Towards sugar- and lignin-based polyesters and polyurethanes with enhanced properties

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Towards sugar- and lignin-based polyesters and polyurethanes with enhanced properties

NIKLAS WARLIN
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Virtually all objects we encounter in our daily life contain plastics, and it has been estimated that close to 400 million tons are produced every year. This enormous production volume causes significant environmental problems when plastic waste ends up in nature since there is often no natural way for it to decompose. Certain types of plastics can last for thousands of years, and it has been estimated that there will be more plastic than fish in the ocean by 2050 if we continue to produce and use plastics in the same way as we do today.

There are many approaches for solving this problem, but I have primarily used two different strategies in this thesis: Designing plastics for chemical recycling, and synthesizing bio-based plastics from renewable sources. To evaluate and demonstrate the properties of these new materials, I have prepared various fibers, coatings, and films. Hopefully the results achieved in this thesis can facilitate commercialization of bio-based products in the near future.

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Towards sugar- and lignin-based polyesters and polyurethanes with enhanced properties

Niklas Warlin

LUND
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DOCTORAL DISSERTATION

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Abstract

The enormous production and consumption of fossil-based plastics has caused severe environmental challenges such as pollution of the ocean, increased CO_2-emissions, and various health problems. Many of these concerns are intimately connected to the use of fossil fuels in the production of polymers. For this reason, there is a considerable interest to develop bio-based monomers to mitigate some of the issues connected to fossil-based plastics. However, new bio-based monomers are often expensive and need some material advantages to facilitate their market entry. In this context, we have designed several new monomers by converting bio-based molecules such as 5-chloromethylfurfural (CMF), 5-hydroxymethylfurfural (HMF) and vanillin into rigid diols for polyester and polyurethane synthesis. This thesis has been divided into 5 chapters describing the most important findings from each underlying project.

In Chapter 1 and 2, HMF was reacted with pentaerythritol and di(trimethylolpropane) to make two rigid diols with cyclic acetal structures. The monomer made from HMF and pentaerythritol was predicted to have an exceptionally low carbon footprint according to our LCA calculations. These diols were further used to synthesize a series of polyesters and polyurethanes with increased glass transition temperatures. Polyurethane synthesis was deemed more suitable for this type of monomers, since degradation occurred at the high temperatures required for polyester synthesis. The obtained polyurethanes were used to prepare coatings and textile fibers. Furthermore, the cyclic acetal structure of the monomers enabled chemical recycling under acidic conditions. In Chapter 3, HMF was produced in a continuous process from fructose, using water and dimethylcarbonate (DMC) in a biphasic system. Both yield and conversion were excellent, demonstrating the utility of DMC for HMF synthesis. The HMF synthesized by this method was sufficiently pure for preparation of the monomers in Chapters 1 and 2 in comparable yields to commercial HMF. In Chapter 4, three rigid diols were prepared from CMF and various lignin-based monomeric aldehydes including 4-hydroxybenzaldehyde, vanillin and syringaldehyde. The diol made from vanillin and CMF was used to prepare a series of thermoplastic polyurethanes with increased glass transition temperatures. The polymers were then cross-linked with Diels-Alder chemistry, which could be reversed at higher temperature. This may facilitate its reprocessing and recycling. In Chapter 5, two rigid monomers were produced from potentially lignin-derived phenols, and used to prepare a series of polyesters with tunable thermal properties. The polymers could potentially be chemically recycled by acid hydrolysis.

Key words: Polyester, Polyurethane, bio-based, HMF, Recycling

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“If we knew what it was we were doing,
it would not be called research,
would it?”
— Albert Einstein

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Populärvetenskaplig sammanfattning

Plast är kanske det allra vanligaste och därmed också viktigaste material vi använder i dagens samhälle. Så gott som alla föremål vi stöter på i vardagen innehåller någon typ av plast och 2019 tillverkades hela 368 miljoner ton, en siffra som har ökat stadigt sedan 50-talet. Denna enorma konsumtion orsakar stora miljöproblem när plast släpps ut i naturen, då det oftast inte finns något naturligt sätt för den att brytas ned på. Vissa sorters plast kan bestå flera tusen år ute i naturen och man räknar med att det kommer finnas mer plast än fisk i havet år 2050 om vi fortsätter producera och använda plast på samma sätt som vi gör i dagsläget.

Återvinning är ett bra sätt att minska plastutsläpp till miljön, men eftersom olika plastsorter inte kan blandas med varandra i återvinningsprocessen utan att kvalitén på materialet sänks, måste den därför sorteras innan den återvinns. Detta är dyrt, vilket leder till att endast en liten del av all plast återvinns genom mekanisk återvinning (dvs att plasten smälts ned och omformas till en ny produkt). Det allra vanligaste är att man eldar upp plasten för att få ut värmeenergi i stället. Detta leder dock till andra problem då plast huvudsakligen är oljebaserad och plastförbränning bidrar därmed till en ökad växthuseffekt.

Det finns flera strategier för att angripa dessa problem. Jag har använt främst två i min forskning: utveckling av biobaserade plaster och kemisk återvinning. Biobaserade plaster tillverkas från förnyelsebara källor i stället för från olja och genererar därför generellt sett en mindre mängd växthusgaser än konventionella oljebaserade plaster. I denna avhandling har jag främst utnyttjat den sockerbaserade molekylen 5-hydroxymetylfurfural (HMF) för att tillverka olika plaster. På kemisk väg har jag omvandlat denna molekyl till olika byggstenar lämpliga för tillverkning av olika plaster (såsom polyestrar och polyuretaner). Därefter har jag syntetiserat dessa material. Eftersom biobaserade plaster ofta är dyrare än oljebaserade plaster är det viktigt att de har någon materiell fördel för att kunna tävla kommersiellt på marknaden. Vi har därför fokuserat på att förbättra plastens värmeegenskaper samt dess mekaniska egenskaper. Vi har även designat plaster som kan brytas ned vid kontakt med syra, vilket möjliggör kemisk återvinning av startmaterialet. Detta kan därefter återanvändas till att skapa nya plaster och material. Generellt sätt kan denna metod utnyttjas som ett alternativ för att återvinna plaster som inte kan återvinnas genom vanlig mekanisk återvinning. För att utvärdera och demonstrera egenskaperna av de plaster vi tillverkat har vi spunnit fibrer, tillverkat lacker, gjutit plast-filmer och förhoppningsvis kan de resultat vi kommit fram till bana väg för kommersiella bio-baserade produkter i framtiden.

Popular scientific summary

Plastics are among the most common and therefore also most important materials we use in modern society. Virtually all objects we encounter in our daily life contain plastics and in 2019 a total of 368 million tons were produced, a number that has been growing steadily since the 1950s. This enormous consumption give rise to significant environmental challenges when plastics end up in nature, since there is often no natural way for plastics to decompose. Certain types of plastics can last for thousands of years, and it has been estimated that there will be more plastics than fish in the ocean by 2050 if we continue to produce and use plastics in the same way as we do today.

Recycling is a good way to minimize the accumulation of plastic waste in the environment but since different types of plastics cannot be mixed in the recycling process without lowering the quality of the material, they need to be sorted before recycling. This is expensive, leading to that only a small fraction of all plastics is being recycled by mechanical recycling (meaning that plastics are melted and reshaped into another product). Instead, most plastics are incinerated for heat energy. Since plastics are made from fossil-resources and their production generates large amount of greenhouse gases, this will lead to other challenges such as increased global warming.

There are many strategies for tackling these issues, but I have primarily used two in my research: Development of bio-based plastics, and chemical recycling. Bio-based plastics are made from renewable sources instead of oil and generate therefore less greenhouse gas emissions than conventional plastics. In this thesis I have primarily used the sugar-based molecule 5-hydroxymethylfurfural (HMF) as starting material. I have chemically transformed this molecule into suitable building blocks for different types of plastics (such as polyesters and polyurethanes) and then synthesized these materials. Since bio-based plastics are often more expensive than oil-based plastics, it is important that they possess some additional feature to be financially competitive.

Therefore, I have focused on improving the thermal and mechanical properties of plastics aimed for textile fiber or coating applications. I have also designed plastics that can be broken up by acid into smaller molecules, which enables chemical recycling. The starting material can then be used to create other plastics and materials. Generally, this method can be used as an alternative for materials that cannot be recycled by conventional methods. To evaluate and demonstrate the properties of these materials, I have prepared various fibers, coatings, and films. Hopefully the results achieved in this work will facilitate commercialization of bio-based products in the future.

List of papers

Paper 1: **N. Warlin**, M. N. Garcia Gonzalez, S. Mankar, N. G. Valsange, M. Sayed, S. H. Pyo, N. Rehnberg, S. Lundmark, R. Hatti-Kaul, P. Jannasch and B. Zhang, *A rigid spirocyclic diol from fructose-based 5-hydroxymethylfurfural: Synthesis, life-cycle assessment, and polymerization for renewable polyesters and poly(urethane-urea)s.* Green Chem., 2019, 21, 6667–6684.

Paper 2: **N. Warlin**, E. Nilsson, Z. Guo, S. V. Mankar, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang, *Synthesis and melt-spinning of partly bio-based thermoplastic poly(cycloacetal-urethane)s toward sustainable textiles.* Polym. Chem., 2021, 12, 4942–4953.

Paper 3: M. Sayed, **N. Warlin**, C. Hulteberg, I. Munslow, S. Lundmark, O. Pajalic, P. Tunå, B. Zhang, S.-H. Pyo and R. Hatti-Kaul, *5-Hydroxymethylfurfural from fructose: an efficient continuous process in a water-dimethyl carbonate biphasic system with high yield product recovery.* Green Chem., 2020, 22, 5402–5413.

Paper 4: **N. Warlin**, Andras Karajos, Emma Olsson, Caroline Almqvist, S. V. Mankar, N. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch, B. Zhang. *Synthesis of bio-based polyurethanes using diol monomers derived from 5-chloromethylfurfural and lignin-based phenols*
(Manuscript unpublished)

Paper 5: **N. Warlin**, S. Subramaniyan, N.Valsange, S. V. Mankar, N. Rehnberg, P. Jannasch, B. Zhang. *Polyesters with acetal units derived from potentially bio-based methyl paraben and methyl vanillate.*
(Manuscript unpublished)

Publications not included in this thesis:

Paper 6: S. V. Mankar, M. N. Garcia Gonzalez, **N. Warlin**, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang., *Synthesis, Life Cycle Assessment, and Polymerization of a Vanillin-Based Spirocyclic Diol toward Polyesters with Increased Glass-Transition Temperature.* ACS Sustain. Chem. Eng., 2019, 7, 19090–19103.

Paper 7: N. G. Valsange, M. N. G. Gonzalez, **N. Warlin**, S. V. Mankar, N. Rehnberg, S. Lundmark, B. Zhang and P. Jannasch, *Bio-based aliphatic polyesters from a spirocyclic dicarboxylate monomer derived from levulinic acid.* Green Chem., 2021, 23, 5706–5723.

Paper 8: Z. Guo, **N. Warlin**, S. V Mankar, M. Sidqi, M. Andersson, B. Zhang and E. Nilsson, *Development of Circularly Recyclable Low Melting Temperature Bicomponent Fibers toward a Sustainable Nonwoven Application*. ACS Sustain. Chem. Eng., 2021, 9, 16778–16785.

My contributions:

Paper 1: I performed most of the experimental work, including the monomer synthesis, all polymerizations, and characterization. The LCA was performed by Nelly Garcia Gonzales. I wrote the first draft of the paper.

Paper 2: I performed most of the experimental work, including monomer synthesis, polymerization, chemical recycling study and characterization. I wrote the first draft of the paper. Spinning and characterization of the fiber was performed by RISE. I wrote the first draft of the paper

Paper 3: I performed the NMR - analysis, and the synthesis of Monomer S using bio-based HMF. Most experimental work was performed by Mahmoud Sayed.

Paper 4: I performed the polymerizations and characterizations. I performed the Diels-Alder cross-linking reactions. I wrote the first draft of the manuscript.

Paper 5: Monomer synthesis and polyester synthesis was performed by Sathiyaraj Subramaniyan. I performed the annealing study and chemical recycling experiments. I wrote the first draft of the manuscript.

