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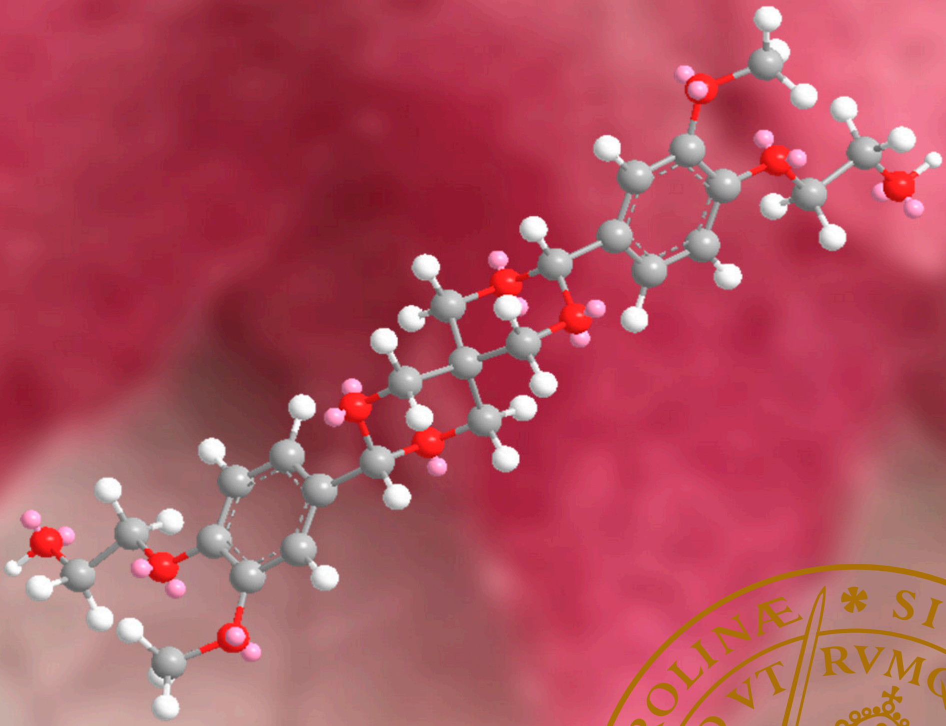

Toward Biomass-Derived Recyclable Polyesters

Smita Vamdev Mankar

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DOCTORAL DISSERTATION

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Faculty opponent
Prof. Katrien V. Bernaert, Masstricht University

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Abstract

Fossil-based plastics have become a matter of concern due to their negative environmental impacts such as greenhouse gas emissions and threats to the health of living beings. Alternative polymers derived from sustainable biomass resources have thus become an attractive research field since the last decade. Currently, there is a strong demand in the development of new bio-based polymers with enhanced properties (e.g., thermal, mechanical, and barrier properties) and recycling possibilities. This thesis focuses on the design and synthesis of various monomers and polymers using bio-based starting molecules, particularly those derived from lignin fragments such as vanillin. Attention was paid to unravel the impacts of certain molecular structures such as spirocyclic acetals on the polymer properties and recyclability. This thesis includes five papers that describe the important findings of various bio-based polyesters.

In Papers I, II, and III, diol and dicarboxylate ester monomers with spirocyclic acetal structures have been synthesized by coupling vanillin with pentaerythritol and derivation by S_N2 reactions. Preliminary life cycle assessment (LCA) results indicated that the production of the diol monomer with spiroacetal structures generates low greenhouse gases (Paper I). This diol monomer was used to synthesize copolyesters together with dimethyl terephthalate and 1,6-hexanediol (Paper I) and neopentyl glycol (Paper II). The glass transition temperatures of these polyesters were significantly enhanced by the incorporation of the spiroacetal monomeric units in the backbone. Furthermore, the spiroacetal units could be selectively cleaved under mild acidic conditions, yielding telechelic polymers with aldehyde end groups (Paper II). The resulting telechelic polymers could be conveniently converted back to the original polymers by polyacetalization with pentaerythritol, which showed their potential in the development of a new energy efficient chemical recycling process. We have also demonstrated that polyesters with spiroacetal units could be effectively hydrolyzed using an enzyme *Humicola insolens* cutinase, which suggested its potential in enzymatic recycling or biodegradation (Paper III). The effectiveness of the same enzyme on a commercial polyester with spiroacetal units (Akestra^{TM}, Paper IV), as well as newly synthesized methoxyhydroquinone-based polyesters without spiroacetal units (Paper V), was also demonstrated.

Key words: Polyester, polycondensation, spiroacetal, chemical recycling, enzymatic degradation

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To my parents,

Pramila and Vamdev Mankar

The Future depends on what we do in the present.

Mahatma Gandhi

Table of Content

Popular Science

Plastics are inescapable and versatile materials that are widely used in our daily lives. Many industries, such as textiles, food packaging, building and construction, kitchen appliances, electronics, and automobiles, produce and employ a variety of plastics to fulfill human needs. In 2021, approximately 390 million tons of plastics were produced globally, of which about 99% were based on the use of fossil-based resources. This is not renewable and can contribute to the greenhouse gas emissions and global warming effect. Therefore, production of new plastic materials from renewable recourses such as various biomass resource has attracted growing attention. Another problem of plastic materials is their accumulation in the environment, as most of them do not degrade naturally. Therefore, it is highly interesting to develop bio-based plastics that can be either effectively recycled or degraded naturally.

This thesis focuses on tackling the plastic challenges by designing and developing suitable building blocks and plastics from biomass resources and investigating possible energy efficient recycling methods for those specifically designed polymer structures. In this thesis, various bio-based monomers have been designed and synthesized. Preliminary environmental assessment indicated that these monomers can produce much less greenhouse gases compared to some other commercial monomers. We also demonstrated that strategically designed monomers can help to improve the quality of the resulting polymers as well as making them recyclable. Regarding the quality, I have investigated the impacts of particular structures of bio-based monomers on the materials properties, such as how much they can resist heat and how well they can block oxygen. Regarding recyclability, we investigated the methods for fragmenting bio-based plastics using chemicals or enzymes, which resulted in small sized polymers and building blocks that can be used to make polymers again. This design-for-recycling concept could potentially facilitate the bioplastics circular economy.

List of Papers

This thesis is based on the publication/papers listed below.

I. Synthesis, Life Cycle Assessment, and Polymerization of a Vanillin-Based Spirocyclic Diol toward Polyesters with Increased Glass Transition Temperature

Smita V. Mankar, M. N. Garcia Gonzalez, N. Warlin, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang, *ACS Sustainable Chemistry and Engineering*, 2019, **7**, 19090–19103.

II. Shorter Loop Chemical Recycling via Telechelic Polymers for Bio-based Polyesters with Spiroacetal Units

Smita V. Mankar, Jan Wahlberg, N. Warlin, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang. (Revision submitted)

III. A Vanillin-Based Dicarboxylate Monomer with a Spiroacetal Unit as a Potential Substitution for Dimethyl Terephthalate in Polyester Synthesis

Smita V. Mankar, Javier A. Linares-Pastén, Jan Wahlberg, N. Warlin, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang. (Manusript submitted)

IV. Comparison of the Enzymatic Depolymerization of Polyethylene Terephthalate and Akestra^{TM} using *Humicola insolens* Cutinase

Lucía Aristizábal-Lanza, **Smita V. Mankar**, Cecilia Tullberg, Baozhong Zhang and Javier A. Linares-Pastén, *Frontiers in Chemical Engineering*, **4**, 1048744, 2022.

V. Synthesis, Polymerization and Enzymatic Degradation of Methoxyhydroquinone-Based polyesters

Smita V. Mankar, N. Warlin, N. G. Valsange, N. Rehnberg, P. Jannasch and B. Zhang. (Manuscript)

My contributions

Paper I. I planned and performed all the synthesis and characterization of monomer and polymers. I participated in the discussion and interpretation of LCA results together with Nelly Garcia Gonzales. I wrote the first draft of the manuscript.

Paper II. I synthesized all the new polyesters and performed the investigations related to chemical recycling. I discussed and interpreted the data about barrier properties measured at Tetra Pak by J. Wahlberg. I wrote the first draft of the paper.

Paper III. I participated in developing the idea for this project and synthesized new dicarboxylate monomer and polyesters. I carried out enzymatic degradations with the help from J. A. Linares-Pastén. I discussed and interpreted the data about oxygen transmission rate measured at Tetra Pak by J. Wahlberg. I wrote the first draft of the manuscript.

Paper IV. I analyzed the molecular structure and thermal properties of polymers and participated in writing and revising the manuscript.

Paper V. I designed and synthesized the new monomer and polyesters, and performed the analysis of molecular structures and thermal properties. I carried out enzymatic degradations with the help from J. A. Linares-Pastén. I wrote the first draft of the manuscript.

Publications not included in this thesis.

I. A Rigid Spirocyclic Diol from Fructose-Based 5-Hydroxymethylfurfural: Synthesis, Life-cycle assessment, and Polymerization for Renewable Polyesters and Poly(urethane-urea)s

N. Warlin, M. N. Garcia Gonzalez, **S. Mankar**, N. G. Valsange, M. Sayed, S. H. Pyo, N. Rehnberg, S. Lundmark, R. Hatti-Kaul, P. Jannasch and B. Zhang, *Green Chemistry*, 2019, 21, 6667–6684.

II. Synthesis and Melt-Spinning of Partly Bio-Based Thermoplastic Poly(cycloacetal-urethane)s Toward Sustainable Textiles

N. Warlin, E. Nilsson, Z. Guo, **S. V. Mankar**, N. G. Valsange, N. Rehnberg, S. Lundmark, P. Jannasch and B. Zhang, *Polymer Chemistry*, 2021, 12, 4942–4953.

III. Bio-based Aliphatic Polyesters from a Spirocyclic Dicarboxylate Monomer Derived from Levulinic Acid

N. G. Valsange, M. N. G. Gonzalez, N. Warlin, **S. V. Mankar**, N. Rehnberg, S. Lundmark, B. Zhang and P. Jannasch, *Green Chemistry*, 2021, 23, 5706–5723.

IV. Development of Circularly Recyclable Low Melting Temperature Bicomponent Fibers toward a Sustainable Nonwoven Application

Z. Guo, N. Warlin, **S. V. Mankar**, M. Sidqi, M. Andersson, B. Zhang and E. Nilsson, *ACS Sustainable Chemistry and Engineering*, 2021, 9, 16778–16785.

