 as a doctoral candidate after she graduated in chemistry from RWTH Aachen University. For her master's thesis, she obtained the DECHEMA student award 2013. Her current research relates to the catalytic functionalization of isohexides.

Li Deng (fourth from left) received his bachelor degree in applied chemistry from Qingdao University of Science and Technology in 2006. He subsequently joined the group of Prof. Qing-Xiang Guo at the University of Science and Technology of China and completed his Ph.D. thesis in 2011. Afterward, he moved to Guangzhou Institute of Chemistry, CAS, where he was promoted as an associate professor. Since 2014, he has been a postdoctoral fellow sponsored by the Alexander von Humboldt foundation in Prof. Regina Palkovits's group at RWTH Aachen.

Irina Delidovich (fifth from left) is a postdoctoral fellow at RWTH Aachen University. She received her diploma in chemistry in 2008 from Novosibirsk State University. In 2011 she obtained her Ph.D. from Borekov Institute of Catalysis under the supervision of Dr. Oxana Taran. In 2012 she joined the research group of Prof. Regina Palkovits at RWTH Aachen University. In 2013, she became an Alexander von Humboldt fellow in cooperation with the Bayer Foundation.

Marcus Rose (right) is group leader at the Chair of Heterogeneous Catalysis and Chemical Technology at RWTH Aachen University. He graduated in chemistry from Dresden University of Technology in 2007, where he also carried out his Ph.D. under the supervision of Prof. Stefan Kaskel from 2007 to 2010 with an intermediate research visit at the Georgia Institute of Technology. Afterward, he joined the group of Prof. Regina Palkovits at the Max-Planck-Institut für Kohlenforschung as a postdoctoral fellow. In 2011, he moved with the group to RWTH Aachen University as group leader. In 2014 he was temporarily appointed as guest professor at the Department of Chemical Technology at Technische Universität Darmstadt.

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ABBREVIATIONS

AA-TEMPO	4-acetamino-2,2,6,6-tetramethylpiperidine-1-oxyl
AL	α -angelica lactone
ALR	air lift reactor
AMI	acetylated methacrylic isosorbide
BAMF	2,5-bis(aminomethyl)furan
BAMTHF	2,5-bis(aminomethyl)tetrahydrofuran
1,4-BDO	1,4-butanediol
2,3-BDO	2,3-butanediol
BHAMF	bis-oxime of 2,5-diformylfuran
BHMF	2,5-bis(hydroxymethyl)furan

BHMTHF	2,5-bis(hydroxymethyl)tetrahydrofuran
BPA	bisphenol A
CHDA	1,4-cyclohexane dicarboxylic acid
COD	cyclooctadiene
CTF	covalent triazine framework
DAB	1,4-diaminobutane
DAII	diamineisoidide
DAIS	diaminoisosorbide
DB	degree of branching
DBTDL	dibutyltin dilaurate
DDI	2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentyl-cyclohexane
DFF	2,5-diformylfuran
DMFA	<i>N,N</i> -dimethylformamide
DMF	2,5-dimethylfuran
DMPA	dimethylol propionic acid
DMSO	dimethyl sulfoxide
DPA	diphenolic acid
DSC	differential scanning calorimetry
EG	ethylene glycol
F	furan
FA	fumaric acid
FCA	2-furancarboxylic acid
FDCA	furan-2,5-dicarboxylic acid
FF	furfural
FFA	furfuryl alcohol
FFAM	furfurylamine
FFCA	5-formylfuran-2-carboxylic acid
FID	flame ionization detector
GC	gas chromatography
GPC	gel permeation chromatography
GBL	γ -butyrolactone
GVL	γ -valerolactone
HBP	hyperbranched polymer
HDI	hexamethylene diisocyanate
HESA	<i>N,N</i> -bis(2-hydroxyethyl)soybean amide
HPA	heteropoly acid
HMF	5-(hydroxymethyl)furfural
HMFCA	5-hydroxymethylfuran-2-carboxylic acid
HMTHF	2-(hydroxymethyl)tetrahydrofuran
HO-CPAD	4-cyano-4-(phenylcarbonothioylthio)pentanoate
HT	hydrotalcite
IA	itaconic acid
IIDCA	isoidide dicarboxylic acid
IIDM	isoidide-2,5-dimethanol
IIDMA	isoidide-2,5-dimethyleneamine
IIDMC	isoidide dicarboxylic acid dimethyl ester
IL	ionic liquid
LA	lactic acid
LDI	<i>L</i> -lysine ethyl ester diisocyanate
LevA	levulinic acid
MMBL	γ -methyl- α -methylene- γ -butyrolactone
MDI	methylene bis(phenyl isocyanate)
Me-FCA	methyl ester of 2-furancarboxylic acid
Me2-FDCA	methyl ester of furan-2,5-dicarboxylic acid
MF	2-methylfuran
MIBK	methyl isobutyl ketone
MMA	methyl methacrylate
MTBE	methyl <i>tert</i> -butyl ether
nBA	<i>n</i> -butyl acrylate
OMS-2	manganese oxide octahedral molecular sieves
PBF	poly(butylene furoate)
PBS	poly(butylene succinate)

PCL-diol	poly(caprolactonediol)
1,2-PDO	1,2-propanediol
1,3-PDO	1,3-propanediol
PEF	poly(ethylene 2,5-furandicarboxylate)
PEIT	poly(ethylene-co-isosorbide terephthalate)
PET	poly(ethylene terephthalate)
PHA	polyhydroxyalkanoates
PHB	poly(3-hydroxybutyrate)
PHFA	poly(dihydroferulic acid)
PIA	poly(itaconic acid)
PIAD	poly(isosorbide adipate)
PIS	poly(isosorbide sebacate)
PISU	poly(isosorbide succinate)
PIT	poly(isosorbide terephthalate)
PLA	poly(lactic acid)
PMMBL	poly(γ -methyl- α -methylene- γ -butyrolactone)
PMMA	poly(methyl methacrylate)
PTMG	poly(tetramethylene glycol)
PU	polyurethane
PVP	poly(vinylpyridine)
RAFT	reversible addition-fragmentation chain transfer
REM	rare earth metal
SA	succinic acid
SSPC	solid-state postcondensation
STR	stirred tank reactor
TCA cycle	tricarboxylic acid cycle
TDI	toluene-2,4-diisocyanate
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy, free radical
Tf	triflate
THF	tetrahydrofuran
TMPA	<i>N,N,N</i> -trimethyl- <i>n</i> -propylammonium
TOF	turnover frequency
TPA	terephthalic acid
UV	ultraviolet

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