Abbreviations

AC	Activated carbon
BHET	bis (2-hydroxyethyl) terephthalate
BHMF	Bis (hydroxymethyl) furan
BPA	bisphenol A
CMF	5-Chloromethylfurfural
CY	Char Yield
Đ	Dispersity
DBTDL	Dibutyltindilaurate
DBTO	Dibutyltinoxide
DC	Direct concentration
DCM	Dichloromethane
Dissociative CAN	Dissociative covalent network
di-TMP	di-trimethylolpropane
DMAc	Dimethylacetamide
DMC	dimethylcarbonate
DMF	Dimetylformamide
DMSO	Dimethylsulfoxide
DMT	Dimethylterephthalate
DSC	Differential scanning calorimetry
EDA	ethylene diamine
EG	Ethylene glycol
EtOAc	Ethyl acetate
EtOH	Ethanol
FDCA	furandicarboxylic acid
FFCA	5-formyl 2-furancarboxylic acid
FTIR	Fourier transformed Infrared spectroscopy
GHG	Green House Gas
GVL	Gammavalerolactone
HMF	5-hydroxymethylfurfural
HMFCA	5-hydroxymethyl 2-furancarboxylic acid
IPDI	Isophorone diisocyanate
KDa	Kilo Dalton

LCA	Life Cycle Assessment
LOI	Limiting Oxygen Index
MDA	methylene diphenyl diamine
MDI	methylene diphenyl diisocyanate
MeCN	Acetonitrile
MIBK	Methyl isobutyl ketone
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMR	Nuclear magnetic resonance
PBAT	polybutylene adipate terephthalate
PBT	polybutylene terephthalate
PCL	Polycaprolactone
1,3-PD	1,3-propane diol
PEF	Polyethylenefuranoate
PET	Polyethylene terephthalate
PLA	Poly Lactic Acid
POM	Polyoxymethylene
PPO	polypropylene oxide
PrOH	Propanol
p-TsOH	*para*-toluene sulfonic acid
PU	Polyurethane
PVB	Polyvinylbutyral
rt	Room temperature (20 °C)
SEC	Size exclusion chromatography
T_5	temperature at 5 % mass loss (by TGA)
t-BuOH	*tert*-butanol
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	tetrahydrofuran
TPA	Terephthalic acid
TPU	Thermoplastic polyurethane
US DOE	Unites States Department of Energy

Introduction

Plastics are among the most common materials in our society and are used in many commodity and engineering products. In 2019, the annual plastic production was estimated as 368 million tons globally, clearly illustrating our dependence on this class of materials.[1] It has been estimated that approximately 8300 million tons of virgin plastics have been produced throughout human history and close to 6300 million tons ended up as plastic waste after use. Approximately 80 % of this plastic waste has been deposited in landfills. This enormous mass has accumulated in nature since plastics generally are resistant to natural degradation, giving rise to concerns regarding the environmental impacts of plastics but also their adverse effects on human health.[2,3] The primary focus has been the accumulation of plastics in the ocean. It has been estimated that by 2050 there will be more plastic than fish in the ocean by weight, if the current trend for plastic production, consumption and waste handling will be continued.[4] In addition, the greenhouse gas emissions due to plastic production is also a serious environmental threat. Plastics are predominately made from fossil resources and the GHG emissions caused by their production alone will constitute approximately 15 % of the global carbon budget by 2050 if the current trajectory is not changed.[5]

Many different strategies have been developed to tackle these challenges. However, this thesis will primarily focus on the synthesis and development of bio-based monomers and their use in polyester and polyurethane synthesis, and also chemical recycling of these polymers.

Biomass

Biomass encompass all material produced from microorganisms, fungi, plants or animals.[6] It is widely recognized as one of the most essential carbon sources for the future, with a total production of more than 100 billion tons annually.[7] This volume makes biomass a viable alternative to fossil fuels as a carbon source for future plastics production. For example, sugar is already being used to produce monomers such as lactic acid (to make PLA) and ethylene glycol (to make PET).[8–10] This leads to concerns regarding the ethical aspect of using land areal for material production, which could otherwise be used to grow crops to feed the growing human population on earth.[11] However, in 2019 less than 0.02 % of all available agricultural land was used to produce all bioplastics on the market. [12] This is a very small portion of land for this particular purpose, especially considering the enormous amount of food waste generated across the globe (which has been estimated to 30-40 %). Upon comparing these figures, it seems that the criticism about using food sources for material production focuses on the wrong problem.[13]

Nevertheless, it is always beneficial to utilize low value renewable carbon sources that do not compete with any currently valuable market. One particularly interesting source is lignin coming from vascular plants.[14–18] Lignin is an aromatic crosslinked biopolymer that is usually removed during paper production.[19,20] This is usually done by the Kraft process, which breaks the bonds between cellulose and lignin, so that the cellulose can be isolated for paper production, while the lignin is often burnt as cheap fuel.[19,21] If one could further isolate and valorize the aromatic components in lignin, significantly improved profits could be expected.[17,19–23]

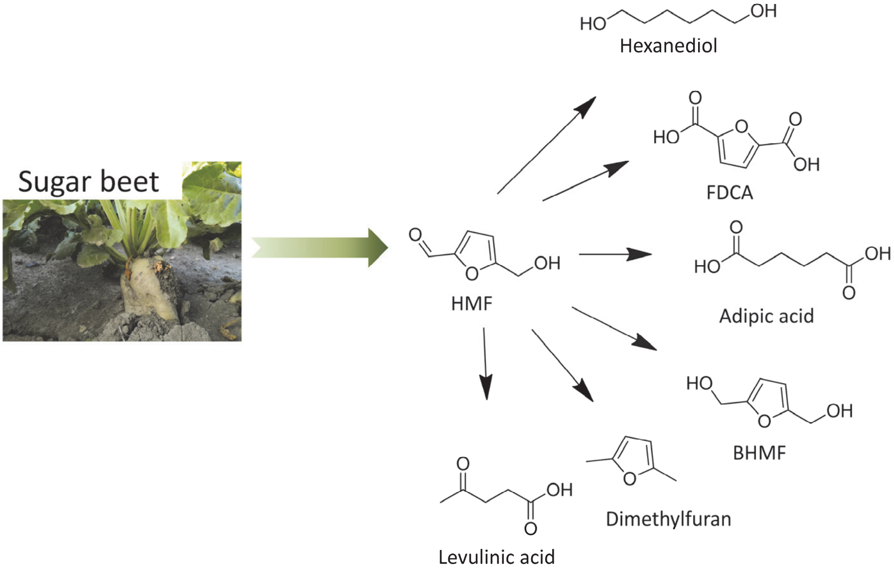
Bio-based plastics

Bio-based plastics are made (entirely or with a significant part) from renewable sources instead of fossil fuels.[12] Even though there have been some progress in the field of bio-based plastics, the vast majority of plastics are still fossil-based.[24] However, fossil resources are not renewable and are restricted by several limitations, such as volatile oil prices caused by political turmoil, environmental concerns due to extraction processes (e.g. fracking), and causation of global warming.[2,12,25,26] The primary reason for the wide use of fossil fuels instead of renewable resources for plastic production is their abundance and low cost.[27] As such, additional advantages (e.g. enhanced physical properties) for new bio-based products are always anticipated in addition to their environmental and sustainability benefits, which will allow them to compete with their cheaper oil-based counter parts. This is often referred to as the “bio-advantage strategy”, which is the concept used in the design of monomers and polymers in this thesis.[28]

5-hydroxymethylfurfural (HMF)

5-hydroxymethylfurfural (HMF) was first synthesized in 1895 by the dehydration of hexose sugars yet has been largely ignored until the 21st century due to difficulties in obtaining a high yield without formation of side products.[29] HMF is notoriously sensitive to both acid and heat and will readily form humins (a black polymeric structure) in the presence of either.[29] It has been shown that the stability of HMF is significantly higher in DMSO than other common solvents, since DMSO forms a protective shell around the aldehyde and hydroxyl group.[30,31]

HMF has recently received growing attention for its potential to serve as a platform chemical, and has been identified by the US DOE as one of the 12 most important molecules for enabling the switch from fossil fuels to renewable resources as raw materials for chemical production.[32] HMF has two different functional groups (aldehyde and alcohol) and can be used to synthesize a wide array of chemicals such as levulinic acid, hexanediol, adipic acid, dimethylfuran, bis(hydroxymethyl)furan (BHMF), and furan dicarboxylic acid (FDCA) (Scheme. 1).[29]



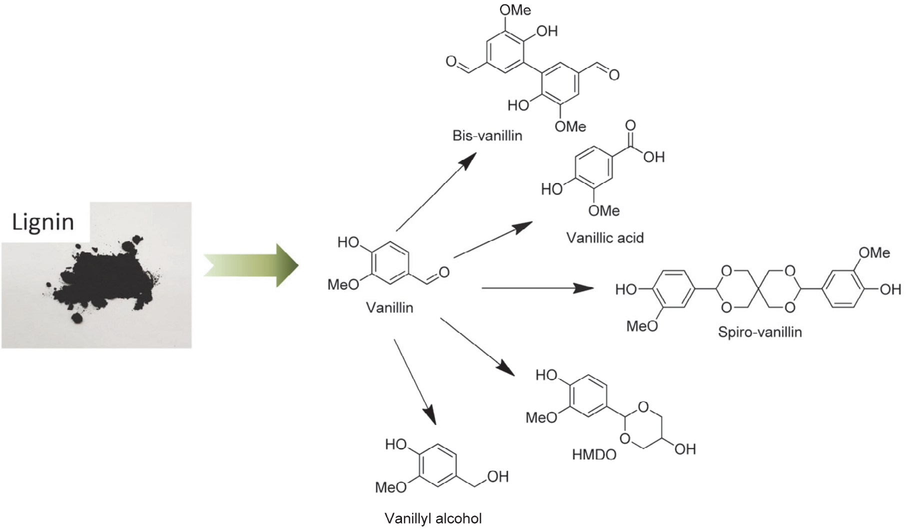
Scheme 1. The platform molecule HMF and potential chemical building blocks derived from HMF.

Many of these chemicals are already commercially available in large volumes. More than 2.5 million tons of adipic acid is produced annually to make Nylon, making it one of the most important dicarboxylic acids in the world.[33] FDCA is another dicarboxylic acid with the potential to replace terephthalic acid in common PET synthesis. As such, FDCA has attracted interest from companies such as Avantium, BASF and Coca Cola, which are actively investigating the pathways to develop and optimize the production of FDCA-based polyester, namely polyethylene furanoate (PEF).[34,35] In academia, new polyesters based on FDCA have also been intensively investigated.[36–39] HMF has also been converted into diols such as bis-hydroxymethylfuran (BHMF) for polyester and polyurethane synthesis. However, these polymers often suffer from discoloration and low molecular weight as a result of poor thermal stability.[40–43] HMF can also be converted into dimethylfuran, which could serve as a biofuel due to its high energy density (even higher than bioethanol).[44] It is also a potential intermediate in the production of bio-based terephthalic acid.[45] Furthermore, the furan structure of HMF is a desirable target for Diels-Alder chemistry. However, since the electron withdrawing aldehyde moiety deactivates the furan on HMF for this type of reaction, it is often first converted into more reactive species.[46]

Unfortunately, the only viable carbon source for HMF synthesis at present date is fructose, which is expensive compared to other carbohydrates such as glucose or cellulose.[47] This has generated a lot of interest for the analogous platform molecule 5-chloromethylfurfural (CMF), which can easily be prepared in high yields from many diverse carbohydrates.[48,49] Furthermore, due to the structural similarity between CMF and HMF both molecules can serve as a platform for production of the same chemicals.[50]

Vanillin

Vanillin is another potentially bio-based molecule which could serve as a platform for rigid monomer production due to its rigid aromatic structure.[51] Vanillin is primarily used by the food industry as a flavoring agent, but can be converted into a large variety of chemicals through different chemical modifications (Scheme 2).[51–57] The majority of commercial vanillin is derived from fossil-based guaiacol, but it can also be produced from lignin waste streams in the pulping industry, which is done at Borregaard in Norway.[18,51] This has triggered a significant interest for the use of vanillin within the field of polymer chemistry.



Scheme 2. Potential vanillin-based monomers.