Abbreviations

BHET	Bis (2-hydroxyethyl) terephthalate
CHDM	Cyclohexanedimethanol
Đ	Dispersity
DBTO	Dibutyltin (IV) oxide
DCM	Dichloromethane
DCTB	*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile
DMA	Dynamic mechanical analysis
DMF	Dimethylformamide
DMFDCA	Dimethyl
DMSO	Dimethyl sulfoxide
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
EC	Ethylene carbonate
EG	Ethylene glycol
FDCA	2,5-Furandicarboxylic acid
FT-IR	Fourier transformed Infrared spectroscopy
GHG	Greenhouse Gas
GPC	Gel permeation chromatography
HD	1,6-Hexanediol
HiCut	*Humicola Insolens*
HMF	5-hydroxymethylfurfural
HPLC	High Performance liquid chromatography
kDa	Kilo Dalton
LCA	Life Cycle Assessment

MALDI-TOF	Matrix-assisted laser desorption/ionization-time of flight
MHET	Mono(2-hydroxyethyl) terephthalic acid
MHQ	Methoxyhydroquinone
M_n	Number average molecular weight
M_w	Weight average molecular weight
NaTFA	Sodium trifluoroacetate
NMR	Nuclear magnetic resonance
NPG	Neopentyl glycol
OTR	Oxygen Transmission Rate
PBAT	Poly(butylene adipate terephthalate)
PBS	Poly(butylene succinate)
PBT	Poly(butylene terephthalate)
PCL	Poly(caprolactone)
PD	1,3-Propanediol
PEF	Poly(ethylene furanoate)
PET	Poly(ethylene terephthalate)
PETG	Poly(ethylene terephthalate) glycol
PGA	Poly(glycolic acid)
PHAs	Poly(hydroxyalkanoates)
PHT	Poly(hexamethylene terephthalate)
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic) acid
PMPT	Poly(2-methyl-1,3-propylene terephthalate)
PNT	Poly(neopentyl terephthalate)
*p*TSA	*p*-Toluene sulfonic acid
PTT	Poly(trimethylene terephthalate)
RI	Refractive index

RH	Relative Humidity
ROP	Ring opening polymerization
RT	Room temperature (20 °C)
SDS	Sodium dodecyl sulphate
SEC	Size exclusion chromatography
SPG	Spiroglycol
T_5	Temperature at 5 % mass loss (by TGA)
T_{dmax}	Temperature at maximum mass loss (by TGA)
T_{g}	Glass transition temperature
TBT	Titanium (IV) butoxide
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMCD	2,2,4,4-Tetramethyl-1,3-cyclobutanediol
TPA	Terephthalic acid

Abstract

Fossil-based plastics have become a matter of concern due to their negative environmental impacts such as greenhouse gas emissions and threats to the health of living beings. Alternative polymers derived from sustainable biomass resources have thus become an attractive research field since the last decade. Currently, there is a strong demand in the development of new bio-based polymers with enhanced properties (e.g., thermal, mechanical, and barrier properties) and recycling possibilities. This thesis focuses on the design and synthesis of various monomers and polymers using bio-based starting molecules, particularly those derived from lignin fragments such as vanillin. Attention was paid to unravel the impacts of certain molecular structures such as spirocyclic acetals on the polymer properties and recyclability. This thesis includes five papers that describe the important findings of various bio-based polyesters.

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Introduction

The properties of different types of plastics such as lightweight, durability, strength, weather resistance, fire resistance, chemical resistance and transparency have made revolutionary changes in our day-to-day life. This has led to the production of nearly 8 billion tons of plastics since 1950's. Among this only 9% have been recycled and all the remaining plastics ended up in nature or incinerated.[1] Today, the world's plastic production has reached 390 million tons per year of which 99% is made up from fossil resources.[2] Even though currently, only 4% of fossil resources are being used for plastics production, it has been estimated to consume 15% of total carbon budget by 2050 if the current production and use of fossil-based plastics is continued.[3] This challenge has been driving researchers in academia and industries to look for alternative plastic materials based on renewable non-fossil-based resources such as biomass resources, industrial and domestic wastes, as well as CO_2.[4–7]

1.1 Bio-based plastics

Bio-based polymers can address the following two important issues related to plastics: 1. Environmental impacts of plastics due to greenhouse gas (GHG) emissions, as bio-based materials have less carbon footprint as they are made up of recently captured CO_2 and the same CO_2 is then released into the atmosphere.[8] 2. Dependency on non-renewable fossil resources of conventional plastics. In addition, the integration of bio-based plastics is quite important and useful for society, as it promotes local and regional economy by providing opportunities of new employment in biomass production and processing.[9]

Despite of these above-mentioned advantages of bio-based plastics, their development has been slower compared to the anticipation from society and industry. Currently, bio-based plastics only constitute ~1% of all plastics. This could be related to the relatively high cost of bio-based polymers and the frequently encountered criticism on the complication of their recyclability.[10,11] Therefore, there are two demands on the development of new bio-based polymers. First, the newly developed bio-based polymers should exhibit enhanced properties so they can out-perform their lower cost fossil-based counter parts. Second, development of bio-based polymers should consider the recycling aspects right at the beginning of the development, during the molecular design of the polymers.

1.2 Lignin

Among all renewable biomass recourses that can be used for the development of new plastics, lignin is particularly important. Lignin is a source of non-fossil carbon, which constitutes about 30% mass in wood of vascular plants.[12] It is made up of various aromatic structures with different functional groups such as phenolic hydroxyl, alcohol hydroxyl, carbonyl, methoxyl, and carboxyl groups, etc. Owing to its high content of aromatics with various functional groups, lignin is thermally and mechanically stable, and also exhibit antimicrobial activity and biodegradability.[12] All of these properties are desirable in the development of value added chemicals and materials.

Annually, over 50 million tons of lignin is produced as a byproduct in the paper and pulp industries, and ~98% of this is burned as a low-grade fuel for the power required during the process.[13] Only about 1 million tons of lignin is used to produce value-added chemicals and products. A particular challenge in the valorisation of lignin toward applications in chemicals and materials, particularly polymers, is the structural complexity and variety of lignin. This makes it difficult to separate large amounts of mixed molecules in cracked lignin fragments. Currently, the only pure molecule that has been produced in commercial scale from lignin resources is vanillin, which is being sold by the Norwegian company Borregaard. Approximately 3 kg of vanillin can be produced from 400 kg of lignin derived from 1000 kg of wood.[13] Currently, bio-based vanillin constitutes ~15% of the global production of vanillin. Isolation of other aromatic molecules (e.g. syringaldehyde, vanillic acid, benzaldehyde, syringic acid, *p*-hydroxybenzoic acid (*p*HBA) from lignin has been achieved in academic research, but not on commercial scale.[14,15]

Vanillin is an aromatic compound containing an aldehyde and a phenolic group, which can be subjected to various chemical modifications.[16] Various vanillin-based monomers have been produced and used in the fabrication of thermoplastics (e.g. polycarbonates, polyesters, polyurethanes), as well as thermosetting materials (e.g. epoxies, adhesives, etc.)[17,18] Due to the increasing demand of bio-based vanillin, biotransformation to vanillin using other naturally abundant substrates such as eugenol, ferulic acid, vanillic acid and sugars have also been actively investigated.[19] Conversion of vanillin into other chemicals such as methoxyhydroquinone, vanillic acid, bisvanilin has also been explored, providing more pathways for valorization of bio-based vanillin in materials applications.[20–22]

Lignin has also shown potential as a starting material for making of acetic acid, quinones, hydroquinones and many other aromatic chemical compounds.[23,24]

1.3 Polyacetals

Polyoxymethylene (POM) is a commonly known polyacetal produced from formaldehyde, which contains carbon atoms bonded to two adjacent oxygen atoms. It is an engineering thermoplastic that is highly crystalline and possesses a high flexural strength, tensile strength, and hardness. Derlin was the first commercial polyacetal to be introduced by Dupont in the 1960s. Since then, it has been used in the automotive, electronics, and consumer goods industries. Tenac, Celcon, Duracon, and Ultraform are commercially available homo- and co-polymers of acetals. These polymers are unstable under UV radiation and change color upon exposure.[25] In recent years, polyacetals have attracted the attention of academic researchers in the development of bio-based polymers. Various bio-based aldehydes or ketones have been used as important building blocks for synthesizing acetals by reacting with polyols.[26,27] To incorporate acetals bond in polymers like polyesters, polyamides, polycarbonates and polyurethanes has also been investigated by making difunctional monomers containing acetal bonds, which were then polymerized.[28–32]

Acetal bonds can be relatively easily broken at lower pH. This property can be used to make the polymer recyclable via acid hydrolysis. Previously, polymers containing acetal bonds have been used for acid-triggered drug delivery.[33] The synthesis of thermosets containing acetal bonds have been reported for chemical recycling of otherwise unrecyclable thermosets.[34] Other polyacetals, such as poly(acetal-ester)s and poly(acetal-urethane)s, have also been subjected to acidic chemical recycling investigations.[34–38]

1.4 Polyesters

Polyesters constitute an important class of polymers with versatile structures and properties. The most important polyester is an aromatic polyester poly(ethylene terephthalate) (PET), which is widely used in fabricating bottles and textiles. The aromatic units (*i.e.,* terephthalates) in the polymer backbone endow desirable thermal and mechanical properties toward various applications. Unfortunately, terephthalates starting materials such as dimethyl terephthalate (DMT) and terephthalic acid (TPA) are currently fossil-based, although successful laboratory-scale synthesis from alternative biomass resources has been reported.[39,40] Currently, 2,5-Furandicarboxylic acid (FDCA) and its methyl ester have shown significant potential as bio-based alternatives for TPA to make polyester poly(ethylene furanoate) *i.e.* PEF. This polyester possesses superior thermal, mechanical and barrier properties as compared to PET.[41–43] Other alternative bio-based aromatic monomers and polyesters with aromatic units such as indole, thiophene, naphthalene, pyridine, etc. have also been actively explored in the past decade.[44–47]
The other difunctional monomers used in polyester synthesis are diols like ethylene glycol (EG), 1,3-propanediol (PD), 1,4-butanediol (BD), 1,4-cyclohexanedimethanol (CHDM), etc., which are used for the production of many important commercial polyesters such as PET, poly(trimethylene terephthalate) PTT, poly(butylene terephthalate) PBT, poly(butylene adipate-co-terephthalate) (PBAT), and poly(ethylene terephthalate) glycol (PETG).[48–51] Depending on the properties, these polyesters are used for different applications in packaging, textiles, three-dimensional (3D) printing, etc. In academia, various synthetic routes have been reported to make above-mentioned diols from bioresources.[48,52–56] In industries like Coca cola, polyester PET bottle *i.e.* PlantBottle™ was produced from biomass-derived ethylene glycol.[57]Akestra™ is a copolyester of PET, produced by Perstorp AB which contains a rigid spirocyclic diol made from bio-based pentaerythritol. This rigid diol significantly improved the thermal and mechanical properties of polyesters and it can be used for hot-filling applications. The current research is directed toward making rigid diol monomers from different biomass resources such as sugar, lignin, agriculture, etc. to improve the properties of new polyesters toward high performance applications.[57–61]

