

Exploring bio-based monomers for UV-curable polymer networks

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To my parents

Abstract

Increased environmental awareness and concern has led to a high demand for sustainable, bio-based materials. Consequently, there is a need for research and development of new bio-based polymeric materials that can be synthesized via routes eliminating excessively toxic reactants and by-products. The work presented in this thesis has focused on the utilization of catalysis, mainly enzymatic, and photopolymerization in order to create efficient synthesis of polymeric networks from bio-based monomers.

Polyesters from bio-based monomers have been polymerized in bulk and thereafter crosslinked by UV initiation to yield polymer networks with tunable properties. The synthesis was also studied more in detail by varying the different types of catalysts and comparing their effect on the polymer products. Polyesters are a promising class of polymers that can be made from bio-based resources due to the wide range of available bio-based carboxylic acids and alcohols that can be combined to yield many polymers with different properties. However, the synthesis of polyesters is rather time-consuming in order to reach high conversions.

As a more efficient alternative, short chain esters monomers and oligomers that have vinyl ether (VE) functionalities were developed. These VE-esters can be synthesized partly from bio-based resources, such as acids, fatty acids and diols, and their synthesis is efficient with enzymatic catalysis. The VE functionality provides a reactive group which can be polymerized rapidly with cationic polymerization. In general, the vinyl ether-esters can be synthesized in less than one hour and crosslinked within a few minutes, which is significantly faster than traditional polyester-synthesis and crosslinking. The enzymatic synthesis of vinyl ether esters also provided a method for developing monomers with orthogonal functionality which was explored by developing functionalizable materials with a variety of macromolecular architectures.

Sammanfattning

Ökad kunskap och miljömedvetenhet har lett till en hög efterfrågan för hållbara, biobaserade material. Följaktligen finns det ett stort behov av forskning och utveckling av nya bio-baserade polymermaterial som kan syntetiseras via hållbara processer som exkluderar giftiga reaktanter och biprodukter. Arbetet som presenteras i denna avhandling har fokuserat på användningen av katalysatorer, främst enzymatisk katalys med *Candida antarctica* Lipase B, och fotopolymerisation för att skapa effektiva synteser av polymera nätverk från bio-baserade monomerer.

Polyestrar från bio-baserade monomerer har polymeriserats och därefter tvärbundits genom UV-initiering för att bilda nätverk med skräddarsydda mekaniska egenskaper. Syntesen studerades också mer i detalj genom att variera de olika formerna av katalysatorer och jämföra deras effekt på polymerprodukterna. Polyestrar är en mycket lovande klass av polymerer som kan tillverkas av bio-baserade resurser på grund av det stora utbudet av bio-baserade karboxylsyror och alkoholer som kan kombineras för att ge många polymerer med olika egenskaper. Syntesen av polyestrar är dock tidskrävande, framförallt då polymerisationen skall nå hög omsättning.

Intresset för att utveckla en effektivare syntes resulterade i utvecklingen av vinyleter-estrar (VE-estrar). VE-estrar kan syntetiseras från delvis biobaserade resurser, såsom; syror, fettsyror och dioler, och deras syntes är mycket snabb med enzymatisk katalys på grund av deras låga molekylvikter. Vidare ger vinyleterfunktionaliteten en reaktiv grupp som kan polymeriseras snabbt med katjonpolymerisation. En stor fördel är även att VE har relativt låg toxicitet jämfört med exempelvis akrylater och metakrylater. VE-estrarna kan syntetiseras på mindre än en timme och tvärbindas inom några få minuter vilket är betydligt snabbare än traditionell polyestersyntes och tvärbindning. Den enzymatiska syntesen av VE-estrar möjliggjorde även utvecklingen av monomerer med ortogonal funktionalitet vilka kunde användas i polymera nätverk som var funktionaliserbara.

List of papers

- I. Biobased UV-curable coatings based on itaconic acid**
Brännström, S., Malmström, E. and Johansson, M., *Journal of Coatings Technology and Research*, (2017), 14, 851-861

- II. Itaconate based polyesters: Selectivity and performance of esterification catalysts**
Brännström, S*, Finnveden, M*, Johansson, M., Martinelle, M. and Malmström, E., *European Polymer Journal*, (2018), 103, 370-377

- III. Novel sustainable synthesis of vinyl ether ester building blocks, directly from carboxylic acids and the corresponding hydroxyl vinyl ether, and their photopolymerization**
Finnveden, M., Brännström, S., Johansson, M., Malmström, E. and Martinelle, M., *RSC Advances*, (2018), 8, 24716–24723

