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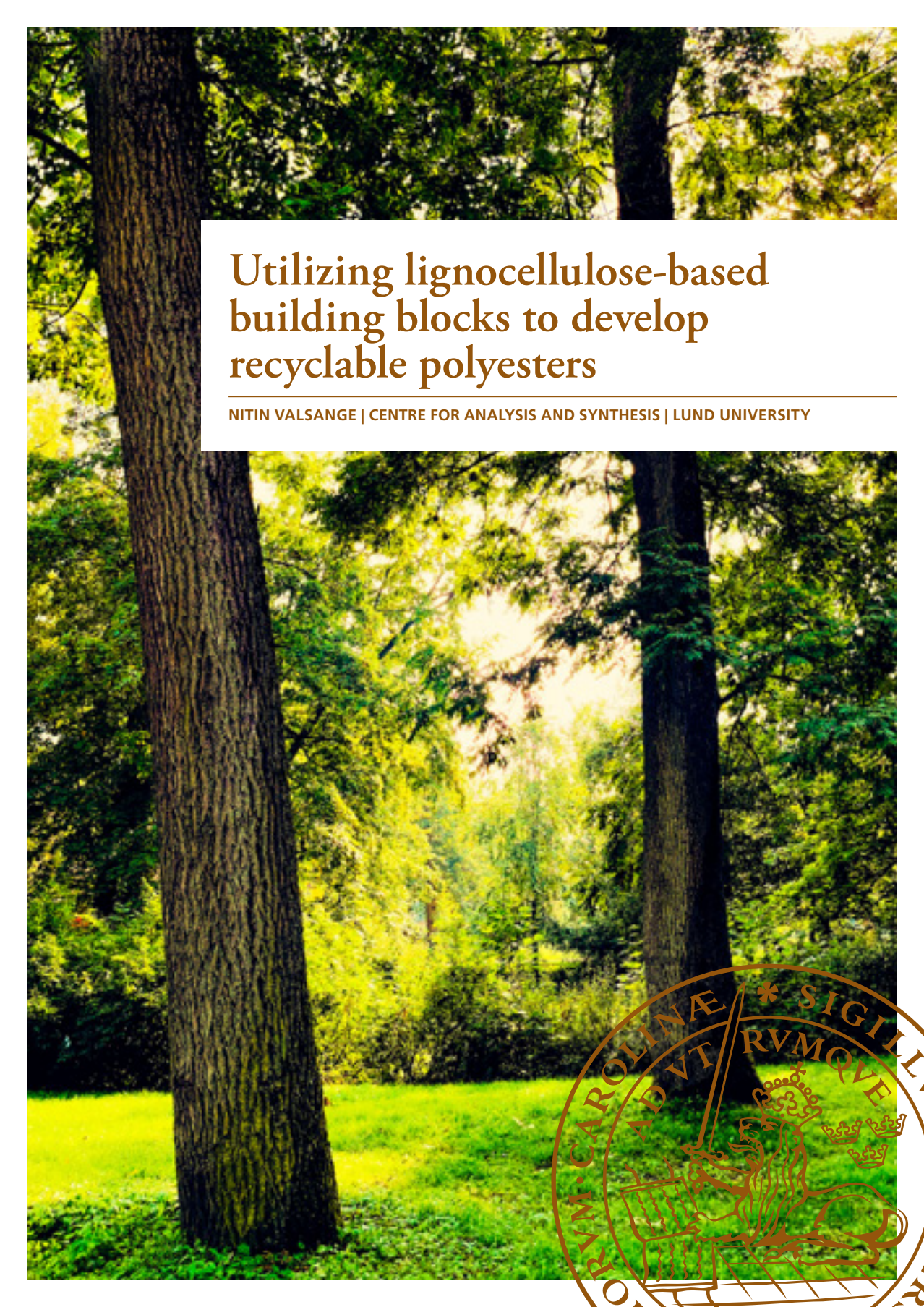
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Utilizing lignocellulose-based building blocks to develop recyclable polyesters

NITIN VALSANGE | CENTRE FOR ANALYSIS AND SYNTHESIS | LUND UNIVERSITY



Utilizing lignocellulose-based building blocks to develop
recyclable polyesters

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Nitin Valsange



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DOCTORAL DISSERTATION

Doctoral dissertation for the degree of Doctor of Philosophy (PhD) at the Faculty of Engineering at Lund University to be publicly defended on November 27, at 13.00 in Lecture Hall K:B, Kemicentrum, Lund.

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Abstract: With the growing global population and the demand for new applications, the production of fossil-based plastics is continuously increasing. This has led to serious environmental concerns about the depletion of fossil resources, land and marine pollution, and generation of greenhouse gas emissions. These undesirable consequences of fossil-based plastics have sparked a significant interest in developing plastics using natural biomass as a sustainable alternative. To successfully compete with the low-cost fossil counterparts, and to mitigate the environmental impacts, biobased plastics with an improved material performance and recyclability are desired. In this context, we have transformed various lignin- and (sugar)cellulose-based building blocks into strategically designed rigid structures for polyester synthesis and investigated efficient pathways for their chemical recycling. This thesis is based on five papers describing key results of new biobased polyesters and their recyclability.

In paper 1 and 2, ketones such as ethyl levulinate and ethyl acetoacetate were combined with pentaerythritol through a ketalization reaction to prepare two rigid spirocyclic diesters with a ketal functionality. A preliminary life cycle assessment (LCA) indicated a lower CO₂ emission for monomer production from ethyl levulinate and pentaerythritol. The spiro-diester were used in melt polycondensations with various diols to produce fully aliphatic polyesters, which showed increasing glass transition temperatures with the rigidity of the diol and spiro-diester. In paper 3, the spiro-diester from ethyl levulinate was incorporated into the structures of poly(butylene 2,5-furandicarboxylate) and poly(hexamethylene 2,5-furandicarboxylate), respectively, to improve the chemical recyclability of these aromatic polyesters. The acid-catalyzed cleavage of the ketal groups in the copolyester structures promoted rapid chain scission to small-sized oligomers, which subsequently showed faster hydrolysis into the starting building blocks than the long chain homopolyesters. Additionally, we demonstrated that the ketone-terminated telechelic oligomers obtained after the selective cleavage of the ketal units could be converted back to the original polymer structures through direct polymerization with pentaerythritol. In paper 4, a series of aromatic dicarboxylates possessing varying substitutions of methoxy groups were synthesized by reacting sugar-based methyl 5-chloromethyl-2-furoate with phenolic carboxylates (methyl paraben, methyl vanillate, and methyl syringate). Some of the polyesters prepared using these monomers showed comparable thermal properties to those based on fossil-based terephthalic acid. Moreover, in paper 5, the same sugar-based methyl 5-chloromethyl-2-furoate was combined with potentially biobased dihydroxy benzenes (hydroquinone and resorcinol) to yield two dicarboxylates which were polycondensed with biobased diols using a slightly different method to enable recycling *via* a telechelic approach. Initially low molecular weight telechelic polyesters with ketone end groups were prepared. Then, chain extension with adipic acid dihydrazide formed high molecular weight polyesters with acylhydrazone bonds as weak links. We demonstrated that acylhydrazone bonds in the polyesters could be selectively hydrolyzed to produce telechelic polyesters, which subsequently could be linked together *via* a chain extension with dihydrazide to recover the original structure.

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Nitin Valsange



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Abstract

With the growing global population and the demand for new applications, the production of fossil-based plastics is continuously increasing. This has led to serious environmental concerns about the depletion of fossil resources, land and marine pollution, and generation of greenhouse gas emissions. These undesirable consequences of fossil-based plastics have sparked a significant interest in developing plastics using natural biomass as a sustainable alternative. To successfully compete with the low-cost fossil counterparts, and to mitigate the environmental impacts, biobased plastics with an improved material performance and recyclability are desired. In this context, we have transformed various lignin- and (sugar)cellulose-based building blocks into strategically designed rigid structures for polyester synthesis and investigated efficient pathways for their chemical recycling. This thesis is based on five papers describing key results of new biobased polyesters and their recyclability.

In paper 1 and 2, ketones such as ethyl levulinate and ethyl acetoacetate were combined with pentaerythritol through a ketalization reaction to prepare two rigid spirocyclic diesters with a ketal functionality. A preliminary life cycle assessment (LCA) indicated a lower CO₂ emission for monomer production from ethyl levulinate and pentaerythritol. The spiro-diester were used in melt polycondensations with various diols to produce fully aliphatic polyesters, which showed increasing glass transition temperatures with the rigidity of the diol and spiro-diester. In paper 3, the spiro-diester from ethyl levulinate was incorporated into the structures of poly(butylene 2,5-furandicarboxylate) and poly(hexamethylene 2,5-furandicarboxylate), respectively, to improve the chemical recyclability of these aromatic polyesters. The acid-catalyzed cleavage of the ketal groups in the copolyester structures promoted rapid chain scission to small-sized oligomers, which subsequently showed faster hydrolysis into the starting building blocks than the long chain homopolyesters. Additionally, we demonstrated that the ketone-terminated telechelic oligomers obtained after the selective cleavage of the ketal units could be converted back to the original polymer structures through direct polymerization with pentaerythritol. In paper 4, a series of aromatic dicarboxylates possessing varying substitutions of methoxy groups were synthesized by reacting sugar-based methyl 5-chloromethyl-2-furoate with phenolic carboxylates (methyl paraben, methyl vanillate, and methyl syringate). Some of the polyesters prepared using these monomers showed comparable thermal properties to those based on fossil-based terephthalic acid. Moreover, in paper 5, the same sugar-based methyl 5-chloromethyl-2-furoate was combined with potentially biobased dihydroxy benzenes (hydroquinone and resorcinol) to yield two dicarboxylates which were polycondensed with biobased diols using a slightly different method to enable recycling *via* a telechelic approach. Initially low molecular weight telechelic polyesters with ketone end groups were prepared. Then, chain extension with adipic

acid dihydrazide formed high molecular weight polyesters with acylhydrazone bonds as weak links. We demonstrated that acylhydrazone bonds in the polyesters could be selectively hydrolyzed to produce telechelic polyesters, which subsequently could be linked together *via* a chain extension with dihydrazide to recover the original structure.

Popular summary

Plastics are very important materials in our modern society due to their widespread use in various industrial areas such as packaging, textiles, electronics, transportation, construction, and healthcare. However, the current practices in the generation and disposal of plastics are unsustainable. More than 95% of plastics are produced from non-renewable and rapidly depleting fossil fuels. Thus, there is an imminent challenge to gradually replace fossil-based plastics with those derived from bio-renewable resources. Moreover, the high durability of plastics has resulted in the accumulation of plastic waste in our ocean, causing serious concerns for marine ecosystems. Methods to address these issues include the development of biodegradable plastics and mechanical recycling. However, many biodegradable polymers that break down effectively in controlled environments do not efficiently degrade in seawater, creating new environmental issues. Mechanical recycling of plastics usually results in substantial loss of material properties, making the recycled material unsuitable for high-performance applications. A particularly attractive and emerging strategy is to develop chemically recyclable polymers that can depolymerize into their constituent monomers for recycling and repolymerization. In this way, the circular use of the materials offers a feasible solution to the end-of-use issue of such materials and provides a closed-loop approach towards a circular economy.

This thesis aims to address the challenges posed by the current plastics by developing new biobased plastics using biomass-derived building blocks and investigating possible pathways for their chemical recycling. Hence, I have designed and synthesized various biobased monomers and polymers, primarily using lignocellulose-based building blocks. The molecular design was particularly focused on creating rigid polymeric structures for improved properties and introducing certain chemical functionalities to facilitate recyclability. Therefore, I have synthesized polymers containing rigid cyclic molecular structures and investigated the impacts of these structures on the material properties. I have also investigated the chemical recycling of the polymers and demonstrated how the incorporation of weak links into the polymer structures facilitates faster degradation into the starting building blocks and small-sized polymers that can be reused to prepare the original polymer.

List of papers

This thesis is based on the following papers:

- I. **Biobased aliphatic polyesters from a spirocyclic dicarboxylate derived from levulinic acid**
Nitin G. Valsange, Maria Nelly Garcia Gonzalez, Niklas Warlin, Smita V. Mankar, Nicola Rehnberg, Stefan Lundmark, Baozhong Zhang and Patric Jannasch, *Green Chemistry*, **2021**, 23(15), 5706-5723.
- II. **Influence of the rigidity of spirocyclic diester monomers on the thermal properties of aliphatic polyesters**
Nitin G. Valsange, Niklas Warlin, Smita V. Mankar, Nicola Rehnberg, Baozhong Zhang and Patric Jannasch, *in manuscript*.
- III. **Improved recyclability of 2,5-furandicarboxylate polyesters enabled by acid-sensitive spirocyclic ketal units**
Nitin G. Valsange, Niklas Warlin, Smita V. Mankar, Nicola Rehnberg, Baozhong Zhang and Patric Jannasch, *submitted for publication*.
- IV. **Lignocellulose-based dicarboxylates for the development of aromatic polyesters: Synthesis, characterization, and properties**
Nitin G. Valsange, Niklas Warlin, Smita V. Mankar, Nicola Rehnberg, Baozhong Zhang and Patric Jannasch, *in manuscript*.
- V. **Semi-crystalline and amorphous polyesters derived from biobased tri-aromatic dicarboxylates and containing cleavable acylhydrazone units for short-loop chemical recycling**
Nitin G. Valsange, Rafael Natal Lima de Menezes, Niklas Warlin, Smita V. Mankar, Nicola Rehnberg, Baozhong Zhang and Patric Jannasch, *in manuscript*.