Another class of polyesters is aliphatic polyesters which contain aliphatic ester groups in the backbone. These polyesters have lower hydrolytic stability and higher flexibility allowing them to fit in the active enzymatic sites which improves their biodegradability compared to aromatic polyesters. Common biodegradable aliphatic polyesters include poly(lactic acid) (PLA), poly(caprolactone) (PCL), poly(glycolic acid) (PGA), poly(lactic-co-glycolic acid) (PLGA), poly(butylene succinate) (PBS), poly(hydroxyalkanoates) (PHAs), etc. These polyesters are used for various applications where degradability is of prime importance, such as reabsorbable sutures, drug delivery, scaffolds for tissue engineering, etc.[62] Incorporating aliphatic ester groups into aromatic polyesters could help improve the biodegradability. For instance, PBAT is a commercial aromatic-aliphatic hybrid polyester which is sold under the brand name Ecoflex or Ecoworld.[49] The relative content of aromatic and aliphatic ester bonds in the polymer backbone decides the thermomechanical properties with the possibility of biodegradation, which is desirable for biodegradable packaging applications.[63]

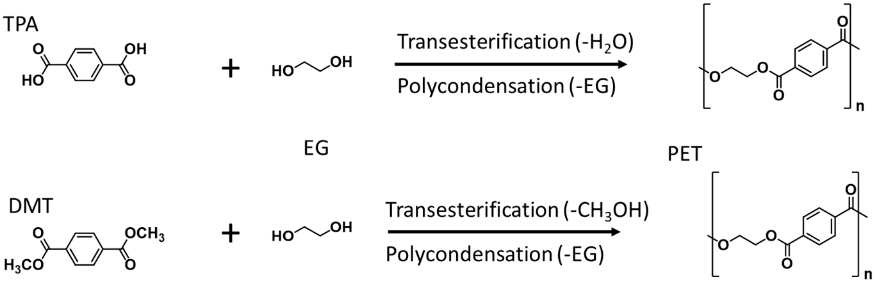
1.4.1 Polyester synthesis

Polyesters can be produced from the polycondensation of carboxylic acid or ester and alcohol functional groups of monomers, with the removal of water or methanol as byproducts. Alternatively, polyesters can also be produced by ring opening polymerization of cyclic ester monomers.

Polycondensation

Polycondensation belongs to step growth polymerizations. The most commonly known polyester PET is commercially produced by polycondensation of terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) (Scheme 1),[64] typically including two steps: transesterification and polycondensation. Many other aromatic polyesters such as PTT, PBT, PBAT, Akestra^{TM} are produced also by this method using corresponding monomers.

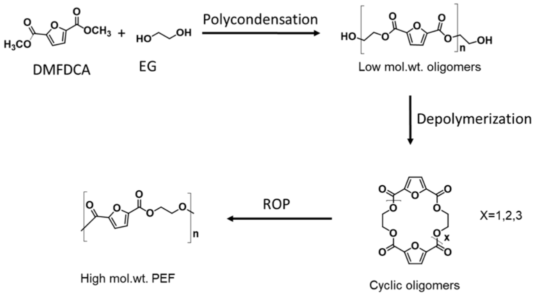
Scheme 1. PET synthesis



The transesterification and polycondensation steps are carried out at high temperatures (~ 200-280 °C) to facilitate the removal of diol and improve the molecular weight.[29,65] Cyclic oligomers are frequently contained as the side products with a few percent in the resulting polymers.[66] In polycondensation, various types of catalysts have been used. For example, antimony-based catalysts are commonly used in industry to produce PET, however, their toxicity for environment and human health has caused concerns. In industry, other catalysts based on titanium and germanium have been also used for polyester synthesis. Titanium-based catalysts have shown promising results in polyester synthesis such as PTT; however, they could cause coloration in PET synthesis.[67,68] Germanium-based catalysts could produce high molecular weight, colourless polyesters like PET, but their relatively high cost is a limitation.[67] In case of small scale (up to ~1 kg) and lab scale polyesters synthesis, dibutyltin (IV) oxide, titanium (IV) butoxide, titanium (IV) isopropoxide, zinc acetate, tin (II) octoate have been frequently used.[29,32,50] In the lab scale polyesters synthesis, adding a small quantity of solvents like xylenes or mesitylene during transesterification step could help reduce the monomer loss due to evaporation, and reduce the reaction temperatures. The polycondensation step was commonly carried out under vacuum, but sometimes also under nitrogen flow, in order to drive the polycondensation forward.[29,46]

Ring opening polymerization (ROP)

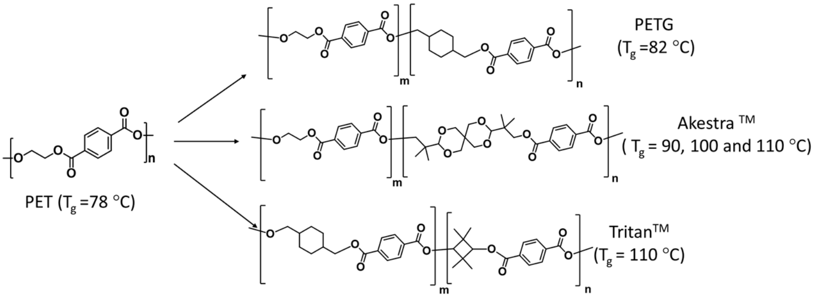
Scheme 2. High molecular weight PEF synthesis by ROP reported by J.G. Rosemboom et.al.[65]



ROP is a chain growth polymerization using a nucleophilic initiator such as alcohol along with catalyst for cyclic monomers. PLA, PGA, PCL are examples of polymers synthesized using ROP.[69–71] By ROP, high molecular weight polymers can be obtained at lower temperatures in relatively shorter time as compared to conventional step-growth polycondensation.[72] Usually, the synthesis of cyclic monomers like lactide, glycolide, etc., is tedious and costly, which somewhat limited the practical use of these polymerizations and the resulting polymers. Research toward new catalysts and enzymes for ROP using aliphatic-aromatic cyclic oligoesters have been reported recently.[73,74] Interestingly, ROP followed by polycondensation, *i.e.* PROP polymerization method, have been recently used to produce several new polyesters including poly(2-methyl-1,3-propylene terephthalate) (PMPT) and poly(neopentylene terephthalate) (PNT), which are difficult to synthesize by conventional polycondensation due to the steric hindrance of the bulky side chains.[75] Recently, this polymerization method was used for making bottle grade PEF by J. Rosenboom et.al. (Scheme 2).[65] In this process, oligomers were synthesized from dimethyl furandicarboxylate (DMFDCA) and ethylene glycol first, which were depolymerized to produce cyclic oligomers. These oligomers were then repolymerized by ROP to obtain colourless PEF with high molecular weight within shorter time (<30 min).[65] This is a smart method that shows potential in overcoming the challenges in PEF synthesis by conventional polycondensations, such as low molecular weight and coloration.[76,77]

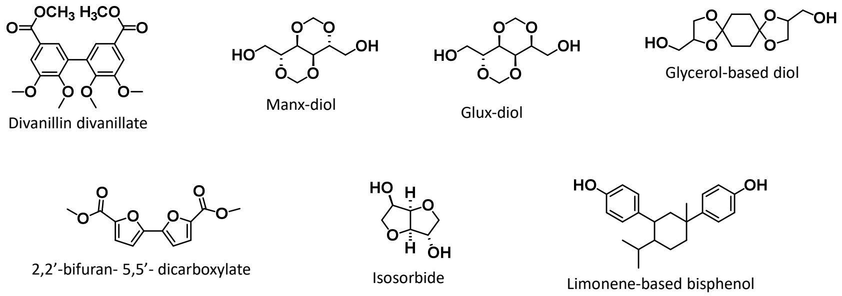
1.5 Enhanced properties

Scheme 3. PET and other high T_g copolyesters using rigid diol monomers.



In order to compete with low-cost fossil-based plastics and enter the market, bio-based polymers could be designed with superior properties such as T_g, barrier performance, recyclability, etc. (so-called "bioadvantage" strategy).[78] Commercial polyesters like PETG, Akestra™, and Tritan were introduced into the market on the basis of enhancement in the properties (T_g, use for 3D printing, etc.), which expanded their use in various applications as compared to PET. In these new polyesters, rigid with cyclic structures, such as 1,4-cyclohexanedimethanol (CHDM), spiroglycol (SPG), and 2,2,4,4-tertamethyl-1,3-cyclobutanediol (TMCD), were used to enhance the thermomechanical performance of resulting polyesters (Scheme 3). However, these monomers used are completely fossil-based or partly bio-based, which led to research for more sustainable bio-based rigid monomers. In academia, various research groups have reported rigid cyclic monomers, aromatic diols and dicarboxylates prepared from biomass resources such as sugars and lignin (Scheme 4) which resulted in new polyesters with enhanced properties suitable for different applications .[79]

Scheme 4. Rigid monomers from biomass used for polyester development.