- IV. Tailoring thermo-mechanical properties of cationically UV-cured systems by a rational design of vinyl ether ester oligomers using enzyme catalysis**
Brännström, S., Finnveden, M., Razza, N., Martinelle, M., Malmström, E., Sangermano, M. and Johansson, M., *Macromolecular chemistry and physics*, (2018), 1800335

- V. Enzymatically synthesized vinyl ether-disulfide monomer enabling an orthogonal combination of free radical and cationic chemistry toward sustainable functional networks**
Brännström, S., Malmström, E., and Johansson, M., *Biomacromolecules*, (2019), 1308-1316

*The authors contributed equally to the work

Author contributions

The appended papers are collaborations with my co-authors, below my contributions are detailed for each individual paper:

- I. All the experimental work, analysis and preparation of the manuscript.
- II. Titanium-catalyzed synthesis of the polyester, the analysis of the polymers, crosslinking and material characterization as well as writing a major part of the manuscript.
- III. Polymerization of the monomers and characterization of the polymers as well as writing the polymer-part in the manuscript.
- IV. All the experimental work, characterization and analysis as well as writing a major part of the manuscript.
- V. All of the experimental work, analyses and manuscript preparation.

Abbreviations

Asp	Aspartic acid
ATR-FTIR	Attenuated total reflectance-Fourier transfer infrared spectroscopy
BD	1,4-Butanediol
BVEMUA	Butanediol vinyl ether mercaptoundecenoic acid
BVEUA	Butanediol vinyl ether undecenoic acid
BDVE	1,4-Butanediol mono vinyl ether
^{13}C	Carbon
CalB	<i>Candida antarctica</i> Lipase B
CDCl_3	Deuterated Chloroform
CyVE	1,4-Cyclohexanedimethanol mono vinyl ether
\bar{D}	Dispersity (M_w/M_n)
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMA	Dynamic mechanical analysis
DMI	Dimethyl itaconate
DMS	Dimethyl succinate
E'	Storage modulus
E''	Loss modulus
^1H	Proton
H_2SO_4	Sulfuric acid
His	Histidine
HDVE	1,6-Hexanediol mono vinyl ether
HVELA	Hexanediolvinyl ether lipoic acid
HVEMUA	Hexanediol vinyl ether mercaptoundecenoic acid
HVEUA	Hexanediol vinyl ether undecenoic acid

IA	Itaconic acid
LA	Lipoic acid
M_n	Number average molecular weight
MUA	Mercaptoundecenoic acid
M_w	Weight average molecular weight
NMR	Nuclear magnetic resonance
<i>p</i> TSA	<i>p</i> -Toluenesulfonic acid
RT-FTIR	Real-time Fourier transfer infrared spectroscopy
SA	Succinic acid
Ser	Serine
SEC	Size exclusion chromatography
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis
TBD	7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
Thr	Threonine
THF	Tetrahydrofuran
Ti(OBu) ₄	Titanium(IV) butoxide
UA	10-Undecenoic acid
UV	Ultraviolet
VE	Vinyl ether

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Aim of study

The development of new sustainable polymeric materials has gained increased attention due to environmental concerns regarding the depletion of natural oil reserves, as well as emission of greenhouse gases and toxic waste that are generated from various industrial processes. In this aspect, developing bio-based monomers that can be polymerized and processed with sustainable procedures is important in order to reach the future sustainability goals and overcome the challenges that are posed on today's society. The purpose of this work has been to demonstrate the possibility to form new polymer networks from bio-based monomers through efficient polymerization and curing processes that have low environmental impact. The main objective was to develop different binder resins utilizing benign synthesis, such as enzyme catalysis, followed by photo-curing to achieve crosslinked polymer networks. It was also of interest to demonstrate that the mechanical properties of the final materials can easily be tuned by combining different monomers during the synthesis.

1. Introduction

1.1 United Nations sustainable development goals

The United Nations (UN) has formulated an agreement on 16 sustainable development goals that should be reached by 2030.¹ Development of bio-based materials and decreasing the use of toxic chemicals can be related to many of these goals; good health and wellbeing (Goal 3), responsible consumption and production (Goal 12), climate action (Goal 13), protection of life on land (Goal 15) and life below water (Goal 14) are some examples. Fossil fuel-derived materials contribute to an increasing amount of greenhouse gases upon combustion and impact the climate. Plant-based materials on the other hand will have a closed carbon cycle as they take up CO₂ when grown which is later released when the end products are burned. Furthermore, oil-prices fluctuate and will continue to do so as fossil reserves are depleted, therefore replacing crude oil with bio-based resources may therefore also have a positive impact on economic growth (Goal 8).