Publications not included

- VI. Synthesis, life cycle assessment, and polymerization of a vanillin-based spirocyclic diol toward polyesters with increased glass transition temperature**
- Smita Mankar, Nelly Garcia Gonzalez, Niklas Warlin, [Nitin Valsange](#), Nicola Rehnberg, Stefan Lundmark, Patric Jannasch and Baozhong Zhang, *ACS Sustainable Chemistry & Engineering*, **2019**, 7(23), 19090-19103.
- VII. A rigid spirocyclic diol from fructose-based 5-hydroxymethylfurfural: synthesis, life-cycle assessment, and polymerization for renewable polyesters and poly(urethane-urea)s**
- Niklas Warlin, Nelly Garcia Gonzalez, Smita Mankar, [Nitin Valsange](#), Mahmoud Sayed Ali Sayed, Sang-Hyun Pyo, Nicola Rehnberg, Stefan Lundmark, Rajni Hatti-Kaul, Patric Jannasch and Baozhong Zhang, *Green Chemistry*, **2019**, 21(24), 6667-6684.
- VIII. Synthesis and melt-spinning of partly bio-based thermoplastic poly(cycloacetal-urethane)s toward sustainable textiles**
- Niklas Warlin, Erik Nilsson, Zengwei Guo, Smita Mankar, [Nitin Valsange](#), Nicola Rehnberg, Stefan Lundmark, Patric Jannasch and Baozhong Zhang, *Polymer Chemistry*, **2021**, 12 (34), 4942-4953.
- IX. Short-loop chemical recycling via telechelic polymers for biobased polyesters with spiroacetal units**
- Smita Mankar, Jan Walhberg, Niklas Warlin, [Nitin Valsange](#), Nicola Rehnberg, Stefan Lundmark, Patric Jannasch and Baozhong Zhang, *ACS Sustainable Chemistry & Engineering*, **2023**, 11(13), 5126-5146.

Author's contribution to the papers

Paper I

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

Paper II

I planned and performed most of the experimental work. I wrote the first draft of the paper.

Paper III

I participated in developing and expanding the idea for this project. I synthesized all the polyesters and performed characterization and chemical recycling studies. I wrote the first draft of the paper.

Paper IV

I designed and synthesized the new monomers and polyesters, and performed the analysis with regard to thermal and mechanical properties. I wrote the first draft of the paper.

Paper V

I performed the synthesis and characterization of new monomers and telechelic polyesters. Chain extensions of telechelic polyesters and chemical recycling was performed by Rafael Natal Lima de Menezes. I wrote the first draft of the paper.

Abbreviations

1,4-BD	1,4-Butanediol
BDA	Biphenyldicarboxylic acid
BFDCA	Bifuran dicarboxylic acid
BHET	Bis (2-hydroxyethyl) terephthalate
BHMF	Bis(hydroxymethyl)furan
CHDM	Cyclohexanedimethanol
CMF	5-Chloromethylfurfural
<i>D</i>	Dispersity
DBTO	Dibutyltin (IV) oxide
DCM	Dichloromethane
DEFDC	Diethyl 2,5-furandicarboxylate
DMA	Dynamic mechanical analysis
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
EG	Ethylene glycol
FDCA	2,5-Furandicarboxylic acid
GHG	Greenhouse Gas
GPC	Gel permeation chromatography
1,6-HD	1,6-Hexanediol
HMF	5-Hydroxymethylfurfural
LA	Levulinic acid
LCA	Life Cycle Assessment
MCMF	Methyl 5-chloromethyl-2-furoate
MHET	Mono(2-hydroxyethyl) terephthalic acid
M_n	Number average molecular weight
M_w	Weight average molecular weight
NMR	Nuclear magnetic resonance
NPG	Neopentyl glycol

PBF	Poly(butylene 2,5-furandicarboxylate)
PBS	Poly(butylene succinate)
PBT	Poly(butylene terephthalate)
1,3-PD	1,3-Propanediol
PE	Polyethylene
PEF	Poly(ethylene 2,5-furandicarboxylate)
PET	Poly(ethylene terephthalate)
PETG	Poly(ethylene terephthalate) glycol
PEV	Poly(ethylene vanillate)
PHAs	Poly(hydroxyalkanoates)
PHF	Poly(hexamethylene 2,5-furandicarboxylate)
PHT	Poly(hexamethylene terephthalate)
PLA	Poly(lactic acid)
PP	Polypropylene
<i>p</i> TSA	<i>p</i> -Toluene sulfonic acid
PTT	Poly(trimethylene terephthalate)
RI	Refractive index
rt	Room temperature (20 °C)
SEC	Size exclusion chromatography
$T_{d,5}$	Temperature at 5 % weight loss
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPA	Terephthalic acid
US DOE	United States Department of Energy

1 Introduction

Considering their widespread usage in various fields such as packaging, textiles, communication, transportation, construction, and healthcare, plastics are very important materials. Most of the plastics we use today is derived from rapidly depleting non-renewable fossil resources. With the growing population and the demand for new applications, the world's plastics production is continuously increasing from 1.7 million tons in 1950 to 390 million tons in 2021.^{1,2} It has been estimated that in total 8300 million tons of virgin plastics has been produced so far, and close to 6300 million tons of plastic waste has been generated.³ About 80 % of this waste has been discarded to landfills. This massive dump has accumulated in nature due to the extreme resistance of plastic toward natural degradation. Another major issue which most of the fossil-based plastics share is the greenhouse gas emissions generated during their production. Today, a small yet non-negligible amount (4-8%) of fossil resources is being consumed for plastic production. However, it has been predicted to contribute 15% of the total carbon budget by 2050 if the current approach to plastic production is not changed.⁴

To address these issues, many different strategies have been developed. However, this thesis will primarily focus on developing new biobased monomers for polyester synthesis and the chemical recycling of these polymers.

1.1 Biobased plastics

Biobased plastics produced from biomass can tackle the serious environmental concerns of fossil-based plastics. The use of renewable chemicals lowers the fossil resources dependency of plastic production.^{5,6} Additionally, biobased plastics can have a carbon-neutral cycle; the CO₂ released in the atmosphere upon their degradation or decomposition can be taken up by plants in the process of photosynthesis to produce biomass again.⁷ Furthermore, some classes of biobased plastics (e.g., aliphatic polyesters) break down naturally into non-hazardous materials.⁸ Despite these obvious advantages, the current share of biobased plastics is around 2%, and the remaining is still fossil-based.⁹ Fossil resources have always been a predominant choice for plastic production due to the abundance and low cost of crude oil.¹⁰ Furthermore, decades of innovation have allowed the production of a huge library of building blocks from oil distillation and cracking, such as styrene,

ethylene, propylene, ethylene glycol, acrylates, terephthalic acid and more.^{11,12} However, fossil resources are non-renewable and are forecasted to deplete relatively soon if their extensive utilization for energy and material production continues. Additionally, the usage of fossil resources is associated with emissions and the generation of hazardous wastes, leading to serious environmental implications such as the greenhouse effect, atmospheric and water pollution, which may eventually cause major health issues.^{3,13,14} Moreover, the extreme volatility of the oil price is another significant disadvantage.¹⁵ Therefore, increasing concerns about the undesirable environmental and socioeconomic consequences of fossil resources have sparked a significant interest in using natural biomass as raw materials for plastic development.^{5,16,17}

Biomass is regarded as a pivotal carbon source of the future and it encompasses all the materials produced from microorganisms, fungi, plants or animals.¹⁸ The worldwide total annual biomass production is estimated to be more than 100 billion tons; such a substantial volume makes biomass a viable substitute of fossil fuels as a source of carbon for plastic production. Some of the biobased plastics are already being produced commercially today, mainly using first generation feedstocks. For example, sugar derived from corn starch is transformed into lactic acid monomer, which is then polymerized to produce polylactic acid (PLA).¹⁹ In addition, biobased polyethylene (bio-PE) is produced using ethylene monomer obtained from the dehydration of biobased ethanol derived from sugar (glucose from sugar cane).²⁰ Similarly, biobased polypropylene (Bio-PP) and poly(ethylene terephthalate) (Bio-PET) are also produced using sugar-derived monomers.^{20,21} However, the utilization of first generation food crops as a source for the plastic production has raised ethical concerns over the use of farm land and its potential impact on the food supply chain, although a very small portion of land is currently used for this purpose. For example, in 2021, less than 0.02% of existing agricultural land was used to produce all the bioplastic on the market (0.8 million tons), which is estimated to be still below 0.06% along with the projected growth of bioplastics production in the next five years.⁹ Yet, this value seems negligible compared to the enormous amounts of food waste generated globally, which is estimated to 30-40%. However, it is always advantageous to use the non-food competing resources for the sustainable future production of plastics. One of the most promising source is lignocellulose, which is abundant and readily available as a part of various waste streams of, e.g., agriculture, forestry, and the paper and pulp industry.^{22,23} However, the process for the production of chemicals from lignocellulose is more demanding than those of corn starch or sugars, particularly due to the challenges associated with the fractionation and depolymerization of lignocellulose. Nevertheless, intensive research in this area has already led to several new approaches towards the valorization of lignocellulose.^{24,25} Therefore, lignocellulose holds great potential as a renewable source of carbon to substitute fossil-resource in the near future.²⁶

1.2 Lignocellulosic biomass and inspired chemicals

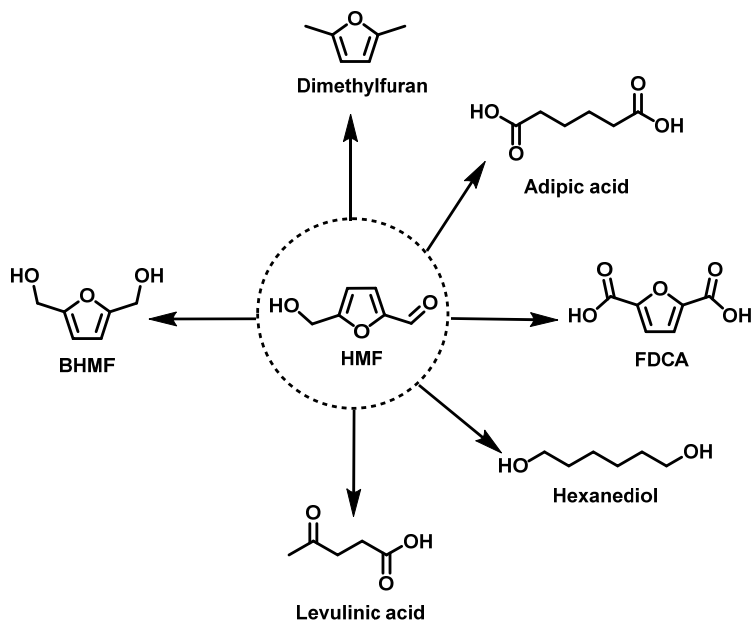
Lignocellulose is one of the most abundant renewable resources existing globally.^{17,26} Approximately 170 billion metric tons per year of lignocellulose are available globally. Lignocellulose mainly consists of cellulose (30–50 wt%), hemicellulose (20–40 wt%), and lignin (15–25 wt%), with the exact composition of each component depending on the feedstock.²⁷ Cellulose is a linear polymer of D-glucose units linked by β -1,4-glycosidic bonds, while hemicellulose is a branched heteropolymer consisting predominantly of pentoses (xylose and arabinose) and hexoses (glucose, galactose, mannose) linked together by different kinds glycosidic bonds. Lignin is a crosslinked amorphous polymer composed of phenylpropanoid monomeric units called monolignols, namely coumaryl alcohol, syringyl alcohol, and coniferyl alcohol.²⁸ Lignin imparts rigidity and recalcitrance to plant cell walls, which makes working directly with lignocellulose usually difficult.²⁹ Therefore, its fractionation into its components is required to provide access to the individual feedstock streams for a subsequent transformation into valuable products. Several methods of lignocellulose fractionation have been reported, and the choice of method is generally depending on the biomass feedstock and the target end products. Some of the common fractionation methods include acidic and alkaline hydrolysis, steam explosion, ammonia fiber explosion, supercritical CO₂ and its explosion, SO₂, hydrothermal pretreatment, organosolv processes, wet oxidation, ozonolysis, biological pretreatments, milling, and microwave irradiation.^{30–33}

Isolated lignocellulose fractions can be converted into a wide range of chemical products through (bio)chemical processes.²⁶ Since polysaccharides (cellulose and hemicellulose) constitute the major fraction (70–85 wt%) of biomass, they have been regarded as key renewable sources for targeted chemical valorization. The cellulose and hemicellulose fractions are hydrolyzed to respective C₆ (glucose) and C₅ (predominantly xylose) sugars, which serve as an intermediate for the production of various biobased building blocks such as 5-hydroxymethylfurfural or HMF, furfural, levulinic acid, and sugar alcohols such as sorbitol and mannitol.³¹ However, some processes directly produce these products in a single stage upon formation of the sugar. On the other hand, lignin has not been valorized to a similar extent as polysaccharides, mainly due to its structural diversity and recalcitrance nature.³³ It is often regarded as a low value by-product by the industries. Over 50 million tons of lignin is extracted annually by the paper and pulp industry, and almost 98% of it is burned as a fuel to power the pulping plant. Only 1 million tons of the isolated lignin is used to create value-added chemicals and products.^{30,34} Thus, lignin utilization is highly undervalued despite being one of the richest sources of aromatic compounds. This has developed increased interest recently in lignin valorisation into the chemical building blocks in order to harness its aromaticity.^{35,36} Lignin can be catalytically depolymerized by various processes such as hydrogenolysis, oxidation and alkaline oxidation to yield chemical building blocks to create

monomers for polymer development.³⁰ More specifically, the substituted phenols including, hydroxybenzaldehyde, hydroxybenzoic acid, vanillin, vanillic acid, syringaldehyde, and syringic acid obtained from the oxidative cleavage of lignin have gained particular attraction in the polymer synthesis.³⁷

1.2.1 5-Hydroxymethylfurfural (HMF)

HMF is a heterocyclic aromatic compound with aldehyde and alcohol functional groups. It has gained increasing interest recently due to its potential to serve as a platform chemical that can be converted into various useful chemicals for polymer production including, levulinic acid, hexanediol, adipic acid, furan dicarboxylic acid (FDCA), dimethylfuran, and bis(hydroxymethyl)furan (BHMF) (**Scheme 1**).³⁸ These biobased chemicals are potential replacements of currently used fossil-based monomers in plastic production. The most promising candidate is FDCA, which is obtained after the oxidation of HMF.³⁹ FDCA has been identified as one of the top 12 biobased platform chemicals by the US DOE. It holds significant potential to replace fossil-based terephthalic acid in PET production.^{40,41} As a result, FDCA-based polyesters have been investigated extensively in recent years. However, the production of HMF with high yields and selectivity is challenging, mainly due to the tendency of HMF towards further reaction and formation of unwanted by-products such as levulinic acid and humins.^{42,43} Furthermore, fructose is currently the only feasible carbohydrate source for HMF synthesis, and is more expensive than other carbohydrates like glucose or cellulose.⁴⁴ Conversion of glucose to HMF is more difficult and results in lower selectivity and yields than that of fructose. Additionally, it requires the isomerisation of glucose to fructose prior to the dehydration of sugar into HMF, making the production uneconomic. An alternative approach to avoid by-product formation in HMF production is to transform it in situ to a more stable analogue, i.e., 5-chloromethylfurfural (CMF), which can be easily prepared in high yields by reacting a wide range of carbohydrates with aq. HCl in dichloromethane.⁴⁵ It can then be converted into the HMF in high yields through a reaction with water or used as a platform for the production of the same chemical as obtained from HMF.⁴⁶ Furthermore, CMF can be transformed into the corresponding carboxylic acid or ester derivatives, which are promising building blocks to synthesize new monomers, *via* a simple and straightforward displacement of chlorine with functional phenols or alcohols.