A wide array of vanillin-based monomers have been synthesized by functionalization of the aldehyde or phenolic groups, while keeping the vanillin structure as the aromatic core. Vanillin can be reduced to make vanillyl alcohol, which has been thoroughly investigated for polyester and polyurethane synthesis.[52,53,56] Vanillin has also been reacted with commercially available triols to prepare cyclic acetal monomers for the synthesis of epoxies.[57,58] Oxidation of vanillin gives vanillic acid which was further modified to prepare diester monomers for polyester synthesis.[59] Bis-vanillin have been used to prepare polyesters a series with high molecular weights and T_g from -5 – 139 °C.[60] Vanillin has also been reacted with pentaerythritol to prepare the spirocyclic diol monomer spiro-vanillin, which was used to synthesize polycycloacetals and polyesters.[61,62] However, many of these monomers suffer from low reactivity due to the phenolic hydroxyl groups, limiting their use in polymer synthesis.

Recycling

Plastics recycling is generally considered to be one of the most important strategies for mitigating plastics littering and pollution. However, different types of plastics waste can be of significantly different quality and purity. Depending on the quality of the waste stream, different methods for recycling are required.[63]

The cleanest type of plastic waste stream is industrial waste, which often contains a single type of uncontaminated polymer. This type of waste can be relatively easily reprocessed (i.e. mechanical recycling) or reused for the same application without a significant amount of pretreatment.[63] However, common plastics waste is often a mixture of contaminated polymers.[63] This means that the waste needs to be thoroughly washed and sorted before it can be mechanically recycled.[64] Because of the intrinsic difficulties connected with obtaining pure waste streams, most common plastic waste is down cycled. This means that the recycled plastics are used to produce lower quality products due to the loss of material properties upon mechanical recycling.[63,65] For some plastics waste, mechanical recycling is impossible. Thermoset polymers are covalently crosslinked and therefore cannot be melted, while polymer blends generally complicate sorting procedures.[64,66–69] For these types of plastics, chemical recycling might be a more suitable option. In chemical recycling, the polymer is depolymerized back to monomers (or chemicals), which can then be used to remake the same polymer or repurposed for other applications. This can be done either by pyrolysis or solvolysis. During pyrolysis, the polymer is heated to very high temperatures (500-900 °C), essentially converting the polymer back into crude oil. During solvolysis, the polymer is reacted with a solvent (often water, methanol, or ethylene glycol) to selectively break the polymer chains. The reformed monomers can then be used for synthesizing the same polymer without extensive purification.[63,68,70,71]

The final solution for plastic waste that cannot be recycled by any other means is energy recovery by incineration.[71]

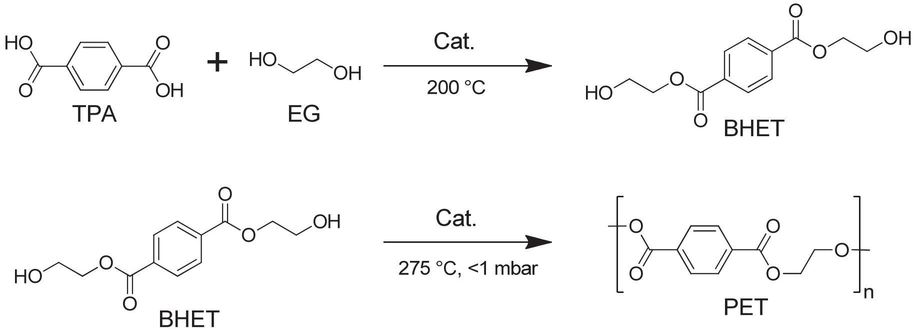
Polyesters

Polyesters are one of the most common types of polymers produced today, making up almost 8 % of all plastics. It is a versatile class of materials used to produce products such as bottles, films, fibers and clothes.[72]

Synthesis

The most common synthesis procedure for polyesters is melt condensation, which is generally carried out in two steps (Scheme 3). For PET this is done by reacting an excess of ethylene glycol with terephthalic acid (TPA) or dimethyl terephthalate (DMT) at 200 °C under inert atmosphere to produce bis (2-hydroxyethyl) terephthalate (BHET) in the presence of a metal catalyst. During this time water is continuously removed via distillation. After this step, the temperature is increased gradually to 275 °C and the pressure is reduced to <1 mbar to form high molecular weight polymers.[73] Other polyesters (eg. PEF, PBT, PBAT) are synthesized similarly.[74–77] This is most often the preferred polymerization procedure at lab scale due to its similarity to the industrial method of producing PET. The most effective catalyst for this procedure is often DBTO which produces colorless polymers with high molecular weight, although titanium based catalysts are also commonly used.[75,78,79] In cases where the monomers are especially sensitive to heat, acyl chlorides are sometimes preferred over carboxylic acids due to their enhanced reactivity allowing polymerization at room temperature.[41,80,81] Furthermore, lab-made polyesters are commonly purified by dissolution in chloroform, HFIP or trifluoroacetic acid and then precipitated into methanol.[78,79,82]

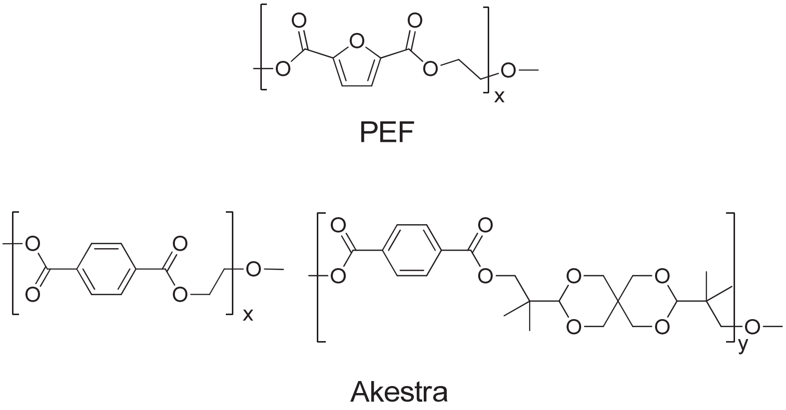
In the industry, polyesters are prepared exclusively by melt condensation and used without extensive purification. For this reason, catalysts such as Sb_2O_3 or titanium compounds are generally preferred over the relatively toxic DBTO.[76,83] Furthermore, different phosphorous-based stabilizers are often needed to minimize coloration.[84] For applications where high molecular weight is essential, solid state polymerization can be applied as a third step.[85–87] During this stage, the solid polymer is cut into flakes, and heated above its glass transition temperature but below the melting point. Then either vacuum or a carrier gas is applied to remove the condensate when the polymer chain ends react. The solid-state polymerization is beneficial since the lower temperatures and low mobility of the polymer chains significantly reduces the risk for unwanted side reactions.[86]



Scheme 3. Polyester synthesis

Bio-based polyesters

Polyesters are particularly interesting targets for developing bio-based polymers.[24] The reason for this is the relatively large oxygen content in the polymer, which facilitates the use of oxygen-rich biomass for monomer synthesis. One particularly significant achievement within this field was the partially bio-based plant bottle made by Coca Cola. This bottle was made from bio-based ethylene glycol, leading to a bio-content of 30 %, while still retaining the same material properties as the original.[9] In 2015 Coca Cola presented a 100 % bio-based plant bottle prototype, however this product has not yet been commercialized.[9] An interesting bio-advantage approach for the next generation of bottles is to replace terephthalic acid with furandicarboxylic acid. This would result in the polymer PEF which has higher T_g, lower melting point, and better barrier properties compared to PET.[34,37,88–90] These advantages might compensate for the higher cost of FDCA and can thus facilitate the market introduction of the new monomer.[91] Another attempt to improve the thermal properties of polyesters using partly bio-based monomers was made in 2013, when Perstorp developed PET copolyester Akestra^{TM} using a spirocyclic bio-based diol (Scheme 4). Akestra^{TM} has a T_g in the range of 90-110 °C depending on the content of the spirocyclic diol.[92]



Scheme 4. Bio-based polyesters

There have been numerous attempts to design novel sugar-based rigid monomers, aiming to improve the thermal properties of the polymer. Sorbitol and galactaric acid have been converted into rigid diacids and dialcohols by acetalation, and then copolymerized with terephthalic acid and various diols to improve the T_g.[74,78,93,94] Tartaric acid and threitol have also been acetalized in a similar reaction and used to prepare copolyesters with either higher T_g (for threitol) or lower T_g (for tartaric acid).[95–97] Camphorquinone and glycerol have been turned into a rigid bio-based diol which was used to increase the T_g for a series of polyesters.[79] Isosorbide has been used to adjust the T_g of a series of polyesters, as well as to improve their biodegradability.[98–102] However, despite the large quantity of papers investigating these rigid diols there has been little success with commercialization, most likely due to complicated reaction procedures, scarcity of raw material, or issues with purification.

Polyester recycling

The mechanical recycling of PET is possibly the most efficient recycling procedure for any major group of polymers in the world. This originates primarily from the collection of PET-bottles, resulting in a comparatively clean waste stream of PET.[68,103] This greatly facilitates mechanical recycling, allowing recycling of almost 60 % of used PET (in Europe).[104] Despite this, the mechanical properties of PET deteriorates with every recycling-cycle preventing closed loop recycling.[105,106] As such, most PET is down-cycled to make sheets and fibers instead of new bottles.[75]

Chemical recycling of PET enables the recovery of pure monomers when conventional mechanical recycling no longer can produce PET of satisfactory quality, and can be used as an end-step solution to produce new PET.[68] Chemical recycling can generally be divided into pyrolysis or solvolysis, depending on the recycling method.[63,70] However for PET-waste, pyrolysis is generally not preferred due to the high costs associated with heating the polymer above its decomposition temperature. Instead, solvolysis is considered more beneficial. Solvolysis can be further divided into hydrolysis, methanolysis, or glycolysis depending on which solvent is used for the depolymerization.

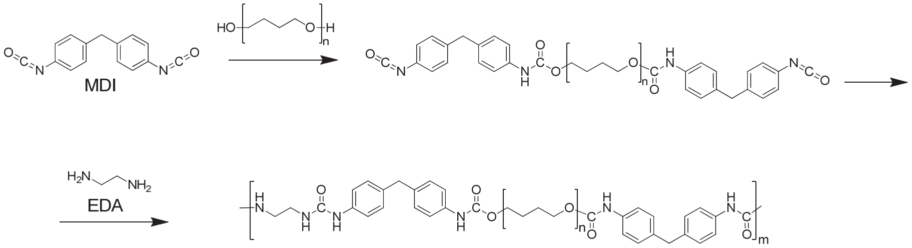
Hydrolysis is performed by depolymerizing PET in water under highly basic or acidic conditions, yielding terephthalic acid and ethylene glycol.[107–109] The main benefit of this method is its low cost, while the main drawback is the requirement of reactors that can resist the corrosive solutions as well as formation of salt as byproducts.[68,70] In methanolysis, PET is depolymerized with methanol at temperatures ranging from 200-300 °C to yield dimethylterephthalate and ethylene glycol.[107,110,111] The main benefit of this method is that dimethylterephthalate can be produced with the same quality as commercial DMT, allowing the recycling step to be directly incorporated into the production facility. The main drawback of this method is its high cost.[68,70] In glycolysis, PET is depolymerized with ethylene glycol to give back the intermediate bis(hydroxyethyl) terephthalate which can be used as an intermediate in conventional polyester synthesis.[112–115] The drawback with this method is that the recovered product is often a mixture of oligomers making purification difficult.[68,70]

All of these methods have been implemented on commercial scale, showing the significant potential of chemically recycling PET-waste.[71]

Polyurethanes

Synthesis

With an annual production of more than 20 million tons, polyurethanes constitute 7.9 % of all plastics and are used to make coatings, foams, shoe soles and medical applications.[72] Polyurethanes can be prepared as thermosets or thermoplastic polymers, yet the work in this thesis will focus on the synthesis of thermoplastic polyurethanes (TPU). Industrially, TPUs are synthesized by polyaddition of an isocyanate with a polyol. In order to reach high molecular weight and good material properties, TPU synthesis usually include two steps (Scheme 5). First, a long flexible diol is reacted with the isocyanate to produce oligomers with isocyanate end groups. Then the oligomer is chain extended by a reaction with a short diol or diamine. This results in a polyurethane with alternating hard and soft segments, where the mechanical properties and processability of the material can be modified by altering the hard/soft ratio.[116]



Scheme 5. Thermoplastic polyurethane synthesis

Recent advances

Isocyanates are extremely toxic and considerable efforts have been made to find alternatives to this route. One example is the ring opening polymerization of carbonates to produce hydroxy urethanes.[117,118] Another possibility is to do transurethanization, yet this requires high temperatures to be industrially viable.[119] Apparently, the main production of polyurethanes will remain the isocyanate route for the foreseeable future despite its toxicity.

