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Exploring different thermoplastics from lignocellulosic building blocks and monomers

Olivier Bonjour

DOCTORAL DISSERTATION

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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 of the polymers. Another possibility is to introduce polar functions to obtain better physical 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 alkanoyl chains were synthesized, and subsequently polymerized. The resulting polymers showed thermal properties depending on the length of the pendant alkanoyl 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

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« 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

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 20th 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 fossil-based 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 glass-transition 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 façon 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 ayant 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
Đ	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_n	Number average molecular weight
M_p	Molecular weight of the highest peak
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
*p*TSA	*p*-Toluene sulfonic acid
RM	Rhizomucor miehei
RT	Room temperature
SAN	Poly(styrene-*co*-acrylonitrile)
SEC	Size exclusion chromatography
T_d	Decomposition temperature at a maximum rate of decomposition
$T_\mathrm{d,95\%}$	Temperature at 5% mass loss (by TGA)
TFA	Trifluoroacetic acid
T_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 20th 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 recovery[8] 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 bio-polypropylene 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 ᴅ-glucose linked through *β*-(1→4) glycosidic bonds. Cellulose can be depolymerized by enzymatic and fermentation processes to afford ᴅ-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 cross-linked 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.

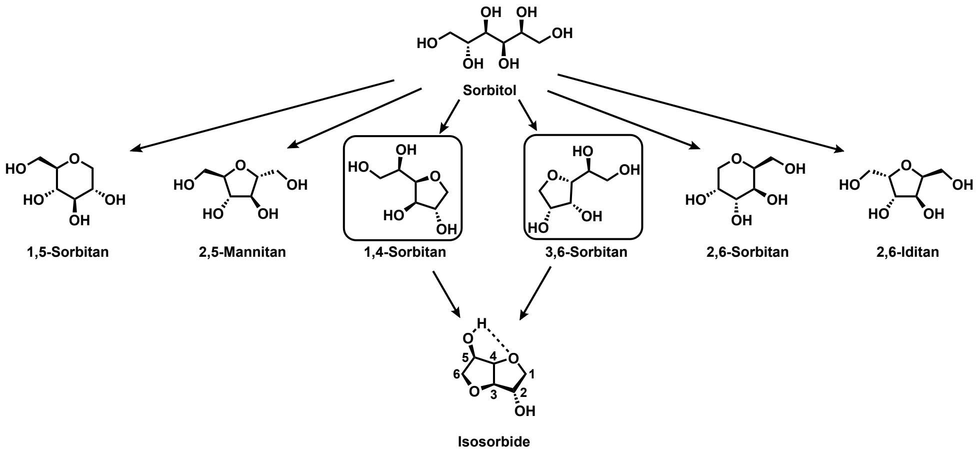
Despite the environmental advantages of shifting the plastic industry towards biobased plastics, the economic viability of such polymer materials is often an impediment. To facilitate the market introduction of biobased plastics, they should present additional advantages compared to conventional fossil-based 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 D-sorbitol, which is obtained from the hydrogenation of D-glucose. D-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 D-glucose to obtain D-sorbitol is well-established and cost-effective.[40,41] The subsequent dehydration of D-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.

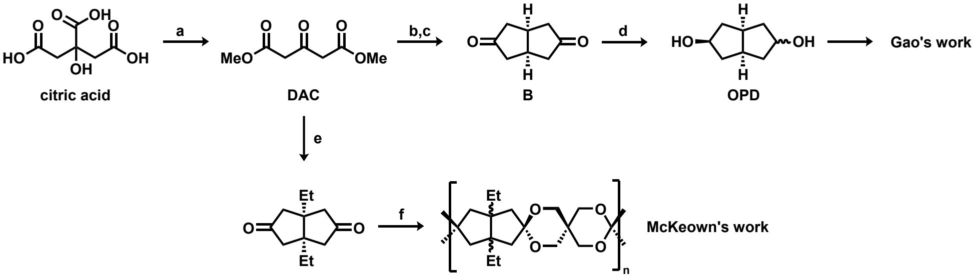


[a]Key: The first intramolecular dehydration yields six different intermediates, of which only 1,4-sorbitan and 3,6-sorbitan can yield isosorbide by a second intramolecular dehydration.

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_gs. 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 (7×10^5 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 *cis*-bicyclo[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 H_2SO_4, 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.

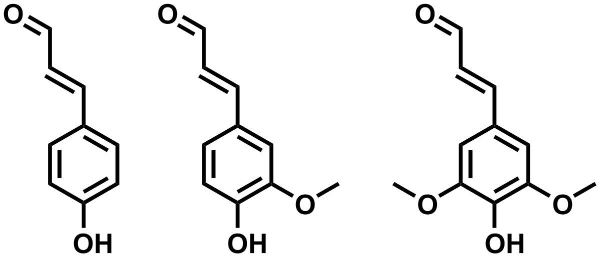


[a]Key: (a) (i) *p*TSA, DCM, 20 °C, 8h, (ii) MeOH, 3 °C, 6 h then 30 °C, 3 h, 95%; (b) NaOH, glyoxal, 65 °C, 1 h, 65%; (c) HCl (aq), AcOH, reflux, 3 h, 80%; (d) $NaBH_4$, MeOH, 0 °C, 12 h, 80%; (e) NaOH, hexane-3,4-dione, 65 °C, (f) pentaerythritol, *p*TSA, toluene, reflux, 48h.