In addition to thermomechanical properties, gas barrier properties are also important to consider when the materials would be used in food packaging.[11] Gas barrier properties depend on not only molecular structures, but also other factors related to compounding, formulation and processing.[82–85] In general, the presence of crystallinity can hinder gas diffusion and penetration more effectively. Thus plastics with higher degree of crystallinity usually exhibit superior gas barrier properties.[86–88] For fully amorphous plastics (e.g., Akestra^{TM}, PETG, Tritan^{TM}), gas barrier properties can be enhanced by lowering the chain mobility and free volume,[89–91] which are usually manifested by higher T_g values. This can be achieved by incorporating rigid monomer units in the polymer structure. For instance, amorphous aliphatic polyesters with enhanced T_g and oxygen barrier have been reported using renewable rigid cyclic monomers.[92] However, if rigid bulky monomers are used for semicrystalline polymers, barrier properties may be reduced due to crystallinity disruption.[87,93]

1.6 Recycling

Recycling of plastics have received growing attention in the past decade due to its potential to reduce GHG emissions and the consumption of primary (e.g., fossil) resources, as well as the amount of total plastic wastes that need to be disposed. Currently, only 9% of plastic wastes are being recycled (mostly by mechanical recycling), and the rest are incinerated or disposed in landfills.[1]

There are a number of possible recycling methods present at the moment which includes mechanical recycling, chemical recycling by pyrolysis, solvolysis, acid/base hydrolysis, etc., and biological recycling by enzymatic degradation/biodegradation, etc. (Fig. 1).[94]

Currently, the most adopted recycling method is mechanical recycling, which means to re-melt and re-shape the collected polymers after use (re-processing). The advantage of this process is that all the chemical bonds in the initial polymers have been preserved, so there is no need to re-build the polymer chains. It is therefore energetically and economically more favourable. However, this kind of mechanical recycling process is limited by the necessity of carefully sorting and separating each different kind of polymers that are collected all together from the mixed plastic wastes.[95] Thermal degradation of the polymers during re-processing is another issue, which lowers the quality of recycled polymers and thus limits the market acceptance.[96,97] Another challenge is that many polymers are frequently used as a part (or component) of complicated materials (e.g. blends, composites, laminates), which are usually difficult to sort out and separate.

Recently, chemical recycling has received growing attention.[98] By chemical recycling, polymers are usually broken into monomers or chemicals, which could be re-polymerized into the same or different polymers.[36] In principle, this allows for the recycling and utilization of polymers particularly polymer mixtures without pre-sorting and separating.[99] Currently, chemical recycling process based on pyrolysis at high temperature is under rapid development.[100] For instance, a project “ChemCycling” led by BASF is focusing on pyrolysis of non-recyclable plastic materials in collaboration with Quantafuel, and the resulting pyrolysis oil will be used as feedstock for new polymers and chemicals.[101] Despite of its advantages of being able to handle various types of plastic mixtures, very high temperatures (~300-900 °C) used for pyrolysis and the resulting complex mixture of chemicals have been the disadvantages.[95,102–104] It has also been reported that the chemical recycling process based on pyrolysis could be difficult if polymers like polyvinyl chloride (PVC) are present in the waste plastics mixture. PVC has chlorinated backbone which would result in acidic, hazardous products during pyrolysis.[105]

Selectively breaking the polymers at certain weak bonds can also make monomers, which can be used for chemical recycling. This process need the presence of particular weak bonds (e.g., acetals, diketoenamine, bifunctional silyl ethers, disulfide, esters, carbonates, etc.).[106–112] Vanillin-based imine thermosets and epoxies have also been cleaved by imine exchange reaction and acidic hydrolysis, respectively, giving rise to monomers for further recycling.[17,113] Chemical recycling of PET by breaking the ester bonds has also been reported, including acidic/alkaline hydrolysis, glycolysis, methanolysis etc., which would yield the corresponding monomers, DMT, TPA, EG, bis (2-hydroxyethyl) terephthalate (BHET) and oligomers.[97,114–117] Recently, Z. Guo et. al., reported methanolysis of bicomponent polyester fibers made from two polyesters poly(hexamethylene terephthalate) (PHT) and PBT, resulting in pure DMT along with diols HD and BD.[50]

Recently, a new strategy of chemical recycling by partly breaking chemical bonds in polymer backbone has attracted growing attention, which resulted in oligomers with functional end groups (telechelic polymers). Johansson et.al, recently reported recycling of polyolefins via telechelic polymers.[106] More recently, G. W. Coates et. al. reported chemical recycling of polymers like polypropylene and polyethylene with cleavable linkages which would result in telechelic polymers.[102,118] Compared to the "conventional" chemical recycling by which all the linkage between monomeric units will be broken, this new strategy may have the advantage of preserving the chemical bonding energy and thus can be in principle present a shorter loop energy efficient approach as shown in Fig. 1.[119]

Both mechanical and chemical recycling processes usually require relatively harsh conditions, so there has been an interest in enzymatic recycling that usually needs mild conditions (e.g., temperature, pH). Pioneer work of enzymatic degradation of PET was reported by Yoshida et al., in 2016, where *Ideonella sakaiensis* 201-F6, a bacterium could effectively break PET into TPA, mono(2-hydroxyethyl) terephthalic acid (MHET) and BHET.[120] Afterward, many other enzymes have also been reported with the ability to degrade PET or other polymers.[63,121–123] The enzymatic degradation rate of polymers can be affected by the physical form (powder, films, and fibers) and other factors including the chemical structure, glass transition temperature, and crystallinity. Non-degradable composition of the polymers also plays an important role in the access of degradable parts (or bonds) by the active sites of the enzyme.[124–126] It has been reported that the small molecules as the enzymatic degradation products could sometimes undergo mineralization process, [125–128] which may hinder the characterization and utilization of the resulting molecules.

Enzymatic degradation processes are usually complicated, and frequently there are residue solids and soluble fractions after the degradation. After the enzymatic degradation, it is non-trivial to analyze the products and understand the process. Commonly used characterization methods include analyzing the residue solids (if there are any) by their changes in chemical composition (e.g. by NMR, FT-IR), weight, molecular weight (by SEC or NMR),[129,130] crystallinity and thermal properties (by DSC, TGA etc.).[131–135] Other factors such as water uptake can be measured by the weight of the polymers after degradation.[136] If films were used for degradation studies, the change in surface can be monitored by scanning electron microscopy (SEM) and atomic force microscopy (AFM).[125,129,137–140] Additionally, the chemicals released into the aqueous solution after the enzymatic degradation can be analyzed by NMR and mass spectroscopy.[124,141,142]

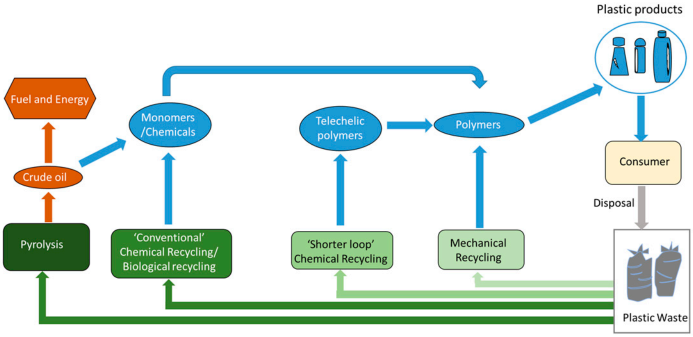


Figure 1. Schematic summary of recycling pathways of plastic wastes.

1.7 Context and scope

The aim of this thesis is to unravel the design principles of new bio-based polyesters with enhanced properties and recyclability. Lignin-based monomeric building blocks have been used to synthesize new monomers and polyesters. The environmental aspects, molecular and materials properties, as well as their chemical and biological recyclability have been investigated.

In Paper I, a rigid diol monomer with spiroacetal structure was synthesized by coupling vanillin and pentaerythritol, followed by conversion of the phenolic groups into primary alcohols. Preliminary LCA results showed lower greenhouse gas emissions of this monomer compared to some other chemically similar monomers used for polyester production. Polyesters incorporating this monomer unit showed high thermal stability, no coloration and enhanced T_g up to 64 °C.

In Paper II, the same monomer in Paper I was used to produce another series of copolyesters with neopentyl glycol and DMT. The resulting polyesters showed superior thermal stability, further enhanced T_g up to 105 °C, and improved oxygen barrier. The acetal bonds of this series of copolyesters could be selectively broken under mild acidic conditions, producing telechelic polyesters that could be repolymerized conveniently by polyacetalization. In principle, this new type of chemical recycling can be more energy efficient than "conventional" chemical recycling.

In Paper III, a dicarboxylate ester monomer with spiroacetal unit was synthesized using vanillin and pentaerythritol, followed by converting the phenolic OH to carboxylate groups. This monomer was investigated as a potential substitution for DMT in polyester synthesis. We discovered that the incorporation of the spirocyclic structure in the polyester backbone could enhance the thermal and oxygen barrier properties of these amorphous polyesters. In addition, we have discovered that these polyesters could be hydrolyzed by *Humicola insolens* cutinase (HiCut) (under ambient conditions), which may indicate their potential in the development of enzymatically recyclable or biodegradable materials.

In Paper IV, a commercially available PET-based copolyester with spiroacetal units (called Akestra^{TM}) was subjected to enzymatic degradation using the same enzyme used for polyesters with vanillin-based spiroacetal (Paper III). A preliminary insight was gained concerning the degradation mechanism of Akestra^{TM} and the impact of spirocyclic structures on the enzymatic degradation of polyesters. Our results suggested that the T_g of the materials, the crystallinity, and the physical forms of the materials have significant impacts on the degradation rate.

In Paper V, a vanillin-based molecule, methoxyhydroquinone, was investigated as the starting material for making a dicarboxylate ester monomer, which was then copolymerized with various diols to yield a series of polyesters with varied rigidity and thermal properties. Enzymatic degradation of this series of polyesters without spiroacetal units was investigated using a thermally stable enzyme HiCut, which resulted in almost complete degradation of the obtained polyesters.

Experimental Work

Monomer synthesis

Acetalization

Acetalization is the organic reaction that involves the formation of an acetal. Acetal are formed from nucleophilic addition of an alcohol to an aldehyde group. In organic synthesis, acetalization is used for protecting aldehyde as it is a reversible reaction with acid as a catalyst. In Paper I-III, spiroacetal monomers were formed from the condensation of aldehyde group of vanillin with pentaerythritol using acid catalyst, pTSA. The reaction was carried out at room temperature in isopropanol (IPA) and ~50-60% of spiroacetal monomers were recovered after recrystallization in ethyl acetate.

Hydroxyethylation of phenol using ethyl carbonate:

In this organic reaction includes nucleophilic attack of phenoxide ion on the electrophilic carbon of ethylene carbonate (EC) to produce hydroxyethylphenol with evolution of CO_2. In industry this type of reaction is carried out using KI as a catalyst and without solvent where EC acts as a solvent. However, to use it as a solvent, thermal stability of starting material should be well above melting point of EC. In Paper I and II, phenolic hydroxyl of vanillin-based spiro-bisphenol monomer was reacted with EC using K_2CO_3 in DMF and reaction was completed in 2 h. After completion of reaction the product was obtained in pure form after straightforward precipitation in water.