Another problem within polyurethane synthesis is that there are few rigid bio-based building blocks available on the market. There has been significant effort in developing new monomers that can be used for polyurethane applications.[120] Oleic acid was used to prepare a linear isocyanate, which showed similar properties as a commercial oil-based sample.[121] Various plant oils have been used as the soft segment and showed superior thermal stability compared to PPO.[122] Soybean oil has been used to prepare cross-linked polyurethane thermosets, however the polymer showed poor mechanical strength due to the heterogeneity of the sample.[123] Cotton seed oil has been used to prepare polyurethane coatings with improved or comparable gloss, adhesion and pencil hardness compared to petrol based alternatives.[124]

Many different bio-based rigid monomers have also been used to prepare polyurethanes with improved properties. Isosorbide has been used as a chain extender to improve the T_g,[125] and as a potential replacement for BPA in dental applications.[126] Isomannide has been used to prepare polyurethanes for medical applications as the polymers showed reasonable degradation in phosphate buffer at 37 °C without inhibiting cell growth.[127] Various cyclic acetalized sugar-based monomers have been used to prepare polyurethanes with improved thermal properties and faster hydrolysis rate.[128,129] Rigid cyclic diols have been synthesized from glycerol and ketones and then been used to make polyurethanes with good thermal properties and high moduli.[130] Despite these efforts there has been little to no commercial success of any of these monomers most likely due to issues concerning purification, expensive starting material or scalability.

Polyurethane recycling

Recycling of polyurethanes is significantly more difficult than for polyesters since the PU waste stream is considerably more contaminated.[65,131,132] In addition, many polyurethanes are crosslinked thermosets, which complicates conventional mechanical recycling.[133] As such, the current market for commercial recycling of polyurethanes is negligible compared to that of PET. Current research focuses especially on chemical recycling of polyurethane resin. The recycling of polyurethanes can be divided into pyrolysis or solvolysis depending on the depolymerization conditions.[132]

Pyrolysis of PU-waste is done by heating the polymer above its degradation temperature to decompose it to oil and gases which can be purified and used for other applications. This is generally not considered an optimal method, considering the large amount of side reactions present during PU-degradation.[132] Furthermore, many polyurethane applications contain halogenated flame retardants which decomposes into corrosive gases.[134] Therefore, solvolysis is often the preferred method for chemically recycling polyurethanes, with the most popular solvents being ethylene glycol (glycolysis), water (hydrolysis), or different amines (aminolysis). Glycolysis is the most common method for recycling PU-waste and is performed by heating the polyurethane with ethylene glycol at elevated temperatures. This causes the urethane bond to rupture, resulting in formation of a polyol that can be reacted with common isocyanate reagents to prepare new polyurethanes.[135] Hydrolysis is performed by reacting PU-waste with water at high temperature and high pressure. This results in formation of the polyol and diamine, both of which can be isolated and reused.[136] The most important type of aminolysis is called Dow’s aminolysis, and is performed by dissolving PU-waste in a KOH

- alkanolamine solution at 120 °C.[137] This gives a mixture of polycarbonates, polyols, amines and ureas that can be recovered and used for production of new polyurethanes.

Polyacetals

Synthetic polyacetals constitute an interesting class of polymers with excellent mechanical properties that are used mainly in specialty engineering parts within the automotive industry or for safety glasses.[138–143] At present date, there are two synthetic polyacetals available at significant commercial scale; polyoxymethylene (POM) and polyvinylbutyral (PVB).[140,142,144] The total production volumes for these two polymers are estimated to 1.1 million tons and 360 thousand tons respectively.[145,146] However, despite the relatively low production volume, the interest for polyacetals have been growing in recent years due to the rising interest for designing bio-based polymers.[142] Because of their high oxygen content and rigid structure, polyacetals make desirable targets as bio-based polymers with excellent properties. Polycycloacetals can be prepared by reacting bio-based dialdehydes with tetraols, yielding polymers with high T_gs and good thermal stability.[143,147,148] However, these polymers often have poor solubility in common solvents, complicating analysis.[149,150] Another strategy for incorporating the acetal-structure into polymers is to prepare difunctional monomers containing acetal groups, and then use these monomers in conventional polyester-, polyamide- or polyurethane synthesis.[151–153] This strategy has been employed by Perstorp to produce the commercial polyester Akestra as a polyester-acetal (Scheme 4).[92]

An especially interesting characteristic of this type of polymers is the sensitivity to acid hydrolysis, which enables selectively breaking the acetal bond. For this reason, polyacetals have also been extensively studied for different types of biomedical applications, especially within the field of drug delivery.[154–156] Furthermore, the acid sensitive acetal bond may also enable chemical recycling of the polymer. Epoxies and phenolic resins exhibit excellent durability, mechanical strength and solvent resistance, but are virtually impossible to recycle due to their cross-linked chemical structure. By incorporating acetal bonds into the polymers, these thermosets can be chemically recycled under acidic conditions after use.[157–160] The possibility to enable chemical recycling of polyurethanes have also been explored.[161,162] A different approach was taken by Abel et al upon designing and demonstrating the recyclability of the new polymer poly(1,3-dioxolane). This polymer exhibited material properties comparable to commercial polyolefins, and could be selectively chemically recycled from a collection of mixed plastic waste.[163]

Context and Scope

The aim of this thesis is to design and synthesize bio-based polymers with enhanced properties. This has been done by using starting material from abundant sources of biomass such as lignin and sugar to design several different monomers. These monomers were used to prepare polyesters and polyurethanes in order to investigate the relationship between their chemical structure and the physical properties.

In paper 1 we reacted HMF with pentaerythritol to prepare a rigid spirocyclic acetal diol monomer. The synthesis of this monomer was analyzed by LCA which predicted a remarkably low carbon footprint. This monomer was then used to prepare a series of polyesters and polyurethanes with increased T_gs. This monomer was found to be more suitable for polyurethane synthesis due to thermal degradation at high temperatures.

In paper 2 we reacted HMF with di-TMP to synthesize another cyclic acetal monomer diol and used it to prepare a series of thermoplastic polyurethanes. One of the polymers were successfully spun into a ~150m long fiber with a tenacity similar to commercial Elastane. The fiber could be chemically degraded under acidic conditions and the relevant chemical building blocks were partially recovered.

In paper 3 HMF was synthesized from fructose using a biphasic water/DMC system in a continuous reactor. This procedure produced HMF in high yield, and the HMF could be used to synthesize the monomer from paper 1 after purification.

In paper 4 we reacted CMF with potentially lignin-based phenols to synthesize a series of furan diol monomers. These monomers were used to synthesize a series of polyurethanes that could be reversibly cross-linked with bis-maleimide to produce a series of dissociative CANs.

In paper 5 we produced two lignin-based diester monomers with a central acetal unit. These monomers were used to prepare two series of polyesters with varying T_gs. These polyesters could be hydrolyzed under acidic conditions, yielding the relevant monomers or chemical building blocks, demonstrating its potential for chemical recycling.

Experimental Methods

Monomer Synthesis

Acetal formation

In paper 1 and 2, HMF was reacted with pentaerythritol in an acid catalyzed acetalization with the tetraols pentaerythritol and di-TMP respectively. This type of reaction is commonly performed in refluxing toluene with a dean-stark apparatus to ensure removal of water and drive the reaction to completion. However, due to the inherent instability of HMF at elevated temperatures, especially in the presence of acid, this method yielded significant humin formation and poor yield. For this reason, an alternative approach was developed, which consisted of performing the reaction at room temperature using alcohols as solvents. Despite no technique was used for removal of water, the desired product precipitated, which drove the equilibrium to high yield instead.

S_N2 nucleophilic substitution

In paper 4 and 5, S_N2 reactions was used to prepare the monomers by reacting a phenol with an organic halogen. In paper 5 KI was used as catalyst. K_2CO_3 was used to deprotonate the phenol, thus improving its nucleophilicity. A polar aprotic solvent such as DMSO or acetonitrile was used for the reaction.

$NaBH_4$ reduction

The aldehydes were reduced with $NaBH_4$ in methanol. Methanol was used since it can solvate $NaBH_4$, even though $NaBH_4$ reacts with methanol to form hydrogen gas and $NaB(OMe)_4$, or lead to the formation of methyl acetals. These side reactions are accelerated by acid, and for this reason a catalytic amount of base (NaOMe) was added to ensure reduction to the desired molecule.

Polymer Synthesis

In this thesis two different types of polymerizations were performed: polyester synthesis and polyurethane synthesis.

Polyesters

The polyesters were prepared using a two-step melt condensation reaction. First, the monomers were melted under a nitrogen atmosphere to produce oligomers with the removal of methanol. A slight excess of the diol was used to compensate for losses by evaporation. Afterwards, the temperature was increased while applying a strong nitrogen flow or high vacuum to facilitate removal of the excess diol used in the synthesis, in order to drive the reaction towards high molecular weight polymers.

Polyurethanes

The polyurethanes in this thesis were produced by solution polymerization. The solvents used were either 2-butanone or DMAc depending on the solubility of the monomers. DBTDL was used as catalyst. In paper 1 the polymers were chain extended with ethylenediamine since this significantly increased the molecular weight. In paper 3, 4 and 5 no chain extension step was applied, and all reagents were directly mixed in the solution instead. The reaction was monitored by FTIR and when no isocyanates could be observed, it was quenched by dibutylamine.

Characterization

The most important characterization methods are described below. For a more detailed description, please see the experimental section of the corresponding paper.

^{1}H and ^{13}C NMR measurements were performed on a Bruker DR X400 spectrometer at 400.13 MHz and 100.61 MHz, respectively. Chemical shifts were reported as δ values (ppm). HRMS was taken on a Micromass QTOF mass spectrometer (ESI). Size exclusion chromatography (SEC) measurements were carried out on two different systems depending on in which solvent the polymers were soluble in. The polyesters were analyzed using a Malvern Viscotek TDAmax instrument with a 2 × PL-Gel Mix-B LS column set (2 × 30 cm) equipped with OmniSEC triple detectors (refractive index, viscosity and light scattering). Chloroform was used as eluent at 35 °C at a flow rate of 1 mL min^{-1}. Calibration was performed with a narrow polystyrene standard M_p = 96 000 Da, $Đ$ = 1.03 (Polymer Laboratories Ltd, Agilent Technologies and Water Associates). The intrinsic viscosity [η], Mark–Houwink–Sakurada parameters (K and a), and the hydrodynamic radii (R_h) of polymers were measured by SEC. Size exclusion chromatography (SEC) measurements for the polyurethanes were carried out using Agilent 1100/1200 Infinity HPLC System equipped with three columns (GPC column PSS GRAM 3000 Å, 10 µm; GPC column PSS GRAM 1000 Å, 10 µm; GPC column PSS GRAM 30 Å, 10 µm) connected in sequence at 40 °C in DMAc with LiBr (5 g L^{-1}) at a flow rate of 1 mL min^{-1}. Calibration was carried out with ReadyCal-Kit poly(methyl methacrylate) standards M_p = 202–2 200 000 Da. Fourier transform infrared (FTIR) spectra were measured with an attenuated total reflection (ATR) setup using a Bruker Alpha FT-IR spectrometer. The polyesters were dissolved in DCM and successively placed on the cell. The poly(urethane-urea)s were taken directly from the reaction solution and placed on the cell. The measurement was performed after evaporation of the solvent. For all samples 64 successive scans over the range of 400–4000 cm^{-1} was recorded. TGA measurements were carried out on a TA instrument mode TGA Q500. The samples were first dried extensively to remove any trace of solvent, and the measurement was performed by heating from 50 °C to 600 °C with a rate of 10 °C min^{-1}. DSC measurements were performed on a DSC Q2000 analyzer from TA instruments. The T_g was determined from the second heating cycle. DMA measurements were performed in a stretching mode using TA instruments Q800 analyzer.

