

LUND UNIVERSITY

Exploring different thermoplastics from lignocellulosic building blocks and monomers

Bonjour, Olivier

2023

Document Version: Publisher's PDF, also known as Version of record

Link to publication

Citation for published version (APA): Bonjour, O. (2023). Exploring different thermoplastics from lignocellulosic building blocks and monomers. Lund University.

Total number of authors: 1

Creative Commons License: CC BY

General rights

Unless other specific re-use rights are stated the following general rights apply:

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights. • Users may download and print one copy of any publication from the public portal for the purpose of private study

or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: https://creativecommons.org/licenses/

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117 221 00 Lund +46 46-222 00 00

Exploring different thermoplastics from lignocellulosic building blocks and monomers

OLIVIER BONJOUR | CENTRE FOR ANALYSIS AND SYNTHESIS | LUND UNIVERSITY



ISBN 978-91-7422-968-4

Centre for Analysis and Synthesis Department of Chemistry Faculty of Engineering Lund University



Exploring different thermoplastics from lignocellulosic building blocks and monomers

Olivier Bonjour



DOCTORAL DISSERTATION

Doctoral dissertation for the degree of Doctor of Philosophy (Ph.D.) at the Faculty of Engineering at Lund University to be publicly defended on September 29th, 2023, at 09.00 in Lecture Hall KC: A, Kemicentrum

Faculty opponent Prof. Karin Odelius, KTH, Royal Institute of Technology

Organization	Document name
LUND UNIVERSITY	Doctoral Dissertation
Faculty of Engineering	Date of issue
Department of Chemistry	2023-09-29
Centre for Analysis and Synthesis	
Author: Olivier Bonjour	Sponsoring organization
Title and subtitle	

Exploring different thermoplastics from lignocellulosic building blocks and monomers

Abstract

The need to replace conventional fossil-based plastics is becoming more imperative. As climate change is more visibly affecting our society, employing non-sustainable resources to produce plastics is aggravating the problem. Moreover, these long-lasting, non-recycled wastes end up in our oceans, creating an intrinsic environmental pollution problem. Researching new biobased building blocks to enable the production of plastics with better properties than conventional plastics has been a long and evolving process. Such bioadvantage strategy usually focuses on designing rigid monomers to improve the thermal and mechanical properties. This thesis focuses on the design of several new lignocellulosic monomers and building blocks to produce thermoplastics. The two strategies mentioned (rigidity and polarity) were explored and are reported here.

In Paper I, isosorbide-based methacrylate monomers with varying pendant alkanovl chains were synthesized, and subsequently polymerized. The resulting polymers showed thermal properties depending on the length of the pendant alkanovl chain. Shorter chains yielded amorphous materials, while longer chains afforded semi-crystalline polymers, even showing liquid crystalline behavior in some cases. In Paper II, a rigid spirocyclic diol derived from citric acid was synthesized and used to produce polycarbonates of different molecular weights. The thermal properties of the higher molecular weight were significantly better. In Paper III, the spirocyclic diol from Paper II was, alongside two other spirocyclic diols derived from citric acid, (meth)acrylated to obtain rigid di(meth)acrylate monomers of different structures. These monomers were polymerized by thiol-Michael polymerization with dithiols of various rigidity, affording a library of polymers. Their thermal properties were successfully correlated to their chemical structure. Additionally, the ketals units were successfully cleaved in a mixture of aqueous acid and acetone, opening the way for potential chemical recycling. In Paper IV. besides using rigid structures, polar groups such as nitrile functions were introduced in lignin-inspired polymers, leading to polymers and copolymers with improved thermal properties, as well as solvent resistance. In Paper V, using a similar strategy, a bis-vanillin monomer containing nitrile functions was employed to produce polyesters with improved thermal properties.

Keywords: Biobased, polymethacrylates, polycarbonates, polyesters, poly(β -thioether ester)s, chemical recycling

Classification system and/or index terms (if any)		
Supplementary bibliographical information		Language: English
ISSN and key title:		ISBN: 978-91-7422-968-4 (printed)
		ISBN: 978-91-7422-969-1 (digital)
Recipient's notes	Number of pages: 79	Price
	Security classification	

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature

Exploring different thermoplastics from lignocellulosic building blocks and monomers

Olivier Bonjour



Cover photo by Olivier Bonjour Copyright pp 1-79 Olivier Bonjour

Paper I © American Chemical Society (open access) Paper II © Royal Society of Chemistry (open access) Paper III © American Chemical Society (open access) Paper IV © American Chemical Society (open access) Paper V © by the Authors (Unpublished manuscript)

Lund University Faculty of Engineering Department of Chemistry Centre for Analysis and Synthesis

ISBN 978-91-7422-968-4 (Print) ISBN 978-91-7422-969-1 (Digital)

Printed in Sweden by Media-Tryck, Lund University Lund 2023



Media-Tryck is a Nordic Swan Ecolabel certified provider of printed material. Read more about our environmental work at www.mediatryck.lu.se

MADE IN SWEDEN 📲

« Je suis de ceux qui pensent que la science est d'une grande beauté. Un scientifique dans son laboratoire est non seulement un technicien :il est aussi un enfant placé devant des phénomènes naturels qui l'impressionnent comme des contes de fées. »

– Marie Skłodowska-Curie

Table of Contents

	1.1	Populärvetenskaplig sammanfattning	8
	1.2	Popular scientific summary	9
	1.3	Résumé scientifique simplifié	10
	1.4	List of Papers	11
	1.5	Author's contribution to the papers	12
	1.6	Abbreviations	13
2	Intr	roduction	15
	2.1	The interest in biobased polymers	15
	2.2	Isosorbide	18
	2.3	Alicyclic diols and diketones	19
	2.4	Vanillin and lignin-inspired monomers	20
	2.5	Polyacrylates and polymethacrylates	21
		2.5.1 Synthesis	22
		2.5.2 Biobased polyacrylates and polymethacrylates	23
	2.6	Polycarbonates	23
		2.6.1 Synthesis	23
		2.6.2 Biobased polycarbonates	24
	2.7	Thiol-Michael polymerization	
	2.0	2.7.1 Biobased poly(<i>p</i> -thioether ester)s	25
	2.8	Polyesters	26
		2.8.1 Synthesis 2.8.2 Biobased polyesters	20 27
	2.9	Recycling	
	2.10	0 Context and Scope	
3	Exp	perimental work	31
	3.1	Monomers syntheses	
		3.1.1 Esterification	
		3.1.2 Ketalization	31
		3.1.3 Aldehyde conversion to nitrile	32
		3.1.4 Oxidative radical coupling	32

		3.1.5	Williamson ether synthesis	.32
	3.2	Polym 3.2.1 3.2.2	er syntheses Poly(meth)acrylates Polycarbonates	32 32 33
		3.2.3	Poly(β -thioether ester)s	.33
	33	Charac	terizations	.55
4	5.5 S			.55
4	Sum	imary of	appended papers	
	4.1 (Pan	Isosort er I)	bide-based polymethacrylates with tunable phase transitions	; 35
	(1 ap	4.1.1	Monomer synthesis.	.35
		4.1.2 methac	Synthesis and characterization of the poly(alkanoyl isosorb	vide 36
	4.2	Citric	acid-derived spirocyclic diols for polycarbonates synthesis	.50
	(Pap	er II)		.40
		4.2.1 4.2.2	Synthesis and characterization of polycarbonates (PCs)	.40 41
	4.3 thio	Citric ether est	acid-derived spirocyclic diols for chemically recyclable polyeer)s (Paper III)	(β- 43
		4.3.1	Monomers synthesis	.43
		4.3.2 4.3.3	Poly(β -thioether ester)s synthesis and characterization Chemical recyclability of the poly(β -thioether ester)s	.45
	4.4	Lignin	-inspired nitrile-containing aromatic monomers for	•••
	poly	methacr	ylates synthesis (Paper IV)	48
		4.4.1	Monomers design and synthesis	.48
		4.4.2 charact	erizations	49
	4.5 (Pap	Vanill	in-based nitrile-containing monomer for polyesters synthesi	S 51
	(I ap	4.5.1	Monomer design and synthesis	.51
		4.5.2	Polyesters and copolyesters synthesis and characterization	52
5	Con	clusions		
6	Out	look		.57
7	Ack	nowledg	ments	59
8	Refe	erences .		62

1.1 Populärvetenskaplig sammanfattning

Sedan upptäckten av syntetisk plast i början av 1900-talet har dess konsumtionen ökat exponentiellt och dessa material är idag oumbärliga för olika industrier. Nödvändiga för förpackningar, råvaruanvändning, medicinska tillämpningar, konstruktion och fordonsproduktion, plaster finns överallt i vårt samhälle. År 2021 producerades 390 miljoner ton plast, och den årliga plastproduktionen har bara ökat sedan dess, allt eftersom länder antar den västerländska samhällsmodellen. Tyvärr är det mesta av plasten som produceras över hela världen olje- eller naturgasbaserad. För närvarande kan storskalig plastproduktion endast uppnås genom användning av fossila resurser, och cirka 5 % av världens fossila förbrukas för detta ändamål årligen. Med det växande behovet av plast och den obönhörliga bristen på fossila resurser är det en nödvändighet att hitta alternativ. En annan nackdel med att använda fossil-baserad plast är deras dåliga nedbrytbarhet. En betydande mängd plast återvinns för närvarande inte och som därför förbränns, begravd i soptippar eller går förlorad i naturen, hamnar sig i våra hav och skapar "nya kontinenter". Men även när plast återvinns är processen sällan miljövänlig. Till exempel, det allt populärare sättet att återvinna plastavfall är att förbränna det. Den frigjorda förbränningsenergin används sedan för andra ändamål som till exempel uppvärmning av hushåll. Men eftersom plast huvudsakligen är baserad på fossila bränslen frigör denna process nya växthusgaser vilket inte är hållbart.

Därför verkar biobaserad plast vara ett önskvärt mål eftersom de kommer från förnybara källor. Produktion av biobaserad plast kan vara ett sätt att minska förbrukningen av fossila bränslen. Dessutom kan förbränning av biobaserad plast ha en lägre miljöpåverkan än förbränning av fossil-baserad plast eftersom kolatomerna som bildar polymererna kommer från koldioxid som absorberat av växter i första hand. I detta doktorsarbete är syftet att designa och utveckla nya lignocellulosabaserade byggstenar från isosorbid, citronsyra och lignin för att tillverka polymerer med stort biobaserat innehåll. Monomererna utformades med rigida molekylära strukturer för att förbättra de termiska och mekaniska egenskaperna hos de resulterande polymererna. Att utveckla bioplaster med hög glasövergångstemperatur är utmanande för industrin. Dessutom prioriterades användningen av gröna kemiska reaktioner, eftersom det är önskvärt med miljövänliga processer. Den kemiska återvinningsbarhen för några av polymererna undersöktes, vilket kan öppna vägen för en cirkulär ekonomi för dessa bioplaster.

1.2 Popular scientific summary

Since the discovery of synthetic plastics at the beginning of the 20^{th} century, the consumption of plastics has increased exponentially, and these materials are essential for various industries. Essential for packaging, commodity use, medical applications, construction, and vehicle production, plastics are everywhere in our society. In 2021, 390 million tons of plastics were produced, and the annual plastic production has only grown since, as countries adopt the Western society model. Unfortunately, most of the plastics produced worldwide are petroleum or natural gas-based. Currently, large plastic production can only be achieved through fossil feedstock consumption, and approximately 5% of extracted fossil feedstocks are consumed to this end annually. With the growing need for plastics and the inexorable scarcity of fossil feedstocks, finding an alternative is a necessity. In addition, another drawback of using fossil fuel-based plastics is their poor degradability. Currently, a significant amount of plastics is not recycled, but is either burned or lost in nature, settling in our oceans, creating "new continents." However, even when plastics are recycled, the process is rarely environmentally friendly. For example, an increasingly popular way of recycling plastic waste is to incinerate it, and the combustion energy released is then used for other purposes such as heating households. But since plastics are mainly fossil fuel-based, this process releases new greenhouse gases which is not sustainable.

Hence, biobased plastics seem to be a desirable target because they come from renewable sources. Large-scale production of biobased plastics may be a way to reduce fossil feedstock consumption. Additionally, the incineration of biobased plastics could have a lower environmental impact than the incineration of fossilbased plastics since the carbon atoms forming the polymers come from carbon dioxide absorbed by plants in the first place. In this thesis, the aim is to design and develop new lignocellulosic building blocks derived from isosorbide, citric acid, and lignin to make polymers with high biobased content. The monomers were designed with rigid molecular structures to improve the thermal and mechanical properties of the resulting polymers. Developing bioplastics with high glasstransition temperatures is a generally great challenge for the industry. Furthermore, the use of green chemical reactions was also considered, as environmentally friendly processes are desirable. The potential chemical recyclability of some of the polymers was investigated, opening the way to a circular economy for these bioplastics.

1.3 Résumé scientifique simplifié

Depuis leur découverte au début du XX^e siècle, les plastiques de synthèse sont devenus essentiels pour diverses industries et ont vu leur consommation croître de facon exponentielle. Incontournables pour l'emballage, les produits de base, certaines applications médicales, la construction et la production de véhicules, le plastique est partout dans notre société. En 2021, 390 millions de tonnes de plastique ont été produites, et la production annuelle de plastique continue de croître à mesure que de nouveaux pays adoptent le modèle de société occidentale. Malheureusement, la plupart des plastiques produits dans le monde sont issus du pétrole ou du gaz naturel. Actuellement, les besoins croissants en plastiques ne peuvent être adressés que par l'utilisation de ressources fossiles, et environ 5% des ressources fossiles sont consommées à cette fin chaque année. Cependant, la raréfaction inexorable des stocks de ressources fossiles nous oblige à trouver des alternatives. Par ailleurs, les plastiques produits à partir de ressources fossiles sont réputés pour leur faible dégradabilité, ce qui représente un problème supplémentaire. Aujourd'hui, une quantité importante de plastique n'est pas recyclée et par conséquent perdue dans la nature, se déposant dans nos océans, créant ainsi de « nouveaux continents ». Cependant, même lorsqu'il est recyclé, le processus est rarement respectueux de l'environnement. C'est le cas par exemple de l'incinération des déchets plastiques. qui est de plus en plus populaire. L'énergie de combustion libérée est récupérée afin, entre autres, de chauffer des ménages. Mais comme le plastique est principalement produit à base de ressources fossiles, ce processus libère des gaz à effet de serre supplémentaires dans l'atmosphère, ce qui n'est pas durable.

Par conséquent, concevoir des plastiques à partir de ressources renouvelables est souhaitable. La production à grande échelle de ces plastiques dits biosourcés pourrait aider à réduire la consommation de ressources fossiles. En outre, l'incinération de plastique biosourcé pourrait avoir un impact environnemental moindre que pour du plastique issu de ressources fossiles. En effet, l'incinération du plastique biosourcé libère dans l'atmosphère du dioxyde de carbone qui avait été préalablement absorbé et assimilé par des plantes. Dans cette thèse, l'objectif est de concevoir et développer de nouveau monomères dits lignocellulosiques, c'est-à-dire issus de lignocellulose, principal composant des cellules végétales. Les monomères présentés ici sont dérivés d'isosorbide, d'acide citrique et de lignine, et ont été utilisés pour fabriquer des polymères à haute teneur biosourcée. Ces monomères ont été conçus pour avoir une structure moléculaire rigide afin d'améliorer les propriétés thermiques et mécaniques des polymères subséquemment produits. Obtenir des bioplastiques avant une température de transition vitreuse élevée est souhaitable pour l'industrie. Par ailleurs, l'emploi de réactions chimiques vertes a également été considéré, car il est désirable d'avoir des processus respectueux de l'environnement. Enfin, le potentiel de recycle chimique de certains polymères a été étudié, ouvrant la voie à une économie circulaire pour ces bioplastiques.

1.4 List of Papers

Paper I

S. Laanesoo, **O. Bonjour**, J. Parve, O. Parve, L. Matt, L. Vares and P. Jannasch, *Poly(alkanoyl isosorbide methacrylate)s: From Amorphous to Semicrystalline and Liquid Crystalline Bio-based Materials.* Biomacromolecules, 2021, 22, 640–648.

Paper II

O. Bonjour, I. Liblikas, T. Pehk, T. Khai-Nghi, K. Rissanen, L. Vares and P. Jannasch, *Rigid biobased polycarbonates with good processability based on a spirocyclic diol derived from citric acid.* Green Chem., 2020, 22, 3940–3951.

Paper III

R. Sedrik, **O. Bonjour**, S. Laanesoo, I. Liblikas, T. Pehk, P. Jannasch, and L. Vares, *Chemically Recyclable Poly*(β -thioether ester)s Based on Rigid Spirocyclic Ketal Diols Derived from Citric Acid. Biomacromolecules, 2022, 23, 2685–2696.

Paper IV

O. Bonjour, H. Nederstedt, M. V. Arcos-Hernandez, S. Laanesoo, L. Vares and P. Jannasch, *Lignin-Inspired Polymers with High Glass Transition Temperature and Solvent Resistance from 4-Hydroxybenzonitrile, Vanillonitrile, and Syringonitrile Methacrylates*. ACS Sustainable Chem. Eng., 2021, 9, 16874–16880.

Paper V

O. Bonjour, Ilme Liblikas, L. Vares and P. Jannasch, *Synthesis and thermal properties of polyesters based on a bis-vanillonitrile diester monomer*. (Unpublished manuscript)

Publications not included in this thesis:

Paper VI

L. Matt, I. Liblikas, **O. Bonjour**, P. Jannasch and L. Vares, *Synthesis and anionic polymerization of isosorbide mono-epoxides for linear biobased polyethers*. Polym. Chem., 2021, 12, 41, 5937–5941.

Paper VII

L. Matt, R. Sedrik, **O. Bonjour**, M. Vasiliauskaité, P. Jannasch and L. Vares, *Covalent Adaptable Polymethacrylate Networks by Hydrazine Crosslinking via Isosorbide Levulinate Side Groups*. ACS. Sustainable Chem. Eng., 2023, 11, 22, 8294–8307.

1.5 Author's contribution to the papers

Paper I

Monomers and polymers synthesis were performed by Siim Laanesoo. I performed all thermal characterizations and dynamic mechanical measurements. I performed the rheological and microscopical study of the liquid crystalline phase behavior. I participated in writing and revising the manuscript.

Paper II

Monomer and polymers syntheses were performed by Ilme Liblikas. Structural elucidation of the monomer by NMR spectroscopy was performed by Toñis Pehk, and X-ray scattering by Truong Khai-Nghi and Kari Rissanen. I performed all thermal characterizations as well as dynamic mechanical measurements. I also performed the thermal stability study by TGA and rheology, the hydrolytic study being performed by Ilme Liblikas. I participated in writing and revising the manuscript.

Paper III

Monomer and polymer syntheses were performed by Rauno Sedrik and Siim Laanesoo, as well as the hydrolytic stability study. I performed all thermal characterizations and dynamic mechanical measurements. I participated in writing and revising the manuscript.

Paper IV

I performed most of the monomer and polymer syntheses and all thermal characterizations, including dynamic melt rheology. I also performed the solvent resistance study. I wrote the first draft of the manuscript.

Paper V

I planned and performed most of the syntheses and characterizations of the monomers and polymers. Ilme Liblikas performed part of the monomer synthesis. I performed all thermal and structural characterizations. I wrote the first draft of the manuscript.

1.6 Abbreviations

AA	Acrylic acid
ACH	Acetone cyanohydrin process
AcOH	Acetic acid
ACN	Acetonitrile
BHET	Bis (2-hydroxyethyl) terephthalate
BPA	Bisphenol A
BPA-PC	Bisphenol A polycarbonate
Ð	Dispersity
DAC	Dimethyl 1,3-acetone dicarboxylate
DBTO	Dibutyltin oxide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DEFDC	Diethyl 2,5-furan dicarboxylate
DMA	Dynamic mechanical analysis
DMAc	Dimethylacetamide
DMAP	4-(Dimethylamino)pyridine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DMT	Dimethyl terephthalate
DPC	Diphenyl carbonate
DSC	Differential scanning calorimetry
EG	Ethylene glycol
EtOAc	Ethyl acetate
EtOH	Ethanol
FDCA	2,5-Furan dicarboxylic acid
FTIR	Fourier transform infrared
HR-MS	High-resolution mass spectrometry
IPCC	Intergovernmental Panel on climate change

LVR	Linear viscoelastic region
MAA	Methacrylic acid
MeOH	Methanol
MMA	Methyl methacrylate
$M_{ m n}$	Number average molecular weight
$M_{ m p}$	Molecular weight of the highest peak
$M_{ m w}$	Weight average molecular weight
n.d.	Not Determined
NMR	Nuclear magnetic resonance
OPD	Octahydro-2,5-pentalenediol
PBF	Poly(butylene 2,5-furan dicarboxylate)
PC	Polycarbonate
PEth	Petroleum ether
PET	Polyethylene terephthalate
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
pTSA	<i>p</i> -Toluene sulfonic acid
RM	Rhizomucor miehei
RT	Room temperature
SAN	Poly(styrene-co-acrylonitrile)
SEC	Size exclusion chromatography
Td	Decomposition temperature at a maximum rate of decomposition
$T_{ m d,95\%}$	Temperature at 5% mass loss (by TGA)
TFA	Trifluoroacetic acid
$T_{ m g}$	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPA	Terephthalic acid

2 Introduction

Plastics have a prominent place in our modern society. They can be found everywhere, in all shapes and colors. They are employed in a wide variety of applications, like building and construction, electronics, automotive, medical, packaging, and more.¹ Since their first appearance and beginning of mass production in 1950, global production has increased at a steady 8.4% annual growth rate.² and was estimated to be about 390 million tons in 2021.³ We are today strongly dependent on these materials. It is estimated that since the beginning of the 20^{th} century, a total of 8300 million tons of virgin plastic materials have been produced, essentially from fossil resources, generating close to 6300 million tons of plastic waste. Unfortunately, about 80% of this gigantic amount of waste has ended up either in landfills or lost in nature. As plastics are very resilient to natural degradation, they are greatly damaging the environment.^{2,4} One example of plastic waste impacting the environment is the estimation that our oceans will contain more plastic than fish, by weight, in 2050.⁵ Hence, plastic waste management has raised a lot of environmental and economic concerns, forcing governments to take action.^{6,7} Unfortunately, the current strategies for recycling plastics are onerous and time-consuming. Despite the vast global effort in recycling as much as possible, the sheer amount of plastic waste, as well as the multiplicity of plastic types, make it challenging to scale up and is not economically viable long-term. Even growing, more economical methods like energy recovery⁸ are not environmentally friendly. A new solution is needed.