1.2 The twelve principles of green chemistry

The twelve principles of green chemistry were published as a guideline to practice safer and more sustainable chemistry.² These principles address ways to minimize the negative impact of chemicals on the environment and health. With increasing concerns over use of plastics and toxicity of chemicals, it is important to consider these principles when designing new materials. In this thesis, the principles of green chemistry have been considered when the materials were developed. The twelve principles of green chemistry are:

1. Prevent waste
2. Atom economy
3. Less hazardous synthesis
4. Design benign chemicals
5. Benign solvents and auxiliaries
6. Design for energy efficiency
7. Use of renewable feedstocks
8. Reduce derivatives

9. Catalysis (vs. stoichiometric)
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Inherently benign chemistry for accident prevention

1.3 Monomers from renewable resources

Fossil fuel-based resources have dominated raw materials for the production of polymers and plastics since the advent of polymer science in the first half of the 20th century. However, due to increasing awareness of the negative impact associated with the fossil-based materials, the interest for bio-based materials continues to grow.³⁻¹⁰ A further aspect of bio-based monomers is that they offer a wide variety of complex compounds with significant potential for new functional materials.^{6, 11} For example, the naturally occurring ring structures of glucose, cyclodextrin, has been used to make self-healing materials due to their abilities to form inclusion complexes with hydrophobic compounds.¹²⁻¹⁴ Another example is the use of chemical motifs inspired by those in mussel proteins to form materials with good adhesive properties.¹⁵ However, an important aspect to consider is to also combine the use of bio-based raw materials with synthetic procedures that are sustainable.

Another issue is the fluctuating prices of the fossil resources, and that the industry associated with their transformation to commodity chemicals will be severely affected by the predicted depletion.¹⁶ Development of systems that are capable of converting, for example, plant-derived resources into higher value products is a promising solution, but it should not compete with food or feed production as this will cause a negative impact on the social sustainability. With this in mind, there are alternative strategies such as: converting food waste to monomer feedstocks through bio-refineries, and using parts from trees such as the bark, which is normally only combusted, to extract useful compounds.^{17, 18}

1.4 Renewable carboxylic acids and alcohols

Many carboxylic acids and alcohols are found in nature or can be produced from renewable resources through fermentation processes, amongst others.¹⁷ In Figure 1 some examples of carboxylic acids and alcohols that can be derived from biomass are presented. These can be combined to form polyesters with different macromolecular structures in order to fine-tune the

material properties. Itaconic acid (IA) is an unsaturated dicarboxylic acid that can be produced from bio-based resources using fermentation of carbohydrates by the fungi *Aspergillus terreus*.^{17, 19} This monomer is a dicarboxylic acid that contains an unsaturation which makes it suitable as a monomer for polyesters in applications such as coatings, where it is desirable to have a functional group that can be crosslinked after pre-polymerization.²⁰⁻²⁶

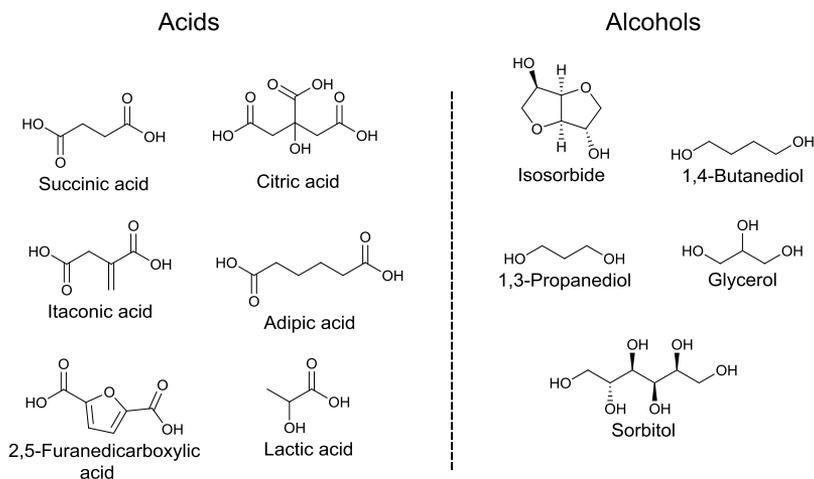


Figure 1. Examples of carboxylic acids and diols/polyols that can be produced from bio-based resources.