The concentrations of fructose, 5-HMF and by-products were determined using HPLC (JASCO, Tokyo, Japan) equipped with a RI detector (ERC, Kawaguchi, Japan), a JASCO UV detector operating at 215 nm and a JASCO intelligent autosampler. Separation of the compounds was carried out on a fast acid analysis chromatographic column connected to a guard column (Biorad, Richmond, CA, USA). The column temperature was maintained at 65 °C using a chromatographic oven (Shimadzu, Tokyo, Japan). Samples were diluted with Milli-Q quality water and mixed with 10% v/v sulfuric acid (25 µL mL^{-1} sample) and then filtered through 0.45 µm filters. A 40 µL aliquot was injected in 10 mM H_2SO_4 mobile phase flowing at a rate of 0.6 mL min^{-1}. The peaks for the different compounds were confirmed and quantified using external standards.

The purity of 5-HMF and the diol monomer produced from HMF was further confirmed using UHPLC-MS with UV–VIS detection on a Waters Acquity UHPLC + Waters XEVO-G2 QTOF mass spectrometer using a Waters Acquity CSH C18, 1.7 μm, 2.1 × 100 mm column. Samples were run using a gradient with water (0.1% formic acid) and acetonitrile at a flow rate of 0.50 mL min^{-1} and a column temperature of 60 °C.

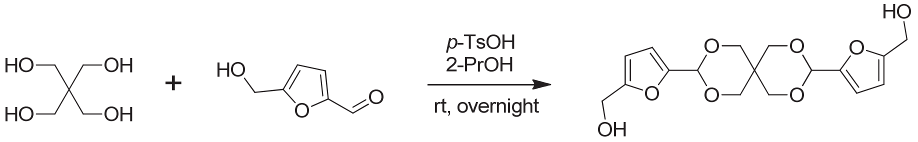
5-HMF stability in DMC, DMSO, 1-butanol, GVL, MIBK and water was investigated by determining the red and blue-shifts of 5-HMF C═O and H–O, using Fourier-transform infrared spectroscopy.[164] The spectra of samples were obtained in a region of 500–4000 cm^{-1} using Nicolet-iS5 (Thermo Scientific, USA). An air background spectrum was collected before the analysis of the sample and subtracted from each sample spectrum.

Rheology measurements were carried out on Advanced Rheometer AR2000 ETC from TA Instruments, using parallel plates with a diameter of 20 mm under nitrogen atmosphere to prevent oxidative degradation. The temperature sweep experiment was performed in the interval 140–220 °C with a heating rate of 3 °C min^{-1}. The measurement was performed with a strain of 1% and a frequency of 1 Hz. The cross-polarized light microscopy images were taken with an Olympus BX50 microscope.

Summary of appended papers

HMF-based cyclic acetal monomer for polyester and polyurethane synthesis (Paper 1)

In this project, HMF was reacted with pentaerythritol to form a spirocyclic acetal diol (Monomer S, Scheme 6).



Scheme 6. Synthesis of Monomer S

Since HMF is notoriously sensitive to both acidic conditions and elevated temperatures, an initial screening was performed to determine suitable reaction conditions. HMF was dissolved in several common solvents, at various temperatures and in the presence of acid. After 5 hours the vials were visually inspected since pure HMF is light yellow but turns black when degraded into humins. It was observed that HMF remained yellow in protic solvents as well as DMF and DMSO (Fig. 1). This can be explained by the solvent forming a protective layer around the HMF molecules preventing it from side reactions (solvent cage effect).[30]

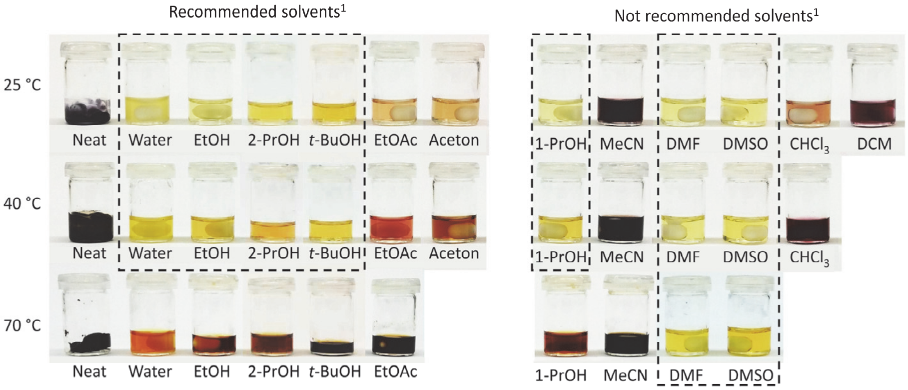


Figure 1. Solvent screening for HMF – stability. [1]Recommended according to the CHEM 21 guide.[165]

After this initial study, the acetalation (Monomer S synthesis) was investigated in several alcohols as well as in DMSO and DMF to optimize reaction conditions. It was observed that the desired product precipitated in ethanol and 2-propanol. This facilitated isolation and purification, and could drive the equilibrium towards higher conversion of Monomer S. Finally, 2-propanol was selected as the best solvent since it generated fewer side reactions than ethanol, while still resulting in high conversion. In addition, 2-propanol is also recommended by the CHEM21 guide as a green solvent.[165] Afterwards, the environmental impacts of Monomer S was preliminarily evaluated using a cradle-to-gate life cycle assessment to estimate the GHG-emissions. The results showed that the synthesis of Monomer S generates 46 % less GHG-emissions than commercial bio-based 1,3-propanediol and 76 % less than fossil-based 1,3-propanediol. These diols are used to produce commercial PTT (Sorona^{TM}). This result indicated the potential environmental benefits of the new monomer (Fig. 2).

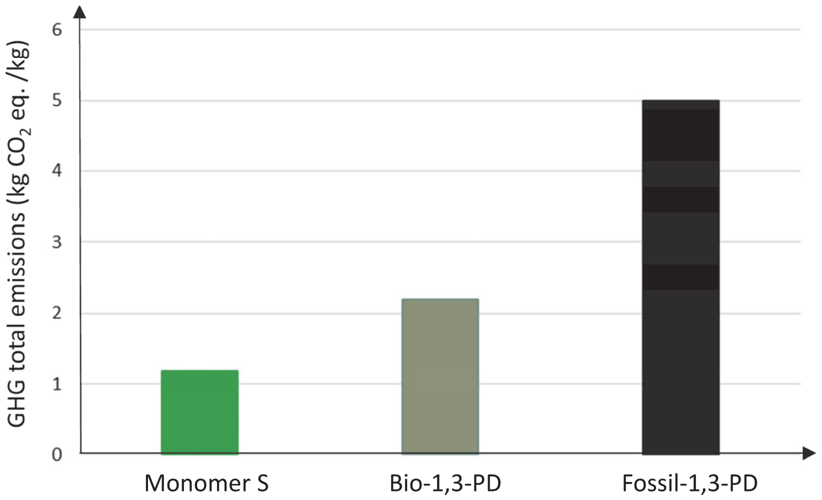
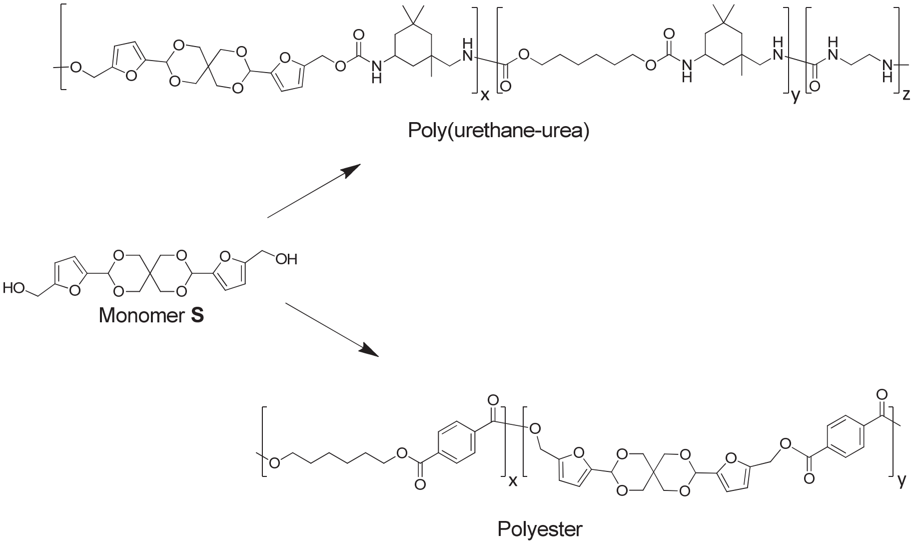


Figure 2. Carbon footprint of Monomer S compared to commercial 1,3-propanediol.

Monomer S was then copolymerized with hexanediol and terephthalic acid to produce a series of polyesters containing up to 19 mol% of the monomer, with M_n = 9.1 - 15.4 KDa. However, it was observed that the polydispersity (Đ) increased with the S-content, indicating that Monomer S caused side reactions during the polymerization. Furthermore, attempts to synthesize polymers containing more than 20 mol% of Monomer S resulted in discolored, insoluble materials. This was assumed to be caused by crosslinked humins due to the monomer degradation.

Another potential market for rigid bio-based diols are polyurethanes. Since polyurethanes are made at 60 - 80 °C, the low thermal stability of Monomer S might cause less problems. To verify this, Monomer S was reacted with hexanediol and IPDI in the presence of the catalyst DBTDL to produce oligomers end-capped with isocyanates. The oligomers were then chain extended with ethylenediamine to produce a series of colorless and transparent poly(urethane-urea)s with an S-content up to 62 % (Scheme 7).

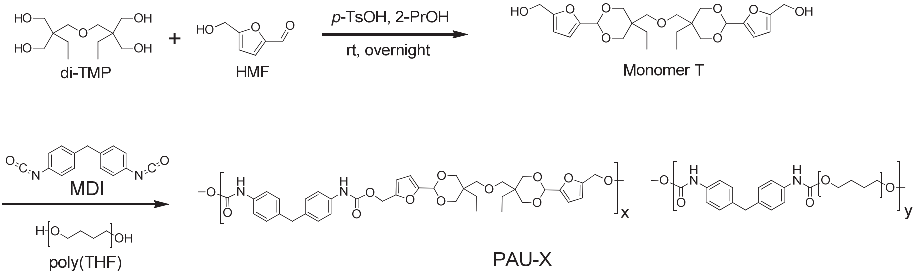


Scheme 7. Synthesis of Monomer S and its use in polyester and poly(urethane-urea) synthesis.

The T_g increased from 79 °C for the homopolymer to 131 °C for PSU-62. However, this cannot entirely be attributed to the bulkiness of Monomer S since there was also a significant increase in molecular weight of the polymers. The T_5 value was largely the same for all poly(urethane-urea)s, which indicates that the initial thermal degradation occurs at the urethane bonds. These results clearly indicate that Monomer S is more suitable for polyurethane synthesis than it is for polyester synthesis.

Synthesis and fiber spinning of thermoplastic polyurethanes (Paper 2)

The acetalation procedure developed in paper 1 was used to synthesize a diol similar to Monomer S, yet with some crucial differences. By using di-trimethylolpropane (di-TMP) instead of pentaerythritol, we prepared the comparatively more hydrophobic and thermally stable Monomer T in better yield (Scheme 8). Monomer T was then polymerized with MDI and H12-MDI to investigate the preliminary properties of the resulting polyurethanes. Since MDI produced significantly higher molecular weights and it was chosen for further analysis.



Scheme 8. Synthesis of Monomer T and polyurethanes. The X indicates the content of Monomer T in the polymer.

Afterwards, a series of thermoplastic polyurethanes was synthesized by copolymerizing MDI, Monomer T and polyTHF (a long flexible diol used in many commercial elastic polyurethanes).[166,167] This yielded a series of polyurethanes with M_n = 41.5 - 98.9 KDa. TGA results indicated that the thermal stability of these polymers decreased with the Monomer T content, most likely due to the increased aromatic contents near the urethane bond.[168–170] Interestingly, the char yield (CY) was relatively high for these polymers (up to 33 % for PAU-100), which could indicate inherent flame resistance (relatively high LOI values) .[171]

Table 1. Molecular and thermal properties of the thermoplastic polyurethanes.