Several strategies are available to lower the environmental footprint of plastics. One strategy, the development of biobased polymers, has raised a lot of attention. Using natural resources, plastic production would become more sustainable, enabling a transition to a circular economy. This thesis will focus mainly on developing new biobased monomers, their polymerizations, and their properties. Chemical recycling of some of the presented polymers will also be discussed.

2.1 The interest in biobased polymers

Today, most plastics are fossil-based. In 2021, biobased polymers constituted less than 2% of all plastics.³ Historically, fossil resources were primarily used to synthesize polymers since oil was a relatively inexpensive and abundant resource.

Also, decades of innovation made it possible to obtain a vast catalog of building blocks from oil distillation and cracking (e.g.; styrene, ethylene, propylene, ethylene glycol, acrylates, terephthalic acid, etc).⁹⁻¹¹ However, the finite nature of oil and its forecasted depletion incite us to develop sustainable ways of producing plastics.¹² Moreover, there are many environmental concerns about using oil. Extraction techniques like fracking can lead to groundwater and soil contamination.^{13,14} and have been shown to induce tremors and earthquakes.¹⁵ In addition, refining and petrochemical production are energy-intensive industries, contributing to greenhouse gas emissions. Besides production, plastics also present drawbacks regarding their end-of-life. Fossil-based plastics have a long degradation lifetime. which is intrinsically problematic. Plastic waste cannot be left to degrade naturally, it needs to be collected and processed. However, modern plastic waste management techniques are not necessarily sustainable. Recycling is time and energy-consuming, and more modern methods, like the increasingly popular incineration of collected plastic waste, also called "energy recovery,"⁸ are not environmentally friendly. Indeed, such incineration inevitably releases carbon dioxide into the atmosphere. Since the plastics are fossil-based, the released carbon was previously stored underground for millions of years. Consequently, burning plastic waste increases the overall amount of greenhouse gases in the atmosphere, contributing to climate change. We need to find a solution to replace fossil-based plastics.

Although fossil-based plastics have a lot of environmental drawbacks, it is difficult to stop using plastic entirely because they are deeply intertwined with human life and indispensable in modern society. One strategy to make greener plastics is using biomass to make so-called biobased polymers. The term biomass refers to all materials produced from microorganisms, plants, or animals.¹⁶ Biomass is viewed as the greatest alternative to fossil fuels and is forecasted to become an essential carbon source in the future. It is estimated that the net primary production of the biosphere is about 100 billion tons of carbon annually, with roughly equal contributions from land and oceans.¹⁷ Several plastics are already being produced by biomass. For example, sugars obtained from corn or potato starch are used to produce monomers like lactic acid, which is polymerized to make polylactic acid (PLA).¹⁸ In addition, some conventional fossil-based plastics can also be derived from biomass. The resulting polymers are chemically identical to their fossil-based counterparts, except that the carbon atoms they contain originated from renewable sources. For example, polyethylene can be biobased, using ethylene derived from glucose. Similarly, sugars can be used to make bio-propylene to produce biopolypropylene and bio-ethylene glycol to produce bio-polyethylene terephthalate (PET).¹⁹ Making conventional fossil-based polymers from biomass is called the *bio*replacement strategy. However, some concerns have been raised about the use of farming land for the production of plastics or biofuels, in a world where not all the population has sufficient access to food.^{20,21} Reports on biobased plastic production and corresponding land use show that in 2021 bioplastics represented less than 1% of the global plastic market while requiring only 0.02% of the current farming

land.²² Although it may seem that there is no apparent rivalry between the feedstock for food, feed, and bioplastic production, the Intergovernmental Panel on climate change (IPCC), in their 2019 special report, warned that desertification and land degradation caused by climate change and human activity could threaten global food production, inducing competition between food and bioplastics.²³ To mitigate these effects, one solution to reduce carbon emissions is to modify our food consumption habits. Today, approximately 70% of farming land is used to raise animals. Animal farming requires a lot of resources (crops, water) and is contributing significantly to greenhouse gas emissions. Therefore, moving to a diet heavier on plant-based foods could redirect resource consumption from animals directly to people, freeing up to 50% of farmland at the same time, and reducing greenhouse gas emissions related to food production by 50%.^{24,25} Additionally, 30–40% of global food production is wasted annually. Consequently, reducing food waste could save more resources for bioplastic production. Besides reduction, the remaining food waste could be reused. Several value-added chemical building blocks can be obtained by fermentation of food wastes and employed to make bioplastics.²⁶

Instead of employing food (i.e., starch, sugars, fats, and oils) as a raw material source for plastic production, alternatives are investigated. The most promising and investigated type of biomass is lignocellulosic biomass. The term "lignocellulose" refers to plant-dried matter (e.g., wood, energy grasses, agricultural waste) and is the most abundantly available raw material to produce biofuels and chemicals.²⁷ Lignocellulose is composed of three types of polymers, two carbohydrate polymers: cellulose and hemicellulose, and one aromatic-rich polymer: lignin. Cellulose is an organic polysaccharide. It consists of a linear chain of D-glucose linked through β - $(1\rightarrow 4)$ glycosidic bonds. Cellulose can be depolymerized by enzymatic and fermentation processes to afford p-glucose and cellobiose.^{28,29} Hemicellulose is a branched heteropolymer consisting of different sugar units. Those sugars are predominantly pentoses (xylose and arabinose) and hexoses (mannose, glucose, galactose, and rhamnose), as well as acetylated sugars.²⁸ Hemicellulose is crosslinked to either cellulose or lignin, reinforcing the plant-cell walls. Due to its structural diversity, hemicellulose is less employed, despite being widely available. Lignin is a branched cross-linked phenolic polymer. Its chemical structure makes it quite rigid and hard, which plays an important role in the sturdiness of plant cell walls. Lignin is mainly composed of three phenolic monomers, called monolignols, that are present in different ratios depending on the plant type. Lignin depolymerization remains challenging, as it yields a mixture of phenols that are difficult to separate.^{30–36} Despite global efforts in developing the lignocellulosic biomass conversion to biofuels and chemicals, scalable production has yet to occur. In this thesis, the reported building blocks and monomers are either derived from sugars or consist of aromatic compounds that can potentially be obtained by lignin depolymerization. Therefore, they can be considered as lignocellulosic building blocks.

Despite the environmental advantages of shifting the plastic industry towards biobased plastics, the economic viability of such polymer materials is often an impediment. To facilitate the market introduction of biobased plastics, they should present additional advantages compared to conventional fossil-based plastics, for example, having high glass transition temperature (T_g) ,³⁷ improved mechanical properties, chemical resistance, or recyclability. This concept is called the *bio-advantage* strategy and is behind the design of the novel monomers reported in this thesis.³⁸

2.2 Isosorbide

Isosorbide is a renewable, nontoxic diol, considered to be a promising building block for biopolymer production.³⁹ It consists of a rigid bicyclic structure with two fused furan rings, forming a V-shaped backbone (Scheme 1). It is industrially produced by double dehydration of p-sorbitol, which is obtained from the hydrogenation of p-glucose. p-glucose is a starting material easily accessible from biomass by hydrolysis of starch, making isosorbide an interesting target for biobased polymers. The hydrogenation process of p-glucose to obtain p-sorbitol is well-established and cost-effective.^{40,41} The subsequent dehydration of p-sorbitol to form isosorbide is more complex, as it requires complete conversion and selectivity. This reaction is promoted by acids but is well-known to yield the formation of various side-products due to chemo- and regioselectivity (Scheme 1).⁴² Several dehydration products can indeed be obtained from the first dehydration step. Among all the intermediates, only 1,4-monoanhydrosorbitol (1,4-sorbitan) and 3,6-monoanhydrosorbitol (3,6-sorbitan) can lead to isosorbide after the internal second dehydration.

The dehydration steps retain the chirality of the D-sorbitol asymmetric carbons; therefore, isosorbide is also chiral. Its asymmetric carbons bear two sterically different secondary hydroxyl groups in *endo* and *exo* positions. Their different steric environments yield somewhat different reactivities. The *endo*-position is sterically shielded and more acidic than the *exo*-position.⁴³ This difference in acidity can be explained by an intramolecular hydrogen bond between the *endo*-hydroxyl group and the oxygen of the neighboring furan ring (Scheme 1). Such reactivity difference enables selective monofunctionalization of the diol, such as alkylation^{44,45} or acetylation.^{46–48} Isosorbide is an interesting diol building block for polycondensation as its bicyclic structure rigidifies the polymer backbone, thus increasing T_g . However, the secondary hydroxyl groups of the isosorbide present a low reactivity for step-growth polymerization.^{49,50} Isosorbide was nonetheless successfully employed to produce polycarbonates,^{51,52} polyesters,^{53–55} and polyurethanes.^{56,57}

Scheme 1. Isosorbide production from sorbitol.



^aKey: The first intramolecular dehydration yields six different intermediates, of which only 1,4-sorbitan and 3,6-sorbitan can yield isosorbide by a second intramolecular dehydration.

2.3 Alicyclic diols and diketones

Sugar-derived cyclic structures like isosorbide have been extensively studied due to their natural origin and their ability to produce transparent polymers with relatively high $T_{\rm s}$ s. However, two major drawbacks of isosorbide limit their development. First, the poor reactivity of the secondary hydroxyl groups in isosorbide tends to yield the formation of oligomers.⁵⁸ The second drawback results from the poor thermal stability of the fused tetrahydrofuran rings of isosorbide, leading to discolored and cross-linked materials when high temperatures are employed.⁵⁹ For these reasons, it is interesting to explore new alicyclic diols from renewable sources. Recently, Gao et al. have reported the synthesis of octahydro-2,5-pentalenediol (OPD), an alicyclic diol derived from citric acid.⁶⁰ Citric acid is a biobased compound produced by fermentation of sugar in high scales (7 \times 10⁵ tons annually),^{61,62} It is usually employed by the plastic industry as a chemical modifier, plasticizer of starch, and a functionality-enhancing monomer for high-tech coatings.^{63,64} To produce OPD, citric acid is readily transformed by decarboxylation and esterification in dimethyl 1,3-acetone dicarboxylate (DAC). ^{65–67} DAC is a promising biobased platform suitable for designing new structures. DAC is, in turn, converted via a two-step reaction into a stiff bicyclic diketone cisbicyclo[3.3.0]octane-3,7-dione B (Scheme 2). This diketone is obtained via Weiss-Cook condensation between glyoxal and DAC.⁶⁸ Aqueous glyoxal can be prepared by oxidation of ethylene glycol,⁶⁹ which can be produced from natural resources, for example by a process still under development by Avantium.⁷⁰ Hence, the synthesis of diketone **B** from citric acid is well-developed and employs only inexpensive acids (cat. *p*TSA or H₂SO₄, HCl, AcOH), a base (e.g., NaOH), and MeOH. Subsequent reduction of the diketone **B** finally yields the diol OPD, that Gao et al. employed to produce copolycarbonates with recycled bisphenol A (BPA), aliphatic or alicyclic bisphenols.^{60,71} Cyclic ketals and acetals are also interesting targets as the rigid alicyclic rings yield polymers with rigid macromolecular chain structures. Thus, polycycloacetals and polycycloketals have been obtained by direct polycondensation reaction of tetraols with dialdehydes or diketones, respectively.^{72–} ⁷⁵ McKeown et al. employed a similar structure to diketone **B** to achieve a high T_g spiro-polymer by polycondensation with pentaerythritol (Scheme 2).⁷⁶

Scheme 2. Synthesis of the diketone B derived from citric acid, and reported works by McKeown ⁷⁶ and Gao,^{60,71} respectively.



^aKey: (a) (i) *p*TSA, DCM, 20 °C, 8h, (ii) MeOH, 3 °C, 6 h then 30 °C, 3 h, 95%; (b) NaOH, glyoxal, 65 °C, 1 h, 65%; (c) HCl (aq), AcOH, reflux, 3 h, 80%; (d) NaBH₄, MeOH, 0 °C, 12 h, 80%; (e) NaOH, hexane-3,4-dione, 65 °C, (f) pentaerythritol, *p*TSA, toluene, reflux, 48h.

2.4 Vanillin and lignin-inspired monomers

Lignin is one of three biopolymers in wood, together with cellulose and hemicellulose, and is the most abundant bio-source of aromatic compounds. As aromatics are rigid structures, their incorporation in polymer materials restricts the macromolecular chain mobility and is a common and efficient strategy to increase T_g . Lignin is mainly composed of three aromatic monolignols: *p*-coumaryl, coniferyl, and synapyl alcohols (Figure 1), which are connected by carbon-carbon and ether bonds, in varying ratios depending on the natural source (i.e., hardwood, softwood or herbaceous sources). ^{35,77,78} Lignin is of great interest because it is a largely undervalued by-product from the paper and pulp industry and is mostly burned as fuel. A possible valorization of lignin that is under investigation is its depolymerization to obtain various renewable chemicals. However, lignin depolymerization and subsequent purifications remain a challenge.^{34,35} Today, only vanillin is isolated on a relatively large scale (ca. 3000 tons/year) from softwood.⁷⁹ Vanillin is primarily used by the food industry as a flavoring agent, and the yearly production is ca. 20,000 tons, most of which is derived from petroleum-based guaiacol.^{79–81} Vanillin is among the most studied building blocks to produce biobased polymers. Many vanillin-based monomers have been synthesized by either functionalization of the aldehyde or phenolic groups.^{80,82} For example, the aldehyde function can be reduced to obtain vanillyl alcohol that can be employed for making polyurethanes.^{83–85} Moreover, further functionalization of the phenolic group and/or primary alcohol can be performed to subsequently produce polyesters⁸⁵ or epoxy resins.⁸² Additionally, the aldehyde can be oxidized to yield vanillic acid, which can be employed for making polyesters⁸⁰ and epoxy resins.^{80,82} Finally, the aldehyde function can be transformed into acetal units by reacting with various diols. Recently Mankar et al. reported the synthesis of a spiro-diol monomer produced from vanillin and pentaerythritol, which yielded polyesters with enhanced thermal properties.⁸⁶

Figure 1. Molecular structure of the monolignols forming lignin.



Key: (from left to right) p-coumaryl, coniferyl, and synapyl alcohols.

2.5 Polyacrylates and polymethacrylates

The *acrylics* family includes polymers and copolymers of acrylic acid (AA), methacrylic acid (MAA), and their corresponding esters, acrylonitrile, and acrylamide.^{87–90} The global production of AA reached 7.65 million tons in 2021 and is forecasted to exceed 10 million tons by 2027.⁹¹ Acrylate polymers, even though they represent a small fraction of the global plastic market, exhibit interesting properties that can be tuned by the functionalization of the acid group to ester. For example, acrylate polymer materials can reach high T_g values,^{92–94} have appealing mechanical⁹⁵ and thermal properties,^{92,93,96} and transparency,^{94,96,97} which makes them useful in various applications. As such, 55% of AA production is used to prepare superabsorbent polymers for diapers, 30% is used for plastic, adhesives, and synthetic rubbers, and the remaining 15% is used for coating and paint formulations.^{98,99} Concerning methacrylic polymers, the methyl ester of MAA, methyl methacrylate (MMA), is a specialty monomer used to produce poly(methyl

methacrylate) (PMMA). It is a transparent and resistant material employed in the safety glass industry¹⁰⁰ and as bone cement in medical applications.^{101,102} In 2018, the global production PMMA reached 3.9 million tons and is forecasted to increase to 5.7 million tons by 2028.¹⁰³

2.5.1 Synthesis

Acrylate and methacrylate monomers are susceptible to undergoing chain-growth polymerization as they possess a carbon-carbon double bond. They are primarily polymerized by a free radical initiation mechanism, ^{94,104,105} either by bulk, solution, or emulsion polymerization, depending on the final application. For instance, rigid PMMA products, such as sheets, rods, and tubes, are produced by bulk polymerization via a controlled casting process to avoid shrinkage. Solution and emulsion polymerizations are employed for nonrigid applications, such as coatings. paints, textiles, adhesives, and sealants.⁹⁴ Free radical polymerizations are initiated by radicals produced by radical initiators. A variety of initiator systems can be used to generate radicals and promote polymerization. The thermal, homolytic dissociation of initiators is the most common way of generating radicals, either for industrial purposes or theoretical studies.⁹⁴ Such polymerizations are referred to as thermal initiated or thermal catalyzed polymerizations, and the initiator as a thermal *initiator*. To be able to generate radicals, thermal initiators require a chemical bond with a dissociation energy in the range of 100–170 kJ mol⁻¹. Only a few classes of compounds fall under this range of dissociation energy, such as O–O, S–S, or N–O bonds (Scheme 3). Peroxides are among the most used thermal initiators as well as azo compounds.^{94,106,107} Although the dissociation energy of the C–N bond is higher than the typical weak bonds of peroxy compounds (~290 kJ mol⁻¹), the dissociation is facilitated by the formation of a highly stable nitrogen molecule.

Scheme 3. Examples of thermal initiators and their radical formation.



Key: from top to bottom: benzoyl peroxide, t-butyl peroxide, and 2,2'-azobisisobutyronitrile (AIBN).

2.5.2 Biobased polyacrylates and polymethacrylates

AA, MAA, and their corresponding esters are essentially fossil-based monomers produced by energy-intensive and non-sustainable processes. AA is obtained by a two-step gas-phase process, starting with the oxidation of propylene to acrolein using a Bi/Mo–O catalyst, followed by a second oxidation in another reactor using a Bi/V-O catalyst.^{99,108,109} MMA, on the other hand, is produced by a different process called the acetone-cyanohydrin process (ACH).^{110,111} Novel routes have been developed to obtain biobased AA and MMA. Biobased AA can be produced from starch, glycerol, glutamic acid, or glucose,^{98,99} while biobased MMA can be obtained from itaconic acid, which is derived from glucose.^{112–114} Despite several strategies to develop the production of biobased AA, MAA, and their respective esters, industrial-scale production has not yet been achieved due to high costs and multi-step procedures. In addition to investigating biobased AA and MAA production, research efforts are made in making partially biobased poly(meth)acrylates. It consists of using renewable hydroxyl-containing molecules to form the corresponding esters of AA or MAA, to obtain materials with improved thermal and mechanical properties compared conventional to poly(meth)acrylates.¹¹⁵

2.6 Polycarbonates

Polycarbonates are polyesters of carbonic acid, usually hard polymers with high $T_{\rm gs}$ due to the strong polar interactions and rigid structures. The most important commercial polycarbonate is based on 2,2'-bis(4-hydroxyphenyl)propane, also called bisphenol A (BPA).^{116,117} It is usually referred to as *polycarbonate* or PC. Most PCs are amorphous ($T_{\rm g} = 150$ °C) and present exceptional transparency, high heat–, chemical–, and impact–resistance, making them suitable for glazing (windows, sunglasses, aircraft, NASA astronaut's helmet…), automotive, and medical applications (blood collection, surgical devices…).¹¹⁷

2.6.1 Synthesis

BPA-based polycarbonate (BPA–PC) is conventionally synthesized by two very different processes: interfacial (solvent-based) and melt condensation polymerizations.^{117–119} In the interfacial method (Scheme 4), BPA–PC is produced by adding a solution of phosgene in dichloromethane (DCM) to an aqueous alkali solution of BPA. DCM prevents the phosgene hydrolysis and precipitation of the polymer before reaching a sufficiently high molecular weight, while the alkali aqueous solution enables to form the phenolate salt. The melt condensation route consists of an ester interchange with diphenyl carbonate (DPC), in a similar way to

the two-stage melt polymerization to produce PET. Overall, economics and easier control of the molecular weight favors the phosgene route over the melt condensation. However, the toxicity of phosgene (used as a chemical weapon during World War I) and chlorinated solvents remain strong drawbacks of BPA–PC production, which is not considered to be environmentally friendly. In addition, the discovery of the endocrine-disrupting effects of BPA^{120,121} pushed for a progressive ban on its use in some PC applications, especially for food and beverage containers. This BPA ban drives research toward new monomers, notably biobased, to replace it in PC production.

Scheme 4. Industrial production of BPA–PC by interfacial polymerization of BPA with phosgene (top), and melt polycondensation with DPC (bottom).



2.6.2 Biobased polycarbonates

BPA is a fossil-based chemical and presents several drawbacks, especially for health. Therefore, efforts have been made to produce biobased alternatives to BPA. Thus, several rigid biobased diols have been reported to give polymers with high $T_{\rm g}$ s.^{122–124} Alternatively, biobased PCs can be made by replacing the toxic phosgene or poorly atom-efficient DPC with other carbonate sources. For example, carbon dioxide can be employed to produce PCs, by reaction with epoxides, which could be part of a carbon fixating strategy to fight climate change.^{125–128}

2.7 Thiol-Michael polymerization

The thiol-Michael addition reaction is the addition reaction of a thiolate nucleophile to an α,β -unsaturated carbonyl, catalyzed by a basic or nucleophilic catalyst (Scheme 5).¹²⁹ It has been used for over 100 years to synthesize small molecules. This reaction is thermodynamically favored, easy to perform, highly regioselective, and can be carried out under mild conditions. For these reasons, it has become increasingly popular over the years, especially in the medical field, ^{129,130} and is considered to be a "click" reaction.¹³¹ Thiol-Michael polymerizations require an

electron-deficient Michael acceptor, such as acrylates, methacrylates and acrylamides, vinyl sulfones, acrylonitriles, or any other electron-deficient alkene bearing a non-carbonyl electron-withdrawing group.¹³² Typical basic catalysts are mild organo-bases, such as Et₃N or 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU). In addition, thiol-Michael polymerizations can be performed *via* a radical mechanism, initiated by UV-light or radical initiators like AIBN. In this case, they are called thiol-ene polymerizations and are generally favorable for electron-rich alkenes.¹³² The resulting polymer of a thiol-Michael or thiol-ene polymerization is called a $poly(\beta$ -thioether ester). After completion of the polymerization, the chain ends are either an unsaturated group (e.g., acrylate) or a thiol function, which are potentially reactive, making them useful for post-modification. Having acrylates as chain ends is usually not desirable as they can undergo spontaneous cross-linking reactions. To prevent having acrylates as chain ends, a slight excess of dithiol is employed to ensure thiol terminal functionalities.¹³³ Thiol-Michael polymerizations have been employed to produce various types of cross-linked, star-shaped, hyperbranched, and linear polymers.131





Key: (a) Base-catalyzed mechanism to form the thiolate, (b) example of the thiol-Michael addition reaction mechanism of the thiolate and methyl acrylate.