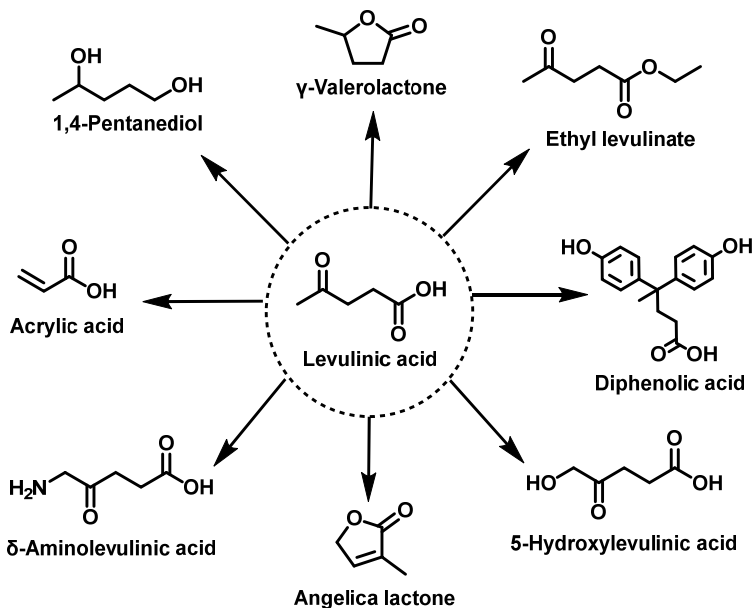


Scheme 1. Potential chemical building blocks derived from HMF.

1.2.2 Levulinic acid

Levulinic acid (LA) is a linear bifunctional molecule containing ketone and carboxylic acid groups. It is an important intermediate for value-added products used in a wide range of applications, such as fuel, additives, pharmaceutical intermediates, solvents, plasticizers, and polymers.⁴⁷ As a result, it has been regarded as one of the top 10 most promising biobased platform chemicals by the US DOE in 2004.⁴¹ LA can be produced by hydration of HMF or directly from sugars, cellulose and lignocellulosic biomass involving HMF formation as an intermediate step. Biofine Technology (Biofine process) and GFBiochemicals are the widely known commercial producers of biobased LA. GFBiochemicals produced LA with a capacity of 10 000 tons/year in 2017 and has planned the scaling up of the facilities for production up to 50 kta by 2025.⁴⁸ These commercial viabilities have promoted an intensive interest in developing LA-based monomers, including γ -valerolactone, acrylic acid, 1,4-pentanediol, angelica lactone, diphenolic acid, δ -aminolevulinic acid, and 5-hydroxylevulinic acid (**Scheme 2**).^{49,50} In addition to these, several other monomers have been prepared, particularly using levulinate esters such as methyl levulinate and ethyl levulinate.^{47,51,52} For example, a number of rigid (spiro)cyclic ketal-esters have been synthesized from levulinate esters and various polyols towards plasticizer preparation.⁵³ Additionally, these (spiro)cyclic ketal-esters were polymerized with various diols, which mainly

resulted in the formation of low molecular weight products. Therefore, a deeper exploration is necessary towards the utilization of these rigid building blocks in polymer synthesis, which would open a new door for the production of high-performance polymers.

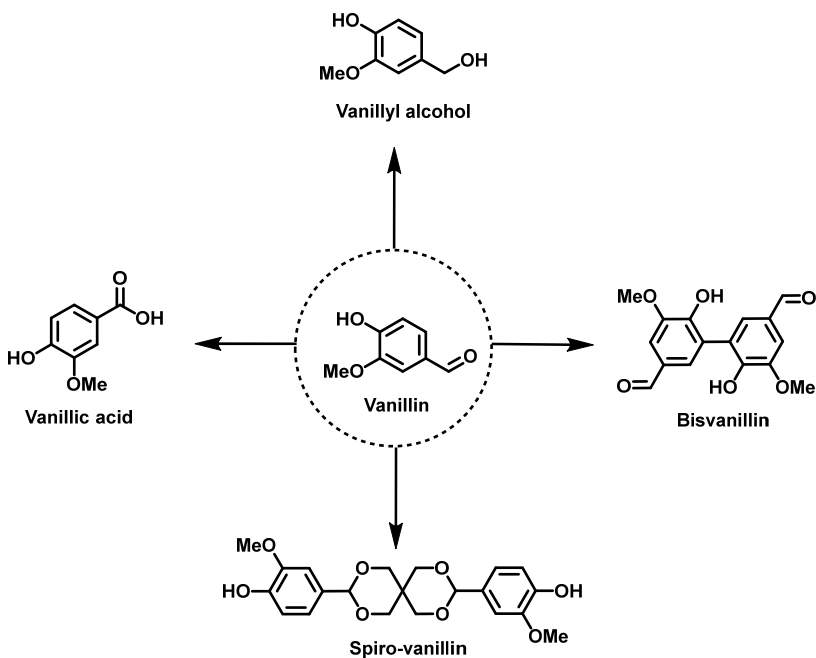


Scheme 2. Potential levulinic acid-based chemicals.

1.2.3 Vanillin

Vanillin is another important building block with a phenolic and an aldehyde group, primarily used as a flavouring agent in food, beverage and pharmaceutical products.^{30,54} It is the only compound which is commercially produced from lignin by the Norwegian company Borregaard, which accounts for ~15% of the global production of vanillin. The remaining percentage is derived from petroleum-based guaiacol.³⁷ Because of the aromatic structure and reactive functionalities, it has been used to produce various rigid monomers for polymer production (**Scheme 3**).^{37,55} Vanillin can be reduced to obtain vanillyl alcohol, which has been employed in polyester and polyurethane synthesis.^{56–58} Oxidation of vanillin leads to vanillic acid, which can be further transformed into dicarboxylic acid and diester monomers to prepare polyesters.^{59–61} Moreover, both vanillyl alcohol and vanillic acid can be functionalized into the diepoxide monomers *via* single-step glycidylation to produce epoxy thermosets.⁶² Bisvanillin monomer was prepared using an enzyme-catalyzed oxidative coupling of two vanillin molecules and was in the polyester synthesis after the functionalization of the aldehyde and phenolic group.⁶³ Vanillin has also been

reacted with various polyols to prepare the (spiro)cyclic vanillin monomers for degradable epoxy thermosets, polycycloacetals, and polyesters.⁶⁴⁻⁶⁷ For instance, a spiro-diol monomer was produced using vanillin and pentaerythritol and employed in copolyester synthesis.⁶⁸ Insertion of the rigid spiro-diol not only improved the physical properties of the polyesters but also facilitated recyclability through selective hydrolysis of the acetal groups.

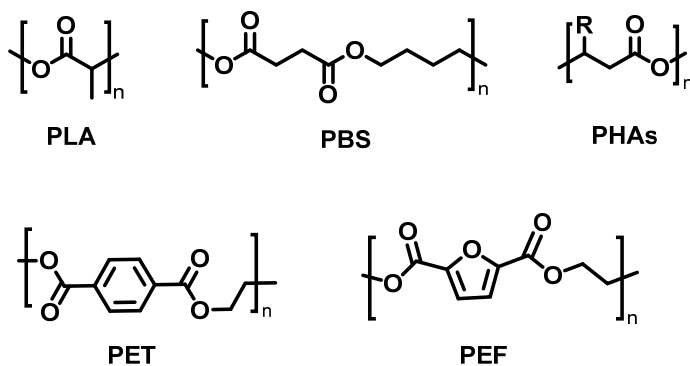


Scheme 3. Potential chemical building blocks derived from vanillin.

1.3 Polyesters

Polyesters are an extremely important class of polymers with applications spanning various sectors, owing to their versatile properties and chemical structures.⁶⁹ Polyesters can be classified as aliphatic or aromatic depending on the structure of the polymer backbone. Aliphatic polyesters are an important subclass of polyesters which can be conveniently produced using readily available biobased monomers from carbohydrates or sugars.⁷⁰ Additionally, the ester bonds in aliphatic polyesters are highly susceptible to hydrolytic degradation under both chemical and enzymatic action, characterizing them as a class of recyclable and (bio)degradable polymers.⁷¹⁻⁷³ Because of their biodegradable properties, they are often presented as a solution to the traditional non-degradable plastics that end up in nature through the leakage

of recycling systems, particularly those used in disposable single-use applications.⁷⁴ However, the natural biodegradation of aliphatic polyesters is generally slow, and it first leads to the generation of tiny microplastics that persist in nature for a long time before they can completely mineralise into CO₂ or CH₄.⁷⁵ In this regard, industrial composting of aliphatic polyesters is being adopted as an eco-friendly alternative to their natural degradation to still utilize the benefits of their biodegradability without harming the environment.⁷⁶ It involves an efficient microbial decomposition of plastics under controlled temperature, moisture, and aeration conditions. Currently, more than 25% of biobased polymers are aliphatic polyesters, although only a small fraction (~2%) of all plastics produced today are biobased.⁷⁷ Poly(L-lactic acid) (PLA), poly(butylene succinate) (PBS) and polyhydroxyalkanoates (PHAs) are notable examples of commercially produced aliphatic polyesters (**Scheme 4**). Among them, PLA is produced on a larger scale using lactic acid monomer obtained after the fermentation of corn starch biomass.¹⁹ Then follows PHAs and PBS. Due to their excellent biocompatibility and biodegradability, these polyesters have found extensive applications in the biomedical field, such as surgical sutures, dental implants, stents, bone screws, and controlled drug delivery systems.^{78,79} In addition, they are used in food packaging, textiles, agriculture mulching films and additive manufacturing (3D printing) applications.^{80,81} Although aliphatic polyesters are deemed suitable for various applications, their large-scale use as commodity plastics is still limited due to their poor thermal and mechanical properties. This has triggered an intense research interest to develop rigid biobased monomers for making aliphatic polyesters with improved thermo-mechanical properties.⁸²



Scheme 4. Examples of prominent aliphatic and aromatic polyesters.

In contrast to aliphatic polyesters, aromatic polyesters possess excellent thermal and mechanical properties due to the rigid aromatic units in their backbone.⁸² One of the most prominent example of aromatic polyester is poly(ethylene terephthalate) (PET) (**Scheme 4**), which constitutes almost 8% of all plastics produced annually and is used extensively in bottle and film packaging and textile fibres.⁸³ In addition, there

are commercial variants of PET, such as poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT), commonly found in textile applications and electronic and electronic components.^{84–86} However, one major drawback of these materials is the use of fossil-based terephthalic acid (TPA) in their production, which present them as environmentally unfriendly materials.^{6,87,88} Recently, linear diol comonomers, such as ethylene glycol, 1,3-propanediol, and 1,4-butanediol, have been produced from biobased resources and used to produce partly biobased aromatic polyesters. For example, the Coca-Cola company introduced a partially biobased PET bottle under the tradename of PlantBottle™ using biobased ethylene glycol.²¹ This bottle contains about 30% of bio-content while retaining the same properties as fossil-based PET bottles. On the other hand, the bio-replacement of terephthalic acid is more complex and still remains a challenge, although several approaches have been described for its biobased production. In 2015, Coca-Cola demonstrated the production of completely biobased PET using biobased TPA, but the product has not yet been commercialised.⁸⁹ In addition, several lab-scale synthesis methods have been reported to produce TPA from biobased isoprene, limonene, sorbic acid, furfural, 5-hydroxymethylfurfural, and dimethyl furan.^{90–95} Due to multi-step synthesis and tedious purification protocol involved, these processes are still far from meeting the industrial standards required to compete with conventional petrochemical method. To tackle this problem and produce aromatic polyesters sustainably, the bio-advantage strategy has been investigated, where 2,5-furan dicarboxylic acid (FDCA) has been developed as a potential substitute for TPA in the PET to yield a 100% biobased polyester called poly(ethylene 2,5-furandicarboxylate) (PEF) (**Scheme 4**).^{40,96} PEF possesses a higher T_g , lower melting point, and superior barrier properties compared to PET.⁹⁷ These advantages may offset the higher cost of FDCA and potentially promote the market adoption of this new monomer.⁹⁸

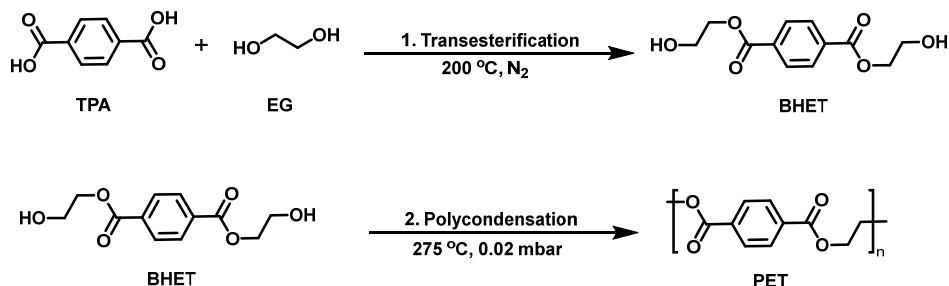
1.3.1 Synthesis

Polyesters can be produced by a polycondensation of diacids or diesters with diols, by self-polycondensation hydroxycarboxylic acids or by employing ring-opening polymerization of lactones or lactides.