Traditionally, maleic acid is used to provide the unsaturation in polyesters. However, this double bond is not able to radically homopolymerize, therefore the addition of another monomer, such as styrene, is needed in the crosslinking step.²⁷ The 1,1-disubstituted unsaturation in IA is more homopolymerizable compared to the double bond in maleate and does not require addition of reactive diluents. Avoiding the use of styrene or other comonomers would yield crosslinked polyesters with significantly improved bio-based content and lower the use of toxic compounds in the production process. There are several recent studies on polymerizing IA with different diols to obtain renewable, unsaturated polyesters for various applications, as reviewed by Robert and Friebl.¹⁹

Succinic acid (SA), is another dicarboxylic acid that can be produced from bio-based resources. Succinic acid is an intermediate in the citric acid cycle and one of the end products in the anaerobic metabolism. Hydrogenation of

succinic acid is also a route to make renewable 1,4-butanediol (BD).²⁸ Other bio-based monomers include furandicarboxylic acid and isosorbide, which can be an alternative to the traditional aromatic compounds that are used today to provide rigidity.^{21, 29, 30}

1.5 Vegetable oils

Vegetable oils are amongst the most accessible and versatile renewable raw materials available, making them attractive for use in polymers and polymeric networks.^{31, 32} Not only are they bio-based, but they may also provide new properties and functionalities that could be used in new types of materials.³²⁻³⁷ Some examples are: soybean oil, castor oil and sunflower oil.^{31, 38} A wide range of compounds can be derived from these oils such as acrylated epoxidized soybean oil, epoxidized soy bean oil, undecenoic acid (UA), and mercapto-undecenoic acid (MUA). Lipoic acid (LA) is another interesting compound which is found naturally in animals. Though it is not available in its free form, it can be synthesized from caprylic acid which is present in for example coconut oil and butter.³⁹ LA is normally bound to enzymes where it functions as a co-factor.⁴⁰ Some examples of fatty acids or compounds that can be derived from bio-based fatty acids can be found in Figure 2.

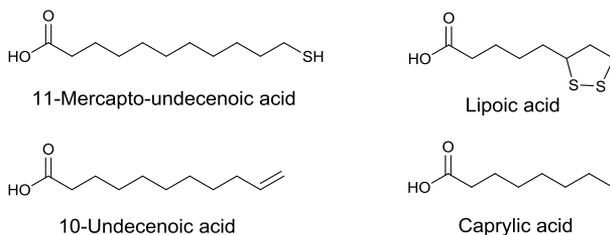


Figure 2. Examples of fatty acids that are found in nature or compounds that can be derived from bio-based fatty acids.

1.6 Polymers

When monomers are covalently linked into long chains these form macromolecules which are called polymers. These chains can be assembled into many different molecular topologies, such as linear, branched or hyper-branched (Figure 3). If the polymer consists of only one type of monomer, it is called a homopolymer and if it is composed of two or more types of monomers it is called a copolymer. Polymers are often associated with

plastics, but in fact, they appear all around us. DNA, proteins, cellulose and hemicelluloses in wood, silk and wool are all examples of natural polymers.

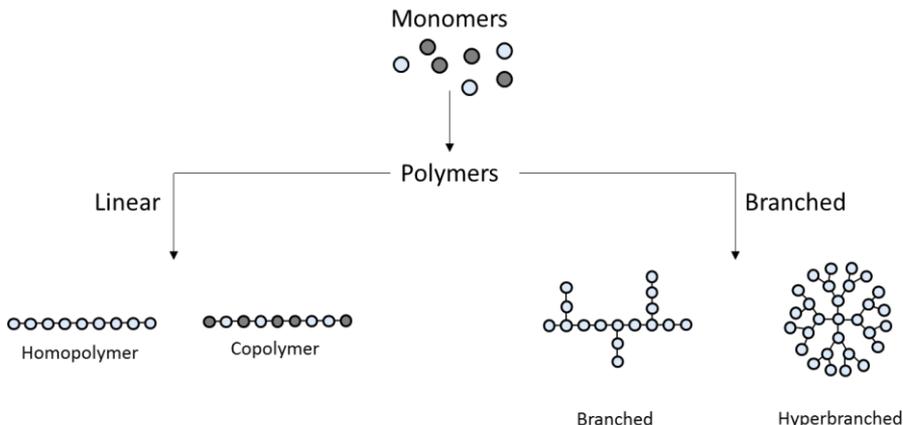


Figure 3. Different kinds of polymers formed from monomers.

1.7 Polymeric networks

Thermoset polymers are polymers, oligomers or multifunctional monomers that have been crosslinked through a process that covalently binds the polymer chains to each other to form an irreversible network (Figure 4).⁴¹⁻⁴³ Polymer networks can also be made to have reversible covalent bonds. Some examples of reversible networks are those containing disulfide-bonds or Diels-alder based systems.^{44, 45}



Figure 4. Schematic structure of polymer networks. In reality these are 3D-structures and look very different, but in principle polymer networks are polymer chains connected together by crosslinks, either covalent or physical.