	Mass % T [a]	M_n [b] (kDa)	M_w [b] (kDa)	Đ	T_g [c] (°C)	T_5 [d] (°C)	CY[e] (%)	LOI[f]
PAU-0	0	85.7	201	2.35	-	337	2.0	0.18
PAU-25	25	98.9	333	3.37	-	281	11.0	0.22
PAU-51	51	49.5	94.9	1.92	-	275	18.8	0.25
PAU-71	71	41.5	99.6	2.40	91	268	23.3	0.27
PAU-86	86	48.2	94.4	1.96	104	268	26.0	0.28
PAU-100	100	62.6	97.3	1.55	104	253	32.9	0.31

[a]The incorporated mass% of Monomer T in the polymer according to ^{1}H-NMR spectroscopy, [b] measured by SEC in DMAc containing 5 g/L LiBr, [c] measured from the second heating curve in DSC, [d] The temperature at 5 % weight loss measured by TGA, [e] Residual mass at 850 °C in TGA, [f] Limiting oxygen index calculated by the van Krevelen - method.[171]

Furthermore, DSC was used to investigate the thermal transitions of the polymers (Tab. 1). PAU-0 was semi-crystalline, while the other polymers were completely amorphous. Polymers with a relatively high Monomer T content (above 70 %) exhibited a relatively high T_g (above 91 °C), which can be explained by the increased backbone rigidity. It was also observed that the T_g was broadened with decreasing Monomer T content, indicating a miscible polymer phase. For polymers with lower than 70 % Monomer T content, the T_g value was too broad to be measured meaningfully.

Fiber spinning

PAU-86 was chosen as the model polymer to use for fiber spinning experiments due to its similarity to the commercial polyurethane Elastane in terms of the ratio between hard and soft segments.[172,173] The rheological properties of PAU-86 were then analyzed by a temperature sweep experiment between 140 °C and 220 °C (Figure 3) to find a suitable processing window. It was observed that G'' exceeded G' at 165 °C, indicating that the material started to flow at this temperature. Furthermore, a maximum in tan (δ) was observed at 186 °C, meaning that the material exhibited the most viscous character at this temperature. These results suggested a suitable processing temperature between 165 – 186 °C.

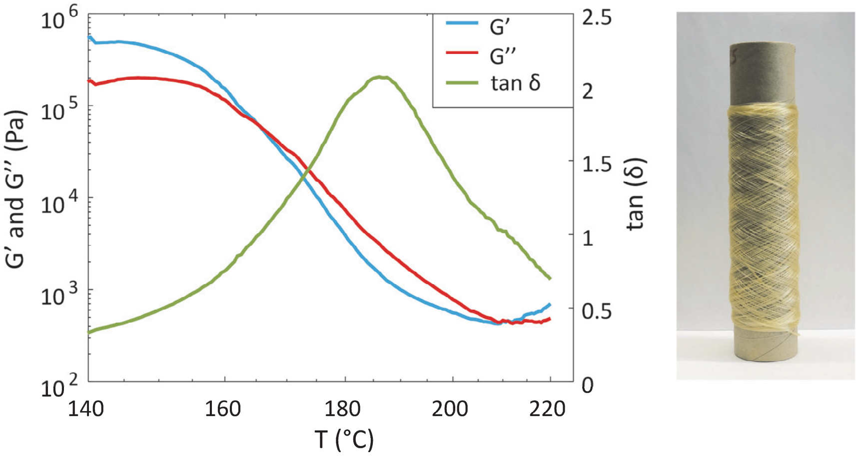


Figure 3. Temperature sweep experiment of PAU-86 (left) and successfully spun TPU fiber (right)

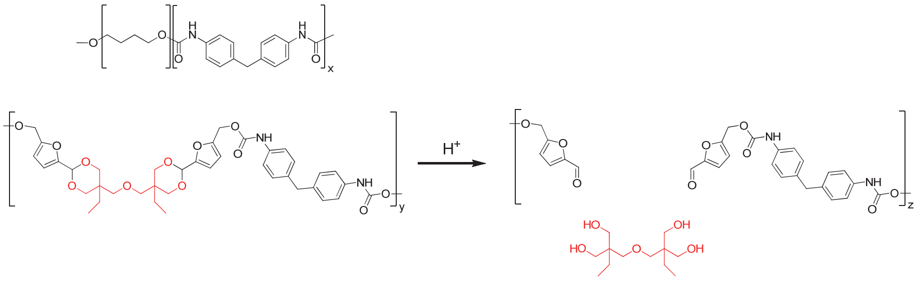
The first attempt to spin the fiber was conducted at 175 °C, yet at this temperature the melt viscosity was too high to sustain a molten flow of polymer. Therefore, the temperature was raised to 185 °C where the flow of polymer was significantly higher, and ~150 m of fiber could be successfully spun from 10 g of polymer.

Fiber properties

The tenacity of the fibers was measured to 6.7 - 7.8 cN /tex, which is comparable to commercial thermosetting elastane fibers.[173] It was also observed that the obtained fiber was slightly yellowish, which may indicate thermal decomposition to some extent. This was verified by reduced molecular weight after spinning (M_n = 16.7 KDa, measured by SEC in DMAc containing 5 g/L LiBr). Furthermore, trace amounts of Monomer T was detected by ^{1}H-NMR analysis of the fibers, indicating the occurrence of chain scission or depolymerization processes during melt spinning.

Chemical recycling of the fibers

Finally, the possibility to chemically recycle the polymers by acid hydrolysis was investigated (Scheme 9). The fiber spun from PAU-86 was submerged in HCl (6M) at 60 °C for 24 h to give a brown slurry. After neutralization of the reaction mixture, up to 84 % of di-TMP and 20 % MDA could be recovered by extraction with THF. Unfortunately, no HMF was recovered, most likely due to humin formation under these acidic conditions. By contrast, commercial Elastane was not hydrolyzed after 10 days in HCl (6M) at 60 °C.



Scheme 9. Chemical hydrolysis of the PAU-86 fiber

Bio-based HMF production from fructose (Paper 3)

HMF is widely considered one of the most important platform molecules for transitioning towards a sustainable bio-based chemical industry. It is also the crucial starting material for synthesis of the monomers in paper 1 and 2.[32] However, despite a significant amount of available literature on HMF synthesis, large scale synthesis is still affected by many problems.[174] The reason for this is related to the low stability of HMF during acidic conditions and high temperatures, both of which are needed to synthesize HMF. This commonly results in low yields of HMF and significant formation of side products unless special (and often expensive) reaction conditions are applied.

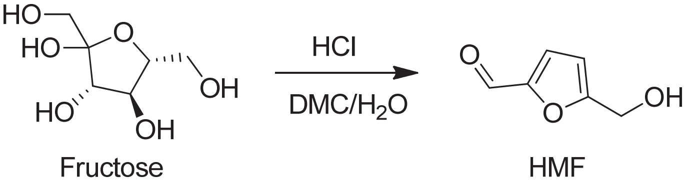
Upon considering these factors, we decided to further investigate the synthesis of HMF in common solvents to facilitate scale up and commercialization.

Screening of solvents

First, several solvents were screened with respect to fructose conversion and selectivity towards HMF. The highest conversion was obtained in gamma valerolactone (GVL), tetrahydrofuran (THF) and dimethylcarbonate (DMC). However, GVL has a high boiling point and separating it from pure HMF is energy consuming. THF has a low boiling point, but unfortunately produced low yield. However, DMC produced both high productivity and high selectivity, while having a low boiling point. It was therefore selected as the preferred solvent despite moderate fructose conversion.

Continuous reaction of fructose to HMF using water/DMC as solvent

Fructose was then converted into HMF using a water/DMC biphasic system in a continuous reactor (Scheme 10). It was observed that the two most important parameters were the temperature and the ratio between DMC and water. The highest HMF yield was obtained at 200 °C, which was also the highest operating temperature. This high temperature increases the risk of HMF degradation and humin formation, but the side reactions could be minimized by keeping a reaction time of 1 minute in the reactor. The selectivity towards HMF was in general quite high in the organic phase, however since HMF is quite polar, a considerable amount partitioned into the water phase. This explains why the total HMF yield was increased when a higher content of DMC was used (up to 89 % when a ratio of 1:5 was used). However, the HMF conversion was considerably lower when a mixture of glucose and fructose was used in the feed stream. Even though the fructose was converted to HMF in high yield, only 37 % of the glucose was converted to HMF. This indicates that it may be more economical to separate the carbohydrates prior to HMF-synthesis.



Scheme 10. Synthesis of HMF from fructose.

HMF stability in the DMC/water system

To elucidate the reason behind the stabilizing effect of DMC on HMF, we analyzed the dependence of the O-H shift on the HMF-concentration by ^{1}H-NMR spectroscopy. It was observed that there was no significant concentration dependence in DMSO-d_6, acetone-d_6 and DMC-d_6, while a clear concentration dependence was observed in $CDCl_3$. This indicated that the solvents may form a protective solvent cage around HMF due to hydrogen bonding.[175] Furthermore, HMF was analyzed by ATR-FTIR spectroscopy by comparing the peak-shift of HMF's functional groups in different solvents.[164] The largest blue shift was observed for HMF in DMC, which indicated the C=O bond was the shortest (and therefore also strongest) in this solvent.

Larger tube reactor

The reaction was then performed in a larger tube reactor, to investigate the impact of scale-up. Three different flow rates were tested (7.5, 9 and 10 mL / min) for the biphasic system with a feed containing 30% w/v fructose in the water phase. The temperature was set to 180 °C which was the highest possible operating temperature of the equipment. The conversion was above 98% in all cases, while the yield and selectivity were slightly higher at higher flow rates. When the system was run continuously for 7 hours, the total HMF yield was calculated to 74 %. However, since the presence of difructose anhydrides was observed in the water phase, the yield and selectivity may be improved by further raising the temperature or residence time in the reactor.

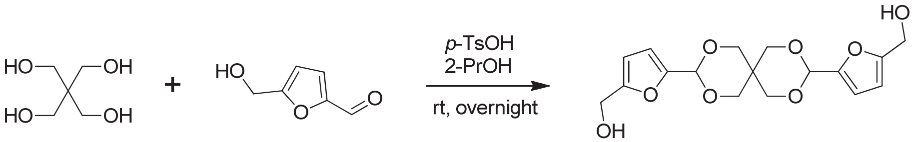
By comparing the length of the reactor for both the small scale and large scale experiment, one can conclude that maximum conversion of fructose is reached before 60 seconds and that the HMF yield decreases with time. This indicated that the ideal reactor would be shorter than 80 cm and operated at a flow rate resulting in approximately 60 seconds residence time.

HMF recovery from DMC-phase

The DMC and aqueous phase were separated using a conventional separating funnel after which the organic phase was concentrated in vacuo. This resulted in a dark solution containing 93 % HMF. Unfortunately, the purity decreased to 82 % after 3 days at room temperature due to leftover acid from the reaction. However, this problem could be mitigated by using activated carbon to purify the organic phase. If the organic phase was neutralized using bases such as NaOH or Na_2CO_3, the purity still decreased to 78 % over 3 days.

Monomer synthesis using fructose-based HMF

The different batches of purified HMF were then used to synthesize Monomer S from paper 1 (Scheme 11, Tab. 2). Commercial HMF (purchased from Nanjing Confidence chemicals) was used as reference. It was observed that commercial HMF resulted in 69 % conversion, while HMF purified by activated carbon and neutralized with Na_2CO_3 gave the second-best conversion (66 %). HMF purified with activated carbon gave 63 % conversion, and directly concentrated HMF gave the lowest conversion (42 %). This clearly demonstrates the importance of purifying the HMF, as trace amounts of acid can initiate degradation to unwanted side products.



Scheme 11. Synthesis of Monomer S from fructose-based HMF.

Table 2. Conversion of Monomer S using different HMF

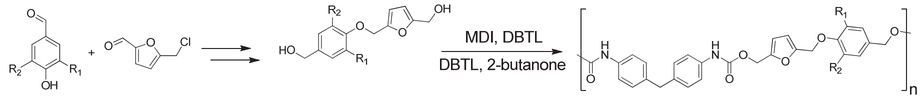
	Purification method			Commercial HMF[4]
Type of HMF	DC[1]	AC[2]	AC + Na_2CO_3[3]	
Conversion (%)	42	63	66	69

The conversion was calculated by ^{1}H NMR.[1] The HMF was directly concentrated,[2] The HMF was purified using activated carbon,[3] The HMF was purified using activated carbon and neutralized by Na_2CO_3,[4] The HMF was purchased from Nanjing Confidence Chemical Co.