Polycondensation

It is a step growth polymerization and most common industrial synthesis method of polyesters which is generally performed *via* a two-step procedure. A typical synthesis of commercial polyester polyethylene terephthalate (PET) is done by polycondensation of terephthalic acid (TPA) or dimethyl terephthalate (DMT) with excess of ethylene glycol (**Scheme 5**). The first (trans)esterification step is carried out at 200 °C under inert conditions to produce bis(2-hydroxyethyl) terephthalate (BHET) intermediate, in the presence of a metal catalyst. Then, temperature is

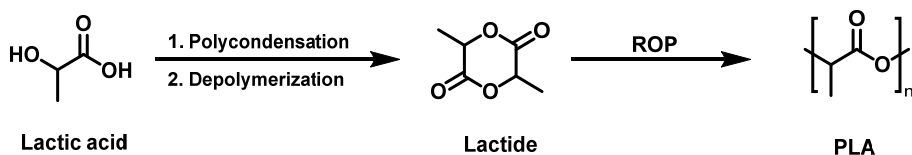
gradually increased to 275 °C and the pressure is reduced to <0.02 mbar to produce high molecular weight polymer during the polycondensation step. The high temperature is necessary to remove the water and lower the viscosity of the melt, as PET has a melting point of 250 °C.⁹⁹ Other polyesters, such as PEF, PBT, and PBAT, are also synthesized using a similar method.^{100–102} Melt polycondensation is the most preferred method for laboratory-scale polyester synthesis, as it closely resembles the industrial process for producing PET. DBTO and titanium-based catalysts are frequently used in these syntheses.^{103–105} In industrial PET production, antimony trioxide (Sb₂O₃) is typically employed as a catalyst.¹⁰⁶



Scheme 5. Synthesis of PET using a two-step melt polycondensation of terephthalic acid and ethylene glycol.

Ring opening polymerization (ROP)

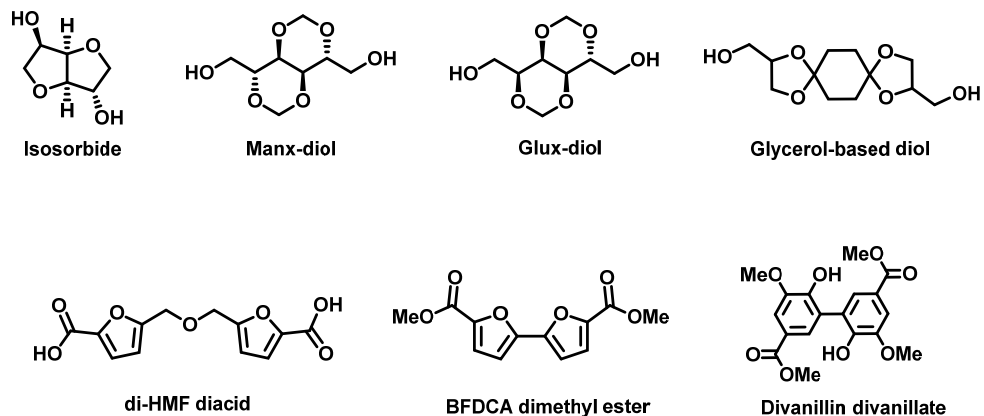
ROP is a form of chain-growth polymerization, in which the terminus of a polymer chain attacks cyclic monomers to form a longer polymer. It offers an alternative to step growth polymerization for the synthesis of high molecular weight polymers at relatively milder conditions.^{107,108} In addition, the molecular weight of polymers can be controlled by changing initiator to monomer ratio. Still, ROP of polyesters is not widely adopted in industry, probably due to the tedious procedure and high cost related to the synthesis of cyclic monomers. Polylactic acid (PLA) is an example of polymers synthesized using ROP of cyclic diester i.e., lactide (**Scheme 6**).¹⁰⁹



Scheme 6. Synthesis of PLA by ROP of lactide obtained from lactic acid.

1.3.2 Recent developments

The recent interest in polyester synthesis has focused on the development of high-performance polyesters with superior thermal and mechanical properties and improved recyclability *via* the bio-advantage strategy.¹¹⁰ In this regard, rigid cyclic monomers have attracted significant attention due to their ability to restrict conformational flexibility and hence increase the polymer chain stiffness, which consequently results in polymers with improved thermo-mechanical properties. Several fossil-based monomers have been utilized for this purpose. For example, the rigid diol 1,4-cyclohexanedimethanol (CHDM) has been utilized as a comonomer to produce a PET-like polyester (PETG) with a higher T_g and alkaline resistance than PET.¹¹¹ Another cyclic diol, *cis/trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), has been used to prepare polyesters with high impact resistance and superior optical clarity.¹¹² Eastman Chemical company produces a commercial high-performance amorphous polyester (Tritan™) using both CHDM and CBDO.¹¹³ However, the fossil-based nature of these monomers has promoted an interest to look for alternative monomers from biomass resources. One significant development in this direction is a partially biobased rigid diol with a spirocyclic acetal structure introduced by Perstorp AB to produce polyesters with high transparency and heat resistance ($T_g > 100$ °C) for hot-filling applications.¹¹⁴ Isosorbide is a commercially available sugar-based bicyclic rigid diol extensively used to enhance T_g values of polyesters (**Scheme 7**).¹¹⁵ Inspired by this example, numerous studies concerning the development of biobased alicyclic/rigid monomers have been carried out, particularly using sugar-based building blocks. For example, two bicyclic diols derived from D-glucose (Glux-diol) and D-mannose (Manx-diol) were polymerized with various linear aliphatic dicarboxylates to obtain high T_g polyesters.¹¹⁶ These diols were also investigated in copolymerizations with dimethyl succinate and dimethyl terephthalate with various diols to produce copolyesters with improved T_g s.^{104,117–119} Several other sugar-based molecules such as galactaric acid, tartaric acid, and threitol were converted into rigid cyclic and bicyclic monomers by acetalization reaction and used to prepare polyesters.^{120–126} Besides improving thermo-mechanical properties, the cyclic sugar moiety in the polymer chain enhances its susceptibility to hydrolysis and biodegradation.^{122,127} In addition to cyclic and bicyclic structures, several spirocyclic monomers have been reported lately. A spirocyclic diol obtained by acetalization of 5-hydroxymethylfurfural (HMF) and biobased pentaerythritol was employed as a comonomer in the preparation of polyesters and poly(urethane-urea)s, the resulting polymers showed an increase in T_g values with the content of spiro-diol.¹²⁸ In addition, various spiro-diol based on glycerol and citric acid have been reported to prepare polyesters and other condensation polymers.^{105,129,130}



Scheme 7. Biobased rigid alicyclic and aromatic monomers.

Although FDCA-based PEF is forecasted to replace PET in the market, it is yet to arrive. Therefore, in the meantime, the development of new biobased aromatic diacids or dicarboxylates is being researched. Several lignocellulose-based aromatic monomers have been studied (**Scheme 7**). For example, a two-step catalytic synthesis of a difuranic-diacid was reported for the polyester synthesis, which was received after the oxidation of di-HMF intermediate obtained from D-fructose.¹³¹ Recently, a furfural-based bifuran diacid (BFDCA) has been prepared as a renewable substitute of fossil-based biphenyldicarboxylic acid (BDA) used to improve PET properties.¹³² The polymerization of its corresponding methyl diester with ethylene glycol resulted in polyester PEBF with glass transition (107 °C) and melting temperature (240 °C) higher than that of PEF and PET due to the more stiff nature of the bifuran moiety in the polymer.¹³³ Moreover, the excellent barrier and UV-blocking properties of PEBF over PET made it deem as a suitable packaging material. In addition, the BFDCA diester has been utilized to produce several other polyesters and copolyesters with improved properties.^{134–137} Further bisfuranic diesters and diols with different bridge linkages between the furan rings have been reported for polyester preparation.^{138–143} In addition to the sugar-based furanics, lignin-derived aromatics have also been studied to develop monomers for polyester synthesis, particularly vanillin, and its corresponding acid derivative (vanillic acid) have been investigated extensively. For example, vanillin was converted into acetyldihydroferulic acid monomer in a two-step synthesis, and the polymerization of this A-B monomer gave polyester poly(dihydroferulic acid) (PHFA) with a glass transition temperature (T_g) of 73 °C and a melting temperature (T_m) of 234 °C, closely mimicking PET.¹⁴⁴ Several vanillic acid-derived hydroxyacid monomers (A-B type) were prepared by reactions with various chloroalcohols, which were then polymerized to obtain the corresponding poly(alkylene vanillate)s.^{145–149} Among them, poly(ethylene vanillate) (PEV) demonstrated comparable thermal and mechanical properties to PET, and was hence presented as a potential replacement

of PET.¹⁴⁵ Apart from hydroxyacid monomers, vanillin and vanillic acid were also used in the synthesis of various diacids and dicarboxylates.^{61,63,150,151} Particularly the symmetrical biphenyl monomers, namely methylated divanillyl diol and methylated dimethylvanillate dimer were able to yield high T_g polyesters owing to the rigidity of the biphenyl structure.^{63,151}

1.4 Recycling

In conjunction with developing plastics from biomass, their recycling is equally important to mitigate the environmental impacts such as plastic littering and pollution. Today, a gigantic amount of plastic waste is being generated due to growing use of plastics in different sectors, of which only 10% is recycled, while the remaining is incinerated to recover the energy or buried in the landfills.¹⁵² Incineration of plastics normally generates toxic and unsafe gases in the atmosphere while possessing low energy recovery efficiency. On the other hand, landfilling usually leads to no degradability or the extremely slow degradation of most plastic wastes. Therefore, plastic recycling is only a sustainable way to deal with the plastic waste issue.

Plastic waste is often a mixture of different polymers.¹⁵³ Hence, it needs to be cleaned and sorted before recycled by various methods such as mechanical recycling, chemical recycling by pyrolysis, solvolysis, or hydrolysis, and biological recycling by enzymatic degradation and biodegradation.¹⁵⁴ Among these, mechanical recycling is the most commonly adopted method industrially. It requires reprocessing of sorted polymer waste by melting and reshaping into the new plastic products. Since it involves no re-polymerization, it is energetically and economically viable. However, a significant disadvantage of this method is the decrease of molecular weight of the polymers during the reprocessing due to thermal degradation at high temperatures. This results in the lower quality of the recycled material. Consequently, the plastic waste is down cycled and used for lower-end applications.^{153,154} Another challenge in this method is the recycling of coloured polymer products, which suffer from poor market acceptance and consequently end up in the incineration or landfills.

When plastic is no longer acceptable for mechanical recycling due to considerably deteriorated quality and the presence of undesired additives, chemical recycling is a promising option.¹⁵⁵ In chemical recycling, polymers are broken down into the starting monomers/building blocks or oligomers, which can then be repolymerized to same or new polymer.¹⁵⁶ Chemical recycling can be done using various approaches, such as pyrolysis, solvolysis and acid/base hydrolysis.¹⁵⁷ Pyrolysis involves heating polymer wastes to high temperatures, typically ranging from 500 to 900 °C, which effectively converts polymer back into crude oil that can serve as

raw materials for plastics and other chemicals.¹⁵⁸ The main disadvantage of this method is the use of extremely high temperatures and the formation of complex chemical mixtures. On the other hand, in solvolysis, the polymers are depolymerized to the monomers by selectively breaking down the weak bonds (ester or acetal and ketal) by reaction with a solvent, which is frequently water, methanol or ethylene glycol. The regenerated monomers can then be used to make same polymer without extensive purification requirements.^{159,160}

Polyesters are attractive candidates for solvolysis, in which the ester group can be cleaved by either acidic/alkaline or enzymatic hydrolysis, methanolysis or glycolysis to form the corresponding monomers and oligomers.¹⁶¹ The solvolysis of PET has been thoroughly studied. It can be hydrolyzed using acidic and basic conditions to the terephthalic acid and ethylene glycol.^{162,163} However, the process requires highly acidic/basic solutions and elevated temperature and pressures, which is a significant drawback of this method despite being cost-competitive. The main reason behind the use of such harsh conditions is related to the high hydrophobicity and degree of crystallinity of PET, leading to a slower degradation. One strategy to enhance the hydrolysis rate of PET or aromatic polyesters is to insert chemically labile units such as acetal or ketal structures in the polymer chain, which being more prone towards hydrolysis than the ester group can cause an efficient fragmentation of the polymer chain into small oligomers.¹⁶⁴ These shorter oligomers chains can degrade faster due to the reduced hydrophilicity and steric hindrance for water molecules reaching the ester group. Methanolysis of PET is another common method to depolymerize PET into dimethyl terephthalate and ethylene glycol. Still, it involves use of high temperature (200-300 °C) and pressures similar as hydrolysis to depolymerize PET completely.^{165,166} High monomer recovery is however an advantage of this method. Glycolysis of PET is another method similar to methanolysis, in which ethylene glycol is used instead of methanol to give back the bis(hydroxyethyl) terephthalate intermediate used in conventional polyester production.^{167,168} However, the product is often mixed with oligomers, which makes the purification challenging.