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 polyesters[85] or epoxy resins.[82] Additionally, the aldehyde can be oxidized to yield vanillic acid, which can be employed for making polyesters[80] 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.

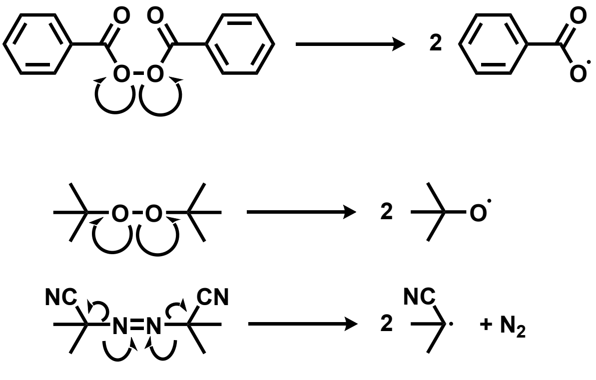
2.5 Polyacrylates and polymethacrylates

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 mechanical[95] 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 industry[100] 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 to conventional poly(meth)acrylates.[115]

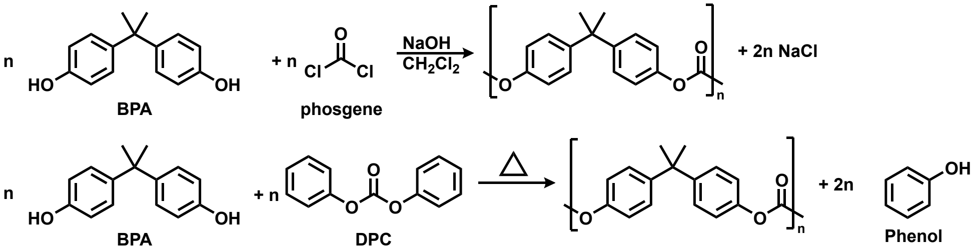
2.6 Polycarbonates

Polycarbonates are polyesters of carbonic acid, usually hard polymers with high T_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_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).



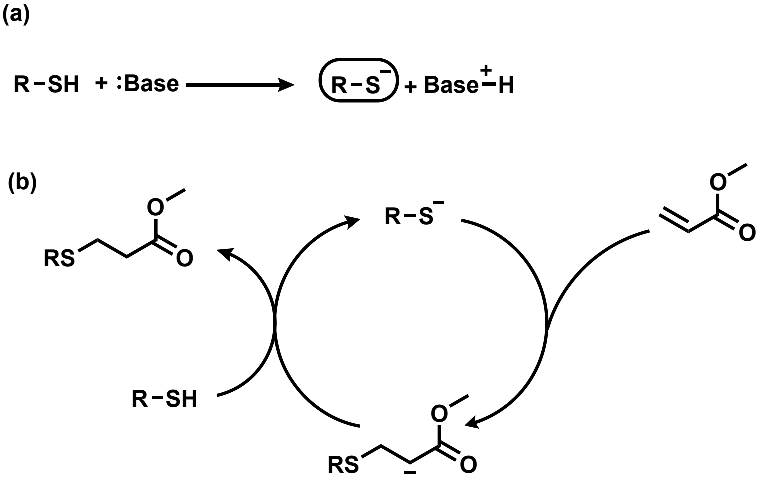
2.6.2 Biobased polycarbonates

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_gs.[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 Et_3N 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(*β*-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]

Scheme 5. Base-catalyzed mechanism of a thiol-Michael reaction involving methyl acrylate.



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(*β*-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(*β*-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.

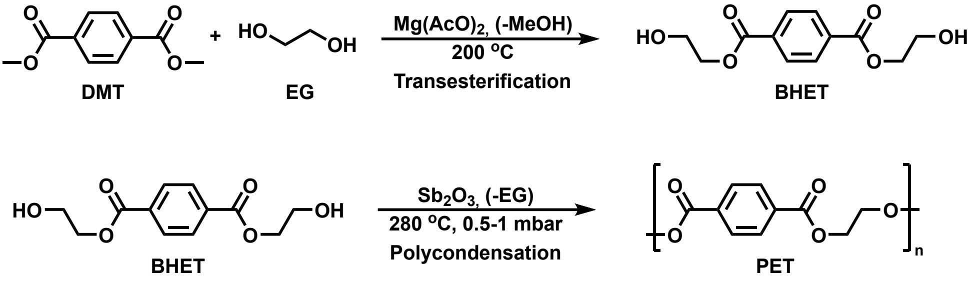
2.8 Polyesters

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 PlantBottle™ 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 Akestra™. 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 biodegradation[176] (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.