Williamson ether synthesis

In this synthesis, ether group is formed from a reaction between primary alkyl halide and alkoxide ion via S_N2 mechanism. A good leaving group with strong electronegativity (commonly a halide) is required for the S_N2 reaction to take place. This reaction is widely used in industrial synthesis. In Paper III and IV, bromomethyl acetate was reacted with phenolic group of vanillin and methoxyhydroquinone in presence of base K_2CO_3 to produce, alkylated vanillin derivative and methoxyhydroquinone-based diester, respectively. The reaction was straightforward and the product was purified by direct precipitation in water or recrystallization in ethyl acetate: heptane (90:10) mixture.

Polymer synthesis and characterization

Polyesters

Polyesters were synthesized using a conventional polycondensation method in two steps:1. transesterification, and 2. Polycondensation in a three neck round bottom flask equipped with inlet, mechanical stirrer and outlet attached to condenser. In the first step, a mixture of monomers (dicarboxylate and diol) and catalyst (DBTO/TBT) was heated above the melting temperature of the monomers for 5 h. In second step of polycondensation, temperature was raised by 20 °C and vacuum was applied to remove excess of diols. In both steps, mixture was constantly stirred using mechanical stirrer with speed of 60-100 rpm.

In Paper II, III and IV, the conventional method was slightly modified by adding a small amount of xylenes to the reaction mixture to avoid evaporation of the diol during first step. Xylenes were collected in a condensation flask later. This step was performed under nitrogen flow with constant stirring (60-100 rpm), and transesterification required approximately 5 h. In the modified method, the second step was carried out with an increasing rate of nitrogen flow with constant stirring (60-100 rpm).

Polyacetals

The polyacetalization of aldehyde-functionalized telechelic polyesters was carried out at room temperature. In a round-bottom flask, telechelic polyester powder was dissolved in dichloromethane and it was mixed with partially solubilized pentaerythritol in isopropanol with catalytic amount of *p*TSA. Polymerization was carried out until equilibrium was achieved (~80% conversion of aldehyde to acetal). Subsequently, the acid was quenched using potassium carbonate and the polymerization mixture was filtered and evaporated to obtain a crude polymer powder.

Characterizations

The most important instruments that I used for characterizations of monomers and polymers are described below. For more detailed information, please see attached publications/manuscripts.

Molecular weight of polyesters (Paper I to III) was measured by size exclusion chromatography (SEC) using a Malvern Viscotek instrument with a 2×PL-Gel Mix-B LS column set (2 × 30 cm) and chloroform as the eluent at 35 °C, equipped with OmniSEC refractive index, viscosity, light scattering Triple Detectors. A polystyrene standard with molecular weight 96 kDa and Đ = 1.03 was used for calibration. In paper V, the molecular weights of all the polyesters were analyzed by size exclusion chromatography (SEC) using OMNISEC from a Malvern instrument equipped with one TGuard, Org Guard, col 10 x 4.6 mm as a guard column, 2 × T6000M, general mixed Org. 300 × 8.0 mm as an analytical column and refractive index (RI) detector. For the conventional calibration, six polystyrene standard samples with M_n equal to 96, 52.4, 30 and 3 kDa from Poplymer Laboratories Ltd., Agilent Technologies, and Water Associates, and M_n = 17.5 and 3.5 kDa from Inc. Warringtons, PA18976) were used. Nuclear magnetic resonance (NMR) spectroscopy was performed (^{1}H and ^{13}C NMR) on a Bruker DR X400 spectrometer at 400.13 MHz proton frequency and at 100.61 MHz carbon frequency. MALDI-TOF analysis was performed using a 4700 Proteomics Analyzer (Applied Biosystems/MDSSCIEX) in the positive reflectron mode between 1000 and 5000 m/z. The polymer or oligomer sample (0.1 mg/mL), matrix DCTB (5 mg/mL), and salt NaTFA (0.05 mg/mL) were dissolved in suitable volatile solvents. 1uL of the sample solution, matrix, and salt was mixed and spotted on a stainless-steel plate used for MALDI-TOF analysis after complete evaporation of the solvents. A Nicolet IS5 spectrophotometer was used for attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) analysis. All spectra were collected at room temperature within the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. Thermogravimetric analysis (TGA) was performed on a TA instrument mode TGA Q500. The samples were heated with a heating rate of 10 °C min^{-1} from room temperature to 600 °C. T_5 was determined at 5% weight loss of polyester at the same rate of heating. The decomposition temperature (T_d) was determined at the maximum decomposition rates. As well as isothermal stability of polyesters was studied at 300 °C for 600 min. Differential scanning calorimetry (DSC) measurements were performed using a DSC Q2000 analyzer (TA Instruments) with heating rate of 10 °C /min under nitrogen atmosphere. The T_g, T_m, and crystallinity of the polyesters were determined from the second heating, in which the sample was heated from -50 to 200 °C. DMA measurements were performed in the stretching mode using a TA Instruments Q800 analyzer. A strain sweep was performed for all the samples, and the linear viscoelastic region (LVR) was determined. A strain of 0.1% was applied within the LVR and was used for further sample analysis. The measured samples were heated from room temperature to 100-120 °C (~10-20 °C above the T_g of the PNT and PNVT) at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz with a strain of 0.1%. A Micromass QTOF mass spectrometer (ESI) was used for determining exact mass of the monomer. An Ultimate 3000 RS (Dionex) equipped with a UV/Vis detector (SPD-20A) and a hydrophobic C18 column (Kinetex® 1.7 µm XB-C18 100 Å, LC Column 50 × 2.1 mm) was used to analyze the components of hydrolyzed sample. The HPLC method and data were processed with Chromeleon v. 6.8 software. Oxygen transmission rate (OTR) analysis was carried at 23 °C with 21% O_2 and 50% relative humidity (RH) with partial pressure of 0.21 atm on instrument Ox-Tran 2/21 from Ametek.

Summary of Appended Papers

Synthesis, LCA and polymerization of a diol monomer with a spiroacetal unit (Paper I)

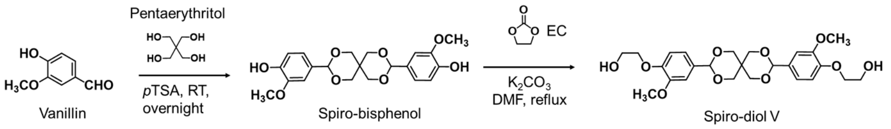
PET is widely used in the applications of beverage bottles, films and textiles.[143] The T_g of PET ranges between 72-78 °C, which restricts its applications where relatively high temperature are needed (*e.g.* hot-filling packaging, coffee mugs, etc.). Terephthalate polyesters with enhanced T_g have been developed and commercialized (e.g. Tritan^{TM}, PETG, and Akestra^{TM}), which have T_g in the range of 90-110 °C.[124] Particularly, Akestra^{TM} is a PET-based copolyester using a partly bio-based diol monomer with spirocyclic acetal unit (spiroglycol unit, Scheme 3).[144] As this spirocyclic monomer is partially bio-based and aliphatic in nature, it would be interesting to see if we could use biomass-derived aromatic aldehydes to make a fully bio-based rigid spirocyclic diol that can be used to fabricate high T_g polyesters like Akestra^{TM}.

In Paper I, a new diol monomer with spirocyclic acetal unit was synthesized using vanillin (a lignin-based molecule) and pentaerythritol. The GHG emissions of the new vanillin-based diol were studied by preliminary Life cycle assessment (LCA), and the polymerizability of this diol in polyester synthesis was investigated.

Monomer synthesis and LCA

A rigid diol monomer with a spirocyclic acetal unit (Spiro-diol V) was synthesized in two steps (Scheme 5). First, a bisphenol with spirocyclic acetal unit was synthesized conveniently by coupling pentaerythritol with vanillin in 2-propanol, a green solvent recommended by the CHEM21 guide.[145] This bisphenol has been previously reported as a green component for making epoxies and thermosets. However, the phenolic OH groups are usually unsuitable for polyester synthesis due to their relatively weak nucleophilicity and higher tendency as leaving groups[146] so this bisphenol has not been used for polyester synthesized by melt polycondensation. In this work, we converted the phenolic OH groups into primary alcohols using ethylene carbonate (EC), which yielded the desirable Monomer V with two primary alcohols.

Scheme 5. Synthesis of spiro-diol V.



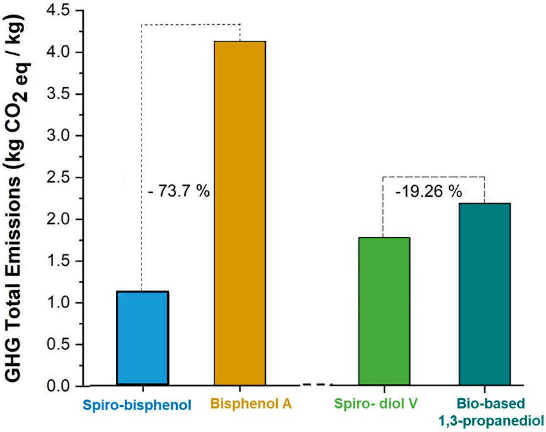
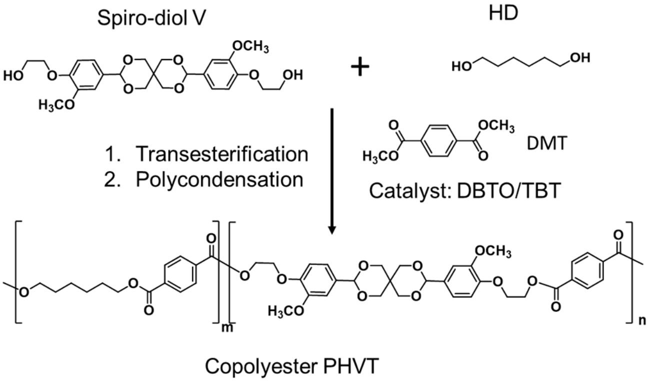


Figure 2. Preliminary life cycle assessment of spiro-bisphenol, spiro diol V and two commercially available monomers bisphenol A and 1,3- propanediol.

The GHG emissions of spiro-diol monomer V and its precursor bisphenol monomer were preliminarily investigated and compared with those of their commercially available counterparts (*i.e.,* bio-based 1,3-propanediol and bisphenol A, respectively, Fig. 2). As a result, the spiro-bisphenol showed ~74% lower GHG emissions than Bisphenol A, which is widely used in industry to fabricate polycarbonates, aromatic polyesters, and epoxies. Spiro-diol V showed 20 % less GHG emissions than bio-based 1,3-propanediol, which is the monomer used for making Sorona^{TM} fibers by DuPont.