All of the above-described methods have been employed commercially for the chemical recycling of PET waste.¹⁵⁹ However, large-scale recycling is still restricted due to the uneconomic and energy intensive nature of these processes. Additionally, the consumption of large amounts of chemicals and generation of huge quantities of waste are other problems. Therefore, alternative methods are being investigated to depolymerize the polyesters under milder conditions. In this context, enzymatic or biological recycling has gained particular attention as it uses lower pH and temperature to break the bonds in polymers. Although the concept of enzymatic recycling of PET has been known since 2005, the boost in this area took place in 2016 after a breakthrough discovery by a Yoshida et. al., who reported that an enzyme found in a bacterium *Ideonella sakaiensis* 201-F6 could effectively break PET into monomeric and intermediate products such as TPA, mono(2-

hydroxyethyl) terephthalic acid (MHET) and BHET.¹⁶⁹ Since then, several other enzymes have been discovered to degrade PET or other polymers.¹⁷⁰⁻¹⁷² In fact, the biological recycling of PET appears to be close to implementation on a commercial scale, although more research is still required to ensure the industrial scalability and energy efficiency of the process.^{173,174}

As discussed above, chemical recycling is often breaking polymers into small molecules or monomers, which leads to the loss of initial chemical bonding energy, making it both environmentally and economically undesirable. A new chemical recycling strategy has emerged that involves partially breaking the chemical bonds in the polymer backbone to produce telechelic oligomers/polymers with functional end groups and then converting them back to polymers by reforming only a small number of chemical bonds.¹⁷⁵ This telechelic approach of recycling is proposed as a more energy efficient and shorter loop than conventional chemical recycling since only fewer bonds are broken and reformed during the recycling. Strategically incorporating weak bonds or units in the polymer structure provides the possibility of recycling *via* telechelic polymers. For example, polystyrene and polypropylene with cleavable thionolactones or ester links have been reported to recycle by telechelic polymers.^{176,177} Polyesters containing cleavable spiroacetal structures have been recycled using similar approach.⁶⁸ Therefore, incorporating chemically sensitive bonds as weak links in the polymer backbone is an attractive strategy towards more energy efficient chemical recycling of polymers *via* the telechelic polymer approach.

2 Experimental work

2.1 Monomer synthesis

2.1.1 Ketalization

In paper 1 and 2, ketones such as ethyl levulinate and ethyl acetoacetate respectively, were reacted with the tetraol pentaerythritol using an acid catalyzed ketalization reaction. The reactions were performed at 120 °C for 4 h under high vacuum, and involved solvent-free conditions. However, an excess of ketone reactants was employed to facilitate the azeotropic removal of the by-product water to drive the reaction forward. This gave monomers in ~65-74% isolated yields after simple extraction using heptane.

2.1.2 S_N2 nucleophilic substitution

In paper 4 and 5, the monomers were prepared by an S_N2 reaction between phenol and an organic halide. The reactions were carried out at room temperature using K₂CO₃ as base and dimethyl sulfoxide (DMSO) as solvent. The crude products were obtained after quenching the reaction mixture by adding water were purified by straightforward recrystallization in ethanol or acetone to obtain the pure monomers in reasonably high yields.

2.2 Polymer synthesis

2.2.1 Polyesters

Conventional melt polymerization is the most adopted method for the synthesis of polyesters. It involves two steps, i.e., (trans)esterification and polycondensation. The first step is performed under nitrogen environment to form oligomers and during second the step a high vacuum is applied to build up high molecular weight polymers by removing the excess diols. Due to issues with volatility and sublimation of some of the diols, conventional melt polymerization was only used in paper 3. In

paper 1, 2, 4, and 5, a modified melt polymerization was used to produce the polyesters, in which small amounts of solvents was used. Xylene was added during the transesterification step to avoid loss of the diols *via* evaporation or sublimation, while mesitylene was added during polycondensation, which facilitated the increase of the molecular weight by removing excess diol azeotropically. In all the papers, DBTO was used as catalyst and an excess of diol was employed to compensate for any loss. The reaction temperatures and times for the polymerizations described in each paper vary from monomer to monomer.

2.2.2 Polyketalization

Ketone-terminated telechelic oligomers in paper 3 were polymerized with pentaerythritol in melt state *via* cycloketalization reaction to recover the original copolyesters with spirocyclic ketal units. The reaction was performed at 170 °C for 3 h using high vacuum to remove the water formed.

2.2.3 Chain extension

In paper 5, telechelic polyesters with ketone end groups were chain extended with adipic acid dihydrazide. The reactions were performed at 75-130 °C under nitrogen using dry DMSO.

2.3 Characterizations

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

The molecular structure of monomers and polymers was confirmed using ¹H and ¹³C NMR measurements performed on a Bruker DR X400 spectrometer at 400.13 MHz and 100.61 MHz, respectively. Chemical shifts were reported as δ values (ppm). A Micromass QTOF mass spectrometer (ESI) was used for determining the exact mass of the monomers. The molecular weights of the polyesters in paper 1 were determined by size exclusion chromatography (SEC) in THF. The SEC setup included three Shodex columns coupled in series (KF-805, -804, and -802.5) in a Shimadzu CTO-20A prominence column oven, a Shimadzu RID-20A refractive index detector, using the Shimadzu LabSolution software. All samples were run at 40 °C at an elution rate of 1 mL min⁻¹. Calibration was done by using poly(ethylene oxide) standards ($M_n = 3.86, 12.60, 49.64$ and 96.1 kg mol⁻¹). The SEC measurements for the polyesters in paper 2 and 4 were carried out using the Malvern OMNISEC instrument equipped with one TGuard, Org Guard, col 10 × 4.6 mm as a guard column, 2 × T6000M, general mixed Org. 300 x 8.0 mm as an analytical

column, and refractive index (RI) detector and THF as eluent at 40 °C at an elution rate of 1 mL min⁻¹. Calibration was performed with narrow polystyrene standards ($M_n = 96, 52.4, 30, 17.5, 3.5$ and 3.0 kg mol^{-1}). The intrinsic viscosity ($[\eta]$) of the polymers in paper 3 and 5 was measured at 25 °C by using an Ubbelohde viscometer. Dried polymer samples were weighed before being dissolved in the solvent. The efflux time of the sample solutions with four different concentrations through the capillary was measured four times. The intrinsic viscosity ($[\eta]$) was calculated by extrapolating η_{red} and η_{inh} to $c = 0$, and their intersection value with the y-axis was taken. TGA was performed on a TA Instruments model Q500 TGA system. The samples were heated from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Thermal decomposition temperatures ($T_{\text{d}s}$) were determined at the maximum decomposition rates. $T_{\text{d},5}$ is the temperature taken at 5% weight loss, and the char yield is the remaining weight % at 600 °C. DSC measurements were performed on a DSC Q2000 analyzer from TA Instruments. Glass transition temperatures ($T_{\text{g}s}$), melting temperatures ($T_{\text{m}s}$) and heats of fusion ($\Delta H_{\text{m}s}$) were determined from the second heating cycle. The crystallization temperature (T_{c}) was measured from the DSC cooling curve. DMA measurements were performed in tensile mode using a TA Instruments Q800 analyzer. The samples (17.5 mm between the clamps) were heated at a heating rate of 3 °C min⁻¹ and a frequency of 1 Hz with a constant strain of 0.1%. Rheology measurements were carried out on an Advanced Rheometer AR2000 ETC from TA Instruments, using parallel plates with a diameter of 15 mm under air. The time sweep experiment was performed constant strain (1%) and oscillation (1 Hz) for 25 min.

3 Scope and context

The scope of this thesis is exclusively focused on biobased polyesters, and it aims to provide a comprehensive understanding of the molecular design, synthesis, properties, and recyclability of new biobased polyesters. Several monomers have been synthesised by utilizing lignocellulose-based building blocks and employed in the preparation of these polyesters. The resulting materials were investigated regarding their molecular and physical properties, as well as their chemical recyclability.

Papers 1 and 2 were focused on the preparation of aliphatic polyester from rigid diester monomers. In paper 1, ethyl levulinate was reacted with pentaerythritol through a ketalization reaction to synthesize a rigid spirocyclic diester monomer with ketal units. A preliminary life cycle assessment (LCA) indicated a lower CO₂ emission for the monomer synthesis compared to biobased succinic acid and adipic acid. This spiro-diester monomer was then used in melt polycondensations with various diols to produce fully aliphatic polyesters, which showed increasing T_g s with the rigidity of the diols. In paper 2, another spiro-diester monomer was prepared by reacting ethyl acetoacetate and pentaerythritol in a similar manner as for the spiro-diester in paper 1. The polyesters made from this monomer showed slightly improved T_g s compared to those in paper 1.

In paper 3, two series of copolyesters were prepared by incorporating the spiro-diester described in paper 1 into the structures of benchmark FDCA-based polyesters (PBF and PHF). The copolyesters showed almost comparable thermal and mechanical properties to their corresponding homopolyesters when small percentages of the spiro-diester was incorporated. Acid-catalyzed cleavage of ketal groups in the copolyesters resulted in accelerated hydrolysis into the starting building blocks in comparison with the long chain homopolyesters, indicating an improved recyclability of FDCA-based polyesters. Additionally, the selective cleavage of the ketal units produced ketone-terminated telechelic oligomers, which were subsequently repolymerized back to the original polymer structures. This demonstrated the closed-loop recycling of the polyesters *via* an energetically more favourable method compared to conventional chemical recycling to monomers.

Paper 4 and 5, were focused on the synthesis of aromatic polyesters using dicarboxylate monomers derived from lignin- and sugar-based chemicals. In paper 4, a series of di-aromatic dicarboxylate monomers were produced by reacting sugar-

based methyl 5-chloromethyl-2-furoate with lignin-based hydroxybenzoates. These monomers were used to prepare two series of polyesters which were completely amorphous in nature and some of them showed comparable T_g s to that of PET. In paper 5, the same sugar-based methyl 5-chloromethyl-2-furoate was used as a starting material to prepare tri-aromatic dicarboxylate monomers by combination with potentially biobased dihydroxy benzenes. Using these monomers, polyesters were synthesized while strategically incorporating acylhydrazone units as weak links in the polymer backbone. Some of these polymers were semi-crystalline due to the symmetrical nature of the polymer chain. In addition, the selective cleavage of the acylhydrazone bonds yielded telechelic polyesters with ketone end groups, which were subsequently coupled together in a chain extension reaction with dihydrazide to recover the original structure.

4 Summary of appended papers

4.1 Rigid spirocyclic dicarboxylates for aliphatic polyesters (Paper 1 and 2)

As mentioned in the introduction, while aliphatic polyesters offer a unique combination of sustainability and biodegradability, their application in various fields is limited due to their poor thermal and mechanical properties. One strategy to improve their properties is to enhance chain stiffness by incorporating rigid cyclic structures in the backbone. Several cyclic aliphatic monomers have been commercially utilized to produce terephthalate-based high-performance polymers (Tritan™, PETG, Akestra™). These polymers have a higher T_g than PET (85-120 °C), due to the partial replacement of flexible ethylene glycol with rigid cyclic diols. Among them, Akestra™ is produced using a partially biobased spirocyclic acetal diol and is marketed as a polymer for hot-filling applications. Inspired by the molecular design of this monomer, we have explored the synthesis of rigid spirocyclic dicarboxylate monomers using biobased building blocks and used them to prepare aliphatic polyesters.

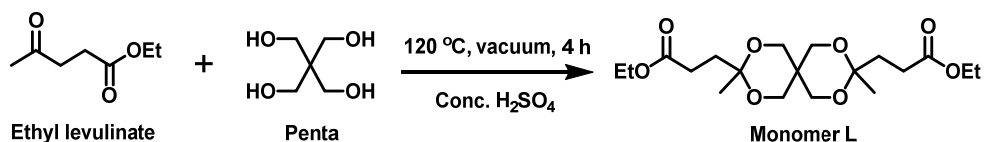
4.1.1 Polyesters from levulinic acid derived spirocyclic dicarboxylate (Paper 1)

In this paper, a new spirocyclic diester (Monomer L) with ketal functionality was synthesized using biobased ethyl levulinate (can be derived from esterification of levulinic acid or potentially from sugars and cellulose) and pentaerythritol and its polymerizability with different diols was investigated. In addition, a preliminary life cycle assessment (LCA) study was performed to evaluate greenhouse gas emissions (GHG) for monomer production.

Monomer synthesis and GHG emissions

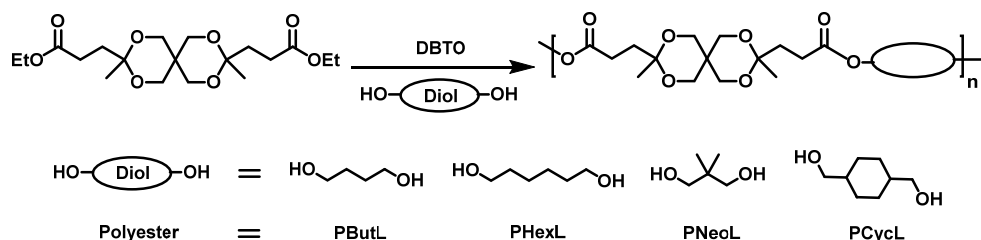
The spiro-diester (Monomer L) was synthesized in a single step by combining ethyl levulinate and pentaerythritol (penta) through an acid-catalyzed ketalization reaction (**Scheme 8**). The reaction was carried out at 120 °C for 4 h using conc. sulfuric acid as a catalyst and followed a green chemistry protocol involving

completely solvent-free conditions. However, an excess of ethyl levulinate (5.5-fold with regard to penta) was utilized to ensure complete ketalization and avoid transesterification side products. Meanwhile, it drove the ketalization reaction forward by removing the by-product water by forming an azeotrope. This facilitated a high conversion to ketal and resulted in a crude reaction mixture containing up to 95% of Monomer L and a small amount of partially ketalized product. However, only up to 74% of Monomer L was isolated in the pure state by a straightforward extraction using heptane as a solvent. More extraction resulted in Monomer L containing a partially ketalized product as an impurity. In any case, the straightforward synthesis and purification of Monomer L, together with the green nature of the reaction, would be favourable in a large-scale industrial production.



Scheme 8. Synthesis of Monomer L.

To investigate if the production of Monomer L is eco-friendly, we performed a preliminary cradle-to-gate life cycle assessment to estimate GHG emissions. Due to the unavailability of reasonable data for the GHG emission of ethyl levulinate production, we assumed an alternative synthesis approach for Monomer L. In this, we first considered the preparation of the diacid form in a reaction of levulinic acid and penta, followed by a subsequent esterification using ethanol to obtain Monomer L. The GHG emission calculated after accounting for the contributions from all the reactants and synthesis steps gave a low value of 2.50 kg CO_{2eq} per kg of Monomer L. The value for the diacid form was 2.34 kg CO_{2eq} per kg in its production, which was comparatively lower than biobased succinic acid and adipic acid. Therefore, the initial results indicated the tendency of Monomer L production to generate less CO₂ and be environmentally friendly. It should be noted that the LCA analysis was only aimed at obtaining an initial assessment of the environmental impact of Monomer L production. Hence, a deeper investigation is required to obtain more precise results, particularly focusing on the source and production of levulinic acid with a lower carbon footprint as it had the largest share in the GHG emission of Monomer L.