Synthesis of monomers and thermoplastic polyurethanes by combining sugar- and lignin-based building blocks (Paper 4)

As demonstrated in Paper 3, it is difficult to produce HMF in good yield from carbon sources other than fructose. This limits the financial gains of industrial HMF-production since there are abundant cheap waste streams from agriculture rich in carbohydrates such as cellulose and glucose. An interesting strategy for potentially valorizing these carbohydrates is to use them for producing 5-chloromethylfurfural (CMF) instead of HMF. CMF can be produced directly from cellulose or glucose by treating them with HCl and DCM. Since CMF is very hydrophobic, it will migrate into the organic phase upon formation, where it cannot undergo further side reactions with water. This method allows production of CMF in high yield from a variety of carbohydrates without some of the problems associated with HMF production.

Because of this, we decided to use CMF as starting material in the production of another furan-based diol monomer, by reacting it with some potentially lignin-based phenolic aldehydes (Scheme 12).



1a $R_1 = R_2 = H$
1b $R_1 = OCH_3$ $R_2 = H$
1c $R_1 = R_2 = OCH_3$

3a $R_1=R_2=H$
3b $R_1=OCH_3$ $R_2=H$
3c $R_1=R_2=OCH_3$

P3a $R_1=R_2=H$
P3b $R_1=OCH_3$ $R_2=H$
P3c $R_1=R_2=OCH_3$

Scheme 12. Synthesis of diol monomers and subsequent polymerization towards polyurethanes.

Monomer synthesis

To optimize the reaction conditions, CMF and vanillin was reacted in different solvents in the presence of a mild base (K_2CO_3). It was observed that the highest yield was achieved in DMSO since it could efficiently solvate all reagents while simultaneously protecting the furan from undergoing side reactions. This solvent was then used to scale up all monomers.

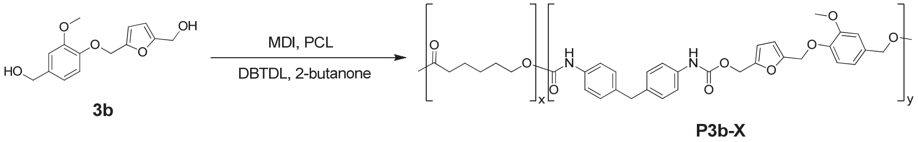
The dialdehydes were then reduced to the corresponding diols using $NaBH_4$ in methanol with a catalytic amount of NaOMe to prevent side reactions. However, for **2b** some side reactions to the corresponding methyl acetal were observed. Because of this, acetonitrile was used as solvent instead, which resulted in high conversion to **3b**.

Polyurethane synthesis & characterization

The diols were then reacted with MDI to produce a series of polyurethanes with M_n = 15-47 KDa (Scheme 13). The thermal properties of the resulting polymers were investigated by TGA and DSC. All polymers showed a T_5 ~ 200 °C which is commonly observed for polyurethanes made from an aromatic isocyanate and a furfuryl alcohol.[81,168,169,176,177] Furthermore, the polymers were fully amorphous with a T_g = 110 – 113 °C. This indicates that the methoxy group had a negligible effect on the structural rigidity of the polymer. This is most likely a combined effect of two factors. Methoxy groups can introduce sterical hindrance inhibiting the rotation of the chain which would increase the T_g, but they can also increase the free volume of the polymer, resulting in increased flexibility. In this case, the combination of these effects seem to have cancelled out.

Thermoplastic polyurethane synthesis & characterization

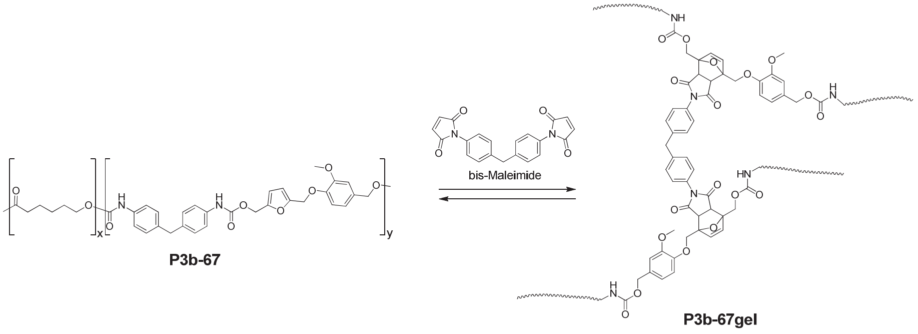
Many polyurethanes contain a soft segment in form of a long flexible diol to improve the mechanical properties of the polymer. Because of this, **3b** was reacted with MDI and PCL in different ratios to form a series of thermoplastic polyurethanes (Scheme 13). The thermal properties of these polymers were then analyzed by TGA and DSC. The T_5 increased with the PCL-content (from 200 °C for P3b-100 to 272 °C for P3b-0), which can be explained by that the urethane bond between PCL and MDI was more stable than the urethane bond between MDI and **2b** (Tab. 3). Furthermore, the polymers were fully amorphous with a T_g that increased from 17 to 110 °C depending on the content of **3b**. This was expected considering **3b** is a significantly bulkier monomer than PCL.



Scheme 13. Synthesis of thermoplastic polyurethanes from **3b**, MDI and PCL. X indicates the content of **3b** in the polymer.

Crosslinking using Diels-Alder chemistry

The backbone of the thermoplastic polyurethanes contain many furan units, which can act as dienes for the Diels-Alder reaction with a dienophile (e.g. bis-maleimide, Scheme 14). This can cause thermally induced crosslinking, which will enhance the T_g and the thermal stability of the polymers. Furthermore, Diels-Alder reactions can be reversed at elevated temperatures (e.g. 120 °C), which could lead to dissociation of the crosslinking. This could yield a material with the excellent properties of a thermoset at room temperature, while still being malleable at elevated temperatures.



Scheme 14. Crosslinking of TPUs with Diels-Alder chemistry using bis-maleimide.

To investigate this, the thermoplastic polyurethanes were reacted with a stoichiometric amount of bis-maleimide in THF. The solution was heated at 60 °C for 24 h, forming a swollen gel. When the reaction was cooled down, the solvent was decanted and the swollen gel was collected, weighed, and dried to yield a yellow solid. The thermal properties of the crosslinked material were then investigated by TGA and DSC (Tab. 3). Interestingly, the T_5 value was almost unchanged after crosslinking. This could be explained by the fact that the initial degradation occurred at the urethane bonds, which were not changed by the Diels Alder crosslinking. Furthermore, the T_g values of all polymers were increased by 6-26 °C, which was consistent with the crosslinking. In addition, the retro-Diels-Alder reaction was observed at 120-150 °C for all polymers by DSC measurements (Fig. 4).

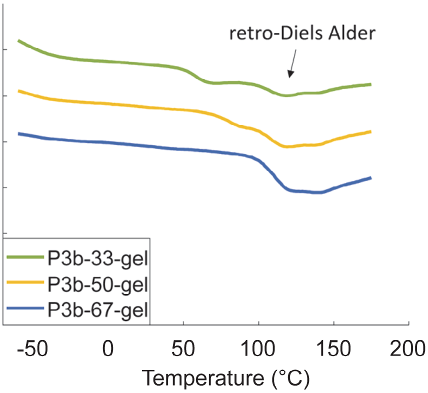
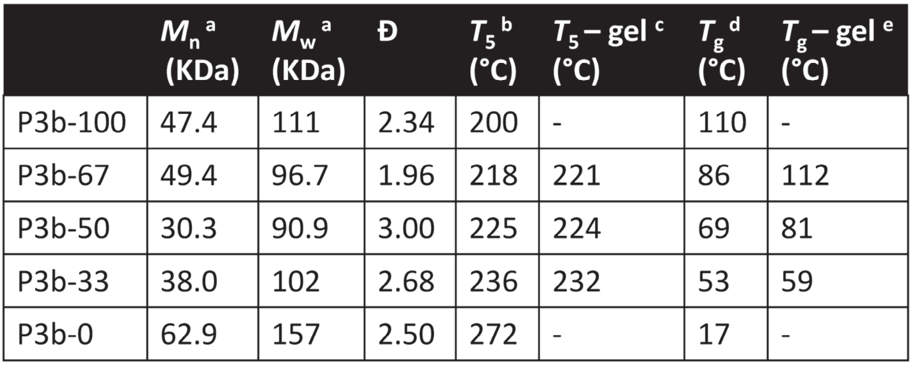


Figure 4. DSC curves of the crosslinked materials.

Finally, the obtained crosslinked polymer (P3b-67gel) was heated at 140 °C for 10 minutes in DMSO-d_6 solution, which resulted in complete dissolution of the polymer. ^{1}H NMR-spectroscopy of the solution confirmed the formation of the initial bis-maleimide and the polymer P3b-67, which indicated successful dissociation of the crosslinking bonds.

Table 3. Thermal properties of the polyurethanes

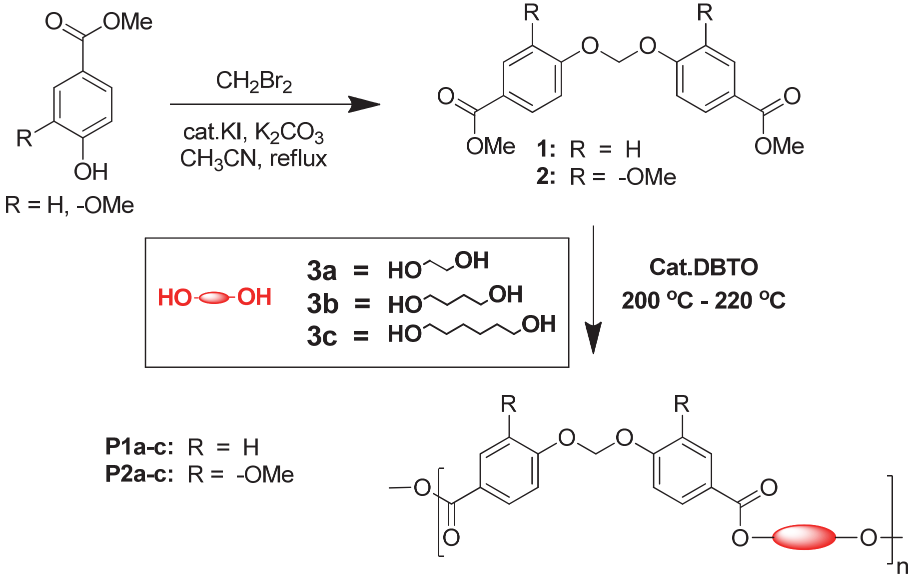


	M_n [a] (KDa)	M_w [a] (KDa)	Đ	T_5 [b] (°C)	T_5 – gel [c] (°C)	T_g [d] (°C)	T_g – gel [e] (°C)
P3b-100	47.4	111	2.34	200	-	110	-
P3b-67	49.4	96.7	1.96	218	221	86	112
P3b-50	30.3	90.9	3.00	225	224	69	81
P3b-33	38.0	102	2.68	236	232	53	59
P3b-0	62.9	157	2.50	272	-	17	-

[a] measured by SEC in DMAc containing 5 g/L LiBr, [b] temperature measured at 5 % mass loss by TGA, [c] temperature measured at 5 % mass loss by TGA for the cross-linked materials, [d] measured from the second heating cycle by DSC, measured from the second heating cycle by DSC for the cross-linked materials.

Lignin-based polyesters with a central acetal unit (Paper 5)

The monomers in paper 1,2 and 4 were all based on thermally unstable HMF structures, which made them inherently unsuitable for high temperature polyester synthesis. For this reason, we designed potentially lignin-based molecules for polyester synthesis using methyl vanillate and methyl paraben, (Scheme 15) both of which are potentially bio-sourced molecules.[178–181] These monomers with a central acetal unit were then reacted with three common diols with varying lengths (ethylene glycol, butanediol, and hexanediol) in a two-step melt condensation polymerization to form two series of polyesters with a central acetal unit.



Scheme 15. Synthesis of lignin-based dimethylesters and polyester synthesis.

Polymer Characterization

The molecular weights of the obtained polymers were in the range from 10.2 KDa – 18.8 KDa, according to SEC measurements in chloroform. The chemical structure was determined by ^{1}H NMR spectroscopy and FTIR.