Scheme 6: Synthesis of polyester with spirocyclic acetal units using monomer diol V.



Synthesis and characterization of polyesters with spiroacetal units

Spiro-diol V was successfully employed as a comonomer in the synthesis of copolyesters PHVT (semicrystalline as well as amorphous) by conventional polycondensation using DMT and 1,6-hexanediol (HD) (Scheme 6). HD was used for investigation because it can be conveniently produced from biomass resource, and the corresponding homopolymer, PHT, has great potential in textile, nanocomposites applications as it is semicrystalline polyester which is resistant to chemicals.[50,147,148] Two catalysts, dibutyltin (IV) oxide (DBTO) and titanium (IV) butoxide (TBT), were investigated for the polymerization. By using DBTO, copolyesters showed moderately high molecular weights (~10–30 kg/mol) with up to 30 % incorporation of spiro-diol V. When the more environmentally friendly TBT catalyst was used, high molecular weight PHT was achieved, however the copolymer containing acetal monomers showed significant decrease in molecular weight than the polyesters synthesized by DBTO catalyst. This result suggested that DBTO was more efficient for the polymerization of bulky monomer V, which was consistent with other reported monomers.[149]

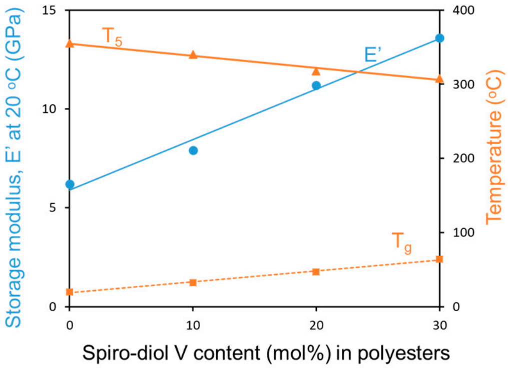


Figure 3. Thermal and dynamic mechanical properties of polyesters

The obtained series of polyesters with varied content of spirocyclic acetal units were subjected to TGA, DSC and DMA measurements to unravel the impacts of spiroacetal structures on the properties of the materials. According to TGA results, the initial thermal decomposition temperature for all polymers were rather high ($T_5 \geq 300$ °C, Fig. 3) with a slight decreasing trend upon the increased content of spiroacetal units. According to DSC results, T_g of the polyesters was significantly improved upon the incorporation of spiro-diol V (from 20 °C to 64 °C). According to DMA results, the storage moduli (E') of the new polyesters was also improved with increasing spirocyclic content (Fig. 3).

Currently, a partially bio-based diol monomer is used for the production of a commercial high performance polyester, Akestra^{TM}.[58,150,151] Our preliminary investigations in this paper demonstrated that the bio-based diol monomer V with similar spiroacetal units could potentially also be used to fabricate Akestra^{TM}-like copolyesters. However, the molecular design of this series of polyesters in this paper is not really optimal concerning the relatively low T_g (20-64 °C) compared to that of Akestra^{TM} (T_g~90-110 °C). The impacts of the spiroacetal units on other materials properties and recyclability are also interesting to study, which will be investigated in the next papers/manuscripts.

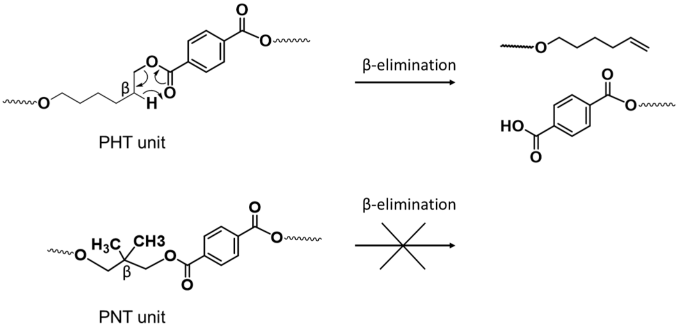
Chemical recycling of polyesters via selective hydrolysis of spiroacetal units (Paper II)

Molecular design and aim

In this study, the previously synthesized spirocyclic diol V (Paper I) was further investigated to fabricate a new series of polyesters with molecular design toward further enhanced materials properties and recyclability. Specifically, there are two key considerations in this work:

1. A more rigid bio-based diol, neopentyl glycol (NPG) was used instead of the more flexible 1,6-hexanediol (in Paper I). This was supposed to enhance the T_g to a comparable range as that of Akestra^{TM}. Furthermore, NPG does not have β-hydrogens, which should improve the thermal stability of the new series of polyesters by avoiding possible degradation by β-elimination mechanism as shown in scheme 7.

Scheme 7. Thermal degradation of PHT units by β-hydrogen transfer mechanism. Due to the absence of β-hydrogen, PNT units do not undergo this type of thermal degradation.[152,153]



2. Chemical recycling of the polyesters with spiroacetal units could be interesting to study. Previously, acidic hydrolysis of acetal-containing polymers always led to the formation of monomers, which means a complete loss of the bonding energy. We hypothesized that the acetal bonds in these polyesters could be selectively broken under mild conditions, which will lead to preservation of most of the bonding energy after hydrolysis. This is potentially a more energy efficient shorter loop chemical recycling.

Synthesis and characterization

A modified polycondensation protocol was used in this paper by using nitrogen flow instead of vacuum for the second step, and a higher reaction temperature (180-200 °C) than that in Paper I (140-160 °C), Amorphous copolyesters containing up to 50% spiro-diol V were produced and a decent molecular weight (~13-10 kDa) were obtained up to 30 % spirocyclic content (Table 1). These can be easily processed to make films by solution cast method, as well as thermally pressed to make specimens for DMA measurements without any visible sign of degradation. High T_g (105 °C) was obtained for the copolyester with 50% spiro-diol units. The thermal stability and mechanical properties of these new polyesters were significantly improved compared with those in Paper I. The T_g of 105 °C was achieved with 50% incorporation of spiro-diol whereas T_g of 96 °C was achieved with decent molecular weight copolyester with 30% Spiro diol in the backbone. As expected, investigation on isothermal stability at 300 °C showed that the new polyesters containing NPG units were more stable than the polyesters containing HD units reported in the Paper I.[152]

Table 1: Molecular, thermal, mechanical, and barrier properties of PNVT series polyesters

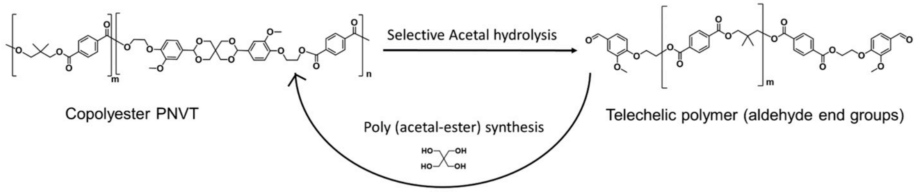
Polyester	M_n (kg/mol)	Đ	T_5 (TGA) (°C)	T_g (DSC) (°C)	E' at 35 °C (DMA) (GPa)	OTR (ml/m^2/day) (0.21 atm)
PNT	12.7	1.9	369	73	1.86	28.6
PNVT5	13.3	2.2	351	81	1.46	25.6
PNVT10	13.2	2.1	340	84	1.53	37.5
PNVT20	9.7	2.1	324	86	1.60	15.7
PNVT30	11.7	3.2	321	96	1.71	ND
PNVT40	7.4	2.8	311	96	ND	ND
PNVT50	4.1	2.1	300	105	ND	ND

The oxygen barrier of the obtained polyesters was preliminarily investigated using the solution-cast films (~ 2.5 cm diameter and 0.12-0.15 mm thickness). As a result, the OTR values showed a decreasing trend upon increased content of diol V in the polyesters, which was consistent with the enhanced rigidity and T_g (Table 1). It should be noted that larger hot-pressed films are usually used for the standard analysis of barrier properties[154–156]. Therefore, the values we reported should not be directly compared with other reported OTR values using different samples under different measurement conditions. However, in this work, all the polymer films were prepared and measured under similar conditions, so these data could be compared.

Chemical recycling via telechelic polymers

Selective hydrolysis of acetal bonds was investigated. The reaction parameters including the temperature, time, and the selection of acid catalyst were investigated (details see the appended Paper II). As a result, the acetal bonds in these copolyesters could be completely hydrolysed under certain mild acidic conditions using conc. HCl (*i.e.,* ≥40 °C, 3 h). Even weaker organic acids, such as citric acid, could also be used, but it would require higher temperature (80 °C) and longer reaction time (60 h) to completely hydrolyse the acetal bonds. The ester bonds in these polymers could be largely preserved. According to NMR and MALDI-TOF results (details see the appended Paper II), the resulting molecular species after hydrolysis contain well-defined telechelic polyesters with precisely two aldehyde groups (Scheme 8). The length of the telechelic polyesters is consistent with the subsequent sequence lengths of the PNT structures in the initial polymers. Repolymerization of the obtained telechelic polyesters via polyacetalization was performed under mild reaction conditions, which produced the original PNVTs conveniently (Scheme 8). This result indicated the potential for the incorporation of spirocyclic acetal units in the development of polyesters recyclable via a shorter loop chemical recycling.

Scheme 8. Chemical recycling of polyesters with spirocyclic structures via telechelic polymers.



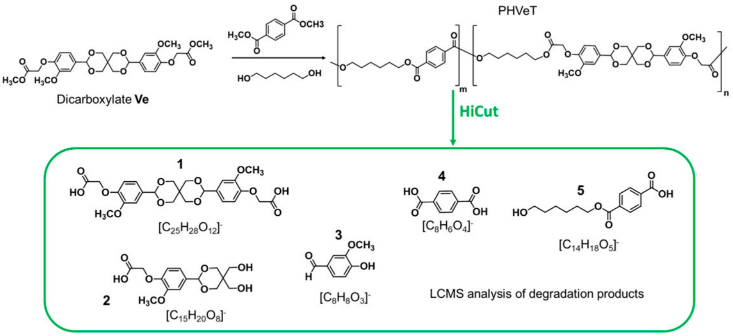
Synthesis and enzymatic degradation of polyesters using a dicarboxylate ester monomer with a spiroacetal unit (Paper III)

Ester bonds can be cleaved by enzymes. It is well known that aliphatic polyesters (PHAs, PBS, PLA) can be cleaved by many enzymes (e.g. esterase, cutinase, lipases, etc.),[124,157,158] which made them biodegradable or compostable under certain conditions.[159–161] Aromatic polyesters such as PET have been commonly understood as non-biodegradable. However, recent reports have revealed activity of certain enzymes (e.g. esterase, cutinases) on PET degradation, which shed light on the development of new polyesters that could be biodegradable or bio-recyclable using certain enzymes. In this work, we synthesized a new bio-based dicarboxylate monomer (Ve) with a spiroacetal unit, which could be used as a comonomer or substitution of terephthalates (DMT) in polyesters. The enzymatic degradation of the resulting polyesters containing the bulky spirocyclic acetal units using the enzyme *Humicola insolens* cutinase (HiCut) was also investigated.