2.7.1 Biobased poly(β -thioether ester)s

Biobased Michael acceptors can be employed to produce $poly(\beta$ -thioether ester)s. For example, isosorbide diacrylate copolymers with linear dithiols were reported with T_{gs} ranging from -14 to 15 °C.¹³⁴ Other sugar-based $poly(\beta$ -thioether ester)s were also reported with T_{g} values from -8 to 19 °C,¹³⁵ as well as soybean oil-based cross-linked networks.^{136,137} Additionally, biobased poly(β -thioether ester)s were obtained by using biobased dithiols. However, the conventional industrial production of thiols uses hydrogen sulfide, a toxic gas mostly obtained from natural gas,¹³⁸ which currently makes thiol production non-sustainable.

2.8 Polyesters

Polyesters are among the most common polymers produced today, accounting for about 8% of global plastic production.⁸ Among the polyester class, poly(ethylene terephthalate) (PET) is produced in the highest quantities, essentially for packaging purposes, and can be recycled into fibers for clothes.

2.8.1 Synthesis

Polyesters are mostly produced by melt polycondensation, by direct esterification of a diacid and a diol, or self-condensation of a hydroxycarboxylic acid. Esterification is an equilibrium reaction; therefore, water (or alcohol in the case of transesterification) must be continuously removed to achieve high conversions and high molecular weight polymers. Polyesterification is conventionally performed in two steps (Scheme 6). The first step often consists of the reaction of the corresponding dimethyl ester of the dicarboxylic acid, with a slight excess diol, in an ester interchange. This reaction has the advantage of being fast, and the removal of methanol is easier than water. The second step is usually carried out at higher temperatures under a partial vacuum to remove the excess diol. The synthesis of PET is industrially performed according to two processes. One process is based on dimethyl terephthalate (DMT), and the first stage is performed as described above. First, the reactants are heated to 150 °C, and the reactor temperature is progressively increased to 210 °C while methanol is distilled off. In this step, the intermediate bis (2-hydroxyethyl) terephthalate (BHET) is formed. In the second stage, the temperature is increased to 270-280 °C, and a partial vacuum is applied. The other process employs terephthalic acid (TPA) instead of DMT, using similar conditions.¹¹⁷ In industrial PET production, a dual metal catalyst system is employed (Scheme 6). At the laboratory scale, a simpler single-metal catalyst like dibutyltin (IV) oxide (DBTO), titanium (IV) butoxide, or titanium (IV) isopropoxide is commonly used in polyester synthesis.^{122,139,140}

Scheme 6. Two-step industrial polyesterification of PET from DMT.



2.8.2 Biobased polyesters

As PET is one of the most important synthetic polyesters, the production of biobased PET (bio-PET) has been extensively investigated. For example, Coca-Cola developed a partially biobased PET bottle, using biobased ethylene glycol. This PlantBottleTM contains about 30% of bio-content while retaining the desired properties of a conventional PET bottle.¹⁴¹ Producing biobased TPA is however more complex. Several approaches have been reported toward the production of biobased TPA, from muconic acid,¹⁴² isoprene,¹⁴³ sorbic acid,^{144,145} coumalic acid,¹⁴⁶ furfural,¹⁴⁷ 5-hydroxymethylfurfural,^{148,149} dimethyl furan,^{149–151} and limonene.¹⁵² They mostly consist of a Diels-Alder cycloaddition between a renewable diene and a dienophile, forming a six-membered aliphatic ring, which is subsequently subjected to dehydrogenative aromatization. In addition, a direct catalyzed pyrolysis of lignocellulosic biomass is even possible to produce the *p*-xylene intermediate necessary to produce TPA.¹⁵³ Coca-Cola recently presented the synthesis of entirely biobased PET in 2015. Unfortunately, a commercial product has yet to appear on the market.¹⁴¹

Instead of using the bio-replacement strategy, the bio-advantage approach is also researched. One good candidate is 2,5-furan dicarboxylic acid (FDCA), which could replace TPA. The resulting polymer, called PEF, presents the advantages of having a higher T_g (86 °C vs 74 °C), lower melting point (235 °C vs 265 °C), and better barrier properties than PET.^{154–157} In addition, other monomers have been developed over the last decade to replace conventional polyesters. For example, Perstorp developed a rigid biobased spirocyclic diol, which was successfully employed to form PET-based copolymers. The resulting copolyesters containing small fractions of this new spirocyclic diol are named AkestraTM. They presented an increased T_g compared to conventional PET, ranging from 90 to 110 °C depending on the content of the spirocyclic monomer.¹⁵⁸ Moreover, other biobased rigid monomers have been designed using the bio-advantage strategy. For example, monomers with spirocyclic units^{86,139,159} or aromatic moieties like ferulic acid,^{160–164} coumaric acid,^{164–166} caffeic acid,^{166–169} and vanillin^{85,86,165,170–173} have been designed to obtain high- T_g polyesters.

2.9 Recycling

Although more biobased plastics are being developed, the question of their disposal remains. As mentioned at the beginning of this introduction, the gigantic amounts of plastics produced poses environmental issues, especially if they are lost in nature or buried in landfills. Therefore, tremendous efforts are being made to develop plastic recycling strategies. Currently, it is estimated that about 10% of plastic waste is recycled.⁸ This fraction is expected to grow as new recycling facilities and technologies are being developed. For example, the latest recycling plants in construction are fully automated and use near IR detectors to more efficiently sort the different types of plastics.^{174,175}

After being collected, the plastic waste can be recycled according to different methods: mechanical recycling, chemical recycling by pyrolysis, solvolysis, or acid/base hydrolysis, and biological recycling by enzymatic degradation and biodegradation¹⁷⁶ (Scheme 7). Mechanical recycling is the most common recycling method and consists in first grinding the collected plastic waste. The resulting pellets are subsequently melted and re-shaped into plastic products. It is advantageous as this method avoids re-polymerization. However, the molecular weight tends to decrease after melting and remolding, reducing the thermal and mechanical properties. This recycling method is often called "downgrading" or "downcycling", as it yields inferior materials.^{177–179} Thus, plastics can only be recycled by this method a finite number of times. This drawback is usually compensated for by adding virgin plastic material.

Chemical recycling is another method for recycling plastic waste. The polymers are chemically broken down to obtain the original monomers or other small molecules, which could be re-polymerized into the same or new polymers.¹⁸⁰ Different strategies are being developed for chemical recycling, namely pyrolysis, solvolysis, and acid/base hydrolysis. With pyrolysis, the polymers are heated to high temperatures (300–900 °C) under an oxygen-deprived atmosphere to prevent oxidation reactions, in the presence of a catalyst, which carries out the depolymerization reaction. Pyrolysis leads to the formation of gases, liquids/waxes, and char, which are mixtures of compounds. The pyrolysis gases and liquids can be used as feedstock for new polymers and chemicals.^{177,181–183} However, this process requires high temperatures and leads to mixtures of compounds, which are large disadvantages limiting scalability.

Pyrolysis chemical recycling is interesting for polyolefins, but it is not suitable for all polymers. Polymers containing several hetero atoms are more prone to side reactions and degradation by pyrolysis, leading to more complex mixtures. Another strategy for chemical recycling is to advantageously use weak chemical bonds to depolymerize the polymer chains. For example, acetals and esters are chemical functions that can be cleaved in an acidic or basic aqueous medium, respectively. Acetal and ketal units have successfully been employed as targets to achieve depolymerization.^{180,184–186} For polyesters, PET has been thoroughly investigated. The ester bond can be cleaved by either acidic/alkaline hydrolysis, glycolysis, or methanolysis, forming the corresponding monomers (DMT or TPA, EG, BHET) and oligomers.^{179,187–190} Currently, chemical recycling is hardly scalable as it is not economically viable since it requires a lot of energy and large amounts of chemicals.^{176,187,188} For polyester recycling, research is still ongoing^{185,191} with new catalysts being developed, especially in the case of monomers polymerized by ring-opening polymerizations.¹⁹²

Additionally, a new polymer recycling strategy, i.e., enzymatic recycling, is becoming popular, as both mechanical and chemical recycling methods require harsh conditions. This method uses enzymes, which is advantageous as enzymes usually require milder conditions in terms of pH and temperature to function. One fundamental step was the discovery of an enzyme degrading PET by Yoshida et al.¹⁹³ The reported enzyme was discovered in a bacterium, *Ideonella sakaiensis*, found in a PET bottle landfill. Since then, other enzymes have been discovered with the power to depolymerize PET¹⁷⁶ and other polyesters.^{194,195} With the development of biotechnologies, researchers expect the discovery of new enzymes which enable the recycling of polymers that we cannot currently recycle, like polyurethanes.^{196,197}



Scheme 7. Simplified schematic of the different recycling methods.

2.10Context and Scope

This thesis aims to report on the design, synthesis, and characterization of thermoplastics obtained from lignocellulosic sources. Several monomers derived from sugar or lignin have been produced and employed to synthesize poly(meth)acrylates, polycarbonates, $poly(\beta$ -thioether ester)s, and polyesters. The thermal and mechanical properties of these polymers were investigated and correlated to their chemical structure. In addition, the chemical recyclability of some of the reported materials was studied.

In Paper I, a series of isosorbide methacrylates was synthesized with a varying pendant alkanoyl chains. Polymethacrylates were obtained by conventional freeradical polymerization and showed different phase behaviors depending on the size of the alkanoyl chain. The shorter side-chain polymers were fully amorphous, while the polymers with longer alkanoyl chains became semi-crystalline, eventually showing liquid-crystalline behavior for the longest pendant chains.

In Paper II, a rigid spirocyclic diol monomer was synthesized in a ketalization reaction between TMP and a bicyclic diketone derived from citric acid. The monomer was employed to produce two PCs of different molecular weights. The higher molecular weight PC showed improved thermal properties than the other.

In Paper III, the spirocyclic diol reported in Paper II inspired the design of two additional spirocyclic diols, varied by their diketone origin and the triol employed in the ketalization reaction. The three monomers were subsequently acrylated or methacrylated, and further employed in thiol-Michael polymerization with different dithiols. The resulting poly(β -thioether ester)s library was used to investigate the relationship between their chemical structure and their thermal properties. Additionally, a degradation study of the polymers was conducted, indicating that the polymers were potentially chemically recyclable.

In paper IV, in addition to using rigid moieties, the introduction of a polar nitrile function into three lignin-inspired monomers was investigated to increase $T_{\rm g}$. A series of polymethacrylates was obtained after a relatively green nitrilation of the building blocks and methacrylation. The homopolymers showed improved thermal properties compared to their non-nitrilated equivalents, demonstrating the potential of introducing polar groups in polymer chains. In addition, copolymers of the nitrile-containing monomers with styrene and MMA, respectively, showed improved thermal properties and solvent resistance compared to neat PS and PMMA.

In Paper V, using a similar strategy as in Paper IV, bis-vanillonitrile was synthesized by oxidative coupling, followed by a chain extension to produce a diester monomer. This monomer was then employed to produce polyesters by reaction with different diols. The introduction of this rigid and polar monomer gave polymers with improved thermal properties compared to benchmark polyesters based on FDCA.

3 Experimental work

3.1 Monomers syntheses

3.1.1 Esterification

In Papers I, III, and IV, different esterification processes were employed to form the monomers. In Paper I, the free hydroxyl group of 5-isosorbide methacrylate (5-IMA) and 2-isosorbide methacrylate (2-IMA) were esterified according to two methods to obtain the alkanoyl isosorbide methacrylate monomers as single regioisomers. The first method consisted of the ester formation using a vinyl alkylate and bio-catalyzed with Novozym 435, while the second method corresponded to the conventional chemical acylation with an acyl chloride and Et₃N in an appropriate organic solvent. The resulting monomers were isolated and purified by either a simple extraction/filtration procedure or by flash chromatography. Liquid products were stored in solution at 2-6 °C with a small amount of hydroquinone as a stabilizer. In Paper III, the monomers were exclusively prepared by chemical acylation, either with acryloyl or methacryloyl chloride and Et₃N in DCM or 2-MeTHF. After completion, the reaction mixtures were neutralized and extracted with DCM. The resulting concentrates were purified by flash column chromatography. In Paper IV, the esterification was performed with methacrylic anhydride instead of methacryloyl chloride, in EtOAc and catalyzed by 4-(dimethyl amino)pyridine (DMAP). The products were purified by simple flash column chromatography over aluminum oxide to remove remaining phenols, if necessary.

3.1.2 Ketalization

In Papers II and III, spirocyclic diol monomers were produced by the ketalization of a polycyclic diketone with glycerol or TMP, using pTSA as an acid catalyst, in an organic solvent mixture (cyclohexane/toluene). A Dean-Stark apparatus was employed to drive the equilibrium toward full conversion. In Paper II, the product was isolated either by a double crystallization procedure or by flash column chromatography. A similar procedure was followed in Paper III. After completion, the spirocyclic diols were purified by flash column chromatography only.

3.1.3 Aldehyde conversion to nitrile

In Paper IV, aromatic aldehydes were nitrilated using hydroxylamine-O-sulfonic acid in an acetic acid/water mixture. The products were isolated by simple extraction/filtration and purified by recrystallization. No chromatography was required.

3.1.4 Oxidative radical coupling

In Paper V, vanillonitrile was coupled to obtain bis-vanillonitrile by reaction with $Na_2S_2O_8$. The reaction was catalyzed by FeSO₄, in water, and was relatively fast (1 hour). The product was isolated by filtration and purified by a simple acid/basic dissolution/precipitation workup.

3.1.5 Williamson ether synthesis

In Paper V, the Williamson ether synthesis was used to prepare the monomers by reacting bis-vanillonitrile with ethyl bromoacetate. K_2CO_3 was used to form the phenolates to improve the nucleophilicity of bis-vanillonitrile, in a polar aprotic solvent like DMF. After completion, the reaction mixture was quenched with concentrated HCl to decompose the excess K_2CO_3 . The product was isolated by filtration.

3.2 Polymer syntheses

In this thesis, four different types of polymers were produced: poly(meth)acrylates, polycarbonates, poly(β -thioether ester)s, and polyesters.

3.2.1 Poly(meth)acrylates

In Papers I and IV, poly(meth)acrylates were synthesized by conventional free radical polymerization. After the removal of the inhibitor (Paper I), the monomers and AIBN (0.1–1 mol%) were dissolved in EtOAc or DMSO and purged with an inert gas. The polymerizations were performed at about 60 °C for 24 h. The polymer solutions were precipitated in MeOH. The resulting solids were filtered, washed with additional MeOH, and dried under reduced pressure.

3.2.2 Polycarbonates

In Paper II, the polycarbonates were synthesized by polycondensation using DPC as the carbonyl source and NaHCO₃ as the catalyst. After a purging step under Ar atmosphere in the melt state, the monomers were converted into oligomers by heating to 160 °C under atmospheric pressure. Subsequently, stepwise increases in the reaction temperature and pressure reductions facilitated the removal of the excess DPC. The molecular weight of the polymers was controlled by the final temperature of the reaction, with temperatures up to 280 °C being employed for higher molecular weights. The resulting polymers were dissolved in CHCl₃, precipitated in MeOH, filtered, and dried under reduced pressure.

3.2.3 Poly(β-thioether ester)s

The poly(β -thioether ester)s reported in Paper III were prepared by reacting the di(meth)acrylate monomers with dithiol, either in 2-MeTHF or CHCl₃. After cooling to 0 °C, 0.1 eq of the catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CHCl₃ was added, and the reaction was allowed to process at room temperature for 24–48 h. The resulting polymers were precipitated in MeOH, filtered, and dried under reduced pressure.

3.2.4 Polyesters

The polyesters reported in Paper V were prepared using a two-step melt condensation comparable to the synthesis procedure of the polycarbonates described above. First, the reactants were melted under nitrogen flow to produce oligomers while removing EtOH. After complete transesterification (verified by ¹H NMR), the temperature was increased, and a vacuum was applied to remove the excess of diol and drive the polycondensation toward high molecular weight polymers. The resulting polymers were dissolved in CHCl₃ and subsequently precipitated in MeOH, filtered, and dried under reduced pressure.

3.3 Characterizations

In the following section, the most important characterization methods will be described. More information is found in the experimental section of the corresponding papers/manuscripts.

The monomer and polymer structures were characterized by ¹H and ¹³C NMR spectroscopy. The measurements were performed on Bruker DR X800 and X400 spectrometers at 800.13 or 400.13 MHz for ¹H spectroscopy and 201,21 or 100.61
MHz for ¹³C, with samples dissolved in chloroform-d or DMSO-d₆. In Paper III, the hydrolysis study was performed in acetone- d_6 and acetonitrile- d_3 . High-resolution mass spectroscopy (HR-MS) was taken on a Micromass QTOF mass spectrometer (ESI) or a Thermo Electron LTO Orbitrap XL analyzer. Fourier transform infrared spectroscopy (FTIR) was measured on a Shimadzu IRAffinity-1 spectrometer. Size exclusion chromatography (SEC) measurements were carried out in different solvents depending on polymer solubility. The polymers in Papers I-IV were analyzed using CHCl₃, THF, or DMF/0.05 M LiBr as eluent at 40 °C. The SEC instrument included three Shodex columns coupled in series (KF-805, -804, and -802.5 for CHCl₃ and THF, and KD-804 and -802.5 for DMF) placed in a Shimadzu CTO-20A prominence column oven and a Shimadzu RID-20A refractive index detector. The results were analyzed with the Shimadzu LabSolution software. Calibration was done using poly(ethylene oxide) standards ($M_n = 3.86, 12.6, 21.16,$ 49.64, and 96.1 kg mol⁻¹). In Paper V, the molecular weights of the polyesters were determined by SEC in THF at 35 °C, using an OMNISEC from Malvern Instrument. The SEC instrument was equipped with one TGuard, Org. Guard Col 10×4.6 mm as guard column, $2 \times T6000M$, General mixed Org. 300 $\times 8.0$ mm as analytical column, and a refractive index (RI) detector. Eight PS standards ($M_p = 3530$ and 184.0 kg mol⁻¹ from Polymer Standards Service, $M_p = 1184$ kg mol⁻¹ from Polymer Laboratories, $M_n = 93.8$ and 3.63 kg mol⁻¹ from Sigma-Aldrich, $M_n = 35.0$ kg mol⁻¹ from Waters and $M_n = 17.5$ and 3.0 kg mol⁻¹ from Polysciences Inc.) were used for conventional calibration.

Thermogravimetric analyses (TGA) were carried out on a TA instrument TGA Q500, by heating from 40 °C to 600 °C with a rate of 10 °C min⁻¹. T_{d,95%} was determined at 5% weight loss and the decomposition temperature (T_d) was determined at the maximum decomposition rate. DSC measurements were performed on a DSC Q2000 analyzer from TA instruments. Tg was determined from the second heating cycle, while melting and crystallization temperatures ($T_{\rm m}$ and $T_{\rm c}$) were determined as the maximum of the crystallization and melting peaks in the DSC thermogram, respectively. In Paper I, the isotropization and anisotropization temperatures (T_i and T_a) were determined likewise at the order-to-disorder transition. DMA measurements were performed using a TA instruments Q800 analyzer, either in a tension mode (for films) or in a bending mode (for hot-pressed bars). After the determination of the linear viscoelastic region (LVR) by a strain sweep, a temperature sweep was carried out at a constant strain within the LVR, with a heating rate of 2-3 °C min⁻¹. Rheology analyses were carried out on an Advanced Rheometer AR2000 ETC from TA Instruments, using parallel plates of diameter $\emptyset = 15-25$ mm, under a nitrogen atmosphere to prevent oxidative degradation. The LVR was determined similarly to DMA, and then thermal stability studies were performed at a constant strain within the LVR and a frequency of 1 Hz. The cross-polarized light microscopy images were taken with an Olympus BX50 microscope equipped with a Linkam THMS 600 hot stage controlled by a Linkam TMS 93 temperature controller.

4 Summary of appended papers

4.1 Isosorbide-based polymethacrylates with tunable phase transitions (Paper I)

4.1.1 Monomer syntheses

In this project, isosorbide was employed to produce methacrylate monomers. Isosorbide was successfully methacrylated as single regioisomers since the two hydroxyl functional groups have different reactivities. In general, the 5-OH group (*endo*) of isosorbide is sterically hindered but has a stronger nucleophilicity than the 2-OH group (*exo*), which is invested in an intramolecular hydrogen bond (Scheme 8).⁴³ Thus, a simple chemical acylation of isosorbide usually favors the reaction with the 5-OH group. Here, the methacrylation of the 5-OH group was performed using *Rhizomucor miehei* (RM) lipase as a catalyst, providing isosorbide-5-methacrylate (5-**IMA**) with a 93% yield. Isosorbide-2-methacrylate (2-**IMA**) on the other hand was synthesized following a previously reported procedure.⁹³ Both pathways afforded the respective single regioisomer using a straightforward chromatography-free workup with purity and regioselectivity >99%.

In a second step, the second hydroxyl group of 5-IMA was acylated with linear alkanoates of different lengths to study how the pendant sidechain would affect the thermal and mechanical properties of the polymethacrylates. This second acylation was either performed by a biocatalytic or a conventional chemical procedure. The biocatalytic reaction, called method A, was performed using *Candida antartica* lipase B (Novozym 435), which is a quite versatile enzyme. Thus, it catalyzed the acylation of the 2-OH group of 5-IMA, with a variety of acyl groups. The resulting single regioisomer diesters were isolated in good to excellent yields (79–98%, Table 1). Those alkanoyl isosorbide methacrylate monomers were designated as AIMAx, where x indicates the number of carbon atoms in the pendant alkanoyl chain. The regioisomeric 2-IMA was reacted with stearoyl chloride to produce the regioisomeric monomer r-AIMA18 with a 49% yield.

Scheme 8. Regioselective synthesis of alkanoyl isosorbide monomethacrylates (AIMA) monomers.



^aKey: (i) vinyl methacrylate, RM, 2-Me-THF, 93%; (ii) three-step procedure reported previously;³⁹ Method A: corresponding vinyl alkylate, Novozym 435, ACN/PEth. Method B: corresponding acyl chloride, Et₃N, ACN, or DCM. n = 0–18

4.1.2 Synthesis and characterization of the poly(alkanoyl isosorbide methacrylates)

The polymers were prepared by conventional free-radical polymerization (Scheme 9). The resulting series of poly(alkanoyl isosorbide methacrylate)s were designated as **PAIMA***x*. The number average molecular weight (M_n) and polydispersity D of the polymers were determined by SEC (Table 1). M_n varied between 32 and 81 kg mol⁻¹, which was relatively high and enables further thermal and mechanical characterizations. The decomposition temperature ($T_{d,95}$) of the samples varied between 190 and 259 °C (Table 1), and the TGA traces showed two distinguishable steps. The first decomposition step was attributed to the decomposition of the alkanoyl chains, as they present α -protons, making them more sensitive to degradation. The second step was attributed to the degradation of the isosorbide units, followed by the decomposition of the polymer backbone.⁹³



Scheme 9. Polymerization of the AIMA monomers by conventional free radical mechanism.