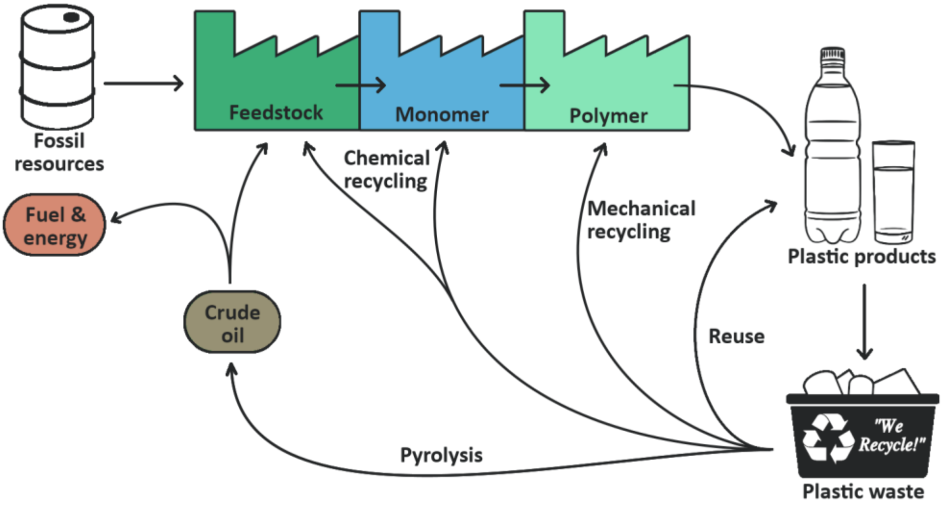
Chemical recycling is another method for recycling plastic waste. The polymers are chemically broken down to obtain the original monomers or other small molecules, which could be re-polymerized into the same or new polymers.[180] Different strategies are being developed for chemical recycling, namely 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 PET[176] 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(β-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 free-radical 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_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 Et_3N 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 Et_3N 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 *p*TSA 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 $FeSO_4$, 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 $NaHCO_3$ 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 $CHCl_3$, 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 $CHCl_3$. After cooling to 0 °C, 0.1 eq of the catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in $CHCl_3$ 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 $CHCl_3$ 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 ^{13}C 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 ^{13}C, with samples dissolved in chloroform-*d* or DMSO-d_6. 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 LTQ 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 $CHCl_3$, 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 $CHCl_3$ 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 × T6000M, General mixed Org. 300 ×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. T_g was determined from the second heating cycle, while melting and crystallization temperatures (T_m and T_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 Ø = 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

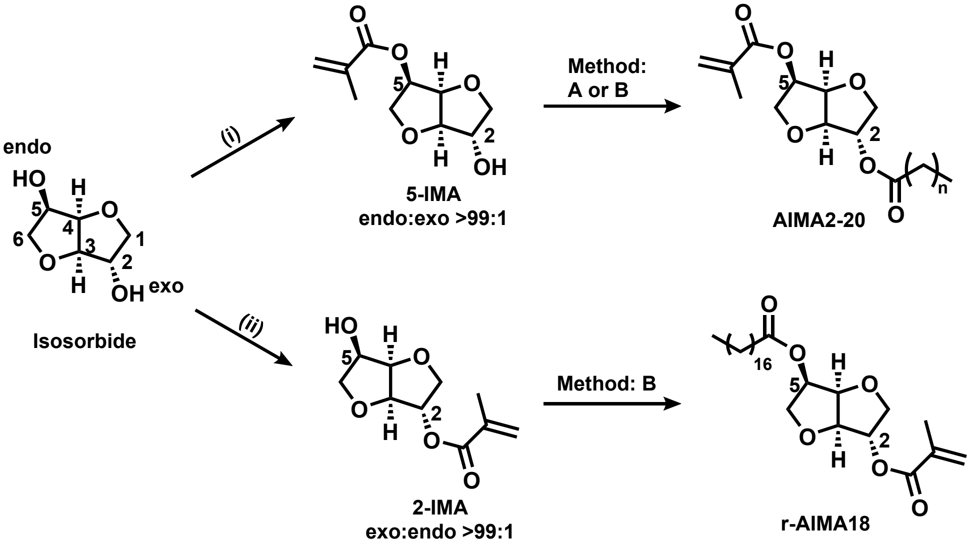
4.1 Isosorbide-based polymethacrylates with tunable phase transitions (Paper I)

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 **AIMA*x***, 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.



[a]Key: (i) vinyl methacrylate, RM, 2-Me-THF, 93%; (ii) three-step procedure reported previously;[93] Method A: corresponding vinyl alkylate, Novozym 435, ACN/PEth. Method B: corresponding acyl chloride, Et_3N, 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 $Đ$ 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.