Synthesis and characterization

The new dicarboxylate ester monomer (Ve) was synthesized conveniently using vanillin by a straightforward S_N2 reaction followed by acetalization with pentaerytritol (details see appended Paper III). Polymerization of monomer Ve with HD and DMT was carried out according to the polycondensation protocol described in Papers I-II (Scheme 9). This resulted in series of polyesters including the homopolyesters PHVe (using only Ve and HD) and copolyesters PHVeT (using Ve, DMT and HD) with moderately high molecular weights (M_n~10-21 kg/mol, Table 2).

Scheme 9: Spirocyclic dicarboxylate Ve based copolyester PHVeT and enzymatic degradation products.



The T_g of polyesters was enhanced with increasing amount of spiroacetal structures in the polymer backbone. Copolyesters PHVeT with T_g up to 61 °C was achieved with up to 80% of spiro-diester units in the backbone (with respect to TPA units). The homopolymer PHVe showed the highest $T_g \sim 67$ °C. All the obtained polyesters were thermally stable up to ≥300 °C (see Table 2 for T_5). The storage modulus (E') and T_g of these polyesters were analysed by DMA. For all polyesters, the storage moduli at the glassy plateau at 35 °C showed a linear increment from 0.76 to 2.28 GPa with the increased amount of spirocyclic units in the polymer backbone. OTR was also successfully measured for the solution-cast films of some polymers (diameter, ~3.4 cm and 0.12-0.15 mm thickness), which showed a decreasing trend upon increased content of Ve units (Table 2). The other polymers failed in the preliminary OTR measurements due to insufficient mechanical strength.

Table 2: Thermal, mechanical, barrier and molecular properties of PHVe and PHVeT polyesters.

Polyester	M_n (kg/mol)	Đ	T_5 (TGA) (°C)	T_g (DSC) (°C)	E' at 35 °C (DMA) (GPa)	OTR (ml/m^2/day) (0.21 atm)
PHT	36.0	1.9	354	20	0.76	ND
PHVeT-20	16.2	2.0	319	31	1.45	ND
PHVeT-40	21.4	1.9	304	43	1.98	41.4
PHVeT-60	11.3	1.6	318	52	1.94	ND
PHVeT-80	20.6	1.6	304	61	2.00	28.7
PHVe	10.2	1.9	306	67	2.28	20.1

Enzymatic degradation

The obtained new polyesters were subjected to enzymatic degradation using *Humicola isolens* cutinases. The aqueous media from the enzymatic degradation mixture (test) and negative control (without enzyme) were analysed by HPLC. As a result, in HPLC chromatogram, several peaks for different degradation products were observed in case of enzymatically degraded samples (Fig. 4). Furthermore, mass analysis of same aqueous media, showed presence of various masses as shown in the Scheme 9 (Structures 1-5). Peaks for TPA and vanillin with retention time 0.6-0.7 min and 0.9-1.1 min were identified in the enzymatically degraded samples, which was confirmed by control HPLC measurements of pure TPA and vanillin with the same method. Mass analysis of revealed that the degradation of ester bond between spiro-diester and HD was hydrolysable under the degradation conditions regardless of the presence or absence of the enzyme (negative control), as shown by the observed structures 1- 3 (Scheme 9). However, the intensity of the signals corresponded to degradation products 1-3 was significantly higher when the enzyme was used.

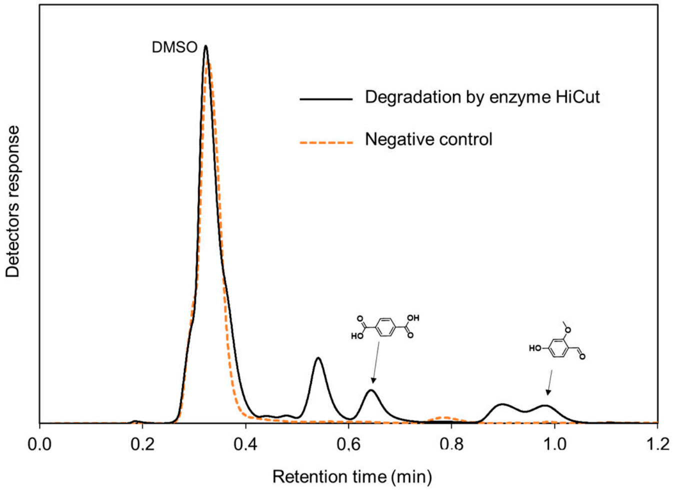


Figure 4. HPLC Chromatograms of samples analyzed from enzymatic degradation by HiCut and non-enzymatic degradation (negative control, orange dotted curve) of copolyester PHVeT-40 (black curve).

Enzymatic degradation of a commercial polyester Akestra$^{\text{TM}}$ with spirocyclic acetal units (Paper IV)

In Paper III, we studied the enzymatic degradability of polyesters containing spirocyclic units. Currently, the only commercialized PET-like polyester with spiroacetal units is Akestra$^{\text{TM}}$ (from Perstorp AB), and it is interesting to study the enzymatic degradability of Akestra$^{\text{TM}}$ using the same enzyme. Comparison of the result with the degradation of PET using the same enzyme is expected to provide further insight into the impact of spirocyclic acetal structures on the enzymatic degradation of polyesters.

In this study, two films (PET and Akestra$^{\text{TM}}$100) and three powders (PET, Akestra$^{\text{TM}}$90 and Akestra$^{\text{TM}}$110) were subjected to the enzyme degradation by HiCut at 70 °C. In general, the rate for enzymatic degradation can be influenced by various factors such as the physical form (film or powder), T_g, and crystallinity. With limited experiments, only similar samples could be meaningfully compared (e.g., film compared to film, powder compared to powder, Table 3).

As shown in Fig. 5, depolymerization of polyester samples was followed by the amount of TPA and TPAeq (MHET and BHET) after degradation. When the results of amorphous PET and Akestra$^{\text{TM}}$ films were compared (Fig. 5A), it was observed that PET film could be depolymerized faster than the Akestra$^{\text{TM}}$ film, which could be mainly attributed to the lower T_g and higher molecular mobility of compared to that of Akestra$^{\text{TM}}$100. When the two Akestra$^{\text{TM}}$ powders (Akestra$^{\text{TM}}$ 90 and 110) were compared (Fig. 5B), it was observed that Akestra$^{\text{TM}}$ 90 was enzymatically degraded faster than Akestra$^{\text{TM}}$ 110, which was likely due to the lower T_g and relatively higher flexibility of the former.

Table 3. Enzymatic degradation of polyesters PET and Akestra$^{\text{TM}}$ by HiCut.

Polymer	Form	IV[a] (dL/g)	T_g [b] (°C)	Crystallinity [b] (%)	Degree of depolymerization (%)
PET	Film	*	73	NA	6.1
Akestra 100	Film	0.63-0.67	102	NA	0.3
PET	Powder	0.80	78	11.3	12.7
Akestra90	Powder	0.64	95	NA	38.3
Akestra 110	Powder	0.63-0.67	108	NA	8.6

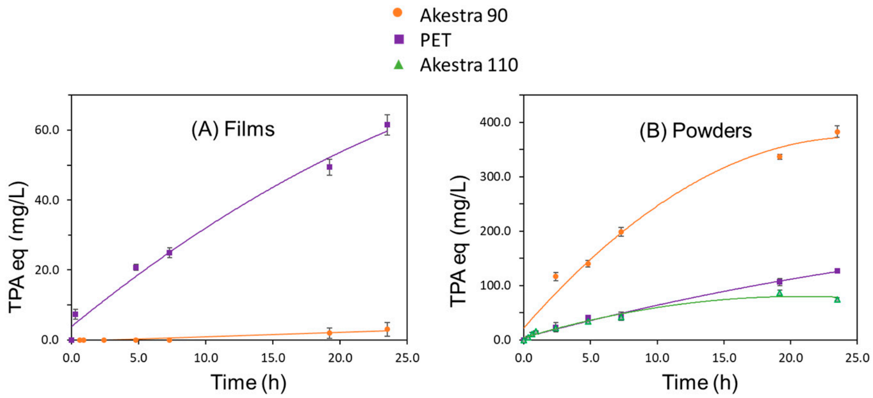


Figure 5. Enzymatic degradation products (TPAeq) for (A) the films of PET (purple squares) and Akestra^{TM} (orange dots) films, and (B) the powders of PET (purple squares), Akestra^{TM} 90 (orange dots) and Akestra^{TM} 110 (green triangles), as a function of time.[124]

In summary, this work has demonstrated that the incorporation of spiroacetal units in polyester backbones could effectively influence the degradation using HiCut enzyme, which could be related to the change in the T_g and crystallinity. Additionally, molecular docking simulation studies showed that the ester group between TPA-EG was easily hydolyzable as compared to the ester group between TPA-SPG.

Methoxyhydroquinone-based dicarboxylate monomer and its derived polyesters (Paper V)

In this work, we used methoxyhydroquinone (can be obtained by oxidation of vanillin or enzymatic depolymerization of lignin)[20,140,162–164] to make a dicarboxylate monomer for substitution of DMT/TPA in polyesters synthesis. Polymerizability of this new monomer and the enzymatic degradation of the resulting polyesters were investigated.

Synthesis and characterization

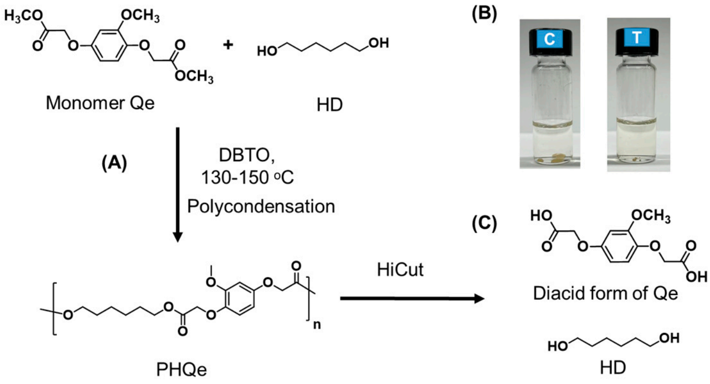


Figure 6. (A) Synthesis of polyester PHQe using methoxyhydroquinone-based dicarboxylate monomer Qe. (B) Visualization of enzymatic degradation of PHQe and negative control (without enzyme). The test sample with enzyme and the negative control without enzyme are marked with the letter *T and C* on the top of the respective vials. (C) Plausible degradation products (note, the shown structure of diacid form of Qe was not observed).