Scheme 9. Polycondensation of Monomer L with different diols.

Polyester synthesis and characterization

Monomer L was investigated in polymerizations with various aliphatic diols including 1,4- butanediol (1,4-BD), 1,6-hexanediol (1,6-HD), neopentyl glycol (NPG), and 1,4-cyclohexanedimethanol (1,4-CHDM) to obtain the polyesters PButL, PHexL, PNeoL, and PCycL, respectively (**Scheme 9**). Dibutyltin oxide (DBTO) was employed as a catalyst (0.5 mol% with respect to Monomer L). The polycondensations were carried out using optimized conditions obtained after a thorough stability evaluation of the monomer. This study indicated the necessity of carefully drying the reaction mixture to remove any moisture since it caused the degradation of Monomer L, which in turn led to crosslinked product. During the stability evaluation, the monomer was heated under nitrogen after the removal moisture, and then it showed almost no degradation up to 130 °C. This may be compared to the same sample without any pre-drying, which degraded even below 100 °C. This indicated that moisture-free conditions are crucial for the polymerization of Monomer L. Therefore, an azeotropic removal of traces of water in the reaction mixtures was performed before heating to 130 °C. The polymerizations were carried using conventional (under vacuum) and modified melt polycondensation methods. The modified melt polycondensation (under nitrogen) was particularly investigated for the preparation PNeoL and was later used for the preparation of PButL, PHexL, and PCycL in order to produce all the polymers using the same method, and to compare with the results from the melt polycondensations (PHexL and PCycL). During the synthesis of PNeoL *via* the conventional method, the loss of NPG was significant due to sublimation, which led to an incomplete transesterification. Therefore, in the modified method, a small amount of xylene was added during the transesterification step under a low nitrogen flow to reduce the loss of the diol. Moreover, in the polycondensation step (under high flow of nitrogen) mesitylene was added to facilitate the azeotropic removal of the diol to increase the molecular weight. SEC analysis of the polyesters prepared by the modified melt polycondensation showed the formation of reasonably high molecular weight polymers with M_n in the range 10.0-18.3 kg mol⁻¹ (**Table 1**). In addition, a molecular weight comparison of the polyesters (PHexL and PCycL) synthesized by both methods suggested that the modified melt polycondensation under nitrogen was

equally efficient to generate high molecular weight polymers as the conventional melt polycondensation using high-vacuum, since comparable molecular weights were obtained using both methods.

Table 1. Molecular, thermal, and mechanical properties of polyesters.

Sample	M_n^a (kg mol ⁻¹)	D^a	$T_{d,5}^b$ (°C)	T_g^c (°C)	E'_d (GPa)	T_g^e (°C)
PHexL	16	2.3	316	12	--	--
PButL	18	2.9	315	25	--	--
PNeoL	17	2.7	308	41	2.36	43
PCycL	10	2.0	318	49	1.91	48

^a Determined by SEC in THF. ^b The temperature at 5% weight loss measured by TGA under N₂. ^c Determined by DSC from the second heating scan. ^d Storage modulus taken at 20 °C. ^e Determined as the peak maximum in the loss modulus (E'') curve.

TGA measurements of the polyesters under nitrogen showed high thermal stability of the polymers with $T_{d,5}$ values exceeding 300 °C in all cases (**Table 1**). This suggested the possibility for the melt processing. DSC analysis revealed the amorphous nature of the polymers with T_g s increasing with increasing rigidity of the polymer backbone. The values were found in the range 12-49 °C, where the highest T_g of 41 and 49 °C were attributed to polyester PNeoL and PCycL, respectively (**Table 1**). Because their T_g s were above room temperature, they formed free-standing and transparent films which were investigated by DMA. Both PNeoL and PCycL showed a moderately high stiffness with storage moduli (E') of 2.36 and 1.91 GPa, respectively. The lower E' of PCycL compared to PNeoL may be related to its lower molecular weight. Furthermore, the T_g values taken at the local maximum of the loss modulus (E'') curve were quite closely comparable to those obtained by DSC.

Although the TGA data suggested that melt processing may be possible for the polyesters, melt processing also involves mechanical shearing of the melt in addition to the heat, which makes to conditions more severe for the polymer. Therefore, the thermo-rheological stability of hot-pressed samples of PNeoL and PCycL was investigated by performing dynamic melt rheological time sweep experiments. The results from the time sweeps carried out at 130 °C for 25 min (using a constant frequency of 1 Hz and strain of 1% within LVR) demonstrated high thermal stability of the polyester under melt shearing, as rheological parameters such as the shear storage modulus (G'), shear loss modulus (G''), and the phase shift (δ) stayed constant during the whole measurement time (**Figure 1**).

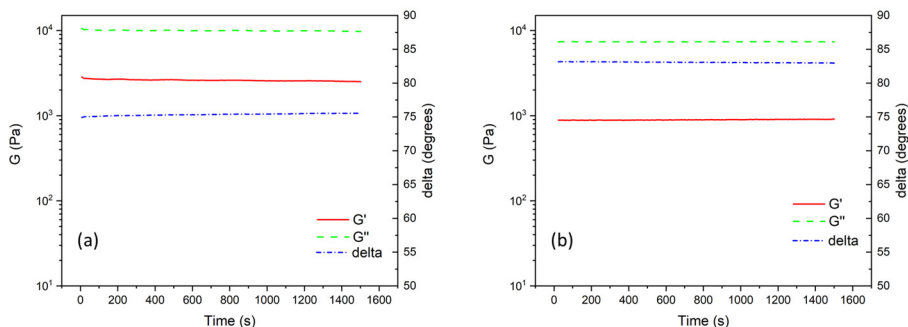


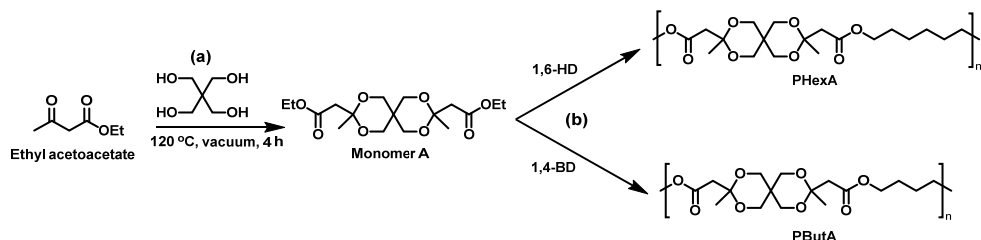
Figure 1. Dynamic melt rheology time sweep traces of PNeOL (a) and PCycl (b) at 130 °C (1 Hz, 1% strain).

4.1.2 Polyesters from ethyl acetoacetic acid derived spirocyclic dicarboxylate (Paper 2)

As discussed in paper 1, the T_g values of the polyesters derived from Monomer L were in the range of 12-49 °C. These values were still moderate despite the highly rigid spirocyclic ring in the polymer backbone. A possible reason for this observation is the presence of methylene groups (spacers) located between the spirocyclic rings and the ester groups. These flexible units partially mitigate the stiffening effect of the rigid spirocyclic rings, resulting in an overall reduction in the polymer chain stiffness and, consequently, the T_g . In this paper, a new spirocyclic diester (Monomer A) was synthesized with less methylene groups between the ester groups and the spirocyclic ring to study the effect of reduced methylene groups on the thermal properties of aliphatic polyesters.

Monomer and polyester synthesis

Monomer A was synthesized by using a similar protocol that employed for Monomer L in paper 1. This was achieved by reacting ethyl acetoacetate and pentaerythritol in a ketalization reaction catalyzed by sulfuric acid at 120 °C during 4 h (**Scheme 10a**). Notably, ethyl acetoacetate is a potentially biobased chemical, as it can be derived from ethanol obtained through sugar fermentation. In a similar manner to the synthesis of Monomer L, a 5.5-fold excess of ethyl acetoacetate with regard to pentaerythritol was used to ensure the complete conversion and facilitate the removal of by-product water by forming an azeotrope. After purification of the crude reaction mixture by extraction using heptane, Monomer A was obtained in a 65% isolated yield.



Scheme 10. Synthesis of Monomer A (a), and its subsequent polycondensation with 1,6-HD and 1,4-BD, respectively (b).

Subsequently, Monomer A was polymerized with two diols 1,6-HD and 1,4-BD, respectively, *via* a modified melt polycondensation method, similar to the procedure described in paper 1 (**Scheme 10b**). A 10 mol% excess of the diols was utilized to ensure complete transesterification. Prior to heating the polymerizations to 130 °C (in both steps), an azeotropic distillation of the reaction mixture was carried out using toluene to remove any traces of moisture that can potentially degrade the spirocyclic ketal units and induce gelation. The viscous reaction mixtures after the polymerizations were dissolved in chloroform, and the resulting products were precipitated in methanol to obtain the polyester PHexA and PButA with isolated yields of 79% and 68%, respectively. The molecular weights were measured by SEC analysis, resulted in values of 17 and 8.3 kg mol⁻¹ for PHexA and PButA, respectively, with corresponding dispersities of 2.2 and 3.0 (**Table 2**).

Table 2. Molecular and thermal data of polyesters based on Monomer A and L, respectively.

Sample	M_n^a (kg mol ⁻¹)	D^a	$T_{d,5}^b$ (°C)	T_g^c (°C)
PHexA	17	2.2	300	20
PButA	8.3	3.0	285	28
PHexL	16	2.3	316	12
PButL	18	2.9	315	25

^a Determined by SEC in THF. ^b The temperature at 5% weight loss measured by TGA under N₂. ^c Determined by DSC from the second heating scan.

Polymer characterization

The thermal properties of PHexA and PButA were investigated by TGA and DSC analysis, and the results were compared with those of PHexL and PButL derived from Monomer L. TGA measurements under nitrogen indicated reasonably high thermal stability of PHexA and PButA with $T_{d,5}$ values above 280 °C (**Table 2**).

However, these values were lower than the corresponding $T_{d,5}$ values of PHexL and PButL, despite the more rigid structure of PHexA and PButA.

DSC analysis confirmed the amorphous nature of the polyesters, with T_g values of 20 °C for PHexA and 28 °C for PButA (**Table 2**). PButA exhibited a higher T_g compared to PHexA due to the shorter 1,4-butylene chain in the backbone. The T_g values of PHexA and PButA were 3-8 °C higher in comparison to PHexL and PButL, highlighting that reducing the number of methylene units between the spirocyclic rings and the ester groups decreased the conformational flexibility of the polymer backbone. However, this difference was quite small for PButA, which showed an increase in T_g of only 3 °C in relation to PButL. In fact, this is almost within the error of the method. PHexA exhibited a slightly noticeable increment of 8 °C, most likely due to its higher molecular weight than PButA. Therefore, the results indicated that the overall chain flexibility of the polyesters was largely dominated by the high flexibility of the diol segments, making the impact of the methylene groups between the ester groups and spirocyclic rings relatively marginal. Thus, the number of these methylene groups is likely to be a significant factor mainly in cases where more rigid diols are employed as a comonomer.

4.2 Improved recyclability of 2,5-furandicarboxylate polyesters (Paper 3)

Although 2,5-furandicarboxylic acid-based polyesters have gained attention as a renewable alternative to those based on fossil-based terephthalic acid, they still have a similar strong resistance against hydrolysis as the terephthalic acid-based ones. The main reason behind their lower hydrodegradability is related to the high crystallinity and hydrophobicity of these aromatic polyesters, hindering efficient water penetration into the polymer matrix to make chemical recycling difficult. Therefore, in this paper, we have focused on improving the recyclability of FDCA-based polyesters by incorporating acid-sensitive ketal units as weak links in the polymer structure. The spirocyclic ketal diester (Monomer L) from paper 1 was used for this purpose and was incorporated in various proportions into the structures of two FDCA-based polyesters, poly(butylene 2,5-furandicarboxylate) (PBF) and poly(hexamethylene 2,5-furandicarboxylate) (PHF), respectively. The choice of Monomer L was primarily due to its completely renewable nature, as it was derived from biobased ethyl levulinate and pentaerythritol. Second, its incorporation into the structure of aromatic polyester will introduce readily cleavable ketal units in the polymer backbone that can lead to the efficient chain scission of the longer polymer into the shorter oligomers when subjected to acid-catalyzed degradation. Subsequently, the shorter oligomer can degrade faster into the monomers/starting building blocks compared to the longer chains due to the reduced hindrance for

TGA measurements under nitrogen suggested a reasonably high thermal stability of the copolyesters with $T_{d,5}$ above 290 °C in all the cases (**Table 3**). The $T_{d,5}$ values decreased with increasing contents of the spiro monomer in both series, presumably due to the aliphatic nature of this monomer. According to DSC data, the melting temperature (T_m) and melt enthalpy (ΔH_m) values of the copolyesters in both series decreased with increasing contents of the spiro monomer. This revealed that the incorporation of rigid and non-planar spiro monomer efficiently suppressed the crystallization in the copolyesters by disrupting any regular close-packing of the polymer chains. In both series, only the copolyesters containing 5 and 10% of spiro monomer could crystallize from the melt. Hence, the small melt endotherms observed for other copolyesters (i.e., PBLF-15 and PHLF-12.5-20) mainly the result of cold crystallizations during the heating scan. However, when these polymers were annealed 10-15 °C below their T_m , a significant enhancement of their melt enthalpies and T_m s was observed because under these conditions the chains had sufficient mobility and time to crystallize more effectively. Still, the appearance of broad endotherms with shoulders implied the presence of different crystallite populations. This was in contrast to the polyesters PBF, PHF, PBLF-5-10 and PHLF-5-10, which crystallized from the melt and displayed comparatively narrow and sharp melting endotherms to hint the presence of nearly homogenous crystallites. Similar to what was observed with T_m and crystallinity, the spiro monomer incorporation in the polyesters also decreased their T_g due to the less rigid nature of spiro monomer than the stiff 2,5-furan dicarboxylate monomer. However, the effect was quite small as only a 4-5 °C reduction of T_g was observed. DMA data showed no particular influence of the spiro monomer content on the stiffness. The E' values (taken at 0 °C) for polyesters in the PBLF and PHLF series were in the narrow range of 2.0-3.0 and 2.3-2.5 GPa, respectively (**Table 3**). Both the E' and T_g values of the copolyesters were quite comparable to their corresponding homopolyesters. This suggested that the incorporation of the spiro monomer yielded copolyesters without a significant trade-off of thermal and mechanical properties of homopolyesters. However, they contain the labile ketal units to favour the hydrolysis for chemical recycling.