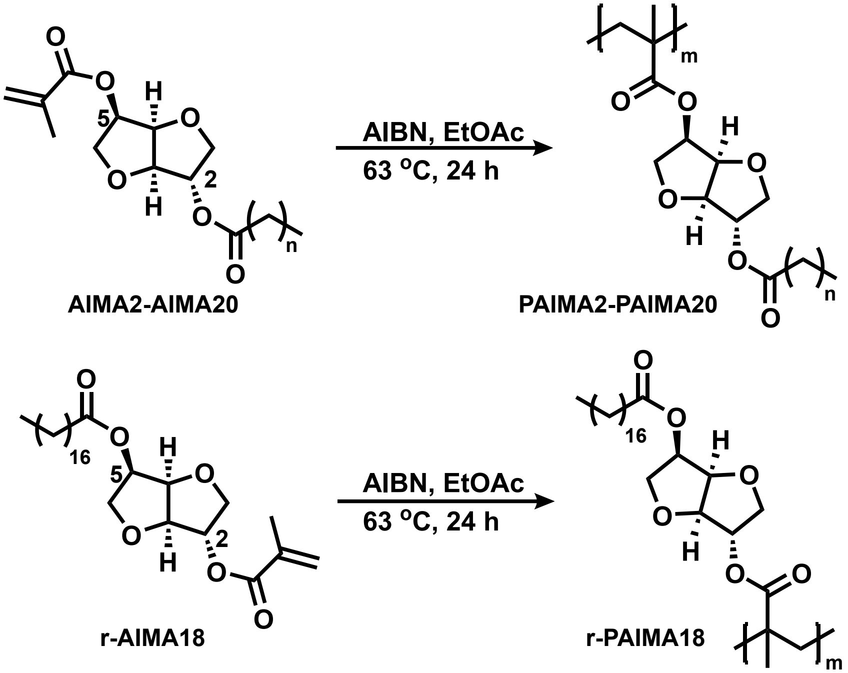


Table 1. Molecular and thermal data of the PAIMA*x* polymers.

Sample	M_n (kg mol^{-1})[b]	$Đ$[b]	$T_{d,95\%}$ (°C)[c]	T_g (°C)[d]	T_m (°C)[d]	T_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

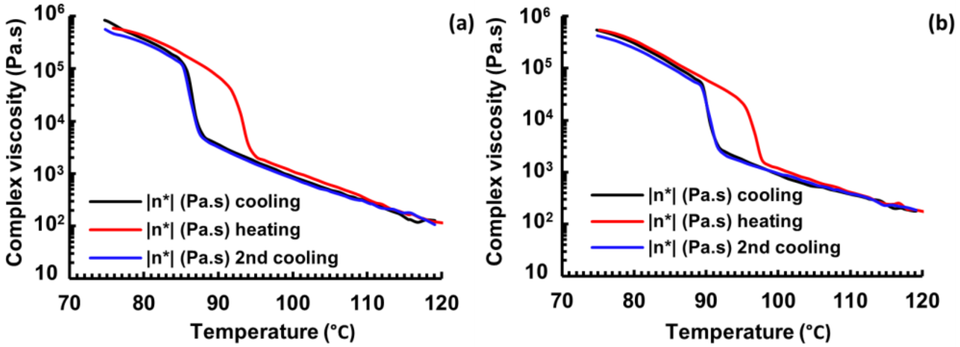
[a]Data taken from previously published work.[93] [b]Measured by SEC in THF using poly(ethylene oxide) standards. [c]Thermal decomposition temperature determined by TGA at 5% weight loss under N_2. [d]Determined by DSC during the second heating scan.

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_gs, 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 **PAIMA*x*** 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.

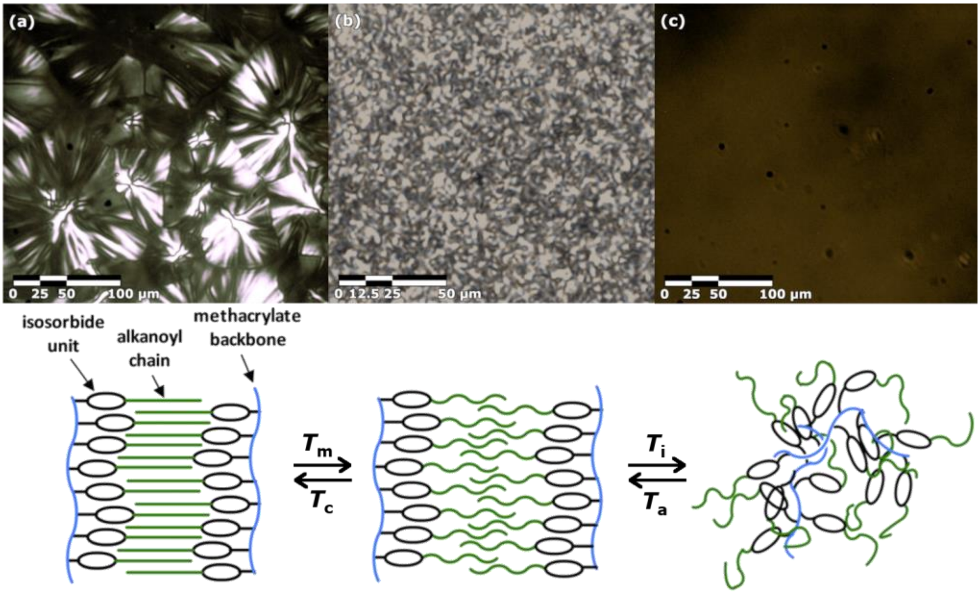
To further investigate the phase behavior, and to confirm the formation of a liquid crystalline mesophase, a rheological study was performed on **PAIMA16**, **PAIMA18**, and **PAIMA20**. Besides demonstrating melt processing without noticeable degradation, dynamic melt rheology showed a sharp and reversible 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 |η*| 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.