When crosslinking polymers, it is necessary that these have two or more functional groups that are able to chemically react with each other or with an external crosslinker. Through crosslinking, the resulting materials will typically have an increased modulus above the glass transition temperature (T_g) compared to the pre-polymer, and the T_g will also increase with

increasing crosslinking density.⁴⁶ T_g , a point where large segments of the chains start moving, is an important property to consider when designing materials for different applications since it defines their operating temperature range.^{47, 48} Depending on the crosslinking density, the resulting materials can have different properties. Lower amount of crosslinks will typically result in a more flexible material while a higher number of crosslinks would yield a material that is more rigid. Commonly the mechanical properties are studied by measuring the displacement when a certain stress is applied. The storage modulus is a measure of elastic response of a material and above the T_g it will reach a plateau for a crosslinked material. The storage modulus at this plateau region can be related to the crosslinking density according to:

$$M_c = \frac{3\rho RT}{E'}$$

where M_c is the molecular weight between crosslinks, ρ is the density, R is the ideal gas constant, T is the temperature and E' is the storage modulus in the plateau region.

1.8 Sustainable synthesis of polymeric materials

Enzyme catalysis in monomer and polymer synthesis

Commonly, polyester synthesis is performed at temperatures above 200 °C, and thus has a relatively high energy demand. Moreover, the production of unsaturated polyesters using high temperatures is associated with some disadvantages: one example is premature thermally initiated radical crosslinking, leading to gelation before the polycondensation has reached sufficient conversion. This is often overcome by the addition of radical inhibitors such as phenolic compounds.⁴⁹ Both organometallic and acid catalysts are commonly used in polycondensation reactions (Figure 5). Base catalysts such as 1,8-diazabicycloundec-7-ene (DBU) and 1,5,7-triazabicyclodec-5-ene (TBD) have also been used as catalysts in ester synthesis, their structures along with some other common catalysts can be seen in Figure 5.⁵⁰ In general, organometallic catalysts have higher rates of reactions, but often require higher temperatures to be active. Thus, in regard to the energy demand, organometallic catalysis can to some extent be associated with undesirable environmental impact.⁵¹ Additionally, residues of the metal catalysts are difficult to separate from the final material and these residual metals may be toxic, thus limiting their use in certain applications.⁵²

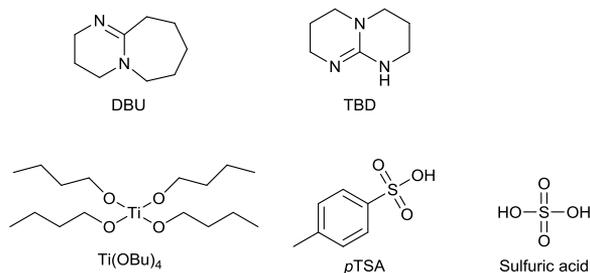


Figure 5. Some catalyst that are commonly used for esterification.

The synthesis of different kinds of esters often requires other reagents such as *N,N'*-dicyclohexylcarbodiimide (DCC), 1,1'-carbonyldiimidazole (CDI), 4-dimethylaminopyridine (DMAP) and pyridine to ensure high yield,⁵³ in particular for the synthesis of products where the structure needs to be flawless such as for dendrimers. These synthetic strategies are efficient and result in high conversions, but when the material cost has to be low and the use of toxic compounds needs to be limited it is not a viable synthetic route. Moreover, these kinds of synthetic strategies often require several purification steps that will result in increased production cost and thus, are no longer profitable for large scale chemical processes.

The use of enzymes as alternatives to traditional catalysts for polyester synthesis has grown due to the advantages they offer over traditional systems. Enzymes are selective and yield no or minimal by-products since they work at mild reaction conditions.⁵⁴⁻⁵⁷ These benefits enable reactions that traditional catalysts cannot perform in one step. For example, chemical transformations can be performed in the presence of groups with high reactivity without the need for protection and deprotection chemistry.⁵⁸ Another advantage of enzyme catalysis is that the radical scavengers can be avoided since the reaction can be performed at low temperatures. Since enzymes can be immobilized, this also means that they can be removed and recycled at the end of the reaction.^{52, 59-64} Ester and polyester synthesis with enzyme catalysis, most commonly by *Candida antarctica* lipase B (CalB), has been proven to be effective for a diverse range of monomers.⁶⁵⁻⁷¹ The active site in CalB contains three amino acids that make up the catalytic triad: aspartic acid, histidine and serine.^{72, 73} The enzyme mechanism for acylation/deacylation can be seen in in Figure 6.