Table 1. Molecular and thermal data of the PAIMAx polymers.

Sample	<i>M</i> _n (kg mol⁻¹) ^b	Ð⊳	<i>T</i> _{d,95%} (°C) ^c	<i>Т</i> _g (°С) ^d	<i>T</i> _m (°C) ^d	<i>T</i> _i (°C) ^d
PAIMA0 ^a	n.d.	n.d.	238	167	-	-
PAIMA2	32	2.97	208	107	-	-
PAIMA 4	60	1.78	190	80	-	-
PAIMA6	56	2.11	188	57	-	-
PAIMA8	38	2.16	199	46	-	-
PAIMA10	47	2.06	201	52	-	-
PAIMA11	56	2.27	209	56	-	-
PAIMA12	43	2.70	226	66	-	-
PAIMA13	32	2.23	228	-	-	75
PAIMA14	61	2.23	233	-	-4	82
PAIMA16	58	2.11	231	76	19	92
PAIMA18	62	2.63	254	79	32	97
r-PAIMA18	49	2.06	251	-	30	-
P(AIMA18-co-r- AIMA18)	81	2.14	247	-	41	69
PAIMA20	46	2.57	259	74	55	94

^aData taken from previously published work.³³ ^bMeasured by SEC in THF using poly(ethylene oxide) standards. ^cThermal decomposition temperature determined by TGA at 5% weight loss under N₂. ^dDetermined by DSC during the second heating scan.

DSC showed that the samples presented large variations in phase behavior depending on the length of the alkanoyl chain. The polymers with short alkanoyl chains are fully amorphous (**PAIMA0–12**), and the DSC traces only showed one glass transition. As expected, T_g decreased with the increasing pendant chain length, as the flexible alkanoyl chains act as internal plasticizers. **PAIMA0** and **PAIMA2** presented the highest T_g s, above 100 °C.

As the length of the alkanoyl chain increased from **PAIMA13**, the polymers became semicrystalline, and a first-order transition was visible on the DSC thermograms. The melting temperature T_m increased with the alkanoyl chain length from -4 °C for **PAIMA14** to 55 °C for **PAIMA20**. A second first-order transition was observed by DSC for the samples of alkanoyl chain length above x = 12. We interpreted this transition as an order-to-disorder transition, connected to the formation of a liquid crystalline mesophase. The isotropization temperature T_i observed upon heating increased from 82 °C for **PAIMA14** to above 97 and 94 °C for **PAIMA18** and **PAIMA20**, respectively. The small variations in T_m and T_i can be explained by differences in molecular weights. As no mesophases have been reported for poly(*n*alkyl methacrylate)s, we inferred that the liquid crystallinity behavior observed for the **PAIMAx** series was most likely induced by the stiff and stereoregular isosorbide units. The substitution of the isosorbide moiety seems also to play an important role, as the polymer *r*-**PAIMA18** prepared from the 2-methacrylic 5-diester regioisomer did not show any order-to-disorder transition.

To further investigate the phase behavior, and to confirm the formation of a liquid crystalline mesophase, a rheological study was performed on **PAIMA16**, **PAIMA18**, and **PAIMA20**. Besides demonstrating melt processing without noticeable degradation, dynamic melt rheology showed a sharp and reversible modification of the complex viscosity at the order-to-disorder transition (Figure 2). An additional study of **PAIMA20** by optical microscopy under cross-polarized light at different temperatures was performed to observe the phase behavior (Figure 3). Below T_m , a semicrystalline spherulitic structure can be observed. At T_m , the crystals melt and a fine granular texture is observed, which was attributed to the formation of mesophases. At T_i , the granular texture disappeared completely. These results demonstrated that the phase behavior of the PAIMA polymers can be tuned by the size of the alkanoyl sidechain. Consequently, these biobased polymers are envisioned to be tailored alternatives to plastics in the coating industry.

Figure 2. Dynamic melt rheology of PAIMA16 and PAIMA18 at the order-to-disorder transition.



Key: Complex viscosity $|\eta^*|$ of **PAIMA16** (a) and **PAIMA18** (b) as a function of temperature (0.01% strain, 1 Hz, 2 °C min⁻¹) showing reversible stepwise changes and hysteresis effects at the order-disorder transition.

Figure 3. Cross-polarized optical microscopy of **PAIMA20** and a simplified representation of the polymers in the different phase structures.



Key: (a) Semicrystalline spherulitic structure at 22.5 °C, (b) fine grainy structure indicating a liquid crystalline mesophase at 52.2 °C, (c) fully isotropic polymer melt at 113 °C showing an absence of texture. Note the scale difference on (b).

4.2 Citric acid-derived spirocyclic diols for polycarbonates synthesis (Paper II)

4.2.1 Monomer synthesis

In this work, the synthesized diketone **B** shown in Scheme 2 was employed to prepare a rigid biobased bis-spirocyclic diol by cycloketalization. The ketalization was carried out with two equivalents of trimethylolpropane (TMP) in the presence of an acid catalyst in toluene/cyclohexane, which yielded a mixture of two isomers of the spiro-diol in a 1:1 ratio (Scheme 10). The two isomers were speculated to be diastereomers differing by the mutual orientation of the terminal ethyl and hydroxymethyl groups. The C_2 symmetric isomer was conveniently named **tB**-trans, and the C_s symmetric **tB**-cis. The ketalization reaction was further optimized to reach higher efficiency for large-scale synthesis. The solvent system, catalyst amount, and stoichiometry were investigated to find better reaction conditions. As a result, a 3:2 (v:v) mixture of cvclohexane/toluene appeared to be the most suitable solvent mixture to afford the products without noticeable by-product formation. It was found that 1 mol% of *p*TSA was sufficient for the reaction and increasing its amount did not show any effect on the reaction. An excess of TMP resulted in a faster conversion. Therefore, a small excess (2.2 eq) in relation to the diketone **B** was employed as it was enough to achieve high conversion within 16h, as well as to avoid the formation of mono-ketalized products. Three methods of product isolation were evaluated. Method (a) consisted of a direct crystallization in EtOAc/hexane, 1:1 (v:v). This method afforded the product with 85% yield, but ¹³C NMR analysis showed traces of unreacted TMP. A second method (b) was investigated to remove the remaining TMP. After the dissolution of the directly crystallized product in EtOAc, the solution was washed with water/brine, followed by a second crystallization. This aqueous wash enabled the removal of the TMP traces, and the final crystallization yielded the pure product tB with a 74% yield. Finally, a direct purification by flash chromatography of the crude reaction mixture was attempted, affording the product with 91% yield. Although this third method, method (c), resulted in the highest yield, it was deemed less attractive for practical and economic reasons if used on an industrial scale. The two isomers were successfully separated by simple flash chromatography on silica gel, to unambiguously confirm the structure of the diastereomers. In the bicyclo[3.3.0]octane moiety, the C and H forming the junction of the two rings are equivalent for the tB-trans isomer, whereas they are not equivalent in the tB-cis isomer. Thus, the chemical shifts of the C and H forming the bicycle junction in tB-cis are separated in the ¹³C and ¹H NMR spectra. These C signals are separated by 2.3 ppm in the ¹³C NMR spectrum and the H signals by 0.03 ppm in the ¹H NMR spectrum. The spectra of **tB**-trans only showed singlets. Further structural characterization and assignment confirmation of the stereoisomers was carried out by X-ray scattering of tB-trans. Single crystals were produced by the slow evaporation of chloroform at room temperature. However, the crystal structure of **tB**-*cis* could not be studied as no suitable single crystals could be obtained.



Scheme 10. Synthesis of the spirocyclic diol monomer tB by ketalization with TMP.

Key: The reaction leads to a mixture of **tB**-*cis* and **tB**-*trans*, isolated with yields of 74 and 91% by crystallization and chromatography, respectively.

4.2.2 Synthesis and characterization of polycarbonates (PCs)

For the rest of this work, we decided to use the diastereomeric mixture of **tB** for practical reasons. Besides, avoiding an extra purification step is relevant from an industry perspective. The mixture of spiro-diols **tB** was employed to produce polycarbonates (**PC**s) using diphenyl carbonate (DPC) as a carbonyl source. After carefully optimizing the reaction conditions, the polymerizations were carried out as solvent-free melt polycondensations using NaHCO₃ as a catalyst and a molar ratio of the diol mixture **tB** and DPC of 1.0:1.1 (Scheme 11). Two samples were produced with specific characteristics regarding their molecular weight by varying the reaction temperature. The molecular weight of the first sample was purposely kept low by limiting the maximum melt polycondensation temperature to 210 °C, while the second one reached a higher molecular weight by applying a temperature of 280 °C. The resulting low- and high-molecular-weight **PC**s were conveniently named **PC**-*l* and **PC**-*h*, respectively.





As expected, **PC**-*l* showed a lower M_n than **PC**-*h*, with $M_n = 7.5$ and 27.7 kg mol⁻¹ and PDI of 3.5 and 3.4 for **PC**-*l* and **PC**-*h*, respectively (Table 2). The measured T_{gs} of the **PC**s were 85 and 99 °C, for **PC**-*l* and **PC**-*h*, respectively, and were confirmed

by DMA. Those values are well below the decomposition temperature which was above 350 °C for both samples.

Table 2. Molecular and thermal properties of the thermoplastic PCs.								
Sample	<i>M</i> _n ^a (kg mol⁻¹)	D^a	<i>Т</i> _{d,95%} ^b (°С)	<i>T</i> _g (DSC) ^c (°C)	<i>Τ</i> g (DMA) ^d (°C)			
PC-/	7.5	3.5	352	85	85			
PC-h	27.7	3.4	360	100	99			

^aMeasured by SEC in CHCl₃. ^bThermal degradation temperature determined by TGA at 5% weight loss under N₂. $^{\circ}T_{g}$ measured using DSC from the second heating scan. $^{d}T_{g}$ measured using DMA.

To further investigate the processability of the **PC**s, dynamic melt rheology was performed, showing that **PC**-*h* had good processability at 170 °C, with a stable shear modulus G' of 42 kPa during the experiment (Figure 4a). However, the sample started to degrade when the temperature reached 200 °C, as a decrease of shear storage modulus G' and an increase of phase angle δ were observed. These observations, corresponding to a less elastic material, were attributed to degradation by chain-scission reactions. On the other hand, PC-l showed an increase of G' over time and a corresponding decrease of δ at 170 °C (Figure 4b). Such variations indicated that the material became more elastic, suggesting that **PC**-*l* underwent cross-linking reactions, which was coherent as the low molecular **PC** had a higher concentration of chain ends. In conclusion, **PC**-*h* showed good processability at 170 °C, which was 70 °C above the T_g and 180 °C below the $T_{d,95}$.





Key: Variation of shear storage modulus (*G*') and phase angle (δ) during the time sweeps of **PC-h** at 170 and 200 °C (a) and **PC-I** at 170 °C (b) as measured by rheology at 1 Hz, 0.2% strain (note the different scales for G').

4.3 Citric acid-derived spirocyclic diols for chemically recyclable poly(β -thioether ester)s (Paper III)

4.3.1 Monomers synthesis

The procedure developed in Paper II to produce the spirocyclic diol tB was employed to design other monomers derived from citric acid. Using glycerol instead of TMP, diketone **B** was converted to the spirocyclic diol **gB** (Scheme 12). The reaction was performed with 2.8 eq of glycerol, 5 mol% of pTSA in a mixture of cyclohexane/DMF, 12.5:1 (v:v) for 15 h. As observed for the synthesis of monomer tB, the reaction led to a mixture of isomers. The desired compound gB was a mixture of six diastereomers resulting from the different orientations of the hydroxymethyl groups. A thorough NMR analysis enabled identification and quantification of the various isomers. In addition, about 10% of a regioisomeric compound with one fivemembered dioxolane ring and one six-membered dioxane ring was identified and consisted of four diastereomers (noted X in Scheme 12). Moreover, about 1% of a spiro diol with two dioxane moieties was also detected and consisted of two diastereomers. Purification of the reaction mixture by flash chromatography afforded the isomeric mixture of gB in 92% yield. An alternative procedure without using DMF was also investigated, employing cyclohexane/toluene, 2:1 (v:v) as a solvent mixture, leading to 82% isolated product.

In a similar strategy, by using a different diketone for the Weiss–Cook condensation, such as cyclohexane-1,2-dione instead of glyoxal, a tricyclic diketone **T** was prepared following a previously reported procedure.^{198–200} After decarboxylation and before neutralizing the organic phase, the reaction mixture was extracted to avoid the neutralization of a large volume of aqueous acid solution. The pure diketone **T** was isolated by crystallization from MeOH. The ketalization reaction of **T** was carried out with TMP (2.2 eq) as triol and 5 mol% *p*TSA in toluene. This step required a longer reaction time (48 h) compared to **tB** and **gB**, probably due to the steric hindrance generated by the tricyclic structure. The resulting rigid spirocyclic diol **tT** was isolated with 88% yield by extraction, followed by crystallization. An NMR analysis demonstrated that the product consisted of two diastereomers in a roughly 1:1 ratio. Those isomers were called **tT**-*trans* for the C₂ symmetric, and **tT**-*cis* for the C_s symmetric (Scheme 12).

Scheme 12. Synthesis of the spirocyclic diols tT and gB.



Key: Both syntheses led to isomeric mixtures. The ratio of gB : X = 9:1, while tT-trans : tT-cis = 1:1.

To simplify the monomer synthesis, the respective isomer mixtures of **tB**, **gB**, and **tT** were employed without further separation. To continue the work reported in Paper II, thiol-Michael polymerizations were performed as the thiol-Michael addition is a very efficient "click" reaction through the reaction of di(meth)acrylates with dithiols. For this reason, the spirocyclic diols **tB**, **gB**, and **tT** were therefore converted to the corresponding diacrylates **tBa**, **gBa**, and **tTa** ("a" for acrylate), respectively, by acrylation with acryloyl chloride/Et₃N in DCM or 2-MeTHF. In addition, the diol **tT** was converted to the dimethacrylate monomer **tTma** ("ma" for methacrylate) using a similar procedure (Scheme 13). As a result, we synthesized four monomers with varying cyclic, spirocyclic, and acrylic structures.

Scheme 13. Preparation of diacrylates and dimethacrylates from the spiro-diols.



4.3.2 Poly(β -thioether ester)s synthesis and characterization

For the thiol-Michael polymerizations, we selected three dithiols; the aliphatic 1,6hexane dithiol (HDT) and 1,3-propanediol (PDT), as well as the aromatic 4,4'thiobisbenzenethiol (TBBT), to influence the chain stiffness (Scheme 14). The polymers were prepared by reacting a di(meth)acrylate monomer with a dithiol in CHCl₃ or 2-MeTHF with DBU as a basic catalyst. The resulting poly(β -thioether ester)s were isolated by precipitation in MeOH, and were named after the corresponding monomers, in the following manner: a polymer prepared from the bicyclic glycerol diacrylate **gBa** and 1,3-propane dithiol **PDT** was named "poly(gBa-PDT)".





4.3.2.1 Influence of the spirocyclic structure

To study the effects of the spirocyclic structure on the polymer properties, we prepared a series of polymers with PDT as dithiol (Table 3). The polymers were isolated with relatively high yields (70–77%). SEC analysis of the polymers showed that the molar masses varied significantly, from 15 to 26 kg mol⁻¹, and poly(tTa-PDT) showed the highest dispersity. TGA analysis of these polymers showed high thermal stability, with $T_{d,95\%}$ close to 320 °C. As expected, the samples were fully amorphous and showed a single T_g of –7, 15, and 24 °C for poly(gBa-PDT), poly(tBa-PDT), and poly(tTa-PDT), respectively. T_g increased with the rigidity of the polymer backbone. The tricyclic structure of poly(tTa-PDT) is more rigid than the bicyclic one of poly(tBa-PDT), thus reaching the highest T_g value. In addition, it appeared that the six-membered ring spirocyclic structure resulting from the ketalization with TMP increased T_g compared to the five-membered ring formed by

ketalization with glycerol. This could be explained by the higher molecular weight of poly(tBa-PDT) compared to poly(gBa-PDT), but it is also possible that the sixmembered ring increased the rotational energy barrier of the polymer backbone, therefore decreasing the segmental mobility of the former polymer opposed to the latter.

Table 3. Polymenzation and thermal data of polymers based on different spirocyclic structures.								
Sample	<i>M</i> _n ^a (kg mol ⁻¹)	D^{a}	<i>Т</i> _{d,95%} ^ь (°С)	T _g (DSC) ^c (°C)	<i>Τ</i> _g (DMA) ^d (°C)			
poly(tBa-PDT)	26	1.8	320	15	-			
poly(gBa-PDT)	15	1.9	322	-7	-			
poly(tTa-PDT)	18	3.6	323	24	17			

^aMeasured by SEC in CHCl₃. ^bThermal degradation temperature determined by TGA at 5% weight loss under N₂. $^{\circ}T_{g}$ measured using DSC from the second heating scan. $^{d}T_{g}$ measured using DMA.

Influence of the (meth)acrylate functionality 4.3.2.2

The monomers based on the tricyclic structure **tT** were chosen to study the effect of the acrylate versus methacrylate group as this rigid structure would likely lead to higher $T_{\rm g}$ values than the bicyclic monomers. Thus, we produced the polymers poly(tTa-PDT) and poly(tTma-PDT), the latter obtained in lower yield and molar mass (Table 4). This observation can be explained by steric hindrance and the electron-donating effect of the supplementary methyl group, which increases the electron density of the double bond, making it a less reactive Michael acceptor. TGA analysis showed that the two samples had similar thermal stability, and DSC analysis demonstrated that both polymers were fully amorphous. In the case of the methacrylate polymer, Tg was 8 °C higher than for the acrylate one. This is a common trend observed between acrylate and methacrylate-based polymers, as the presence of the methyl group increases the rotational barrier of the polymer backbone.²⁰¹ By DMA, poly(tTma-PDT) showed a higher storage modulus (E') than poly(tTa-PDT) in the glassy state. The T_g values measured as the maximum of the loss modulus (E") agreed well with the values determined by DSC.

Table 4. Polymerization and thermal data of polymers based on different diacrylate and dimethacrylate functionalities.

Sample	<i>M</i> n ^ª (kg mol⁻¹)	Ъ	<i>Т</i> _{d,95%} ^b (°С)	T _g (DSC) ^c (°C)	<i>T</i> _g (DMA) ^d (°C)
poly(tTa-PDT)	18	3.6	323	24	17
poly(tTma-PDT)	14	2.6	315	32	27

^aMeasured by SEC in CHCl₃. ^bThermal degradation temperature determined by TGA at 5% weight loss under N₂. $^{c}T_{g}$ measured using DSC. $^{d}T_{g}$ measured using DMA.

Influence of the dithiol structure 4.3.2.3

In addition to the PDT dithiol discussed in the previous sections, the more flexible HDT and the more rigid aromatic TBBT dithiols were investigated in polymerizations with the tricyclic diacrylate **tTa** monomer. The resulting poly(tTaPDT), poly(tTa-HDT), and poly(tTa-TBBT) were analyzed by DSC, which showed that they were fully amorphous, with T_g values of 24, 27, and 40 °C, respectively (Table 5). T_g was expected to increase with the rigidity of the polymer backbone, from the flexible HDT-based polymer to the PDT-based, and finally the aromatic TBBT-based polymer. The difference between poly(tTa-HDT) and poly(tTa-PDT) may be explained by the significantly lower molecular weight of the latter. In addition, DMA was performed on the three polymers. The T_g values determined as the maximum of loss modulus E" confirmed the DSC data (Table 5).

Sample	<i>M</i> n ^a (kg mol⁻¹)	D^{a}	<i>Т</i> _{d,95%} ^b (°С)	<i>T</i> _g (DSC) [°] (°C)	<i>T</i> _g (DMA) ^d (°C)
poly(tTa-HDT)	27	3.6	320	27	22
poly(tTa-PDT)	18	3.6	323	24	17
poly(tTa-TBBT)	22	1.8	317	40	35

Table 5. Polymerization and thermal data of polymers based on different dithiols

^aMeasured by SEC in CHCl₃. ^bThermal degradation temperature determined by TGA at 5% weight loss under N₂. ^c T_g measured using DSC. ^d T_g measured using DMA.

Overall, we report here on polymers with tunable thermal and mechanical properties depending on the structure of the monomers. Furthermore, all the studied poly(β -thioether ester)s showed a decomposition temperature measured by TGA that was relatively high in the region of 317–323 °C, about 200 °C above T_g , indicating the potential melt processability of these samples.

4.3.3 Chemical recyclability of the poly(β -thioether ester)s

The poly(β -thioether ester)s were first immersed in aqueous solutions of pH = 0, 3, 8, and 14 at 37 °C for 14 days to assess their stability. No noticeable change in molecular weight was observed by SEC in CHCl₃. As acetal bonds were previously reported for thiol-ene thermosets to be degraded into the original aldehyde/ketone and alcohol groups in a 1:1 (v:v) mixture of acetic acid and water at 90 °C,²⁰² these conditions were employed on poly(tTma-PDT). After 6 h, TLC analysis showed traces of the diketone **T**. Other conditions were also investigated. The samples poly(tTma-PDT), poly(tTa-TBBT), poly(tBa-HDT), and poly(gBa-PDT) were immersed in a water–acetone mixture [0.1 M aqueous HCl:acetone, 1:9 (v:v)] at 50 °C. After 72 h, SEC analysis showed the presence of only polymer fragments of M_n values lower than 1500 g mol⁻¹, indicating an extensive degradation of the polymer chains. Moreover, ¹H NMR analysis confirmed the presence of the corresponding diketones. These degradation experiments demonstrated that the poly(β -thioether ester)s were potentially chemically recyclable.