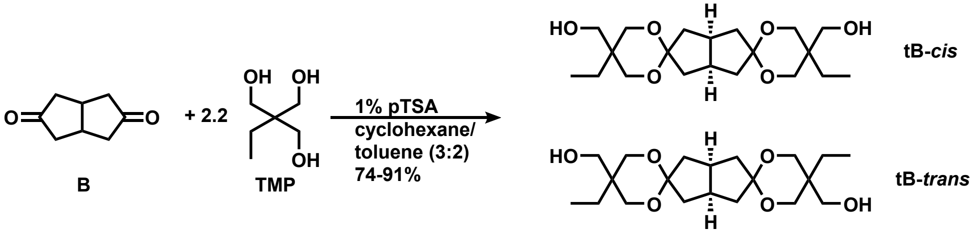
Key: (a) Semicrystalline spherulitic structure at 22.5 °C, (b) fine grainy structure indicating a liquid crystalline mesophase at 52.2 °C, (c) fully isotropic polymer melt at 113 °C showing an absence of texture. Note the scale difference on (b).

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 cyclohexane/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 ^{13}C 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 ^{13}C and ^{1}H NMR spectra. These C signals are separated by 2.3 ppm in the ^{13}C NMR spectrum and the H signals by 0.03 ppm in the ^{1}H 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.

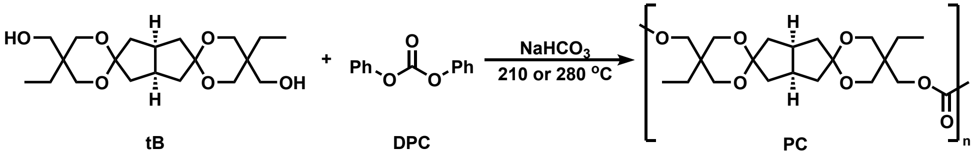


Key: The reaction leads to a mixture of **tB**-*cis* and **tB**-*trans*, isolated with yields of 74 and 91% by crystallization and chromatography, respectively.

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 $NaHCO_3$ 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.

Scheme 11. Synthesis of **PC**-*h* and **PC**-*l* by melt polycondensation of the diol **tB** and DPC.



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.

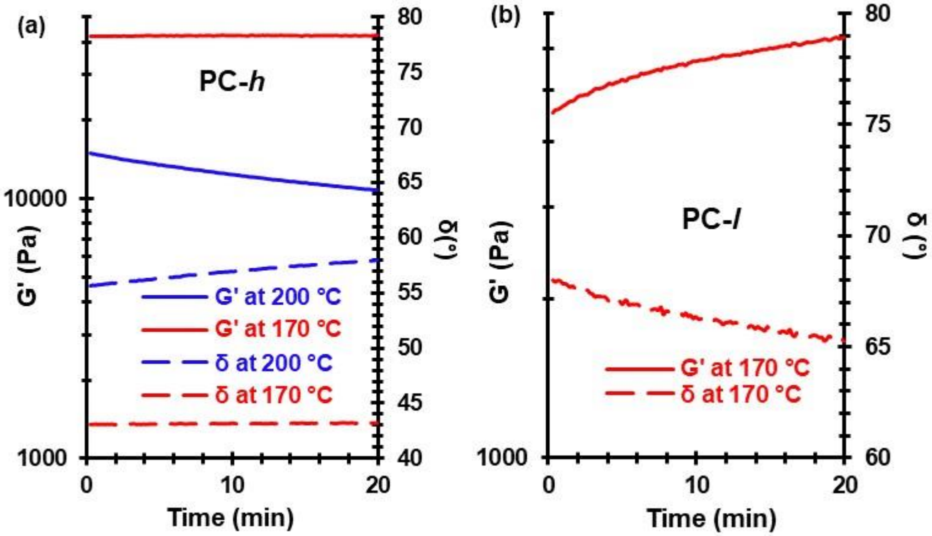
Table 2. Molecular and thermal properties of the thermoplastic PCs.