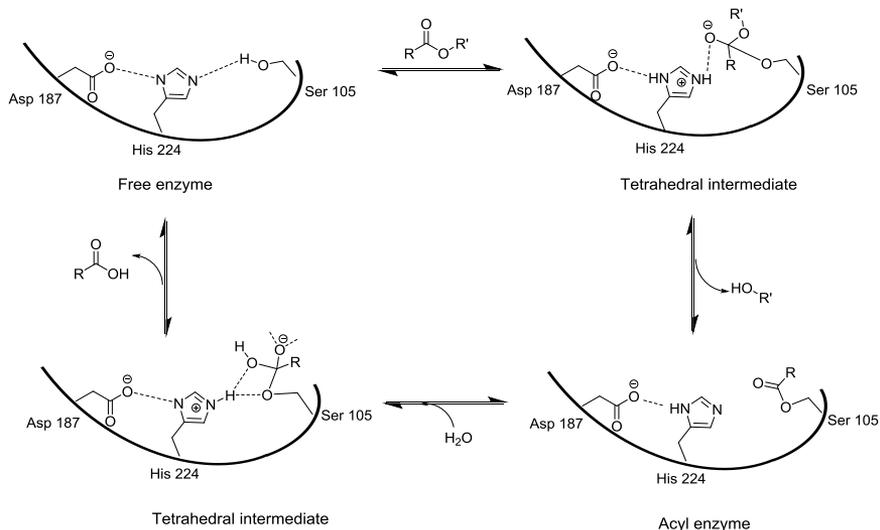


Figure 6. Schematic overview of the catalysis that takes place in the active site of CalB, where the “free enzyme” represents the active site with no bound ligands. While water is normally removed during esterification, some small amount of water is required for CalB to be able to perform the catalysis.

Photopolymerization

Photo-initiated polymerization technologies have received an increased interest during the last 20 years due to the many advantages they provide over thermal processes, including rapid curing, low energy consumption, solvent-free formulations, spatial control and low material cost.⁷⁴⁻⁷⁸ The polymerization proceeds by a chain reaction with an active propagating center that reacts with the monomer. Typically the active center is a radical, a cation or, more rarely, an anion.⁷⁹ UV-initiated free radical polymerizations gained interest early in the development of these technologies due to the availability of existing free radical photoinitiators. Cationic processes became more widely used much later when thermally stable cationic photoinitiator systems were developed.^{80, 81} Common monomers in radical polymerization are acrylates, methacrylates, thiols together with alkene in thiol-ene chemistry, and vinyl monomers such as styrene. For cationic polymerization, epoxides and vinyl ethers are commonly used as monomers.

Cationic photocurable systems have many advantages over radical polymerization. The carbocationic growing chains are not sensitive to oxygen inhibition and cationic polymerization may continue after the light source has

been removed because the formed Lewis acid or protic acid are long lived. Free radicals are typically extinguished by a variety of termination steps and no new radicals are formed from the photoinitiators in the absence of light. One other important advantage of cationic systems is the low toxicity of the monomers, which makes them a good alternative to acrylate and methacrylate systems that are common in radical processes.^{77, 82-85}

Photo initiators that have been used in this thesis are 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651, added as radical initiator) and *p*-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (UVAcure 651, cationic initiator) (Figure 7).

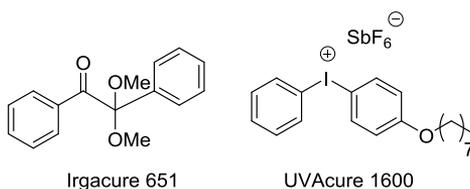
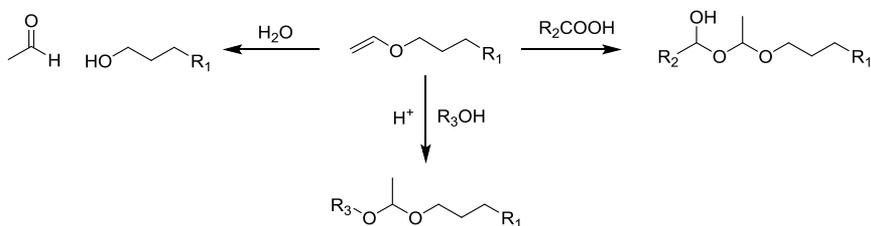


Figure 7. Structures of the radical photoinitiator Irgacure 651 and the cationic photoinitiator UVAcure 1600 used in this work.