4.4 Lignin-inspired nitrile-containing aromatic monomers for polymethacrylates synthesis (Paper IV)

4.4.1 Monomers design and synthesis.

In the projects presented so far, the strategy to obtain high- T_g polymers was to design rigid monomers. Besides influencing the rigidity of the polymer backbone, the polymer scientist can also play with another parameter to increase $T_{\rm g}$, namely the polarity. Introducing strong polar groups will increase T_g as it will increase intermolecular interactions. In this project, we combined both rigid monomers and the introduction of highly polar functional groups. The polar group introduced in this project was the nitrile group. Nitrile functions have previously been introduced into styrenic materials to improve both thermal properties and chemical resistance. Poly(styrene-co-acrylonitrile), for example, has a Tg above 100 °C depending on the acrylonitrile content and is known for improving the chemical resistance of the material, compared to polystyrene.^{89,203} Three nitrile-containing lignin-inspired monomers were designed based on the three monolignols presented in Figure 1. The three monomers were synthesized from 4-hydroxybenzaldehyde 1a, vanillin 1b, and syringaldehyde 1c, which differ by the substitution of the phenolic ring with 0, 1, and 2 methoxy groups, respectively. The monomers were synthesized in two steps (Scheme 15). Step (i) consisted of the nitrilation of the aldehyde group using the inexpensive hydroxylamine-O-sulfonic acid, an approach developed by Quinn et al.²⁰⁴ The reaction also requires acid conditions, which were achieved by using an aqueous acetic acid solution, making it a reaction with a lower environmental impact. Thus, 4hydroxybenzonitrile 2a and syringonitrile 2c were readily synthesized in reasonably high yields (82% and 79% for 2a and 2c, respectively), and 2b was directly bought from a chemical supplier. In step (ii), 2a, 2b, and 2c were methacrylated, by reaction with methacrylic anhydride in EtOAc and using DMAP as a catalyst. The resulting monomers, 4-hydroxybenzonitrile methacrylate **BM**, vanillonitrile methacrylate **VM**, and syringonitrile methacrylate **SM**, were easily isolated by filtration and extraction. Only SM required further purification by flash chromatography on aluminum oxide to remove phenol and acid residues.

Scheme 15. Synthetic pathway to the lignin-inspired nitrile-containing monomers and homopolymers.



^aKey: Reagents and conditions: (i) hydroxylamine-*O*-sulfonic acid (1.1 eq), acetic acid (1 eq)/water, 50 °C, 6 h (yield 79–82%); no column chromatography required; (ii) methacrylic anhydride (1.01 eq), catalytic DMAP (2 mol%), ethyl acetate, 60 °C, 24 h (yield 70-89%); (iii) AIBN (0,1–1 mol%), DMSO, 60 °C, 24 h.

4.4.2 Homopolymers and copolymers synthesis and characterizations

The **BM**, **VM**, and **SM** monomers were polymerized by conventional free radical polymerization to produce the corresponding homopolymers, **PBM**, **PVM**, and **PSM**, respectively. SEC analysis of the homopolymers showed reasonably high M_n of 36, 23, and 44 kg mol⁻¹ for **PBM**, **PVM**, and **PSM**, respectively (Table 6). To investigate the effect of the incorporation of the nitrile-containing monomers on the properties of styrenic and methacrylic materials, three series of copolymers using either **VM** or **SM** were prepared. **VM** was copolymerized with styrene (S) and methyl methacrylate (MMA) to form the **PSVM** and **PMVM** series, respectively, while **SM** was copolymerized with styrene to obtain the **PSSM** series. The copolymers were designated **PSVM-x**, **PMVM-x**, and **PSSM-x** for the **PSVM**, **PMVM**, and **PSSM**, respectively, where *x* represents the nitrile monomer content (in mol%) in the copolymer, determined by ¹H NMR spectroscopy. A general trend showed that the molar fractions of the **VM** and **SM** monomers were higher in the copolymers than in the feeds, indicating that these monomers have a higher reactivity compared to styrene and MMA in the performed copolymerizations.

Sample	<i>M</i> _n (kg mol⁻¹)	Ð	<i>Т</i> _{d,95%} ^с (°С)	<i>Т</i> _g ^d (°С)
PBM	36ª	2.1ª	302	150
PVM	23 ^b /21 ^a	2.8 ^b /2.7 ^a	303	164
PSM	44 ^b /43 ^a	2.3 ^b /2.1 ^a	319	238
PSSM-16	19 ^b	1.8 ^b	317	123
PSSM-25	24 ^b	1.7 ^b	339	139
PSSM-35	21 ^b	1.6 ^b	324	152
PSSM-42	24 ^b	1.9 ^b	322	163
PSSM-50	30 ^b	1.8 ^b	330	173
PSVM-14	20 ^b	1.6 ^b	340	109
PSVM-28	26 ^b	1.7 ^b	341	123
PSVM-45	39 ^b	1.8 ^b	334	128
PMVM-18	85 ^b	1.9 ^b	261	128
PMVM-41	163 ^b	1.5 ^b	247	139

|--|

^aDetermined by SEC in THF. ^bDetermined by SEC in DMF. ^cDetermined by TGA at 5% weight loss under N_2 . ^dDetermined by DSC from the second heating scan.

All polymers and copolymers were fully amorphous and displayed single T_{gs} . The T_{g} values for the homopolymers were 150, 164, and 238 °C for **PBM**, **PVM**, and **PSM**, respectively, which are much higher than conventional PS ($T_{g} = 100$ °C) and PMMA ($T_{g} = 105$ °C). T_{g} increases with the number of methoxy groups present on the aromatic ring, which verifies previous observations on methoxy-substituted polymethacrylates.^{205–207} Besides, **PVM** and **PSM** have significantly higher T_{g} values than the corresponding non-nitrilated polymers, i.e., vanillin- and syringaldehyde polymethacrylates ($T_{g} = 129$ and 201 °C, respectively).²⁰⁶ This can be explained by the higher polarity of the nitrile group ($\mu = 4.18$ D) compared to the aldehyde group ($\mu = 2.77$ D).^{208,209} Regarding the copolymer series, the T_{g} values that the content of the nitrile-containing monomers, showing that the T_{g} of styrenic and methacrylic materials can be tuned and enhanced by incorporating predetermined amounts of biobased nitrile-containing monomers.

Finally, the solvent resistance of the different polymers was assessed by investigating the solubility in various solvents, chosen depending on their solubility parameter (δ) and their hydrogen bonding ability (Table 7). It appeared that the styrenic materials became insoluble in Et₂O and toluene as the nitrile-containing monomer content increased, comparable to SAN characteristics.²⁰³ The methacrylic materials, on the other hand, became insoluble in acetonitrile (ACN) with higher contents of the **VM** monomer. Consequently, both the **VM** and **SM** monomers can be employed to enhance the solvent resistance of the styrenic and acrylic polymer materials.

Sample	Et ₂ O δ = 15 (m)	ACN δ = 24 (p)	Toluene δ = 18 (p)
PS	+	-	+
PBM	-	-	-
PSVM-14	-	-	+
PSVM-28	-	-	+
PSVM-45	-	-	-
PVM	-	-	-
PSSM-16	-	-	+
PSSM-25	-	-	-
PSSM-35	-	-	-
PSSM-42	-	-	-
PSSM-50	-	-	-
PSM	-	+	-
PMMA	-	+	+
PMVM-18	-	+	+
PMVM-41	-	-	+

Table 7. Solubility of the nitrile-containing polymers at 21 °C.

^aThe symbols "+" and "-" indicate solubility and nonsolubility, respectively. Solubility parameters (δ , MPa^{1/2}) were obtained from the *Polymer Handbook*,²¹⁰ and the letters s, *m*, and *p* denote strongly, moderately, and poorly hydrogen-bond-forming solvents, respectively.

4.5 Vanillin-based nitrile-containing monomer for polyesters synthesis (Paper V)

4.5.1 Monomer design and synthesis

The monomers reported in Paper IV were inspired by lignin. Furthermore, we demonstrated that the introduction of nitrile functions, besides the rigid aromatic structure, increases T_g significantly. In the present project, we designed a monomer employing a similar strategy, i.e., using both rigidity and polarity to achieve high- $T_{\rm g}$ polymer materials. We decided to prepare bis-vanillonitrile by oxidative coupling of vanillonitrile. This reaction was efficiently performed in water by FeSO₄, with Na₂S₂O₈ acting as oxidant, at 90 °C. The bis-vanillonitrile precursor (BVN) was easily isolated by filtration and purified by a simple precipitation procedure, with up to 94% yield. This procedure is relatively green as water is used as solvent and benign chemicals are employed. Additionally, this reaction can also be performed by enzymatic catalysis, using either horseradish peroxidase^{211,212} or laccase Trametes versicolor,^{170,213} making it attractive for both industry and environmental purposes. As phenols are not very reactive in polycondensations, bis-vanillonitrile was converted into a diester by nucleophilic substitution of the hydroxyl groups with ethyl bromoacetate in DMF, under mild basic conditions (Scheme 16). The resulting diester monomer of bis-vanillonitrile (**DEBVN**) was easily isolated by precipitation in water and neutralization of the excess K_2CO_3 . After filtration and washing of the KBr salt formed as a side-product, **DEBVN** was obtained with 93% yield. An alternative isolation procedure consisting of extraction with EtOAc followed by purification by flash column chromatography was investigated and yielded similar results.

Scheme 16. Synthesis of the biobased precursor BVN and the diester monomer DEBVN.



4.5.2 Polyesters and copolyesters synthesis and characterization

The **DEBVN** monomer was used in polycondensation with three different diols, namely 1,4- butanediol, 1,6-hexanediol, and neopentyl glycol, forming the corresponding homopolyesters **PBBVN**, **PHBVN**, and **PNBVN**, respectively (Scheme 17). SEC analysis of the homopolymers showed relatively limited M_n values of 10.6, 2.3, and 7.6 kg mol⁻¹ for **PBBVN**, **PHBVN**, and **PNBVN**, respectively (Table 8). To investigate the effect of the incorporation of **DEBVN** as a co-monomer and demonstrate its potential to improve polymer properties, we prepared a series of copolyesters. We decided to synthesize copolyesters of **DEBVN** with 1,4-butanediol and the diethyl ester of FDCA (DEFDC), as **PBBVN** achieved the highest molecular weight, and because FDCA is a promising biobased aromatic compound for replacing terephthalic acid.^{155,156,214} Thus, three copolyesters containing 25, 50, and 75 mol% of **DEBVN** were prepared, as well as a neat poly(butylene 2,5-furan dicarboxylate) (PBF) sample as benchmark. The copolyesters were named **PBBVNF-X**, where "X" indicates the mole percentage of **DEBVN** monomer in the feed, relative to the total amount of diester monomers.

Scheme 17. Polymer synthesis of the bis-vanillonitrile diester monomer by conventional polycondensation with 1,4-butanediol, 1,6-hexanediol, and neopentyl glycol.



Sample	lsolated yield ^a (%)	<i>M</i> n [♭] (kg/mol)	D^{b}	<i>T</i> _{d,95%} (°C) ^c	7 _g (°C) ^d	7 _m (°C)⁴	∆H _m (J/g) ^d	Т _с (°С)е
PBF	69	n.d.	n.d.	332	40	172	41.2	135
PBBVNF-25	86	n.d.	n.d.	316	57	-	-	-
PBBVNF-50	55	3.8	3.1	331	71	-	-	-
PBBVNF-75	78	4.0	4.8	330	77	-	-	-
PBBVN	69	10.6	4.2	335	90	-	-	-
PHBVN	77	2.3	3.7	329	76	-	-	-
PNBVN	60	7.6	4.5	327	101	-	-	-

Table 8. Polymerizations and thermal data of the neat PBF, PBBVN, PHBVN, and PNBVN polyesters and the PBBVNF-X copolyesters.

^aDetermined gravimetrically. ^bDetermined by SEC in THF. ^bDetermined by SEC in DMF. ^cDetermined by TGA at 5% weight loss under N₂. ^dDetermined by DSC from the second heating scan. ^eDetermined by DSC during the cooling cycle.

SEC analysis showed that the M_n values of **PBBVNF-50** and **PBBVNF-75** were low, 3.8, and 4.0 kg mol⁻¹, respectively. **PBBVNF-25** and the neat PBF samples could not be analyzed by SEC as they were not soluble in THF. ¹H NMR spectroscopy demonstrated that the **DEBVN** content in the copolyesters was similar to the feed ratios, indicating similar reactivities of the two diester monomers.

All the polyesters showed single-step decompositions by TGA analysis, with relatively high decomposition temperatures $T_{d,95\%}$, ranging from 316 to 335 °C (Table 8). The variations could be explained by the differences in molecular weight. As expected, the homopolyesters based on **DEBVN** were fully amorphous and exhibited a single T_g by DSC analysis (Figure 5). The T_g values for the homopolyesters were 90, 76, and 101 °C for PBBVN, PHBVN, and PNBVN, respectively (Table 8). The T_g values increased with the rigidity of the diol. Notably, **PNBVN** displayed a $T_{\rm g} > 100$ °C, which is promising, considering its relatively limited M_n value. It is anticipated that with a higher molecular weight, **PNBVN** could attain an even higher $T_{\rm g}$ value, rendering it suitable for hot-fill applications. As predicted, PBF was semi-crystalline with a melting temperature of $T_{\rm m} = 171$ °C and $T_g = 40$ °C, consistent with existing literature reports.^{215–217} The semicrystallinity of PBF disappeared upon copolymerization, resulting in fully amorphous copolyesters. Moreover, the incorporation of the rigid and polar **DEBVN** monomer into the PBF backbone led to improved thermal properties, causing T_g values to increase linearly with the **DEBVN** content (Figure 6). In summary, the findings demonstrate that the $T_{\rm g}$ of PBF can be findly tuned and enhanced by strategically incorporating predetermined quantities of the biobased bis-vanillonitrile monomer. Importantly, all homopolyesters and copolyesters exhibited $T_{\rm g}$ values more than 200 °C below their respective decomposition temperatures, suggesting their potential melt-processability.

Figure 5. Second heating DSC traces of the homopolyesters and copolyesters under $N_{\rm 2}$ atmosphere at 10 °C min 1 .



Figure 6. T_g as a function of the incorporated **DEBVN** monomer in the copolyester series. (Linear trend plotted in red to highlight the linear behavior).



5 Conclusions

In this thesis, new building blocks and monomers from lignocellulose were rationally designed and synthesized. We specifically targeted two physical parameters, the rigidity and polarity of the monomers, to improve the thermal and mechanical properties of the resulting biobased thermoplastics. Thus, several building blocks and monomers derived from sugar and lignin have been produced and employed to synthesize a wide variety of polymers, i.e., poly(meth)acrylates, polycarbonates, poly(β -thioether ester)s, and polyesters. The thermal and mechanical properties of these polymers were investigated and correlated to their chemical structure. In addition, we demonstrated the potential chemical recyclability of some of the reported materials.

In Paper I, we successfully prepared a series of 12 isosorbide-based AIMA monomers with different pendant linear alkanoyl chains ranging from C2 to C20. These monomers were synthesized using biocatalytic and chemical acylation pathways and subsequently polymerized through radical mechanism. The length of the alkanoyl chain had a significant impact on the material properties. Monomers with C2 to C12 chains resulted in fully amorphous, stiff, and transparent materials, while those with longer chains (C13 to C20) became semicrystalline and formed liquid crystalline mesophases above their melting temperatures. Melt processing of the materials was feasible without degradation, and the study demonstrated that the phase behavior and transition temperatures could be controlled by altering the alkanoyl chain length and the regiochemistry of the monomer. The PAIMA class of biobased polymers shows promise for various applications in the plastics and coating industries.

In Paper II, a synthetic pathway to a biobased alicyclic spiro-diol monomer was developed using inexpensive starting materials. The spiro-diol was obtained from a ketalization reaction between a bicyclic ketone derived from citric acid and trimethylolpropane. Melt polycondensations of this monomer with diphenyl carbonate resulted in rigid polycarbonates with high molecular weights and T_g up to 100 °C. The polymer exhibited good transparency, mechanical strength, and processability, making it suitable for high- T_g condensation polymers. Current investigations are focused on using the spiro-diol monomer to prepare polyesters, polyurethanes, and polyacrylates.

In Paper III, the synthetic pathway developed in Paper II was employed to produce two conformationally rigid biobased alicyclic spiro-diols from readily available starting materials. These spiro-diols were converted into di(meth)acrylates and used in thiol-Michael polymerizations with various dithiols. The resulting poly(β thioether ester)s exhibited high thermal stability, T_g values ranging from -7 to 40 °C, and resistance to acidic and basic aqueous conditions. The ketal functionalities could be cleanly hydrolyzed in a mixture of 1 M aqueous HCl/acetone (1:9), opening a path for the chemical recycling of these materials. Overall, this study demonstrated that these novel spiro-diols are a valuable addition to the preparation of highperformance polymers.

In Paper IV, we prepared nitrile-containing methacrylates by nitrilation of lignininspired building blocks like vanillin and syringaldehyde. Copolymerizations with styrene and methyl methacrylate produced materials with enhanced T_g values and solvent resistance. The presence of the highly polar nitrile group and methoxy groups contributed to the exceptionally high T_{gs} reached by the polymethacrylates. Polymers containing vanillonitrile methacrylate (VM) were found to be melt processable and held promise for applications in packaging, coatings, and highperformance plastics due to the accessibility and potentially low cost of vanillin.

In Paper V, using a similar strategy as in Paper IV, bis-vanillonitrile was synthesized by oxidative coupling followed by a chain extension to produce a diester monomer. This monomer was employed to produce polyesters by reaction with different diols. The introduction of this rigid and polar monomer showed that the resulting polymers had improved thermal properties compared to similar polyesters based on FDCA.

Overall, these studies demonstrate the successful synthesis of various biobased monomers and their polymerization into materials with tailored properties, opening new possibilities for environmentally friendly and sustainable materials in diverse industrial applications.

6 Outlook

In the future, further research should focus on fine-tuning the properties of the PAIMA materials reported in Paper I, by exploring different pendant groups and regioisomers. For example, investigating the use of alicyclic, aromatics or branched alkanoyl pendant groups may offer additional control over the phase behavior, transition temperatures, and mechanical properties of these polymers. This could lead to the development of PAIMA variants optimized for specific applications, such as flexible packaging, high-performance coatings, or biomedical materials.

The spirocyclic diols reported in Papers II and III may be further employed to produce polyesters, polyurethanes, and polyacrylates, to propose a library of biobased polymers suitable for different applications and being potentially chemically recyclable. In addition, it is possible to increase the T_g of the poly(β -thioether ester)s by oxidizing the sulfide moieties into more polar sulfoxides or sulfones.²¹⁸ A study of the oxidation of the reported polymers and how it affects their thermal, mechanical, and barrier properties could be carried out.

While the research reported in this thesis has focused on isosorbide-based, citric acid-based, and lignin-inspired monomers, there is potential to explore and develop other biobased monomers from renewable resources. Expanding the repertoire of renewable building blocks for high- T_g polymers is an important avenue for future research. Identifying new alicyclic or aromatic building blocks derived from lignocellulosic biomass, as well as introducing polar functions like the nitrile group reported in Papers IV and V, could offer a wide range of possibilities for high-performance biobased polymers with unique properties and applications.

Considering the increasing emphasis on sustainability and circular economy principles, future research should assess the biodegradability and recyclability of the developed biobased polymers. The recyclability of the polyesters reported in Paper V could be investigated. For example, a study of enzymatic recycling with PETase could be performed, or conventional chemical recycling by acidic or alkaline hydrolysis. Understanding the fate of these materials in different environmental conditions and exploring methods for their efficient recycling will contribute to their viability as green alternatives in various industries.

In the pursuit of sustainable materials, biobased polymers have emerged as a promising alternative to traditional plastics. To determine their economic viability, particularly within industrial processes, the application of life-cycle assessment

(LCA) is pivotal. LCA can offer a comprehensive framework for evaluating the environmental and economic impacts of biobased polymer materials across their entire life cycle – from raw material extraction and production to use and disposal. While the laboratory-scale syntheses reported in this thesis offer valuable insights, they often fail to capture the complexities and efficiencies achievable in optimized industrial settings. This approach considers factors such as scale-up efficiency, resource optimization, and waste reduction, offering a comprehensive view of their viability in real-world applications. Therefore, by focusing on industrial procedures in LCAs, we could gain a more accurate understanding of the potential economic impact of the biobased monomers and polymer materials presented here.

In conclusion, future research in the field of biobased polymers should focus on optimizing material properties, exploring new monomers, developing green polymerization methods, understanding polymer morphology and processing, evaluating sustainability, biodegradability, and recycling potential, and investigating applications in emerging technologies. By addressing these research perspectives, we can accelerate the adoption of sustainable biobased materials in various industries, contributing to a more environmentally friendly and resourceefficient future.

7 Acknowledgments

When I started my Ph.D., I pictured the coming five years as a marathon. I imagined that a Ph.D. was like a long, solo, enduring race, where you must pace your efforts to reach the end, even though I was not a runner myself. How wrong I was! As the end of my Ph.D. draws near, I realize that it is a journey, a voyage, with countless encounters along the way. I would like to express my gratitude to the people I met and who helped me during this journey, but also to those who made me who I am today.

First, I would like to thank Patric Jannasch, my supervisor, for offering me the opportunity to realize a Ph.D. within his research group. When I started, I was freshly out of teaching physics and chemistry in France, having a Master's in Organic Chemistry, and little knowledge about polymers. Five years later, I am now on my way to defend my thesis in Polymer Technology. You have been a great support and guided me when I needed help. Your calm character and the trust you showed me gave me the confidence to pursue my efforts. I learned so much, especially polymer physics and material science, and developed so many skills along this journey. Please accept my deepest gratitude. Secondly, I would like to thank Baozhong Zhang for co-supervising me. I am grateful for learning polymer chemistry with you and for your advice and support on my research work. I also would like to thank Charlotta Turner and Jan-Olle Malm for acting as my department representatives during my Ph.D. Thank you for your positive feedback, suggestions, and encouragement during the ISP meetings.

I would like to thank my Estonian collaborators Lauri Vares, Livia Matt, Siim Laanesoo, Ilme Liblikas, and Rauno Sedrik from the University of Tartu. I appreciated working with you all and discussing our projects in meetings. I am grateful for the fruitful collaboration we had and I hope to visit you in Estonia someday.

There are many people at CAS that I have met along this journey and that are the heart of the department. Without them, CAS would not function properly. Thank you to Maria Levin and Sara Röstlund for your support and guidance with the arcane administrative paperwork. Thank you also to Kornelije Kraguljac for his valuable expertise in various machinery, thus saving several vacuum pumps from premature replacement. Thank you to Ulf Dahlén for your IT skills, troubleshooting our computers, and making them reliable. Many thanks to Katarina Fredriksson and the

purchasing department for their assistance and efficiency with purchasing chemicals, equipment, or anything indispensable for our lab work. Thank you to Sofia Essén and Fiona Nermark for running LC-HRMS at our department and being available to help with understanding the measurements and interpreting results.