After this, the thermal stability of the resulting polyesters was investigated by TGA. All polymers showed relatively high initial thermal decomposition temperatures ($T_5 > 330$ °C) and a single thermal decomposition step, which could be attributed to beta hydrogen degradation, a typical thermal degradation mechanism for many polyesters like PET, PBT, etc.[182] The thermal transitions of the polymers were investigated by DSC (Fig. 5). The polymers were first heated from room temperature to 200 °C, then cooled to -50 °C, and finally re-heated to 200 °C with a rate of 10 °C/min to erase the thermal history. Interestingly, melting peaks were observed in the first heating cycle for polymers **P2b**, **P2c** and **P3c**, while only **P2b** exhibited a melting peak during the second heating cycle. This indicated slow crystallization of these polymers from their melts. To investigate the crystallization behavior further, all the samples were annealed at 20 °C above their respective T_g for 3 hours to induce crystallization. For the annealed P2b, a significantly larger melting peak was observed (ΔH_m =32 J/g compared to ΔH_m = 5 J/g during first heating cycle) at 147 °C. However, this phenomenon was not observed for any other polymer. This indicated that **P2c** and **P3c** could crystallize relatively easily from solution, but not from melt. This behavior has previously been reported for other polyesters.[183]

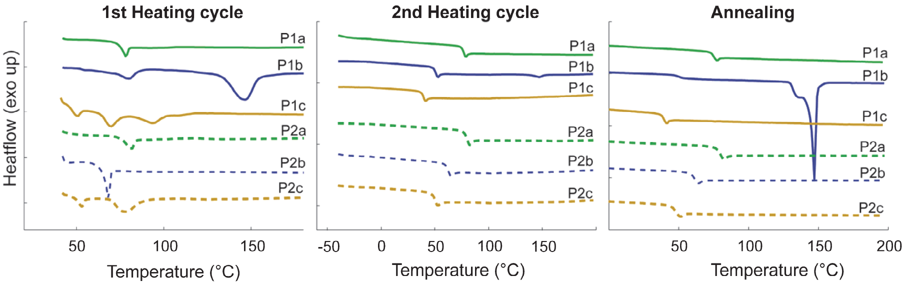


Figure 5. Annealing of semicrystalline polyester.

Finally, **P1a** and **P2a** was selected for chemical recycling investigations. The polymers were hydrolyzed in concentrated HCl for 24 hours to yield a heterogeneous slurry (Fig 6). Afterward, the slurry was filtered to give a solid residue and an aqueous phase. The filtrate was extracted with DCM, which yielded another solid after solvent evaporation.

Interestingly, the hydrolysis of **P2a** was more rapid with deep coloration (Fig. 4), while that of **P1a** remained white throughout the experiment (Fig. 6). This could be explained by the formation of humic acids from vanillic acid structures in **P2a**, which was absent in **P1a**.[184–186] For **P1a**, the main hydrolysis product was obtained in Fraction A, while a minor amount was obtained in Fraction B. ^{1}H-NMR spectroscopy showed that Fraction A was mainly the bis-phenol structure formed by selectively cleaving the acetal bond in the polymer and could be recovered in good yield (77%). However, for **P2a**, the main product was a white solid in Fraction B. ^{1}H-NMR spectroscopy showed that the white solid in Fraction B was relatively pure vanillic acid in rather low yield (31 %). Fraction A was black, which was assumed to be crosslinked humins. The reason for the different hydrolysis processes for **P1a** and **P2a** was likely that the methoxy group accelerated hydrolysis of **P2a**, causing hydrolysis of the esters and the acetals. Furthermore, vanillic acid can form humic acids under highly acidic conditions, which resulted in a significant mass loss of the material due to humin formation.

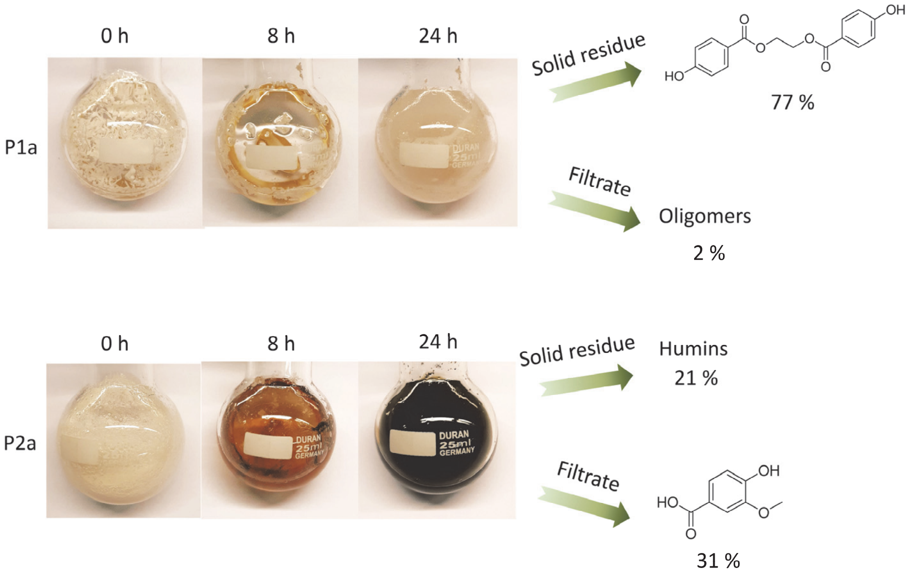


Figure 6. Acid hydrolysis of **P1a** and **P2a** over 24 h.

Conclusions

In this thesis, new bio-based rigid aromatic monomers have been rationally designed and synthesized aiming to improve certain physical properties and recyclability of polyesters and polyurethanes. The relationship between their chemical structures and physical and chemical properties is the focus of this research. Processability and potential applications for the obtained materials were also preliminarily investigated.

In Paper 1, a spirocyclic acetal diol monomer (Monomer S) was synthesized by reacting bio-based HMF and pentaerythritol. Preliminary LCA results indicated favorably low greenhouse gas emissions. This monomer was used to prepare two series of polyesters and polyurethanes, aiming to unravel their polymerizability and their impact on the properties of the resulting polymers. For both series of polymers, the T_g values were significantly enhanced by the incorporation of the rigid spiroacetal structures. However, thermal degradation was observed during the polycondensation to synthesize polyesters due to the inherent thermal instability of the furan structure. This was not a problem for polyurethane synthesis, which was demonstrated by achieving high molecular weight colorless polyurethanes. Such a result indicated that the HMF-based diols are suitable eco-friendly building blocks for polyurethanes.

In Paper 2, a similar diol monomer (Monomer T) was synthesized by reacting HMF and di-TMP, which is another potentially bio-based tetraol. Compared to the previous monomer (S), Monomer T was more hydrophobic and thermally stable, and could be prepared in relatively high yield. This monomer was then reacted with MDI and polyTHF to prepare a series of thermoplastic polyurethanes with good molecular weights, and tuneable T_gs. The obtained polyurethanes could be melt spun into a fiber with a tenacity similar to that of commercial Elastane used in fabrics. The obtained fiber could be conveniently hydrolyzed under acidic conditions, yielding the corresponding monomeric building blocks. This indicated its potential towards chemical recycling, particularly for textiles, something that is challenging to recycle today.

In Paper 3, the synthesis of HMF from various hexose carbohydrates was explored. High quality HMF was synthesized in a flow reactor using a biphasic system of DMC and water as solvent, when fructose was used as substrate. Other carbohydrates such as glucose or cellulose resulted in lower yields. The purified HMF was then used to synthesize Monomer S in comparable yield to the monomer synthesis using commercial HMF.

In Paper 4, CMF was reacted with three potentially lignin-based monomeric aldehydes, and then reduced to prepare three monomer diols in good yields. One diol was then selected for copolymerization with PCL and MDI to produce a series of thermoplastic polyurethanes with high molecular weights and tuneable T_g ranging from 17 - 110 °C. The polyurethanes could be conveniently crosslinked using a reversible Diels-Alder reaction to further increase the T_g. At elevated temperatures, the crosslinked materials could be conveniently reverted back to starting thermoplastic polyurethanes. This property showed the potential of this class of materials in the development of recyclable thermosets.

In Paper 5, polyesters with a central acetal unit were designed using biosourced building blocks other than furan-based ones (e.g. HMF, CMF). To achieve this, methyl vanillate and methyl paraben were used to react with dibromomethane to prepare two rigid diester monomers. As expected, these monomers were more thermally stable than the furan-based monomers from Papers 1-4, and could therefore be used for polyester synthesis at high temperatures. The obtained polyesters showed good thermal stability and tuneable T_g values. Similar to the polymers with acetal units in Papers 1-4, these new polymers could also be hydrolyzed at the acetal bonds, although using higher acid concentration and temperatures.

Future outlook

The furan-based diols in this thesis were relatively unstable at high temperatures, something that limited their use within polyester synthesis. The reason for this is most likely connected to the relatively high electron density of the furan ring. One can compare the thermal stability to FDCA which is widely used to prepare polyesters, since the two electron withdrawing acid groups deactivates the furan ring. For this reason, I think it would be highly interesting to investigate different furan-based monomers with varying electron density, aiming to find a correlation between their thermal stability and electron density. A few examples of such monomers would be HMFCA, BHMF, FFCA, and the spirocyclic monomer formed by reacting pentaerythritol with FFCA. This may facilitate the design of future furan-based monomers for the synthesis of many different types of polymers.

In addition to this, it would be interesting to conduct a deeper investigation in chemical recycling of the polymers synthesized in this thesis. More specifically, to explore what conditions are required to selectively break the acetal bond (using acid hydrolysis) versus the ester/urethane bond (using basic hydrolysis). Furthermore, the recycled monomers could be used to synthesize polyimides (when aromatic diamines were recovered) or polycarbonates (when bis-phenols were recovered) to demonstrate the concept of up-cycling.

The monomeric diols in this thesis could also be used to synthesize polycarbonates, which is especially interesting considering that they can be produced at relatively low temperatures (using phosgene). In addition to this, the bulky structure of the diol monomers mimics the structure of BPA, which may result in polymers with similar physical properties, but without the drawbacks associated with the hormonal toxicity of BPA.

Thermal degradation was observed during fiber spinning (in Paper 2), indicating that a more thermally stable polymer may produce better fibers. This could be accomplished by using different aliphatic isocyanates, or using other non-furan-based diols. Wet-spinning is also an interesting alternative, considering that this is how Elastane fibers are spun. The semi-crystalline polyester in paper 5 (P2b) would also be an interesting candidate for fiber spinning.

Diels-Alder chemistry based crosslinking and the reverse reaction would be interesting to investigate deeper, especially for the monomers and polymers synthesized in Paper 1 and 2. For the polymers in Paper 4 it would be interesting to analyze how the material properties are affected by the reversible Diels-Alder crosslinking. It would be especially interesting to investigate how multiple cycles of processing would impact the material.

Finally, this thesis only investigated lab-scale (<1kg) synthesis of building blocks, monomers, and polymers. Further investigation regarding scale-up and evaluation of suitable applications would be highly interesting. However, large scale synthesis of building blocks, monomers and polymers may require further optimization to minimize waste generation.

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As my time as a PhD student draws to a close, I think of all people who have aided my research in various ways throughout the years and the list is seemingly endless. I will nevertheless try to express my gratitude towards some of the key players and summarize their contribution to the research I've conducted in this thesis.

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Despite my studies being academic, I almost feel like an industrial PhD student due to the vital support I have received from many industrial partners, especially within STEPS.

Bona: Thank you Nicola for our discussions in chemistry, and much insightful advice regarding all sorts of chemistry, Stefan whom I shared office and have had many interesting discussions with, Johan & Dzenana for showing me around the lab, Bartosz for helping me with numerous SEC-analyses, Anna for showing me how to operate analytical equipment, and Cecilia for in depth discussions of catalysts and polyurethane synthesis.

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Finally, I would like to thank MISTRA and Kungliga Fysiografiska Sällskapet for financially supporting my studies.

Newton once wrote: “*If I have seen further, it is by standing on the shoulders of giants*”, and after writing this thesis, I feel very fortunate to have been standing on a whole pile of them. Thank you all, and best of luck in the future,

//Niklas

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