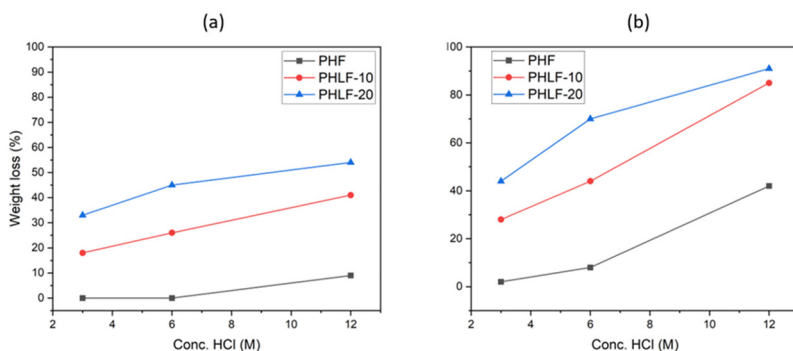
Table 3. Molecular, thermal, and mechanical properties of PBLF and PHLF copolyesters.

Sample	$[\eta]^a$ (dL g ⁻¹)	$T_{d,5}^{b}$ (°C)	T_g^c (°C)	T_m^c (°C)	ΔH_m^c (J/g)	T_c^d (°C)	T_g^e (°C)	E' (GPa) ^f
PBF	1.04	342	39	168	33	104	51	2.71
PBLF-5	0.57	313	37	165	36	113	41	3.04
PBLF-10	0.47	306	34	158	29	99	39	2.31
PBLF-15	0.57	294	34	150	2	--	34	2.67
PBLF-20	0.72	294	34	--	--	--	29	2.03
PBLF-50	0.50	291	28	--	--	--	--	--
PHF	0.94	335	17.5	143	42	94	27	2.33
PHLF-5	0.64	317	13	136	46	73	26	2.39
PHLF-10	0.66	310	12.5	129	38	67	25	2.36
PHLF-12.5	0.64	308	13	125	16	--	23	2.51
PHLF-15	0.57	308	13.5	122	4	--	24	2.32
PHLF-20	0.58	308	13	118	0.4	--	--	--

^a Intrinsic viscosity $[\eta]$ measured in HFIP at 25 °C. ^b Determined by TGA at 5% weight loss under N₂. ^c Determined by DSC from the second heating scan. ^d Measured from the first DSC cooling scan. ^e Determined at the peak maximum in the E'' curve. ^f Storage modulus taken at 0 °C.

Analysis of hydrolytic degradation

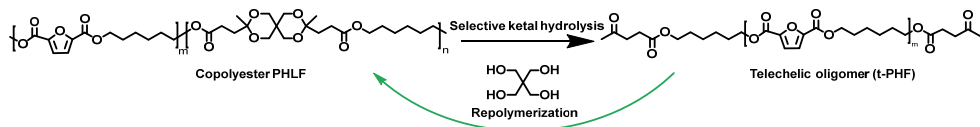
Hydrolytic degradation of the polyesters under acidic conditions was investigated to evaluate how the presence of ketal units from the spiro monomer in the copolyesters influenced their degradation into the starting building blocks. The hydrolysis experiments were conducted on PHF and the copolyesters PHLF-10 and PHLF-20 at 60 and 85 °C, respectively, during 24 h using aq. HCl solutions with the concentrations 3, 6, and 12 M, respectively. After degradation, a solid polymer residue and a filtrate containing the hydrolyzed products (monomers) were obtained, and the rate of hydrolytic degradation was estimated by measuring the weight loss (%) of the sample (**Figure 2**).

**Figure 2.** Weight loss (%) of polyester PHF and the copolyesters (PHLF-10, and PHLF-20) during hydrolytic degradation at 60 (a) and 85 °C (b) in aq. HCl solutions (3, 6, and 12 M) during 24 h.

In general, the weight loss increased with acid concentration and temperature. However, the observed weight loss of PHF was lower than that of the copolyesters (PHLF-10 and PHLF-20) under each tested condition, implying a very sluggish degradation. In contrast, the copolyesters showed notably improved degradation, as indicated by their higher weight loss values compared to PHF. Additionally, the hydrolysis rate increased with increasing contents of the spiro-diester in the backbone, as can be seen from the higher weight loss of PHLF-20 in relation to PHLF-10. This suggested that the ketal units induced an efficient fragmentation of the polymer chains into low molecular weight polymer or oligomer chains, which then proceeded to degrade much faster than the longer polymer chains of PHF. This observation may be explained by a reduced hydrophobicity and an increased water penetration of samples containing short polymer or oligomeric chains. Furthermore, the crude product extracted from the aqueous filtrate of PHLF-20 hydrolysis was analyzed by ^1H NMR spectroscopy, which confirmed the hydrolysis of the polyester into the starting monomers or building blocks by the appearance of signals from 2,5-furandicarboxylic acid, 1,6-hexanediol, and levulinic acid. Notably, pentaerythritol was not recovered due to its very high solubility in the aqueous phase.

Chemical recycling *via* the telechelic approach

Selective hydrolysis of ketal units in the copolyesters yields ketone-terminated oligomers, which may potentially be polymerized with pentaerythritol through cycloketalization to restore the original polymer structure. A preliminary investigation was carried out using PHLF-20 as a representative sample to assess the feasibility and challenges of this process (**Scheme 12**). Milder hydrolysis using 1 M HCl at 60 °C resulted in a telechelic oligomer with predominantly ketone end groups, in an 82% yield. The telechelic oligomer was directly polymerized with pentaerythritol using *p*-TSA as a catalyst at 170 °C for 3 h under a high vacuum to remove by-product water. This resulting repolymer (r-PHLF) contained 8.3% of spiro-units in the polymer structure, which was lower than expected due to an incomplete conversion of ketone to ketal groups, as confirmed by ^1H NMR analysis. As a result, a lower yield (69%) and molecular weight ($[\eta] = 0.34 \text{ dL g}^{-1}$) of the repolymerized product were obtained. This was possibly due to an inefficient mixing of the highly viscous polymerization mixture, suggesting a need for thoroughly optimizing the polymerization conditions to reach improved molecular weights. Still, the initial investigation demonstrated the potential for recycling of polyesters containing spirocyclic ketal units *via* a telechelic approach, which, in practice, represents a closed-loop recycling.



Scheme 12. Chemical recycling of PHLF copolyester *via* the telechelic approach.

4.3 Furanic- and phenolic-based dicarboxylates for aromatic polyesters (Paper 4 and 5)

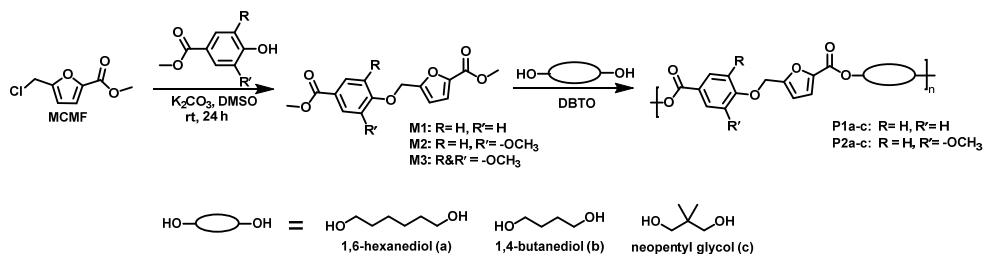
As highlighted in the introduction, the utilization of fossil-based TPA in the production of PET and its related variants has generated substantial concerns regarding the sustainability of these materials. Therefore, it is of utmost importance to develop new aromatic dicarboxylic acids or dicarboxylates by utilizing lignocellulose-based building blocks for the sustainable production of high-performance aromatic polyesters. In paper 4 and 5, the synthesis of new aromatic dicarboxylates has been investigated for the development of aromatic polyesters.

4.3.1 Polyesters from di-aromatic dicarboxylates (Paper 4)

In this paper, a potentially sugar-based chemical, i.e., methyl 5-chloromethyl-2-furoate was reacted with lignin-based *p*-hydroxybenzoates to obtain three asymmetric di-aromatic diester monomers with varying methoxy substitutions on the phenyl ring. These monomers were investigated in polycondensations with various diols to produce polyesters, which were then characterized with regard to structural, thermal and mechanical properties.

Monomer and polyester synthesis

Three different diester monomers (M1, M2, and M3) were synthesized in one-step S_N2 reactions of methyl 5-chloromethyl-2-furoate (MCMF) and three different hydroxybenzoates, namely, methyl paraben, methyl vanillate and methyl syringate, respectively (**Scheme 13**). The reactions were performed in DMSO using K_2CO_3 as a base at room temperature during 24 h. The crude products were purified by a simple recrystallization in ethanol to give the diester monomers in good yields (75–77%).



Scheme 13. Synthesis of diester monomers and their polymerizations with a variety of diols to prepare polyesters.

Afterwards, the diester monomers were investigated in polycondensations with 1,6-HD (a), 1,4-BD (b), and NPG (c), respectively, using a two-step modified melt polycondensation method (**Scheme 13**). DBTO was employed as a catalyst and the polymerizations were conducted using optimized transesterification and polycondensation step temperatures at 160 and 180 °C, respectively. However, only diester M1 and M2 produced two series of polyesters (P1a-c and P2a-c, respectively) with reasonably high molecular weights and yields (**Table 4**). Diester M3 underwent significant degradation which resulted in the formation of a dark-coloured crosslinked product. No crosslinking or gelation was detected in the cases of diester M1 and M2, except for a pale-yellow tint in the polyesters P2a-c obtained from diester M2, which may imply some minor degradation of this monomer. These initial results suggested that the thermal stability of the diester monomers decreased as the methoxy substitution on the phenolic group increased, leading to the formation of coloured or crosslinked products. Still, the diesters M1 and M2 showed excellent stability under the optimized conditions to yield reasonably high molecular weight polyesters without any significant colouration or gelation. The M_n values were in the range 15-37 kg mol⁻¹ for P1a-c and 12-25 kg mol⁻¹ for P2a-c.

Table 4. Polymerization, thermal, and mechanical data of polyesters.

Sample	M_n^a (kg mol ⁻¹)	\mathcal{D}^a	$T_{d,5}^{b,c}$ (°C)	T_g^c (°C)	T_g^d (°C)	E' (GPa) ^e
P1a	37	1.9	312	36	37	1.97
P1b	27	2.0	314	50	48	2.27
P1c	15	2.1	309	75	73	2.01
P2a	25	2.3	290	48	45	2.17
P2b	17	2.3	281	61	54	2.69
P2c	12	2.3	274	75	74	2.05

^a M_n , and \mathcal{D} were measured by SEC in THF. ^b $T_{d,5}$ was measured by TGA. ^c T_g was measured from the second DSC heating curve. ^d Determined at the peak maximum in the E'' curve. ^e Storage modulus (E') taken at 20 °C.

Polymer characterization

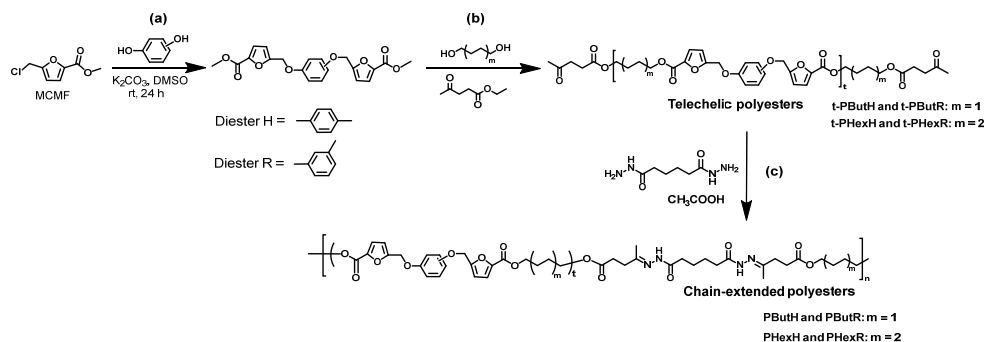
TGA data indicated a relatively high thermal stability of the polyesters with $T_{d,5}$ values above 275 °C in all cases (**Table 4**). The polyesters in the P2a-c series exhibited slightly lower thermal stability than those in the P1a-c series, which might be related to the electron-donating methoxy groups and is consistent with the observations for other methoxy containing polymers. According to the DSC results, the polyesters in both series were fully amorphous, as no melting endotherm was observed. The T_g values of the P1a-c and P2a-c series were in the range 36-75 °C and 48-75 °C, respectively, and increased with decreasing length of the diol unit in the two series of polyesters (**Table 4**). This was expected because of the increased backbone rigidity. Compared to the P1a-c series, the polyesters in the P2a-c series generally exhibited higher T_g s due to the increased chain stiffness by the presence of methoxy substituent that restricted the segmental mobility of the polymer backbones. However, polyester P2c was an exception and showed a similar T_g as P1c (75 °C) despite having the bulky methoxy substituent on the backbone. This could be because P2c (12 kg mol⁻¹) possessed a lower molecular weight than P1c (15 kg mol⁻¹). The T_g value of 75 °C for P1c and P2c was comparable to that of commercial PET (76 °C), indicating an excellent heat resistance of the polymers. Moreover, DMA analysis showed a moderately high stiffness of polyester samples with E' values in the range 1.97-2.01 GPa for P1a-c and 2.05-2.69 GPa for P2a-c (**Table 4**). Similar to what was observed with the T_g values, the E' values also increased with decreasing chain length of the diol unit in both series of polyesters (except P1c and P2c), which may be due to the increased backbone stiffness. The lower E' values of the P1c and P2c samples may be attributed to their lower molecular weight, which restricted the efficient chain entanglement in the polymer sample compared to their longer chain analogues (P1a-b and P2a-b, respectively). The polyesters in the P2a-c series exhibited higher E' values in comparison to the corresponding polymers in the P1a-c series due to the increased stiffness resulting from the bulky methoxy substituents. In addition, the T_g values taken at the local maximum of the loss moduli (E'') in the glass transition region were consistent with the DSC results, showing a good correlation between the two methods.