Besides work-related matters, there are also coworkers at CAS that create a friendly work environment that I would like to thank. First, my comrades of the Feel-Good Committee, Karl-Erik, Cassandra, Laura, Smita, Valtýr, Vicky, Peter, Viveka, Eric, Thamani, Erika, Mynta, and Ronak. Thank you for your enthusiasm for planning team-building activities, barbecues, movie and board game nights, potluck dinners, and more to make our department a better workplace. I would like to thank the other talented researchers I had the opportunity to work alongside and that supported me during these five years. Thank you, Pegah, for your help in the lab and our many discussions in the office. I am grateful for your help with reading through my thesis and giving advice. Thank you to my past and present polymer groups colleagues, Christoffer, Joel, Hannes, Huong, Nitin, Andrit, Dong, Oskar, Haivue, Anuja, Si, Triet, Isabell, Choi, Yifan, Sudhir, Niklas, Smita, Tam, Sathiyaraj, Xugang, Ping, Xiaoya, Rafael, Olga, and Tobias for being great coworkers, helping one way or another, and for the interesting discussions in the lab and the fika room. Thank you to my other Polymat colleagues, Axel, Mikelis, Robin, David, Daniel, Crispin, Johan, Marcus, Kimberly, Reine, Martin, Azemina, Aidas, Mark, Tianyi, Ofentse, Michael, and other colleagues at CAS.

I would like to thank my outside-of-work friends. Thank you to my high school friends, Ambre, Aurélie, Alice, Morgane, Samantha, and Gaëtan for being in my life and supporting me when I needed it. I always look forward to seeing you all when I come back to France. A special thanks to my friend Nathan for spending time while on vacation reading through my thesis and giving me advice on my English writing. I also want to thank Ashley for introducing me to drinking coffee in the last year of my Ph.D., which proved to help me a lot during these long nights of writing.

Je voulais également remercier l'ensemble de mes professeur.e.s qui m'ont guidé tout au long de mon parcours scolaire. En particulier, je souhaite remercier Mme Hénaux, ma professeure de SVT en classe de Seconde, qui m'a fortement incité à aller en filière scientifique. Je tiens aussi à exprimer ma reconnaissance à Mme Pichery, ma professeure de Physique-Chimie en classe de Terminale, pour m'avoir orienté vers les classes préparatoires CPGE à l'issue du baccalauréat, et me donner confiance dans mes capacités pour suivre cette voie d'excellence.

Je voudrais remercier mes parents pour leur amour et leur support tout au long de mes études et de ma vie personnelle et professionnelle. Depuis tout petit, ils ont nourri ma curiosité et ma soif de connaissances, avec entre autres mes abonnements à Images Doc, l'achats de livres d'astronomie, et j'en passe. Ils m'ont permis de devenir qui je suis aujourd'hui. Je leur suis reconnaissant pour la confiance et la liberté qu'ils m'ont accordé dans le choix de mes (très longues) études. Je suis également plein de gratitude envers ma tante Marie pour son soutien tout au long de ma vie, notamment ses incitations à poursuivre mes activités artistiques, aussi bien musicales que picturales. Je n'oublierai jamais la porte ouverte rue Daubenton les vendredi soir lorsque que j'étais au lycée Le Castel, pour me permettre de jouer du piano. Merci aussi pour les superbes peintures à l'huile que je n'ai pas eu l'occasion de mettre à profit pour réaliser la couverture de ma thèse, mais que je compte bien utiliser dans d'autres projets.

I would like to thank my Cookie Monster, who has been a rock in my life for the past eight years. I am immensely grateful for your support and your patience with me when I was studying in France for the Agrégation and throughout my Ph.D. Thank you for being here for me in the past years. You helped me keep my sanity when I was lost, took me away from the lab to relax when I needed it, and is an overall positive presence in my life. You make me a better person and I never regretted "failing" my zebra cake all these years ago.

Finally, I would like to thank Formas, the Estonian research council, and the European fund Mobilitas+ for financially supporting my research and studies.

//Olivier

8 References

- (1) Gibb, B. C. Plastics Are Forever. *Nat Chem* **2019**, *11* (5), 394–395. https://doi.org/10.1038/s41557-019-0260-7.
- (2) Roland, G.; R, J. J.; Lavender, L. K. Production, Use, and Fate of All Plastics Ever Made. *Sci Adv* **2022**, *3* (7), e1700782. https://doi.org/10.1126/sciadv.1700782.
- (3) PlasticsEurope. *Plastics The Facts 2022*; 2022. https://plasticseurope.org/wp-content/uploads/2022/10/PE-PLASTICS-THE-FACTS_V7-Tue_19-10-1.pdf (accessed 2022-11-14).
- (4) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. Plastic Waste Inputs from Land into the Ocean. *Science* (1979) **2015**, 347 (6223), 768 LP 771. https://doi.org/10.1126/science.1260352.
- (5) World Economic Forum. The New Plastics Economy. Rethinking the Future of Plastics. **2016**, 13–14.
- (6) EuropeanCommission. *The European Green Deal*. https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52019DC0640&from=EN.
- (7) EuropeanCommission. A Clean Planet for all: A European strategic long-term vision for a prosperous, modern, competitive and climate neutral economy. https://eur-lex.europa.eu/legalcontent/EN/TXT/HTML/?uri=CELEX:52018DC0773&from=EN.
- (8) PlasticsEurope. *Plastics The Facts 2020*. https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/ (accessed 2023-07-03).
- (9) Waddams, A. L. *Chemicals from Petroleum*, 4th ed.; Murray, J., Ed.; London, 1978.
- (10) Kimberlin, C. N. Chemistry in the Manufacture of Modern Gasoline. *J Chem Educ* 1957, 34 (11), 569. https://doi.org/10.1021/ed034p569.
- (11) Arene, E. O.; Kitwood, T. M. An Introduction to the Chemistry of Carbon Compounds; Longman: London, 1979.
- (12) Heinberg, R.; Campbell, C. *The Oil Depletion Protocol: A Plan to Avert Oil Wars, Terrorism, and Economic Collapse*; New Society Publishers, 2006.
- (13) U.S. EPA. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States; Washington, 2016. https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990 (accessed 2022-03-08).
- (14) Grec, A.; Maior, C. Earth Oil Extraction Major Environmental Pollution Source. *Environ Eng Manag J* 2008, 7 (6), 763–768.

- (15) Ellsworth, W. L. Injection-Induced Earthquakes. *Science (1979)* **2013**, *341* (6142), 1225942. https://doi.org/10.1126/science.1225942.
- (16) IUPAC. *The IUPAC Compendium of Chemical Terminology*; Gold, V., Ed.; International Union of Pure and Applied Chemistry (IUPAC): Research Triangle Park, NC, 2019. https://doi.org/10.1351/goldbook.
- (17) Field, C. B.; Behrenfeld, M. J.; Randerson, J. T.; Falkowski, P. Primary Production of the Biosphere: Integrating Terrestrial and Oceanic Components. *Science (1979)* 1998, *281* (5374), 237–240. https://doi.org/10.1126/science.281.5374.237.
- (18) Castro-Aguirre, E.; Iñiguez-Franco, F.; Samsudin, H.; Fang, X.; Auras, R. Poly(Lactic Acid)—Mass Production, Processing, Industrial Applications, and End of Life. Adv Drug Deliv Rev 2016, 107, 333–366. https://doi.org/10.1016/j.addr.2016.03.010.
- (19) Siracusa, V.; Blanco, I. Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly(Ethylene Terephthalate) (Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. *Polymers (Basel)* **2020**, *12* (8). https://doi.org/10.3390/polym12081641.
- (20) Sidek, I. S.; Draman, S. F. S.; Abdullah, S. R. S.; Anuar, N. Current Development on Bioplastics and Its Future Prospects: An Introductory Review. *i TECH MAG* 2019, 1, 03–08. https://doi.org/10.26480/itechmag.01.2019.03.08.
- (21) Atteberry, J. *Are Food-Based Plastics a Good Idea*?. HowStuffWorks. https://science.howstuffworks.com/food-based-plastics.htm (accessed 2022-03-10).
- (22) European Bioplastics. *Bioplastics market data*. https://www.europeanbioplastics.org/market/ (accessed 2022-03-03).
- (23) IPCC. Climate Change and Land: An IPCC Special Report on Climate Change, Desertification, Land Degradation, Sustainable Land Management, Food Security, and Greenhouse Gas Fluxes in Terrestrial Ecosystems; 2019.
- (24) Hallström, E.; Carlsson-Kanyama, A.; Börjesson, P. Environmental Impact of Dietary Change: A Systematic Review. *J Clean Prod* 2015, 91, 1–11. https://doi.org/10.1016/j.jclepro.2014.12.008.
- (25) Rose, D.; Heller, M. C.; Willits-Smith, A. M.; Meyer, R. J. Carbon Footprint of Self-Selected US Diets: Nutritional, Demographic, and Behavioral Correlates. *Am J Clin Nutr* 2019, *109* (3), 526–534. https://doi.org/10.1093/ajcn/nqy327.
- (26) Tsang, Y. F.; Kumar, V.; Samadar, P.; Yang, Y.; Lee, J.; Ok, Y. S.; Song, H.; Kim, K.-H.; Kwon, E. E.; Jeon, Y. J. Production of Bioplastic through Food Waste Valorization. *Environ Int* **2019**, *127*, 625–644. https://doi.org/10.1016/j.envint.2019.03.076.
- (27) Wyman, C. E.; Dale, B. E.; Elander, R. T.; Holtzapple, M.; Ladisch, M. R.; Lee, Y. Y. Coordinated Development of Leading Biomass Pretreatment Technologies. *Bioresour Technol* 2005, 96 (18), 1959–1966. https://doi.org/10.1016/j.biortech.2005.01.010.

- (28) Yousuf, A.; Pirozzi, D.; Sannino, F. Chapter 1 Fundamentals of Lignocellulosic Biomass. In *Lignocellulosic Biomass to Liquid Biofuels*; Yousuf, A., Pirozzi, D., Sannino, F., Eds.; Academic Press, 2020; pp 1–15. https://doi.org/10.1016/B978-0-12-815936-1.00001-0.
- (29) Bayer, E. A.; Morag, E.; Lamed, R. The Cellulosome A Treasure-Trove for Biotechnology. *Trends Biotechnol* **1994**, *12* (9), 379–386. https://doi.org/10.1016/0167-7799(94)90039-6.
- (30) Li, C.; Zheng, M.; Wang, A.; Zhang, T. One-Pot Catalytic Hydrocracking of Raw Woody Biomass into Chemicals over Supported Carbide Catalysts: Simultaneous Conversion of Cellulose, Hemicellulose and Lignin. *Energy Environ Sci* 2012, 5 (4), 6383–6390. https://doi.org/10.1039/C1EE02684D.
- (31) Kumar, A.; Anushree; Kumar, J.; Bhaskar, T. Utilization of Lignin: A Sustainable and Eco-Friendly Approach. *Journal of the Energy Institute* **2020**, *93* (1), 235–271. https://doi.org/10.1016/j.joei.2019.03.005.
- (32) Abdelaziz, O. Y.; Brink, D. P.; Prothmann, J.; Ravi, K.; Sun, M.; García-Hidalgo, J.; Sandahl, M.; Hulteberg, C. P.; Turner, C.; Lidén, G.; Gorwa-Grauslund, M. F. Biological Valorization of Low Molecular Weight Lignin. *Biotechnol Adv* 2016, 34 (8), 1318–1346. https://doi.org/10.1016/j.biotechadv.2016.10.001.
- (33) Sun, Z.; Fridrich, B.; de Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. *Chem Rev* **2018**, *118* (2), 614–678. https://doi.org/10.1021/acs.chemrev.7b00588.
- (34) Liu, X.; Bouxin, F. P.; Fan, J.; Budarin, V. L.; Hu, C.; Clark, J. H. Recent Advances in the Catalytic Depolymerization of Lignin towards Phenolic Chemicals: A Review. *ChemSusChem* **2020**, *13* (17), 4296–4317. https://doi.org/10.1002/cssc.202001213.
- (35) Becker, J.; Wittmann, C. A Field of Dreams: Lignin Valorization into Chemicals, Materials, Fuels, and Health-Care Products. *Biotechnol. Adv.* **2019**, *37* (6), 107360. https://doi.org/10.1016/j.biotechadv.2019.02.016.
- (36) Abdelaziz, O. Y.; Li, K.; Tunå, P.; Hulteberg, C. P. Continuous Catalytic Depolymerisation and Conversion of Industrial Kraft Lignin into Low-Molecular-Weight Aromatics. *Biomass Convers Biorefin* 2018, 8 (2), 455–470. https://doi.org/10.1007/s13399-017-0294-2.
- (37) Nguyen, H. T. H.; Qi, P.; Rostagno, M.; Feteha, A.; Miller, S. A. The Quest for High Glass Transition Temperature Bioplastics. J. Mater. Chem. A **2018**, 6 (20), 9298–9331. https://doi.org/10.1039/C8TA00377G.
- (38) Hernández, N.; Williams, R. C.; Cochran, E. W. The Battle for the "Green" Polymer. Different Approaches for Biopolymer Synthesis: Bioadvantaged vs. Bioreplacement. Org Biomol Chem 2014, 12 (18), 2834–2849. https://doi.org/10.1039/C3OB42339E.
- (39) Rose, M.; Palkovits, R. Isosorbide as a Renewable Platform Chemical for Versatile Applications—Quo Vadis? *ChemSusChem* **2012**, *5* (1), 167–176. https://doi.org/10.1002/cssc.201100580.

- (40) Romero, A.; Nieto-Márquez, A.; Alonso, E. Bimetallic Ru:Ni/MCM-48 Catalysts for the Effective Hydrogenation of d-Glucose into Sorbitol. *Appl Catal A Gen* 2017, 529, 49–59. https://doi.org/10.1016/j.apcata.2016.10.018.
- (41) Zhang, X.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M. A.; Lee, A. F.; Wilson, K. Platinum-Catalyzed Aqueous-Phase Hydrogenation of d-Glucose to d-Sorbitol. *ACS Catal* **2016**, *6* (11), 7409–7417. https://doi.org/10.1021/acscatal.6b02369.
- (42) Dussenne, C.; Delaunay, T.; Wiatz, V.; Wyart, H.; Suisse, I.; Sauthier, M. Synthesis of Isosorbide: An Overview of Challenging Reactions. *Green Chemistry* 2017, *19* (22), 5332–5344. https://doi.org/10.1039/C7GC01912B.
- (43) Stoss, P.; Hemmer, R. 1,4:3,6-Dianhydrohexitols. In *Advances in Carbohydrate Chemistry and Biochemistry*; Horton, D., Ed.; Academic Press, 1991; Vol. 49, pp 93–173. https://doi.org/10.1016/s0065-2318(08)60182-1.
- (44) Abenhaïm, D.; Loupy, A.; Munnier, L.; Tamion, R.; Marsais, F.; Quéguiner, G. Selective Alkylations of 1,4:3,6-Dianhydro-d-Glucitol (Isosorbide). *Carbohydr Res* 1994, 261 (2), 255–266. https://doi.org/10.1016/0008-6215(94)84022-9.
- (45) Loupy, A.; Monteux, D. A. Isomannide and Isosorbide as New Chiral Auxiliaries for the Stereoselective Synthesis of Tertiary α-Hydroxy Acids. *Tetrahedron* 2002, 58 (8), 1541–1549. https://doi.org/10.1016/S0040-4020(02)00024-8.
- (46) Tamion, R.; Marsais, F.; Ribereau, P.; Queguiner, G.; Abenhaim, D.; Loupy, A.; Munnier, L. Synthesis of New Chiral Auxiliaries Derived from Isosorbide. *Tetrahedron Asymmetry* 1993, 4 (8), 1879–1890. https://doi.org/10.1016/S0957-4166(00)80428-0.
- (47) Seemayer, R.; Bar, N.; Schneider, M. P. Enzymatic Preparation of Isomerically Pure 1,4:3,6-Dianhydro-D-Glucitol Monoacetates - Precursors for Isoglucitol 2and 5-Mononitrates. *Tetrahedron Asymmetry* **1992**, *3* (9), 1123–1126. https://doi.org/10.1016/S0957-4166(00)82092-3.
- (48) Roy, A.; Chawla, H. P. S. Biocatalysis in Organic Solvents: A Process for Multigram Synthesis of 1,4:3,6-Dianhydro-D-Glucitol 2-Acetate and Its Isomeric 5-Acetate Using Immobilized Lipase from P Seudomonas Sp. *Enzyme Microb Technol* 2001, 29 (8), 490–493. https://doi.org/10.1016/S0141-0229(01)00425-2.
- (49) Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J.-P. Polymers from Renewable 1,4:3,6-Dianhydrohexitols (Isosorbide, Isomannide and Isoidide): A Review. *Prog Polym Sci* 2010, *35* (5), 578–622. https://doi.org/10.1016/j.progpolymsci.2009.10.001.
- (50) Saxon, D. J.; Luke, A. M.; Sajjad, H.; Tolman, W. B.; Reineke, T. M. Next-Generation Polymers: Isosorbide as a Renewable Alternative. *Prog Polym Sci* 2020, *101*, 101196. https://doi.org/10.1016/j.progpolymsci.2019.101196.
- (51) Nelson, A. M.; Long, T. E. A Perspective on Emerging Polymer Technologies for Bisphenol-A Replacement. *Polym Int* 2012, 61 (10), 1485–1491. https://doi.org/10.1002/pi.4323.
- (52) Noordover, B. A. J.; Haveman, D.; Duchateau, R.; van Benthem, R. A. T. M.; Koning, C. E. Chemistry, Functionality, and Coating Performance of Biobased Copolycarbonates from 1,4:3,6-Dianhydrohexitols. *J Appl Polym Sci* 2011, *121* (3), 1450–1463. https://doi.org/10.1002/app.33660.

- (53) Kang, H.; Li, M.; Tang, Z.; Xue, J.; Hu, X.; Zhang, L.; Guo, B. Synthesis and Characterization of Biobased Isosorbide-Containing Copolyesters as Shape Memory Polymers for Biomedical Applications. *J Mater Chem B* 2014, 2 (45), 7877–7886. https://doi.org/10.1039/C4TB01304B.
- (54) Caretto, A.; Passoni, V.; Brenna, N.; Sitta, M.; Ogliosi, L.; Catel, G.; Turri, S.; Griffini, G. Fully Biobased Polyesters Based on an Isosorbide Monomer for Coil Coating Applications. ACS Sustain Chem Eng 2018, 6 (11), 14125–14134. https://doi.org/10.1021/acssuschemeng.8b02659.
- (55) Vendamme, R.; Eevers, W. Sweet Solution for Sticky Problems: Chemoreological Design of Self-Adhesive Gel Materials Derived From Lipid Biofeedstocks and Adhesion Tailoring via Incorporation of Isosorbide. *Macromolecules* **2013**, *46* (9), 3395–3405. https://doi.org/10.1021/ma400203v.
- (56) Valdés, B. S. G.; Gomes, C. S. B.; Gomes, P. T.; Ascenso, J. R.; Diogo, H. P.; Gonçalves, L. M.; Dos Santos, R. G.; Ribeiro, H. M.; Bordado, J. C. Synthesis and Characterization of Isosorbide-Based Polyurethanes Exhibiting Low Cytotoxicity towards HaCaT Human Skin Cells. *Polymers (Basel)* **2018**, *10* (10). https://doi.org/10.3390/polym10101170.
- (57) Park, H.; Gong, M.-S.; Knowles, J. C. Catalyst-Free Synthesis of High Elongation Degradable Polyurethanes Containing Varying Ratios of Isosorbide and Polycaprolactone: Physical Properties and Biocompatibility. *J Mater Sci Mater Med* 2013, 24 (2), 281–294. https://doi.org/10.1007/s10856-012-4814-0.
- (58) Wu, J.; Eduard, P.; Jasinska-Walc, L.; Rozanski, A.; Noordover, B. A. J.; van Es, D. S.; Koning, C. E. Fully Isohexide-Based Polyesters: Synthesis, Characterization, and Structure–Properties Relations. *Macromolecules* 2013, 46 (2), 384–394. https://doi.org/10.1021/ma302209f.
- (59) Yokoe, M.; Aoi, K.; Okada, M. Biodegradable Polymers Based on Renewable Resources. VII. Novel Random and Alternating Copolycarbonates from 1,4:3,6-Dianhydrohexitols and Aliphatic Diols. *J Polym Sci A Polym Chem* **2003**, *41* (15), 2312–2321. https://doi.org/10.1002/pola.10772.
- (60) Liu, X.; Pang, C.; Ma, J.; Gao, H. Random Copolycarbonates Based on a Renewable Bicyclic Diol Derived from Citric Acid. *Macromolecules* 2017, 50 (20), 7949–7958. https://doi.org/10.1021/acs.macromol.7b01641.
- (61) Gandini, A. The Irruption of Polymers from Renewable Resources on the Scene of Macromolecular Science and Technology. *Green Chemistry* 2011, 13 (5), 1061– 1083. https://doi.org/10.1039/C0GC00789G.
- (62) Angumeenal, A. R.; Venkappayya, D. An Overview of Citric Acid Production. *LWT - Food Science and Technology* 2013, 50 (2), 367–370. https://doi.org/10.1016/j.lwt.2012.05.016.
- (63) Noordover, B. A. J.; van Staalduinen, V. G.; Duchateau, R.; Koning, C. E.; Benthem, van; Mak, M.; Heise, A.; Frissen, A. E.; van Haveren, J. Co- and Terpolyesters Based on Isosorbide and Succinic Acid for Coating Applications: Synthesis and Characterization. *Biomacromolecules* 2006, 7 (12), 3406–3416. https://doi.org/10.1021/bm060713v.