Sample	M_n[a] (kg mol^{-1})	$Đ$[a]	$T_{d,95\%}$[b] (°C)	T_g (DSC)[c] (°C)	T_g (DMA)[d] (°C)
PC-*l*	7.5	3.5	352	85	85
PC-*h*	27.7	3.4	360	100	99

[a] Measured by SEC in $CHCl_3$. [b] Thermal degradation temperature determined by TGA at 5% weight loss under N_2. [c] 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 $T_{d,95}$.

Figure 4. Dynamic melt rheology of the PCs.



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-*l*** at 170 °C (b) as measured by rheology at 1 Hz, 0.2% strain (note the different scales for G').

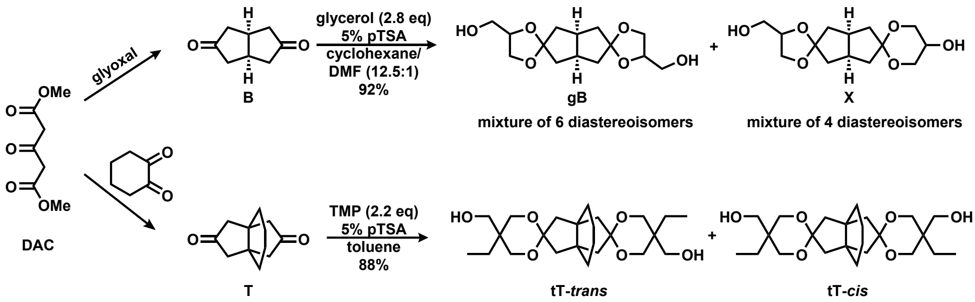
4.3 Citric acid-derived spirocyclic diols for chemically recyclable poly(*β*-thioether ester)s (Paper III)

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 *p*TSA 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 five-membered 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 C_2 symmetric, and **tT**-*cis* for the C_s symmetric (Scheme 12).

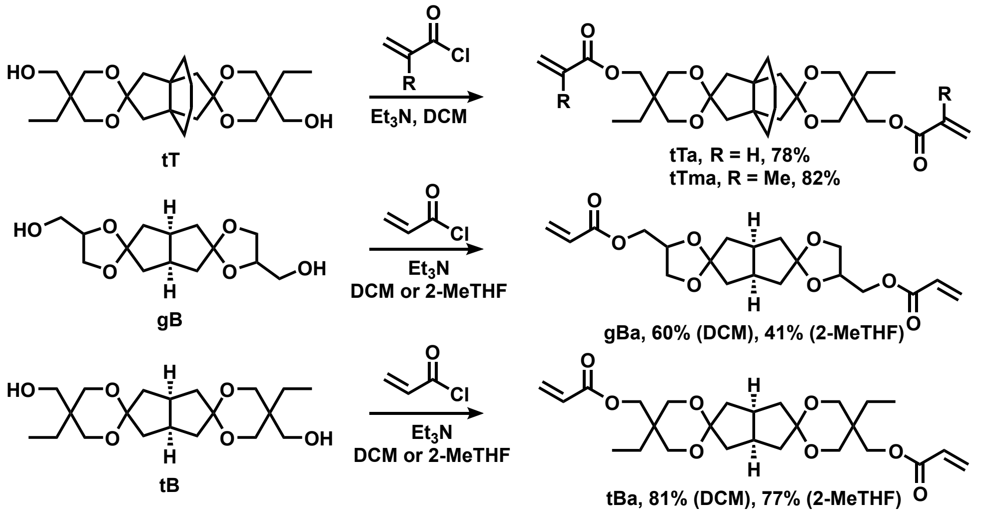
Scheme 12. Synthesis of the spirocyclic diols **tT** and **gB**.



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/Et_3N 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.

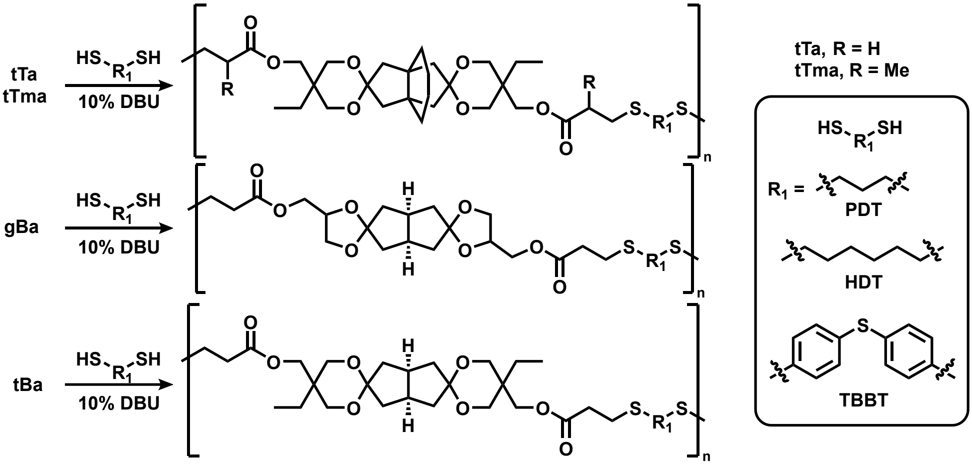
Scheme 13. Preparation of diacrylates and dimethacrylates from the spiro-diols.