Vinyl ethers are of interest for cationic polymerization due to their high curing rate – the electron-rich nature of the double bond gives rise to the high reactivity in cationic polymerization⁸⁶ – but the commercial availability of multifunctional vinyl ether monomers is currently limited and they have therefore found few uses in industrial UV-curing applications. Vinyl ethers are commonly synthesized from alcohols and acetylene in super basic conditions and high pressure.^{87, 88} However, developments of the process have been made and resulted in processes where high pressure systems are no longer required.⁸⁹ Some reasons for the limited availability are the difficulties in synthesis since vinyl ethers are sensitive to hydrolysis and may react with acids as well as with alcohols (see Scheme 1).⁹⁰⁻⁹²

Scheme 1. Possible degradation and side-products that may form when attempting to modify a vinyl ether monomer.



2. Experimental

The experimental procedures are briefly explained in this chapter. Further information can be found in the respective papers.

2.1 Materials

Itaconic acid (IA), succinic acid (SA), 1,4-butanediol (BD), *Candida antarctica* lipase B (CalB) immobilised on an acrylic carrier, >5000 U g⁻¹ (Novozyme 435), dimethyl succinate (DMS), lipoic acid, 1,4-butanediol vinyl ether (BVE), dimethyl itaconate (DMI), undecenoic acid (UA), 11-mercaptoundecenoic acid (MUA), titanium(IV)butoxide (Ti(OBu)₄), 1,8-diazabicycloundec-7-ene (DBU), 1,5,7-triazabicyclodec-5-ene (TBD), 0.1 M potassium hydroxide solution in ethanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol) and benzoic acid were purchased from Sigma Aldrich. 4-methoxyphenol and *p*-toluenesulfonic acid (*p*TSA) were supplied by Merck. Sulfuric acid (H₂SO₄) was purchased from Scharlau, Irgacure 651, 1,6-hexanediol vinyl ether (HVE) and 1,4-cyclohexanedimethanol vinyl ether (CyVE) were supplied by BASF. UVAcure 1600 was purchased from Cytec and phenolphthalein was supplied by KEBO. Acetone, toluene and 2-propanol were supplied by VWR. Dimethyl (83-85%)-diphenyl(15-17%)-siloxane copolymer, vinyl terminated was supplied by Hüls Petrarch Systems. Deuterated chloroform (CDCl₃) was supplied by Larodan.

2.2 Instrumentation

Nuclear magnetic resonance (NMR)

¹H-NMR and ¹³C-NMR spectroscopy was performed with a Bruker Avance 400 MHz spectrometer using CDCl₃ as solvent.

FTIR (Fourier transform infrared spectroscopy)

A Perkin Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate, single reflection ATR system (CPECAC Ltd., London (UK)) equipped with a MKII heated Diamond 45_ATR was used to record the spectra using 8-32 scans per sample.

RT-FTIR (real time FTIR)

The RT-FTIR analysis was performed using a Perkin-Elmer Spectrum 2000 FTIR instrument (Norwalk, CT) equipped with a single reflection (ATR) accessory unit (Golden Gate) from Graseby by Specac LTD (Kent). RT-FTIR continuously recorded the chemical changes over the range 4000–600 cm^{-1} . Spectroscopic data were collected at an optimized scanning rate of 1 scan per 1.67 s with a spectral resolution of 4.0 cm^{-1} using TimeBase software from Perkin-Elmer.

SEC (Size exclusion chromatography)

SEC was performed on a Malvern VISCOTEK GPCmax equipped with a refractive index detector and TGuard column followed by two linear mixed bed columns (LT4000L) (35 °C). Tetrahydrofuran (THF) stabilized with BHT (1 mL/min) was used as mobile phase. The molecular weights were calculated against polystyrene standards (Polymer Laboratories, $M_p = 1000$ Da up to $M = 4.5 \times 10^6$ Da). All samples were filtered through a 0.2 μm PTFE filter (13 mm, PP housing, Alltech) before analysis.

DMTA (Dynamic mechanical thermal analysis)

DMTA was performed using a Mettler-Toledo DMA/Q800 with a tensile fixture. All the samples were parts of thin film coatings that had been removed from glass substrate and cut into test specimens, with approximate dimensions of 20 mm \times 3.5 mm \times 0.1 mm. Temperature ranged from –60 °C to 150 °C at a heating rate of 3 °C min^{-1} and 1 Hz oscillation.

DSC (Differential scanning calorimetry)

A Mettler Toledo differential scanning calorimeter DSCe 820 was used for measurements. Samples (5-15 mg) were placed in 100 μL aluminum pans covered by aluminum lids and the results were analyzed with Mettler Toledo STARe software V9.2 was used to evaluate the results. Insert temperature was -60 °C and end point calibration was set to 5 min. Thereafter samples were heated from -60 °C to 150 °C at a rate of 10 °C/ min with pure nitrogen (flow rate of 30 ml/min), equilibrated at 150 °C for 5 min, cooled to -60 °C and equilibrated for 5 min, thereafter heated again to 150 °C.