- (64) Tisserat, B.; O'kuru, R. H.; Hwang, H.; Mohamed, A. A.; Holser, R. Glycerol Citrate Polyesters Produced through Heating without Catalysis. *J Appl Polym Sci* 2012, *125* (5), 3429–3437. https://doi.org/10.1002/app.36669.
- (65) Adams, R.; Chiles, H. M.; Rassweiler, C. F. Acetonedicarboxylic Acid. *Organic Syntheses* **1925**, *5*, 5. https://doi.org/10.15227/orgsyn.005.0005.
- (66) Jákfalvy, E.; Gregorné Boros, L.; Mórász, T.; Tóth, G.; Szabó, A.; Töreki, J.; Oláh, S. Process for the Preparation of Dialkyl 3-Oxoglutarates. WO2004089867A2, 2004.
- (67) Chen, Y.; Chen, J.; Heng, L. Method for Preparing 1,3-Acetone Dicarboxylic Acid Diester and an Intermediate Thereof by Using Citric Acid to Catalyze Oxidization of Hydrogen Peroxide. CN103288629A, 2013.
- (68) Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U. Condensation of Dimethyl 1,3-Acetonedicarboxylate with 1,2-Dicarbonyl Compounds: Cis-Bicyclo[3.3.0]Octane-3,7-Diones. Organic Syntheses 1986, 64, 27. https://doi.org/10.15227/orgsyn.064.0027.
- (69) Karpov, A.; Walsdorff, C.; Siemer, M.; Mattioda, G.; Blanc, A. Glyoxal. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley, 2021; pp 1–11. https://doi.org/10.1002/14356007.a12_491.pub3.
- (70) Avantium. *Ray Technology*. https://www.avantium.com/technologies/ray/ (accessed 2023-08-14).
- (71) Pang, C.; Jiang, X.; Yu, Y.; Liu, X.; Lian, J.; Ma, J.; Gao, H. Sustainable Polycarbonates from a Citric Acid-Based Rigid Diol and Recycled BPA-PC: From Synthesis to Properties. ACS Sustain Chem Eng 2018, 6 (12), 17059–17067. https://doi.org/10.1021/acssuschemeng.8b04421.
- (72) Hufendiek, A.; Lingier, S.; Espeel, P.; de Wildeman, S.; du Prez, F. E. Polycycloacetals via Polytransacetalization of Diglycerol Bisacetonide. *Polym Chem* 2018, 9 (38), 4789–4797. https://doi.org/10.1039/C8PY01191E.
- (73) Lingier, S.; Nevejans, S.; Espeel, P.; De Wildeman, S.; Du Prez, F. E. High Molecular Weight Poly(Cycloacetals) towards Processable Polymer Materials. *Polymer (Guildf)* 2016, 103, 98–103. https://doi.org/10.1016/j.polymer.2016.09.040.
- (74) Bailey, W. J.; Volpe, A. A. Synthesis of Spiro Polymers, *J Polym Sci A1* 1970, 8 (8), 2109–2122. https://doi.org/10.1002/pol.1970.150080819.
- (75) Alder, R. W.; Reddy, B. S. R. Attempted Equilibration of an Insoluble Spiran Polymer with Monomers and Oligomers through Reversible Chemical Reactions: Transketalization Route to Spiropolymers from 1,4-Cyclohexanedione and Pentaerythritol. *Polymer (Guildf)* **1994**, *35* (26), 5765–5772. https://doi.org/10.1016/S0032-3861(05)80054-0.
- (76) Makhseed, S.; B. McKeown, N. Novel Spiro-Polymers with Enhanced Solubility. *Chemical Communications* 1999, No. 3, 255–256. https://doi.org/10.1039/A808457B.
- (77) Boerjan, W.; Ralph, J.; Baucher, M. Lignin Biosynthesis. Annu. Rev. Plant Biol. 2003, 54 (1), 519–546. https://doi.org/10.1146/annurev.arplant.54.031902.134938.

- (78) Brunow, G. Lignin Chemistry and Its Role in Biomass Conversion. *Biorefineries-Industrial Processes and Products*. December 16, 2005, pp 151–163. https://doi.org/10.1002/9783527619849.ch21.
- (79) Fache, M.; Boutevin, B.; Caillol, S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. *ACS Sustain. Chem. Eng.* **2016**, *4* (1), 35–46. https://doi.org/10.1021/acssuschemeng.5b01344.
- (80) Fache, M.; Boutevin, B.; Caillol, S. Vanillin, a Key-Intermediate of Biobased Polymers. *Eur Polym J* 2015, 68, 488–502. https://doi.org/10.1016/j.eurpolymj.2015.03.050.
- (81) Bomgardner, M. M. Following Many Routes To Naturally Derived Vanillin. *Chem. Eng. News* **2014**, *92* (6), 14–15.
- (82) Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a Promising Biobased Building-Block for Monomer Synthesis. *Green Chemistry* 2014, *16* (4), 1987–1998. https://doi.org/10.1039/C3GC42613K.
- (83) Lee, D.-W.; Kim, H.-N.; Lee, D.-S. Introduction of Reversible Urethane Bonds Based on Vanillyl Alcohol for Efficient Self-Healing of Polyurethane Elastomers. *Molecules* 2019, 24 (12), 2201. https://doi.org/10.3390/molecules24122201.
- (84) Tachibana, K.; Abe, H. Studies on Thermo-Mechanical and Thermal Degradation Properties of Bio-Based Polyurethanes Synthesized from Vanillin-Derived Diol and Lysine Diisocyanate. *Polym Degrad Stab* 2019, *167*, 283–291. https://doi.org/10.1016/j.polymdegradstab.2019.07.014.
- (85) Zhao, C.; Huang, C.; Chen, Q.; Ingram, I. D. V.; Zeng, X.; Ren, T.; Xie, H. Sustainable Aromatic Aliphatic Polyesters and Polyurethanes Prepared from Vanillin-Derived Diols via Green Catalysis. *Polymers (Basel)* **2020**, *12* (3), 586. https://doi.org/10.3390/polym12030586.
- (86) Mankar, S. V; Garcia Gonzalez, M. N.; Warlin, N.; Valsange, N. G.; Rehnberg, N.; Lundmark, S.; Jannasch, P.; Zhang, B. Synthesis, Life Cycle Assessment, and Polymerization of a Vanillin-Based Spirocyclic Diol toward Polyesters with Increased Glass-Transition Temperature. ACS Sustain. Chem. Eng. 2019, 7 (23), 19090–19103. https://doi.org/10.1021/acssuschemeng.9b04930.
- (87) Kine, B. B.; Novak, R. W. Acrylic and Methacrylic Ester Polymers. In Encyclopedia of Polymer Science and Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; New York, 1985; Vol. 1, pp 234–299.
- (88) Nemek, J. W.; Bauer, W. Jr. Acrylic and Methacrylic Polymers. In *Encyclopedia* of Polymer Science and Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1985; Vol. 1, pp 211–234.
- (89) Peng, F. M. Acrylonitrile Polymers. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1985; Vol. 1, pp 426–470.
- (90) Thomas, W. M.; Wang, D. W. Acrylamide Polymers. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1985; Vol. 1, pp 169–211.

- (91) AgileIntel Research (ChemIntel360). *Market volume of acrylic acid worldwide* from 2015 to 2021, with a forecast for 2022 to 2029 (in million metric tons). Statista. https://www.statista.com/statistics/1245262/acrylic-acid-market-volumeworldwide/ (accessed 2023-04-01).
- (92) Wang, S.; Shuai, L.; Saha, B.; Vlachos, D. G.; Epps, T. H. I. I. From Tree to Tape: Direct Synthesis of Pressure Sensitive Adhesives from Depolymerized Raw Lignocellulosic Biomass. ACS Cent Sci 2018, 4 (6), 701–708. https://doi.org/10.1021/acscentsci.8b00140.
- (93) Matt, L.; Parve, J.; Parve, O.; Pehk, T.; Pham, T. H.; Liblikas, I.; Vares, L.; Jannasch, P. Enzymatic Synthesis and Polymerization of Isosorbide-Based Monomethacrylates for High-Tg Plastics. ACS Sustain. Chem. Eng. 2018, 6 (12), 17382–17390. https://doi.org/10.1021/acssuschemeng.8b05074.
- (94) Odian, G. Radical Chain Polymerization. In *Principles of Polymerization*; 2004; pp 198–349. https://doi.org/10.1002/047147875X.ch3.
- (95) Bao, Y.; Ma, J.; Zhang, X.; Shi, C. Recent Advances in the Modification of Polyacrylate Latexes. *J Mater Sci* 2015, 50 (21), 6839–6863. https://doi.org/10.1007/s10853-015-9311-7.
- (96) Tsai, T.-L.; Lin, C.-C.; Guo, G.-L.; Chu, T.-C. Chemical Kinetics of Polymethyl Methacrylate (PMMA) Decomposition Assessed by a Microwave-Assisted Digestion System. *Ind Eng Chem Res* 2008, 47 (8), 2554–2560. https://doi.org/10.1021/ie0714246.
- (97) He, F.; Jin, K.; Sun, J.; Fang, Q. Biobased Anethole/Polyacrylate Cross-Linked Materials with Good Transparency and High Thermostability. *ACS Sustain Chem Eng* **2018**, *6* (3), 3575–3579. https://doi.org/10.1021/acssuschemeng.7b03899.
- (98) Makshina, E. V; Canadell, J.; van Krieken, J.; Peeters, E.; Dusselier, M.; Sels, B. F. Bio-Acrylates Production: Recent Catalytic Advances and Perspectives of the Use of Lactic Acid and Their Derivates. *ChemCatChem* **2019**, *11* (1), 180–201. https://doi.org/10.1002/cctc.201801494.
- (99) Beerthuis, R.; Rothenberg, G.; Shiju, N. R. Catalytic Routes towards Acrylic Acid, Adipic Acid and ε-Caprolactam Starting from Biorenewables. *Green Chemistry* 2015, 17 (3), 1341–1361. https://doi.org/10.1039/C4GC02076F.
- (100)Britannica The Editors of Encyclopaedia. *Polymethyl methacrylate*. Encyclopedia Britannica. https://www.britannica.com/science/polymethyl-methacrylate (accessed 2023-04-03).
- (101)Rey-Vinolas, S.; Engel, E.; Mateos-Timoneda, M. A. 7 Polymers for Bone Repair. In *Bone Repair Biomaterials (Second Edition)*; Pawelec, K. M., Planell, J. A., Eds.; Woodhead Publishing, 2019; pp 179–197. https://doi.org/10.1016/B978-0-08-102451-5.00007-X.
- (102)Lee, C. The Mechanical Properties of PMMA Bone Cement. In *The Well-Cemented Total Hip Arthroplasty: Theory and Practice*; Breusch, S., Malchau, H., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2005; pp 60–66. https://doi.org/10.1007/3-540-28924-0_6.
- (103)Persistence Market Research. *Methyl methacrylate market to reach ~5.7 million tons by the end of 2028*. Inter Press Service News. https://ipsnews.net/business/2020/06/09/methyl-methacrylate-market-to-reach-5-7-million-tons-by-the-end-of-2028/ (accessed 2023-04-03).
- (104)Khelifa, F.; Habibi, Y.; Dubois, P. Chapter 5 Nanocellulose-Based Polymeric Blends for Coating Applications. In *Multifunctional Polymeric Nanocomposites Based on Cellulosic Reinforcements*; Puglia, D., Fortunati, E., Kenny, J. M., Eds.; William Andrew Publishing, 2016; pp 131–175. https://doi.org/10.1016/B978-0-323-44248-0.00005-5.
- (105)Walker, F. H.; Prane, J. W. *Introduction to Polymers and Resins*, 2nd ed.; Federation of Societies for Coatings Technology, 2000.
- (106)Sheppard, C. S. Peroxy Compounds. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, pp 1–21.
- (107)Sheppard, C. S. Azo Compounds. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1985; Vol. 2, pp 143–157.
- (108)Weissermel, K.; Arpe, H.-J. Propene Conversion Products. In *Industrial Organic Chemistry*; 2003; pp 267–312. https://doi.org/10.1002/9783527619191.ch11.
- (109)Wittcoff, H. A.; Reuben, B. G.; Plotkin, J. S. Chemicals and Polymers from Propylene. In *Industrial Organic Chemicals*; 2012; pp 211–271. https://doi.org/10.1002/9781118229996.ch6.
- (110)Darabi Mahboub, M. J.; Dubois, J.-L.; Cavani, F.; Rostamizadeh, M.; Patience, G. S. Catalysis for the Synthesis of Methacrylic Acid and Methyl Methacrylate. *Chem Soc Rev* **2018**, *47* (20), 7703–7738. https://doi.org/10.1039/C8CS00117K.
- (111)Nagai, K. New Developments in the Production of Methyl Methacrylate. *Appl Catal A Gen* **2001**, *221* (1), 367–377. https://doi.org/10.1016/S0926-860X(01)00810-9.
- (112)Lansing, J. C.; Murray, R. E.; Moser, B. R. Biobased Methacrylic Acid via Selective Catalytic Decarboxylation of Itaconic Acid. *ACS Sustain Chem Eng* **2017**, *5* (4), 3132–3140. https://doi.org/10.1021/acssuschemeng.6b02926.
- (113)Bohre, A.; Novak, U.; Grilc, M.; Likozar, B. Synthesis of Bio-Based Methacrylic Acid from Biomass-Derived Itaconic Acid over Barium Hexa-Aluminate Catalyst by Selective Decarboxylation Reaction. *Molecular Catalysis* **2019**, *476*, 110520. https://doi.org/10.1016/j.mcat.2019.110520.
- (114)Lebeau, J.; Efromson, J. P.; Lynch, M. D. A Review of the Biotechnological Production of Methacrylic Acid. *Front Bioeng Biotechnol* **2020**, *8*.
- (115)Veith, C.; Diot-Néant, F.; Miller, S. A.; Allais, F. Synthesis and Polymerization of Bio-Based Acrylates: A Review. *Polym Chem* **2020**, *11* (47), 7452–7470. https://doi.org/10.1039/D0PY01222J.
- (116)Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. Polycarbonates. In Encyclopedia of Polymer Science And Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, pp 648–718.

- (117)Odian, G. Step Polymerization. In *Principles of Polymerization*; 2004; pp 39–197. https://doi.org/10.1002/047147875X.ch2.
- (118)Singh, A. Polycarbonate Synthesis. In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S., Müllen, K., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2014; pp 1–5. https://doi.org/10.1007/978-3-642-36199-9_419-1.
- (119)Brunelle, D. J.; Smigelski, P. M. Jr.; Boden, E. P. Evolution of Polycarbonate Process Technologies. In *Advances in Polycarbonates*; ACS Symposium Series; American Chemical Society, 2005; Vol. 898, pp 8–21. https://doi.org/10.1021/bk-2005-0898.ch002.
- (120)Fenichel, P.; Chevalier, N.; Brucker-Davis, F. Bisphenol A: An Endocrine and Metabolic Disruptor. *Ann Endocrinol (Paris)* **2013**, *74* (3), 211–220. https://doi.org/10.1016/j.ando.2013.04.002.
- (121)Rubin, B. S. Bisphenol A: An Endocrine Disruptor with Widespread Exposure and Multiple Effects. *J Steroid Biochem Mol Biol* **2011**, *127* (1), 27–34. https://doi.org/10.1016/j.jsbmb.2011.05.002.
- (122)Lingier, S.; Spiesschaert, Y.; Dhanis, B.; De Wildeman, S.; Du Prez, F. E. Rigid Polyurethanes, Polyesters, and Polycarbonates from Renewable Ketal Monomers. *Macromolecules* **2017**, *50* (14), 5346–5352. https://doi.org/10.1021/acs.macromol.7b00899.
- (123)Garrison, M. D.; Storch, P. J.; Eck, W. S.; Adams, V. H.; Fedick, P. W.; Harvey, B. G. BPA-Free High-Performance Sustainable Polycarbonates Derived from Non-Estrogenic Bio-Based Phenols. *Green Chemistry* **2021**, *23* (20), 8016–8029. https://doi.org/10.1039/D1GC01500A.
- (124)Zhang, Z.; Xu, F.; Zhang, Y.; Li, C.; He, H.; Yang, Z.; Li, Z. A Non-Phosgene Process for Bioderived Polycarbonate with High Molecular Weight and Advanced Property Profile Synthesized Using Amino Acid Ionic Liquids as Catalysts. *Green Chemistry* **2020**, *22* (8), 2534–2542. https://doi.org/10.1039/D0GC00265H.
- (125)Cui, S.; Borgemenke, J.; Qin, Y.; Liu, Z.; Li, Y. Chapter Five Bio-Based Polycarbonates from Renewable Feedstocks and Carbon Dioxide. In Advances in Bioenergy; Li, Y., Ge, X., Eds.; Elsevier, 2019; Vol. 4, pp 183–208. https://doi.org/10.1016/bs.aibe.2019.04.001.
- (126)Hauenstein, O.; Agarwal, S.; Greiner, A. Bio-Based Polycarbonate as Synthetic Toolbox. *Nat Commun* **2016**, 7 (1), 11862. https://doi.org/10.1038/ncomms11862.
- (127)Cui, S.; Qin, Y.; Li, Y. Sustainable Approach for the Synthesis of Biopolycarbonates from Carbon Dioxide and Soybean Oil. ACS Sustain Chem Eng 2017, 5 (10), 9014–9022. https://doi.org/10.1021/acssuschemeng.7b01819.
- (128)Ye, S.; Wang, S.; Lin, L.; Xiao, M.; Meng, Y. CO2 Derived Biodegradable Polycarbonates: Synthesis, Modification and Applications. Advanced Industrial and Engineering Polymer Research 2019, 2 (4), 143–160. https://doi.org/10.1016/j.aiepr.2019.09.004.
- (129)Nair, D. P.; Podgórski, M.; Chatani, S.; Gong, T.; Xi, W.; Fenoli, C. R.; Bowman, C. N. The Thiol-Michael Addition Click Reaction: A Powerful and Widely Used Tool in Materials Chemistry. *Chemistry of Materials* **2014**, *26* (1), 724–744. https://doi.org/10.1021/cm402180t.

- (130)Lowe, A. B. Thiol-Ene "Click" Reactions and Recent Applications in Polymer and Materials Synthesis. *Polym Chem* **2010**, *1* (1), 17–36. https://doi.org/10.1039/B9PY00216B.
- (131)Hoyle, C. E.; Bowman, C. N. Thiol–Ene Click Chemistry. *Angewandte Chemie International Edition* **2010**, *49* (9), 1540–1573. https://doi.org/10.1002/anie.200903924.
- (132)Hoyle, C. E.; Lee, T. Y.; Roper, T. Thiol–Enes: Chemistry of the Past with Promise for the Future. *J Polym Sci A Polym Chem* **2004**, *42* (21), 5301–5338. https://doi.org/10.1002/pola.20366.
- (133)Hebner, T. S.; Fowler, H. E.; Herbert, K. M.; Skillin, N. P.; Bowman, C. N.; White, T. J. Polymer Network Structure, Properties, and Formation of Liquid Crystalline Elastomers Prepared via Thiol–Acrylate Chain Transfer Reactions. *Macromolecules* **2021**, *54* (23), 11074–11082. https://doi.org/10.1021/acs.macromol.1c01919.
- (134)Moon, N. G.; Mazzini, F.; Pekkanen, A. M.; Wilts, E. M.; Long, T. E. Sugar-Derived Poly(β-Thioester)s as a Biomedical Scaffold. *Macromol Chem Phys* 2018, 219 (16), 1800177. https://doi.org/10.1002/macp.201800177.
- (135)Lillie, L. M.; Tolman, W. B.; Reineke, T. M. Degradable and Renewably-Sourced Poly(Ester-Thioethers) by Photo-Initiated Thiol–Ene Polymerization. *Polym Chem* **2018**, *9* (23), 3272–3278. https://doi.org/10.1039/C8PY00502H.
- (136)Kim, S.-S.; Ha, H.; Ellison, C. J. Soybean Oil-Based Thermoset Films and Fibers with High Biobased Carbon Content via Thiol–Ene Photopolymerization. ACS Sustain Chem Eng 2018, 6 (7), 8364–8373. https://doi.org/10.1021/acssuschemeng.8b00435.
- (137)Kasetaite, S.; De la Flor, S.; Serra, A.; Ostrauskaite, J. Effect of Selected Thiols on Cross-Linking of Acrylated Epoxidized Soybean Oil and Properties of Resulting Polymers. *Polymers (Basel)* **2018**, *10* (4), 439. https://doi.org/10.3390/polym10040439.
- (138)Roberts, J. S. Thiols. In *Kirk-Othmer Encyclopedia of Chemical Technology*; 2000. https://doi.org/https://doi.org/10.1002/0471238961.2008091518150205.a01.
- (139)Warlin, N.; Garcia Gonzalez, M. N.; Mankar, S.; Valsange, N. G.; Sayed, M.; Pyo, S.-H.; Rehnberg, N.; Lundmark, S.; Hatti-Kaul, R.; Jannasch, P.; Zhang, B. A Rigid Spirocyclic Diol from Fructose-Based 5-Hydroxymethylfurfural: Synthesis, Life-Cycle Assessment, and Polymerization for Renewable Polyesters and Poly(Urethane-Urea)s. *Green Chem.* **2019**, *21* (24), 6667–6684. https://doi.org/10.1039/C9GC03055G.
- (140)M. Gruter, G.-J.; Sipos, L.; Adrianus Dam, M. Accelerating Research into Bio-Based FDCA-Polyesters by Using Small Scale Parallel Film Reactors. *Comb Chem High Throughput Screen* **2012**, *15* (2), 180–188. https://doi.org/10.2174/138620712798868374.
- (141)*Coca-Cola Collaborates with Tech Partners to Create Bottle Prototype Made from 100% Plant-Based Sources*. https://www.coca-colacompany.com/mediacenter/100-percent-plant-based-plastic-bottle (accessed 2023-07-04).

- (142)Frost, J. W.; Miermont, A.; Schweitzer, D.; Bui, V.; Paschke, E.; Wicks, D. A. Biobased Polyesters. US 2011/0288263 A1, November 24, 2011.
- (143)Miller, K. K.; Zhang, P.; Nishizawa-Brennen, Y.; Frost, J. W. Synthesis of Biobased Terephthalic Acid from Cycloaddition of Isoprene with Acrylic Acid. ACS Sustain Chem Eng 2014, 2 (8), 2053–2056. https://doi.org/10.1021/sc5003038.
- (144)Bérard, S.; Vallée, C.; Delcroix, D. Sorbic Acid as a Renewable Resource for Atom-Economic and Selective Production of p-Toluic Acid and Alkyl-p-Toluates: Intermediates to Bioterephthalic Acid and Esters. *Ind Eng Chem Res* **2015**, *54* (28), 7164–7168. https://doi.org/10.1021/acs.iecr.5b01972.
- (145)Banella, M. B.; Gioia, C.; Vannini, M.; Colonna, M.; Celli, A.; Gandini, A. A Sustainable Route to a Terephthalic Acid Precursor. *ChemSusChem* **2016**, *9* (9), 942–945. https://doi.org/10.1002/cssc.201600166.
- (146)Kraus, G. A.; Riley, S.; Cordes, T. Aromatics from Pyrones: Para-Substituted Alkyl Benzoates from Alkenes, Coumalic Acid and Methyl Coumalate. *Green Chemistry* **2011**, *13* (10), 2734–2736. https://doi.org/10.1039/C1GC15650K.
- (147)Tachibana, Y.; Kimura, S.; Kasuya, K. Synthesis and Verification of Biobased Terephthalic Acid from Furfural. *Sci Rep* **2015**, *5* (1), 8249. https://doi.org/10.1038/srep08249.
- (148)Lin, Z.; Ierapetritou, M.; Nikolakis, V. Aromatics from Lignocellulosic Biomass: Economic Analysis of the Production of p-Xylene from 5-Hydroxymethylfurfural. *AIChE Journal* **2013**, *59* (6), 2079–2087. https://doi.org/10.1002/aic.13969.
- (149)Pacheco, J. J.; Labinger, J. A.; Sessions, A. L.; Davis, M. E. Route to Renewable PET: Reaction Pathways and Energetics of Diels–Alder and Dehydrative Aromatization Reactions Between Ethylene and Biomass-Derived Furans Catalyzed by Lewis Acid Molecular Sieves. *ACS Catal* **2015**, *5* (10), 5904–5913. https://doi.org/10.1021/acscatal.5b01309.
- (150)Williams, C. L.; Chang, C.-C.; Do, P.; Nikbin, N.; Caratzoulas, S.; Vlachos, D. G.; Lobo, R. F.; Fan, W.; Dauenhauer, P. J. Cycloaddition of Biomass-Derived Furans for Catalytic Production of Renewable p-Xylene. *ACS Catal* **2012**, *2* (6), 935–939. https://doi.org/10.1021/cs300011a.
- (151)Chang, C.-C.; Green, S. K.; Williams, C. L.; Dauenhauer, P. J.; Fan, W. Ultra-Selective Cycloaddition of Dimethylfuran for Renewable p-Xylene with H-BEA. *Green Chemistry* **2014**, *16* (2), 585–588. https://doi.org/10.1039/C3GC40740C.
- (152)Colonna, M.; Berti, C.; Fiorini, M.; Binassi, E.; Mazzacurati, M.; Vannini, M.; Karanam, S. Synthesis and Radiocarbon Evidence of Terephthalate Polyesters Completely Prepared from Renewable Resources. *Green Chemistry* 2011, *13* (9), 2543–2548. https://doi.org/10.1039/C1GC15400A.
- (153)He, Y.; Luo, Y.; Yang, M.; Zhang, Y.; Zhu, L.; Fan, M.; Li, Q. Selective Catalytic Synthesis of Bio-Based Terephthalic Acid from Lignocellulose Biomass. *Appl Catal A Gen* **2022**, *630*, 118440. https://doi.org/10.1016/j.apcata.2021.118440.