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

For the thiol-Michael polymerizations, we selected three dithiols; the aliphatic 1,6-hexane 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 $CHCl_3$ 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)”.

Scheme 14. Thiol-Michael polymerizations involving PDT, HDT, and TBBT of the di(meth)acrylates **tTa**, **tTma**, **gBa**, and **tBa**.



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 six-membered 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. Polymerization and thermal data of polymers based on different spirocyclic structures.

Sample	M_n[a] (kg mol^{-1})	$Đ$[a]	$T_{d,95\%}$[b] (°C)	T_g (DSC)[c] (°C)	T_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

[a]Measured by SEC in $CHCl_3$. [b]Thermal degradation temperature determined by TGA at 5% weight loss under N_2. [c]T_g measured using DSC from the second heating scan. [d]T_g measured using DMA.

4.3.2.2 *Influence of the (meth)acrylate functionality*

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_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, T_g 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	M_n[a] (kg mol^{-1})	$Đ$[a]	$T_{d,95\%}$[b] (°C)	T_g (DSC)[c] (°C)	T_g (DMA)[d] (°C)
poly(tTa-PDT)	18	3.6	323	24	17
poly(tTma-PDT)	14	2.6	315	32	27

[a]Measured by SEC in $CHCl_3$. [b]Thermal degradation temperature determined by TGA at 5% weight loss under N_2. [c]T_g measured using DSC. [d]T_g measured using DMA.

4.3.2.3 *Influence of the dithiol structure*

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(tTa-

PDT), 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).

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

Sample	M_n^a (kg mol^{-1})	$Đ$^a	$T_{d,95\%}$^b (°C)	T_g (DSC)^c (°C)	T_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

[a]Measured by SEC in $CHCl_3$. [b]Thermal degradation temperature determined by TGA at 5% weight loss under N_2. [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

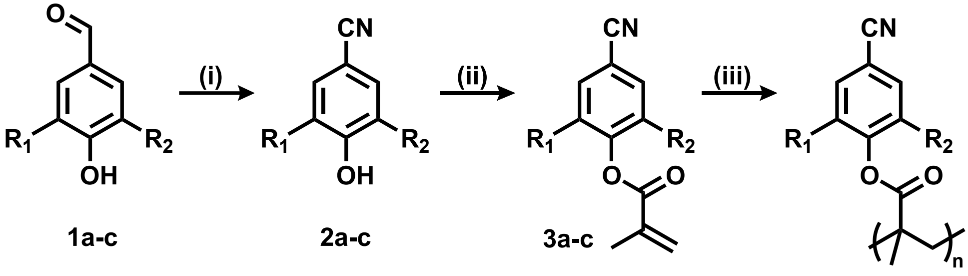
The poly(β-thioether ester)s were first immersed in aqueous solutions of pH = 0, 3, 8, and 14 at 37 °C for 14 days to assess their stability. No noticeable change in molecular weight was observed by SEC in $CHCl_3$. As acetal bonds were previously reported for thiol-ene thermosets to be degraded into 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, ^{1}H 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_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 T_g 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, 4-hydroxybenzonitrile **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.



$R_1 = R_2 = H$; 3a = **BM**
$R_1 = H$, $R_2 = OCH_3$; 3b = **VM**
$R_1 = R_2 = OCH_3$; 3c = **SM**

[a]Key: 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 ^{1}H 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.

Table 6. Polymerization and thermal data of the nitrile-containing polymethacrylates.

Sample	M_n (kg mol^{-1})	$Đ$	$T_{d,95\%}$[c] (°C)	T_g[d] (°C)
PBM	36[a]	2.1[a]	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

[a]Determined by SEC in THF. [b]Determined by SEC in DMF. [c]Determined by TGA at 5% weight loss under N_2. [d]Determined 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 (μ = 4.18 D) compared to the aldehyde group (μ = 2.77 D).[208,209] Regarding the copolymer series, the T_g values gradually increased with 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 Et_2O 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.

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

Sample	Et_2O $\delta = 15$ (m)	ACN $\delta = 24$ (p)	Toluene $\delta = 18$ (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	-	-	+

[a]The 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.