The dicarboxylate monomer (Qe) was synthesized by a one-step reaction from methoxyhydroquinone. Polymerization of monomer Qe with diols with varying structures including three linear aliphatic diols *i.e.*, HD and BD, NPG and a cyclic CHDM (Fig. 6A shows scheme for synthesis of polyester PHQe as an example), resulted in moderately decent molecular weight (~7 -15.6 g/mol) polyesters (PHQe, PBQe, PNQe, and PCQe, Table 4). The T_g of the new series of polyesters varied with the rigidity of the diols used, and the highest T_g (42 °C) was obtained with PCQe, which was due to the rigid structure of monomer CHDM. All the polyesters were thermally stable with T_5 up to 300 °C according to TGA results, except for PHQe which possessed slightly lower T_5 (277 °C, Table 4).

Table 4: Molecular and thermal properties of MHQ-based polyesters.

Polyester	M_n (kg/mol)	Đ	T_5 (TGA) (°C)	T_g (DSC) (°C)
PHQe	11.2	2.2	277	11
PBQe	7.3	2.1	310	17
PNQe	15.6	1.9	310	31
PCQe	13.7	2.3	313	42

Preliminary investigations on enzymatic degradation

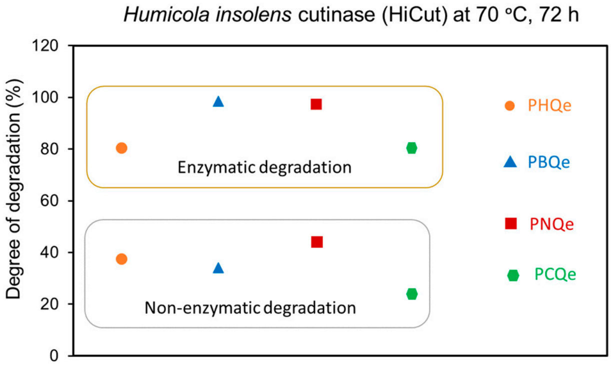


Figure 7. Weight loss of the enzymatic and non-enzymatic degradation of MHQ-based polyesters.

MHQ-based polyesters were subjected to degradation by HiCut enzyme, which has been previously used for the degradation of PET and Akestra^{TM} (Paper III and IV). In this work, the obtained MHQ-based polyesters have aliphatic ester groups, which should be degraded faster compared to aromatic ester groups. By visualization, the suspended polymer powders in the enzyme solution showed considerably smaller size after the enzymatic degradation (3 days, Fig. 6B). The remaining powders were washed with SDS and dried before subjected to weighing. The degree of degradation (%) was calculated based on the remaining weight of polymer residue with respect to initial amount used (*i.e.*, 20 mg). As shown in Fig. 7, the weight loss after 3 days of enzymatic degradation was in the range of 80-99%, while the negative control (without enzyme) showed only 20-45% weight loss after 3 days. The remaining polymer residues were analyzed by ^{1}H NMR spectroscopy, which showed all the signals for respective original polymers. The intensity of the end group signals from protons of respective diols (signals for -OH or -CH_2OH) were significantly increased after degradation, suggesting a decreased molecular weight (for details see ESI of appended Paper V). Unfortunately, the quantity of the residue solid was insufficient for GPC analysis.

The aqueous phase after the enzymatic degradation was extracted with chloroform, which was then subjected to NMR analysis. As a result, all the corresponding diols (e.g., HD, BD, NPG and CHDM) were clearly observed in the NMR spectra, which confirmed the hydrolysis of the ester bonds (Fig. 8 shows presence of HD in aqueous phase of polyester PHQe, is shown as an example). No signals corresponded to the diacid form of monomer Qe (Fig. 6C) has been observed in the NMR spectra of aqueous phase extracted in chloroform, which presumably could be due to the lower solubility of the possible products formed (e.g., the diacid shown in Fig. 6C, or other oligomers).

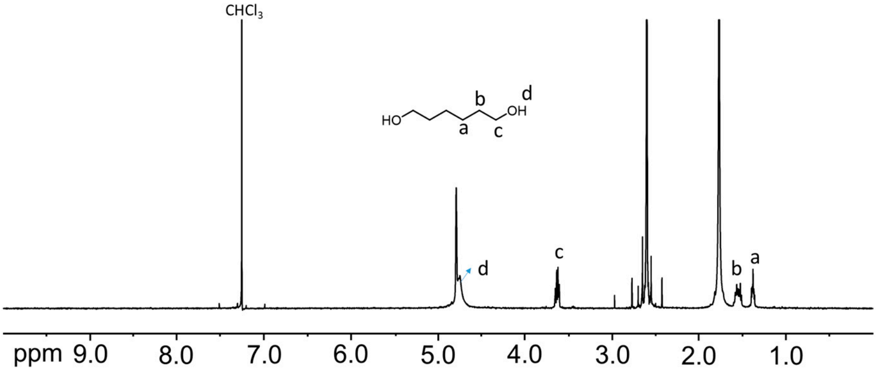


Figure 8. ^{1}H NMR spectrum of the chloroform extract from the aqueous media after the enzymatic degradation of PHQe.

Conclusions

In this thesis, new bio-based monomers were designed and synthesized, which were used to fabricate new polyesters with desirable properties and recyclability. Particularly, we have demonstrated that vanillin-based diols and dicarboxylates with spirocyclic acetal units could be successfully incorporated into polyester backbones to enhance their T_g, as well as the mechanical and barrier properties. We have also demonstrated that the incorporation of spiroacetal units in polyester backbones could be considered as a factor to facilitate the molecular design toward enhanced chemical and biological recyclability.

In Paper I, we synthesized spiro-bisphenol and diol using an environmentally friendly procedure. LCA of spiro-bisphenol and spiro-diol showed low GHG emissions of these monomers. The spiro-diol monomer was used successively to produce semicrystalline and amorphous copolyesters with enhanced T_g and mechanical properties. The storage moduli of these copolyesters were similar to those of Akestra^{TM} 90 and Akestra^{TM} 110. 30% incorporation of the spirocyclic unit in the polyesters resulted in the highest T_g ~64 °C.

In Paper II, spiro-diol V in Paper I was used to synthesize another series of polyesters with NPG and DMT. This improved not only the T_g (81-105 °C) but also the isothermal stability, due to the rigid structure and absence of β-hydrogen. Acidic hydrolysis of these polyesters under mild conditions could completely break the acetal bonds while leave the ester bonds basically intact. This produced telechelic polyesters with aldehyde functional groups, which can be repolymerized back to the initial polymer. This demonstrated the feasibility of using spiroacetal units as a structure element for the design of polyesters with the possibility for shorter loop chemical recycling.

In Paper III, new rigid spirocyclic dicarboxylate monomer was synthesized and investigated as a potential replacement for TPA in polyesters. The new polyesters synthesized from spiro-dicarboxylate monomer showed improved thermal and mechanical and barrier properties due to increasing rigid monomer content. HiCut enzyme used for PET degradation was found to be capable of degradation of the obtained copolyesters with new dicarboxylate units.

In Paper IV, it was observed that a commercial high-performance polyester Akestra^{TM} with spiroacetal units could be degraded by using HiCut, the same enzyme used in Paper III. The degradation rate depended on the molecular structures, thermal properties (T_g), crystallinity and physical forms (film or powder). It was also found that HiCut could hydrolyze ester bonds in Akestra^{TM}, releasing TPA, EG and TPA-SPG units. The results were found to be in correlation with the molecular docking simulations.

In Paper V, one step synthesis was used for producing a dicarboxylate monomer from methoxyhydroquinone. The new monomer showed polymerizibilty with different types of diols. The thermal properties were improved with increasing rigidity of diol structures. Polyesters synthesized using MHQ-based diester and CHDM showed T_g around 42 °C. These polymers in the powder form could be almost completely degraded by *Humicola insolens* at 70 ºC in 3 days.

Future Outlook

In the future, the vanillin-based bisphenol and spirocyclic diol synthesized in the thesis can be used for the synthetic investigations of other types of polymers such as polycarbonates and polyurethanes, and their chemical and enzymatic recyclability could be interesting to investigate. MHQ-based dicarboxylate monomer could also be further investigated as a comonomer together with other sustainable monomers like FDCA. In addition, other aromatic aldehydes and ketones (e.g., benzaldehyde, syrigaldehyde, acetovanillone) derived from lignin can be interesting for designing new acetal/ketal monomers. Mixtures of such compounds that could be directly obtained from lignin fragmentation could also be investigated for monomer and polymer synthesis, if it is not too complicated (e.g., without mono- or tri-functional molecules).

Chemical recycling via telechelic polymers could also be thoroughly investigated using other polymers containing cleavable acetal bonds including the commercial polymer Akestra^{TM}. In the literature, it has been reported that other polyesters with cyclic acetal units could be selectively hydrolyzed at the ester positions.[112] Some other polymers with spiroacetal units could be non-selectively hydrolyzed to monomers.[57] It would be interesting to investigate the applicability and parameters of such a new chemical recycling strategy. Enzymatic degradability of polyesters could also be further explored. Deeper insight into the degradation mechanism could be explored by investigating all the changes in the physical and chemical properties. Re-use and re-polymerization of the degradation products from enzymatic degradation can also be investigated.

Although the polymers synthesized in this thesis are mainly amorphous, we found that polymers with certain crystallinity could be achieved using relatively low amount of spiroacetal monomers. These polymers could be of interest for fiber spinning investigations toward sustainable textiles. Particularly the spiroacetal units in these polymers may facilitate the chemical recycling of textile fibers, which are usually challenging to recycle.

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//Smita

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Plastics are widely used everyday in our clothes, lunch boxes, mobile phones and many other things. But their large production from non-renewable fossil resources and limited recycling methods have been an issue. In my thesis, I have made very interesting biobased building blocks and used them to make biobased plastics. I have also studied new recycling strategies for the biobased plastics by using chemicals or enzymes. These strategies may shed some light on the design of recyclable biobased plastics.

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