- (154)Avantium. *PEF bottles a sustainable packaging material*. https://www.avantium.com/wp-content/uploads/2022/02/20220221-PEF-bottles-%E2%80%93-a-sustainable-packaging-material-ISO-certified-LCA.pdf (accessed 2023-07-04).
- (155)Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon Dioxide Sorption and Transport in Amorphous Poly(Ethylene Furanoate). *Macromolecules* **2015**, *48* (7), 2184–2193. https://doi.org/10.1021/acs.macromol.5b00333.
- (156)Burgess, S. K.; Karvan, O.; Johnson, J. R.; Kriegel, R. M.; Koros, W. J. Oxygen Sorption and Transport in Amorphous Poly(Ethylene Furanoate). *Polymer(Guildf)* 2014, 55 (18), 4748–4756. https://doi.org/10.1016/j.polymer.2014.07.041.
- (157)Burgess, S. K.; Mikkilineni, D. S.; Yu, D. B.; Kim, D. J.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J. Water Sorption in Poly(Ethylene Furanoate) Compared to Poly(Ethylene Terephthalate). Part 2: Kinetic Sorption. *Polymer (Guildf)* **2014**, *55* (26), 6870–6882. https://doi.org/10.1016/j.polymer.2014.10.065.
- (158)Hatti-Kaul, R.; Nilsson, L. J.; Zhang, B.; Rehnberg, N.; Lundmark, S. Designing Biobased Recyclable Polymers for Plastics. *Trends Biotechnol* **2020**, *38* (1), 50– 67. https://doi.org/10.1016/j.tibtech.2019.04.011.
- (159)Valsange, N. G.; Garcia Gonzalez, M. N.; Warlin, N.; Mankar, S. V; Rehnberg, N.; Lundmark, S.; Zhang, B.; Jannasch, P. Biobased Aliphatic Polyesters from a Spirocyclic Dicarboxylate Monomer Derived from Levulinic Acid. *Green Chemistry* 2021, 23 (15), 5706–5723. https://doi.org/10.1039/D1GC00724F.
- (160)Pion, F.; Ducrot, P.-H.; Allais, F. Renewable Alternating Aliphatic–Aromatic Copolyesters Derived from Biobased Ferulic Acid, Diols, and Diacids: Sustainable Polymers with Tunable Thermal Properties. *Macromol Chem Phys* **2014**, *215* (5), 431–439. https://doi.org/10.1002/macp.201300702.
- (161)Nguyen, H. T. H.; Suda, E. R.; Bradic, E. M.; Hvozdovich, J. A.; Miller, S. A. Polyesters from Bio-Aromatics. In *Green Polymer Chemistry: Biobased Materials* and Biocatalysis; ACS Symposium Series; American Chemical Society, 2015; Vol. 1192, pp 401–409. https://doi.org/doi:10.1021/bk-2015-1192.ch024.
- (162)Mialon, L.; Pemba, A. G.; Miller, S. A. Biorenewable Polyethylene Terephthalate Mimics Derived from Lignin and Acetic Acid. *Green Chemistry* **2010**, *12* (10), 1704–1706. https://doi.org/10.1039/C0GC00150C.
- (163)Charbonneau, L. F.; Morris, N. J. Thermotropic Polyesters Derived from Ferulic Acid and a Process for Preparing the Polyesters. US4230817A, October 28, 1980.
- (164)Nguyen, H. T. H.; Reis, M. H.; Qi, P.; Miller, S. A. Polyethylene Ferulate (PEF) and Congeners: Polystyrene Mimics Derived from Biorenewable Aromatics. *Green Chemistry* **2015**, *17* (9), 4512–4517. https://doi.org/10.1039/C5GC01104C.
- (165)Nguyen, H. T. H.; Short, G. N.; Qi, P.; Miller, S. A. Copolymerization of Lactones and Bioaromatics via Concurrent Ring-Opening Polymerization/Polycondensation. *Green Chemistry* **2017**, *19* (8), 1877–1888. https://doi.org/10.1039/C6GC03238A.
- (166)Kaneko, T.; Thi, T. H.; Shi, D. J.; Akashi, M. Environmentally Degradable, High-Performance Thermoplastics from Phenolic Phytomonomers. *Nat Mater* **2006**, *5* (12), 966–970. https://doi.org/10.1038/nmat1778.

- (167)Bazin, A.; Duval, A.; Avérous, L.; Pollet, E. Synthesis of Bio-Based Photo-Cross-Linkable Polyesters Based on Caffeic Acid through Selective Lipase-Catalyzed Polymerization. *Macromolecules* **2022**, *55* (11), 4256–4267. https://doi.org/10.1021/acs.macromol.2c00499.
- (168)Dong, W.; Ren, J.; Lin, L.; Shi, D.; Ni, Z.; Chen, M. Novel Photocrosslinkable and Biodegradable Polyester from Bio-Renewable Resource. *Polym Degrad Stab* 2012, 97 (4), 578–583. https://doi.org/10.1016/j.polymdegradstab.2012.01.008.
- (169)Dong, W.; Li, H.; Chen, M.; Ni, Z.; Zhao, J.; Yang, H.; Gijsman, P. Biodegradable Bio-Based Polyesters with Controllable Photo-Crosslinkability, Thermal and Hydrolytic Stability. *Journal of Polymer Research* **2011**, *18* (6), 1239–1247. https://doi.org/10.1007/s10965-010-9526-x.
- (170)Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. Renewable
 (Semi)Aromatic Polyesters from Symmetrical Vanillin-Based Dimers. *Polym. Chem.* 2015, 6 (33), 6058–6066. https://doi.org/10.1039/C5PY00824G.
- (171)Zhang, S.; Cheng, Z.; Zeng, S.; Li, G.; Xiong, J.; Ding, L.; Gauthier, M. Synthesis and Characterization of Renewable Polyesters Based on Vanillic Acid. *J Appl Polym Sci* **2020**, *137* (39), 49189. https://doi.org/10.1002/app.49189.
- (172)Mialon, L.; Vanderhenst, R.; Pemba, A. G.; Miller, S. A. Polyalkylenehydroxybenzoates (PAHBs): Biorenewable Aromatic/Aliphatic Polyesters from Lignin. *Macromol Rapid Commun* **2011**, *32* (17), 1386–1392. https://doi.org/10.1002/marc.201100242.
- (173)Pang, C.; Zhang, J.; Zhang, Q.; Wu, G.; Wang, Y.; Ma, J. Novel Vanillic Acid-Based Poly(Ether–Ester)s: From Synthesis to Properties. *Polym Chem* **2015**, *6* (5), 797–804. https://doi.org/10.1039/C4PY01090F.
- (174)Recycling Magazine. *Billion investment in plastic recycling in Sweden*. https://www.recycling-magazine.com/2021/08/31/billion-investment-in-plastic-recycling-in-sweden/ (accessed 2023-07-05).
- (175)Swedish Plastic Recycling. *We are building Site Zero*. https://www.svenskplastatervinning.se/en/site-zero/ (accessed 2023-07-05).
- (176)Soong, Y.-H. V.; Sobkowicz, M. J.; Xie, D. Recent Advances in Biological Recycling of Polyethylene Terephthalate (PET) Plastic Wastes. *Bioengineering* **2022**, *9* (3), 98. https://doi.org/10.3390/bioengineering9030098.
- (177)Rahimi, A.; García, J. M. Chemical Recycling of Waste Plastics for New Materials Production. *Nat Rev Chem* **2017**, *1* (6), 0046. https://doi.org/10.1038/s41570-017-0046.
- (178)Dimonie, D.; Socoteanu, R.; Pop, S.; Fierascu, I.; Fierascu, R.; Petrea, C.; Zaharia, C.; Petrache, M. Overview on Mechanical Recycling by Chain Extension of POSTC-PET Bottles. In *Material Recycling*; Achilias, D. S., Ed.; IntechOpen: Rijeka, 2012; p Ch. 3. https://doi.org/10.5772/31841.
- (179)Eriksen, M. K.; Christiansen, J. D.; Daugaard, A. E.; Astrup, T. F. Closing the Loop for PET, PE and PP Waste from Households: Influence of Material Properties and Product Design for Plastic Recycling. *Waste Management* 2019, 96, 75–85. https://doi.org/10.1016/j.wasman.2019.07.005.

- (180)Abel, B. A.; Snyder, R. L.; Coates, G. W. Chemically Recyclable Thermoplastics from Reversible-Deactivation Polymerization of Cyclic Acetals. *Science (1979)* **2021**, *373* (6556), 783–789. https://doi.org/10.1126/science.abh0626.
- (181)Miandad, R.; Rehan, M.; Barakat, M. A.; Aburiazaiza, A. S.; Khan, H.; Ismail, I. M. I.; Dhavamani, J.; Gardy, J.; Hassanpour, A.; Nizami, A.-S. Catalytic Pyrolysis of Plastic Waste: Moving Toward Pyrolysis Based Biorefineries. *Front Energy Res* **2019**, *7*. https://doi.org/10.3389/fenrg.2019.00027.
- (182)Gebre, S. H.; Sendeku, M. G.; Bahri, M. Recent Trends in the Pyrolysis of Non-Degradable Waste Plastics. *ChemistryOpen* **2021**, *10* (12), 1202–1226. https://doi.org/10.1002/open.202100184.
- (183)Hamad, K.; Kaseem, M.; Deri, F. Recycling of Waste from Polymer Materials: An Overview of the Recent Works. *Polym Degrad Stab* **2013**, *98* (12), 2801–2812. https://doi.org/10.1016/j.polymdegradstab.2013.09.025.
- (184)Warlin, N.; Nilsson, E.; Guo, Z.; Mankar, S. V; Valsange, N. G.; Rehnberg, N.; Lundmark, S.; Jannasch, P.; Zhang, B. Synthesis and Melt-Spinning of Partly Bio-Based Thermoplastic Poly(Cycloacetal-Urethane)s toward Sustainable Textiles. *Polym Chem* **2021**, *12* (34), 4942–4953. https://doi.org/10.1039/D1PY00450F.
- (185)Manker, L. P.; Dick, G. R.; Demongeot, A.; Hedou, M. A.; Rayroud, C.; Rambert, T.; Jones, M. J.; Sulaeva, I.; Vieli, M.; Leterrier, Y.; Potthast, A.; Maréchal, F.; Michaud, V.; Klok, H.-A.; Luterbacher, J. S. Sustainable Polyesters via Direct Functionalization of Lignocellulosic Sugars. *Nat Chem* **2022**, *14* (9), 976–984. https://doi.org/10.1038/s41557-022-00974-5.
- (186)Vidal, F.; Williams, C. K. Chemically Recyclable Polyacetals to Deliver Useful Thermoplastics. *Chem* **2021**, 7 (11), 2857–2859. https://doi.org/10.1016/j.chempr.2021.10.013.
- (187)Sinha, V.; Patel, M. R.; Patel, J. V. PET Waste Management by Chemical Recycling: A Review. *J Polym Environ* **2010**, *18* (1), 8–25. https://doi.org/10.1007/s10924-008-0106-7.
- (188)Garcia, J. M.; Robertson, M. L. The Future of Plastics Recycling. *Science (1979)* **2017**, *358* (6365), 870–872. https://doi.org/10.1126/science.aaq0324.
- (189)Geyer, B.; Lorenz, G.; Kandelbauer, A. Recycling of Poly(Ethylene Terephthalate) – A Review Focusing on Chemical Methods. *Express Polym Lett* **2016**, *10* (7), 559–586. https://doi.org/10.3144/expresspolymlett.2016.53.
- (190)Kathalewar, M.; Dhopatkar, N.; Pacharane, B.; Sabnis, A.; Raut, P.; Bhave, V. Chemical Recycling of PET Using Neopentyl Glycol: Reaction Kinetics and Preparation of Polyurethane Coatings. *Prog Org Coat* **2013**, *76* (1), 147–156. https://doi.org/10.1016/j.porgcoat.2012.08.023.
- (191)Dębowski, M.; Iuliano, A.; Plichta, A.; Kowalczyk, S.; Florjańczyk, Z. Chemical Recycling of Polyesters. *Polimery* 2021, 64 (11–12), 764–776. https://doi.org/10.14314/polimery.2019.11.5.
- (192)Xu, G.; Wang, Q. Chemically Recyclable Polymer Materials: Polymerization and Depolymerization Cycles. *Green Chemistry* **2022**, *24* (6), 2321–2346. https://doi.org/10.1039/D1GC03901F.

- (193)Yoshida, S.; Hiraga, K.; Takehana, T.; Taniguchi, I.; Yamaji, H.; Maeda, Y.; Toyohara, K.; Miyamoto, K.; Kimura, Y.; Oda, K. A Bacterium That Degrades and Assimilates Poly(Ethylene Terephthalate). *Science* (1979) **2016**, 351 (6278), 1196–1199. https://doi.org/10.1126/science.aad6359.
- (194)Tang, K. H. D.; Lock, S. S. M.; Yap, P.-S.; Cheah, K. W.; Chan, Y. H.; Yiin, C. L.; Ku, A. Z. E.; Loy, A. C. M.; Chin, B. L. F.; Chai, Y. H. Immobilized Enzyme/Microorganism Complexes for Degradation of Microplastics: A Review of Recent Advances, Feasibility and Future Prospects. *Science of The Total Environment* 2022, 832, 154868. https://doi.org/10.1016/j.scitotenv.2022.154868.
- (195)Dominik, D.; Jennifer, C.; R, S. W. Plastics: Environmental and Biotechnological Perspectives on Microbial Degradation. *Appl Environ Microbiol* **2019**, *85* (19), e01095-19. https://doi.org/10.1128/AEM.01095-19.
- (196)Amobonye, A.; Bhagwat, P.; Singh, S.; Pillai, S. Plastic Biodegradation: Frontline Microbes and Their Enzymes. *Science of The Total Environment* **2021**, *759*, 143536. https://doi.org/10.1016/j.scitotenv.2020.143536.
- (197)Magnin, A.; Entzmann, L.; Pollet, E.; Avérous, L. Breakthrough in Polyurethane Bio-Recycling: An Efficient Laccase-Mediated System for the Degradation of Different Types of Polyurethanes. *Waste Management* 2021, *132*, 23–30. https://doi.org/10.1016/j.wasman.2021.07.011.
- (198)Torres-Gómez, H.; Lehmkuhl, K.; Schepmann, D.; Wünsch, B. Design, Synthesis and Receptor Affinity of Novel Conformationally Restricted σ Ligands Based on the [4.3.3]Propellane Scaffold. *Eur J Med Chem* **2013**, 70, 78–87. https://doi.org/10.1016/j.ejmech.2013.09.021.
- (199)Weber, R. W.; Cook, J. M. General Method for the Synthesis of [n.3.3]Propellanes, $n \ge 3$. Can J Chem **1978**, 56 (2), 189–192. https://doi.org/10.1139/v78-030.
- (200)Weiss, U.; Edwards, J. M. A One-Step Synthesis of Ketonic Compounds of the Pentalane, [3,3,3]- and [4,3,3]-Propellane Series. *Tetrahedron Lett* **1968**, *9* (47), 4885–4887. https://doi.org/10.1016/S0040-4039(00)72784-5.
- (201)Sainz, M. F.; Souto, J. A.; Regentova, D.; Johansson, M. K. G.; Timhagen, S. T.; Irvine, D. J.; Buijsen, P.; Koning, C. E.; Stockman, R. A.; Howdle, S. M. A Facile and Green Route to Terpene Derived Acrylate and Methacrylate Monomers and Simple Free Radical Polymerisation to Yield New Renewable Polymers and Coatings. *Polym Chem* **2016**, *7* (16), 2882–2887. https://doi.org/10.1039/C6PY00357E.
- (202)Ge, M.; Miao, J.-T.; Zhang, K.; Wu, Y.; Zheng, L.; Wu, L. Building Biobased, Degradable, Flexible Polymer Networks from Vanillin via Thiol–Ene "Click" Photopolymerization. *Polym Chem* **2021**, *12* (4), 564–571. https://doi.org/10.1039/D0PY01407A.
- (203)Wu, M. M. Acrylonitrile Polymers, Survey and Styrene-Acrylonitrile (SAN). *Kirk-Othmer Encyclopedia of Chemical Technology*. September 14, 2001. https://doi.org/10.1002/0471238961.1921182202011212.a01.pub2.

- (204)Quinn, D. J.; Haun, G. J.; Moura-Letts, G. Direct Synthesis of Nitriles from Aldehydes with Hydroxylamine-O-Sulfonic Acid in Acidic Water. *Tetrahedron Lett.* **2016**, *57* (34), 3844–3847. https://doi.org/10.1016/j.tetlet.2016.07.047.
- (205)Cowie, J. M. G.; Arrighi, V. Polymers: Chemistry and Physics of Modern Materials, 3rd Ed.; CRC Press., 2007.
- (206)Emerson, J. A.; Garabedian, N. T.; Burris, D. L.; Furst, E. M.; Epps, T. H. Exploiting Feedstock Diversity To Tune the Chemical and Tribological Properties of Lignin-Inspired Polymer Coatings. *ACS Sustain. Chem. Eng.* **2018**, *6* (5), 6856– 6866. https://doi.org/10.1021/acssuschemeng.8b00667.
- (207)Yang, M.; Mao, D.; Chen, S.; Zhang, H. Design, Synthesis and Thermotropic Self-Organization of Dendronized Polystyrenes with Different Length Alkyl Tails. *Polym. Chem.* **2016**, 7 (34), 5445–5455. https://doi.org/10.1039/C6PY01062H.
- (208) Marcus, Y. The Properties of Solvents; John Wiley & Sons, Ed.; 1999; Vol. 4.
- (209)Lide, D. R. Handbook of Chemistry and Physics, 89th ed.; CRC, Ed.; 2008.
- (210)Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 4th ed.; Grulke, E. A., Ed.; Wiley: New York, 2003.
- (211)Antoniotti, S.; Santhanam, L.; Ahuja, D.; Hogg, M. G.; Dordick, J. S. Structural Diversity of Peroxidase-Catalyzed Oxidation Products of o-Methoxyphenols. *Org Lett* **2004**, *6* (12), 1975–1978. https://doi.org/10.1021/ol0494481.
- (212)Nishimura, R. T.; Giammanco, C. H.; Vosburg, D. A. Green, Enzymatic Syntheses of Divanillin and Diapocynin for the Organic, Biochemistry, or Advanced General Chemistry Laboratory. *J Chem Educ* **2010**, *87* (5), 526–527. https://doi.org/10.1021/ed8001607.
- (213)Constantin, M.-A.; Conrad, J.; Beifuss, U. Laccase-Catalyzed Oxidative Phenolic Coupling of Vanillidene Derivatives. *Green Chemistry* **2012**, *14* (9), 2375–2379. https://doi.org/10.1039/C2GC35848D.
- (214)Chen, G.; Wu, L.; Fan, H.; Li, B. Highly Efficient Two-Step Synthesis of 2,5-Furandicarboxylic Acid from Fructose without 5-Hydroxymethylfurfural (HMF) Separation: In Situ Oxidation of HMF in Alkaline Aqueous H2O/DMSO Mixed Solvent under Mild Conditions. *Ind Eng Chem Res* **2018**, *57* (48), 16172–16181. https://doi.org/10.1021/acs.iecr.8b03589.
- (215)Zhu, J.; Cai, J.; Xie, W.; Chen, P.-H.; Gazzano, M.; Scandola, M.; Gross, R. A. Poly(Butylene 2,5-Furan Dicarboxylate), a Biobased Alternative to PBT: Synthesis, Physical Properties, and Crystal Structure. *Macromolecules* 2013, 46 (3), 796–804. https://doi.org/10.1021/ma3023298.
- (216)Poulopoulou, N.; Nikolaidis, G. N.; Ioannidis, R. O.; Efstathiadou, V. L.; Terzopoulou, Z.; Papageorgiou, D. G.; Kapnisti, M.; Papageorgiou, G. Z. Aromatic But Sustainable: Poly(Butylene 2,5-Furandicarboxylate) as a Crystallizing Thermoplastic in the Bioeconomy. *Ind Eng Chem Res* 2022, *61* (36), 13461–13473. https://doi.org/10.1021/acs.iecr.2c02069.
- (217)Kang, H.; Miao, X.; Li, J.; Li, D.; Fang, Q. Synthesis and Characterization of Biobased Thermoplastic Polyester Elastomers Containing Poly(Butylene 2,5-Furandicarboxylate). *RSC Adv* **2021**, *11* (25), 14932–14940. https://doi.org/10.1039/D1RA00066G.

(218)Infante Teixeira, L.; Landfester, K.; Thérien-Aubin, H. Selective Oxidation of Polysulfide Latexes to Produce Polysulfoxide and Polysulfone in a Waterborne Environment. *Macromolecules* **2021**, *54* (8), 3659–3667. https://doi.org/10.1021/acs.macromol.1c00382.