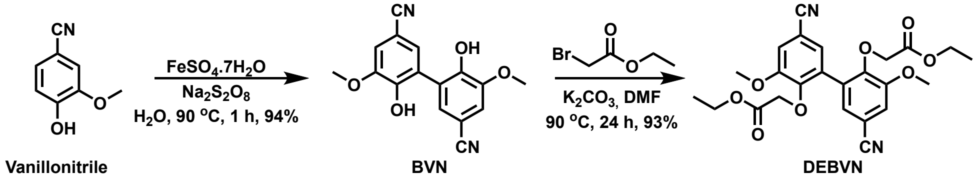
4.5 Vanillin-based nitrile-containing monomer for polyesters synthesis (Paper V)

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_g polymer materials. We decided to prepare bis-vanillonitrile by oxidative coupling of vanillonitrile. This reaction was efficiently performed in water by $FeSO_4$, with $Na_2S_2O_8$ 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.

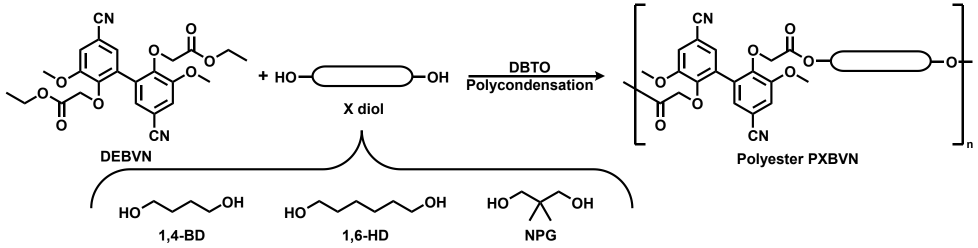


Table 8. Polymerizations and thermal data of the neat PBF, **PBBVN**, **PHBVN**, and **PNBVN** polyesters and the **PBBVNF-X** copolyesters.

Sample	Isolated yield[a] (%)	M_n[b] (kg/mol)	Đ[b]	$T_{d,95\%}$ (°C)[c]	T_g (°C)[d]	T_m (°C)[d]	ΔH_m (J/g)[d]	T_c (°C)[e]
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	-	-	-

[a]Determined gravimetrically. [b]Determined by SEC in THF. [b]Determined by SEC in DMF. [c]Determined by TGA at 5% weight loss under N_2. [d]Determined by DSC from the second heating scan. [e]Determined 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. ^{1}H 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 $T_g > 100$ °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_g value, rendering it suitable for hot-fill applications. As predicted, PBF was semi-crystalline with a melting temperature of $T_m = 171$ °C and $T_g = 40$ °C, consistent with existing literature reports.[215–217] The semi-crystallinity 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_g of PBF can be finely tuned and enhanced by strategically incorporating predetermined quantities of the biobased bis-vanillonitrile monomer. Importantly, all homopolyesters and copolyesters exhibited T_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_2 atmosphere at 10 °C min^{-1}.

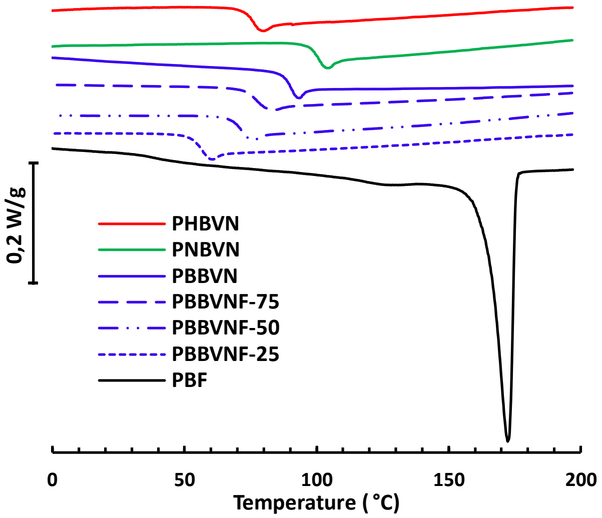
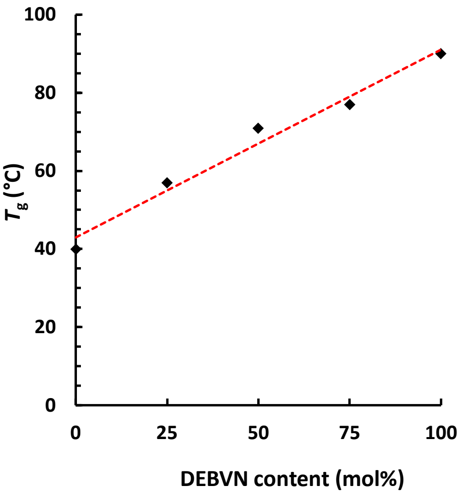


Figure 6. T_g as a function of the incorporated **DEBVN** monomer in the copolyester series. (Linear trend plotted in red to highlight the linear behavior).



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 high-performance polymers.

In Paper IV, we prepared nitrile-containing methacrylates by nitrilation of lignin-inspired 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 high-performance 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 resource-efficient 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.

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