4.3.2 Polyesters from tri-aromatic dicarboxylates (Paper 5)

In this paper, the sugar-based methyl 5-chloromethyl-2-furoate described in paper 4 was combined with two potentially biobased dihydroxy benzenes to prepare symmetrical tri-aromatic diester monomers. Using these monomers, polyesters with acylhydrazone units in the backbone were prepared. The synthesized materials were characterized with regard to primarily structural and thermal properties. Furthermore, chemical recycling *via* telechelic polymer approach was investigated in a similar way as discussed in paper 3.

Monomer and polyester synthesis

Tri-aromatic diester monomer H and R were synthesized *via* S_N2 reactions of methyl 5-chloromethyl-2-furoate (MCMF) with hydroquinone and resorcinol, respectively (**Scheme 14a**). The reactions were conducted at room temperature for 24 h under mild basic conditions (K₂CO₃) in dimethyl sulfoxide (DMSO), which gave diester monomer H and R in good yields, i.e., 57 and 62%, respectively, following a straightforward recrystallization in acetone.



Scheme 14. Synthesis of diester H and R (a). Polyester synthesis *via* a two-step approach involving polycondensation (b) and chain extension (c) reactions.

The polymerizations of diester monomers H and R were conducted *via* a two-step procedure involving transesterification and chain extension reactions. Initially, telechelic polyesters with ketone end groups were synthesized by polymerizing diester H and R with 1,6-HD and 1,4-BD, respectively, in the presence of ethyl levulinate as an end capping agent (**Scheme 14b**). A molecular weight of 4.0 kg mol⁻¹ was targeted in each case. The polymerizations of diester R with the respective diols were then conducted at 160 °C for 24 h. However, in the polymerization of diester H, a slightly higher temperature (180 °C) was utilized to prevent crystallization of the product. Still, the polymerization of diester H with 1,4-BD resulted in crystallization of the oligomers formed after an hour of reaction. The polymerization with 1,6-HD was carried out for 10 h. The polymerizations yielded telechelic polyesters (t-PHexH, t-PButH, t-PHexR, and t-PButR) with an isolated yield in the range 74–88%. These oligomers were then chain extended with adipic acid dihydrazide (**Scheme 14c**). The chain extensions were performed at 75–130 °C using acetic acid as a catalyst in dry DMSO, to prepare the corresponding high molecular weight polyesters (PHexH, PButH, PHexR, and PButR) in 69–89 % isolated yields and with intrinsic viscosities in the range 0.29–0.52 dL g⁻¹ (**Table 5**). This indicated the formation of polymers with moderately high molecular weights.

Polymer characterization

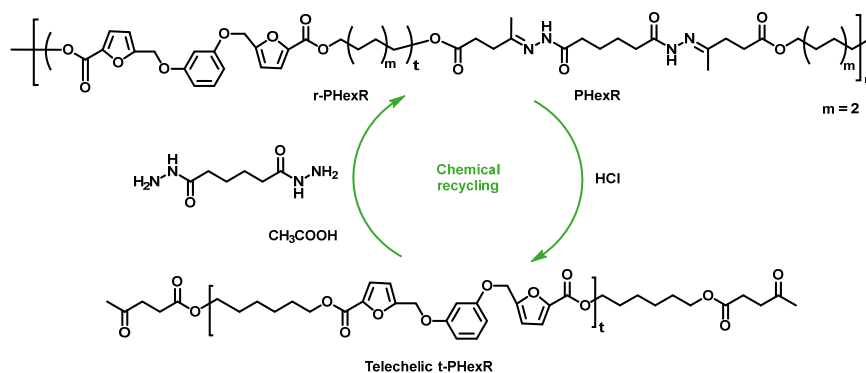
According to TGA, all the polyesters were thermally stable up to ≥ 275 °C (**Table 5**). Furthermore, the char yields of the polyesters were higher than 30%, suggesting inherent flame retardancy. DSC revealed the semicrystalline nature of the polyesters derived from diester H due to the linear chain structure induced by the 1,4-phenolic linkages of hydroquinone. In contrast, polyesters based on diester R were fully amorphous, most probably due to the kinked chain structure caused by the 1,3-phenolic moiety of resorcinol. PHexH and PButH showed melting points at 158 and 192 °C, respectively (**Table 5**). The higher melt enthalpy and crystallization temperature (T_c) of PButH suggested its higher crystallizability than PHexH, possibly due to its lower molecular weight and melt viscosity compared to PHexR. The T_g s of the polyesters varied with the rigidity caused of the diols, as expected. Polyesters based on 1,4-BD had higher T_g s than those based on 1,6-HD. Interestingly, the T_g s of the polyesters derived from both diesters with their respective diols were the same, i.e., 35 °C for polyesters (PHexH and PHexR) based on 1,6-HD and 44 °C for polyesters (PButH and PButR) based on 1,4-BD. This suggested that the substitutions of the phenolic ring had no, or very little, effect on the backbone rigidity.

Table 5. Molecular and thermal properties of polyesters.

Sample	$[\eta]^a$ (dL g ⁻¹)	$T_{d,5}^b$ (°C)	Char yield ^b (wt%)	T_g^c (°C)	T_m^c (°C)	ΔH_m^c (J/g)	T_c^d (°C)
PHexH	0.34	295	33	35	158	34	78
PButH	0.29	276	33	44	192	65	164
PHexR	0.52	305	33	35	--	--	--
PButR	0.39	295	36	44	--	--	--
r-PHexR	0.51	306	33	35	--	--	--

^a Intrinsic viscosity $[\eta]$ measured in HFIP at 25 °C. ^b Determined by TGA at 5% weight loss under N₂. ^c Determined by DSC from the second heating scan. ^d Measured from the first DSC cooling scan.

Chemical recycling *via* the telechelic approach



Scheme 15. Chemical recycling of acylhydrazone-containing polyester *via* the telechelic approach.

Chemical recycling *via* the telechelic approach was investigated using PHexR as a representative, as this sample exhibited higher molecular weight than the other polyesters, indicated by its higher intrinsic viscosity (0.52 dL g^{-1}) (**Scheme 15**). Selective hydrolysis of the acylhydrazone bonds in this polyester using a 1 M HCl/CHCl₃ biphasic system for 24 h gave the corresponding telechelic polyester (t-PHexR) in 63% isolated yield. Subsequently, t-PHexR was repolymerized *via* chain extension with adipic acid dihydrazide, employing a procedure similar to that used in the synthesis of PHexR. This yielded repolymer r-PHexR in an isolated yield of 73% and with an intrinsic viscosity of 0.51 dL g^{-1} , close to that of the initial sample (PHexR). This indicated the successful recovery of the original structure. Furthermore, the thermal properties of r-PHexR were almost comparable to those of initial PHexR (**Table 5**). Hence, the results demonstrated the potential short-loop recyclability of the new acylhydrazone-containing polyester without any significant trade-off in the quality of the recycled material.

Conclusions

In this thesis, new biobased rigid monomers were rationally designed and synthesized with the aim of creating new polymers with improved physical properties and recyclability. Utilizing lignocellulose-based building blocks, several dicarboxylate monomers were synthesized and employed in the preparation of polyesters. The relationship between their chemical structure and physical properties was established. In addition, the potential chemical recyclability of some of the synthesized materials was demonstrated.

In paper 1, a spirocyclic diester (Monomer L or spiro-diester) was synthesized through a straightforward reaction between ethyl levulinate and pentaerythritol. A preliminary life cycle assessment (LCA) indicated a lower CO₂ emission during the production of Monomer L compared to biobased succinic acid and adipic acid. Monomer L was successfully polymerized with various potentially biobased diols to produce a series of aliphatic polyesters with reasonably high molecular weights. The fully amorphous polyesters demonstrated sufficient thermal stability, with T_{as} in the 308-318 °C range, and T_g s in the 12-49 °C range. Furthermore, dynamic melt rheology experiments on hot-pressed films of the polyesters derived from NPG and 1,4-CHDM indicated the feasibility of melt processing. Additionally, both hot-pressed and solvent-cast films of these polyesters displayed high flexibility and mechanical strength, as well as excellent transparency, suggesting their potential suitability for a wide range of applications.

In paper 2, another spiro-diester (Monomer A) with two less methylene groups was prepared by reacting ethyl acetoacetate and pentaerythritol in a similar manner as spiro-diester described in paper 1. The resulting polyesters exhibited slightly improved thermal properties compared to those in paper 1, due to the reduced number of methylene groups between the ester groups and the spirocyclic rings. However, the high chain flexibility of the diol segments played a significant role in influencing the overall chain flexibility of the polyesters. As a result, the presence of methylene groups between the ester groups and the spirocyclic rings had only a marginal impact on T_g . Thus, the influence of the number of these methylene groups can be more significant when employing more rigid diols as a comonomer.

In paper 3, Monomer L discussed in paper 1 was incorporated into the structures of PBF and PHF to obtain two series of copolyesters PBLF and PHLF, respectively. Incorporation of spiro monomer in smaller percentages yielded thermal and

mechanical properties of the copolyester very similar to the corresponding homopolyesters. Compared to the homopolyester PHF, copolyesters showed improved hydrolytic degradation into the starting building blocks, most likely due to the rapid chain fragmentation promoted by the acid-catalyzed cleavage of the ketal units in polymer backbone. Selective hydrolysis of the ketal groups resulted in ketone-terminated telechelic oligomers, which could be repolymerized to recover the original polymer structures. This demonstrated the viability of incorporating the spirocyclic ketal units as a structural element to potentially facilitate short-loop recycling of 2,5-furandicarboxylate polyesters.

In paper 4, MCMF was reacted with three potentially lignin-based hydroxybenzoates to obtain diester monomers in high isolated yields. The polycondensations of diester monomers based on methyl paraben and methyl vanillate with various diols successfully produced two series of polyesters with reasonably high molecular weights. The fully amorphous polyesters possessed T_g s in the range 36-74 °C, and the polyesters based on neopentyl glycol showed comparable T_g s to PET.

In paper 5, two diester monomers were prepared by reacting MCMF with potentially biobased hydroquinone and resorcinol, respectively. The two diesters, having a central phenyl ring flanked by two furan rings, were used to produce high molecular weight polyesters containing acylhydrazone units in the backbone. Polyesters containing the linear hydroquinone units were semi-crystalline, while those containing the kinked resorcinol units were fully amorphous. Chemical recycling investigation revealed that the acylhydrazone bonds in polyesters could be selectively hydrolyzed under milder acidic conditions to obtain the starting ketone-terminated telechelic polyesters. Moreover, the recovered telechelic structures could be transformed into the original high molecular weight polymer by a chain extension with adipic acid dihydrazide.

Future outlook

In the future, developing new spirocyclic monomers without flexible spacers between the spirocyclic ring and the polymerizable functional group can potentially produce more rigid monomers. This reduction of the flexible linkages may result in materials with improved thermal and mechanical properties. Furthermore, combining aromatic and spirocyclic structures in monomers is an attractive strategy to enhance the rigidity of the resulting polymers. The use of lignin-based aromatic aldehydes or ketones for this purpose is a sustainable choice since lignin is a by-product of the paper and pulp industry. These spirocyclic bisphenols can be directly used, or functionalized into polymerizable diol or dicarboxylate monomers, to produce polyester, polycarbonates, and other high-performance polymers.

The spirocyclic and aromatic dicarboxylates synthesized in paper 1-2 and 4-5 may be employed in the preparation of polyamides, which are an important class of polymers known for their strong and versatile properties, and are hence often used in applications including textiles, automotive parts, and more.

It would be interesting to explore the crosslinking of the polyesters in papers 4 and 5 using a reversible Diels-Alder reaction to produce thermoset materials with enhanced physical properties. These crosslinked materials could be easily reverted to their original thermoplastic state at elevated temperatures, paving the way for a new class of recyclable thermosets.

Furthermore, one could explore the chemical recycling of the polyesters in papers 1-2 and 4. Notably, the aliphatic polyesters in papers 1 and 2 hold particular promise for bio-recycling, given their potential susceptibility to enzymatic degradation. Methanolysis could be a promising approach for the chemical recycling of aromatic polyesters synthesized in paper 4, as it could yield the starting dicarboxylate and diol monomers. These recovered monomers could subsequently be repolymerized to demonstrate a closed-loop recycling process.

Utilizing a telechelic method in the context of chemical recycling holds significant promise as an energy-efficient and short-loop approach. This approach could also be explored for the benchmark polyester PEF, which is an eco-friendly alternative to PET. For instance, small quantities of spirocyclic ketal monomers in papers 1 or 2 could be incorporated into the structure of PEF to obtain copolyesters containing ketal units. These ketal units can then be selectively cleaved to generate telechelic PEF, which can subsequently be repolymerized to recover the original polymer.

This thesis primarily focused on laboratory-scale synthesis of monomers and polymers. It would be interesting to further explore the scalability of these syntheses and evaluate the potential applications of the polymers in various contexts. For example, the polyesters with small contents of spirocyclic monomer in paper 3 were semicrystalline, making them suitable for further investigations related to fiber spinning, toward the development of sustainable textiles. Notably, the spiroketal units in these polymers might offer advantages for the chemical recycling of textile fibers, which are typically challenging to recycle efficiently. Furthermore, the amorphous polymers in paper 1-2 and 4-5 may be evaluated concerning their barrier properties to assess their suitability in packaging applications. In particular, the polyesters in paper 4 are of interest since some of them showed a T_g comparable to PET.

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