Acid titration

The conversion for polyesters synthesized from IA, SA and BD were monitored by assessing the acid number (mg potassium hydroxide/g polyester). 0.5 g polyester was dissolved in a solvent-mixture (40 mL, toluene: 2-propanol:distilled water in a 50:50:1 ratio), and the solution was titrated with KOH in ethanol (0.1 M) using phenolphthalein as indicator. The concentration of the potassium hydroxide solution was determined by titrating benzoic acid (0.1 g, known amount) dissolved in distilled water: 2-propanol (40 mL, 1:1). The calculations of the conversion from the acid titration can be found in the supporting information of PAPER I.

2.3 Synthetic procedures

Synthesis of unsaturated polyesters from bio-based monomers

I) Polyester synthesis with acid catalysis (PAPERS I and II)

The monomers were mixed in a diacid to diol ratio of 1:1.2 together with 1 wt% *p*TSA and 1 wt% 4-methoxyphenol (added as radical inhibitor) in a round-bottom, flask equipped with a magnetic stirrer. The flask was placed in an oil bath pre-heated to 160 °C and fitted with a Vigreux column connected to a condenser. The reaction was monitored by acid titration and ¹H-NMR spectroscopy and stopped when the desired conversion was reached. The product was recovered without any purification. In Table 1 the compositions of the itaconic acid-based polyesters that were synthesized can be found.

Table 1. Molar ratios of the monomers used for synthesizing the polyesters and the acid numbers that were reached when the reactions were stopped.

Polyester	Molar ratios			Temperature (°C)	Acid number (mg KOH/g)	Reaction time (h)
	Itaconic acid	Succinic acid	1,4- Butanediol			
PIB-90 ^[a]	1.0	-	1.2	160	90	2.0
PIB-70 ^[a]	1.0	-	1.2	160	70	2.5
PIB-60 ^[a]	1.0	-	1.2	160	60	3.0
PIB-40 ^[a]	1.0	-	1.2	160/170	40	4.5
PISB-85 ^[b]	0.85	0.15	1.2	160/170	40	7.0
PISB-75 ^[b]	0.75	0.25	1.2	160	40	6.5
PISB-50 ^[b]	0.50	0.50	1.2	160	40	5.0

^[a] Polyesters from itaconic acid and 1,4-butanediol are denoted PIB-xx, where xx is the acid number that was reached for the synthesis. ^[b] Polyesters with both IA and SA are denoted PISB-xx where xx corresponds to the ratio of itaconic acid to succinic acid used in the synthesis.

II) Polyester synthesis with organometallic catalysis (PAPER II)

The monomers were mixed in a round bottom flask in a dimethyl ester to diol ratio of 1.3:1 together with Ti(OBu)₄ (1 wt%) and 4-methoxyphenol (1 wt%, added as radical inhibitor). The mixture was placed in a pre-heated oil bath set to 160 °C with a magnetic stirrer and the formed methanol was distilled off. The reaction was monitored by ¹H-NMR spectroscopy and when all the alcohols were reacted, the product was removed from the heat and poured into a glass container and stored in room temperature. An overview of the synthesis can be found in Scheme 2. Polymerization with *p*TSA in PAPER II was performed in the same way but with 1 wt% *p*TSA as catalyst.

III) Polyester synthesis with enzyme catalysis (PAPER II)

The monomers were mixed in a dimethyl ester to diol ratio of 1.3:1 together with immobilized CalB (10 wt% immobilized enzyme) in a round-bottom flask equipped with a magnetic stirrer and fitted with a distillatory. The flask was placed in an oil-bath set to 60 °C and after 5 h the pressure was reduced to 200 mbar and the reaction was left for an additional 6 h. The reaction was monitored by ¹H-NMR spectroscopy and when all the alcohols were reacted, the product was removed from the heat and dissolved in acetone. The solution was filtered to remove the immobilized CalB and the acetone was evaporated. Product was stored in room temperature. A schematic overview

of the synthesis of polyesters (PAPER II) with CalB, Ti(OBu)₄ and *p*TSA can be seen in Table 2.

Scheme 2. Synthesis of unsaturated polyesters with different catalysts. *p*TSA and Ti(OBu)₄ were used at 160 °C and the radical inhibitor 4-methoxyphenol was added. CalB was used at 60 °C and no inhibitor was added.

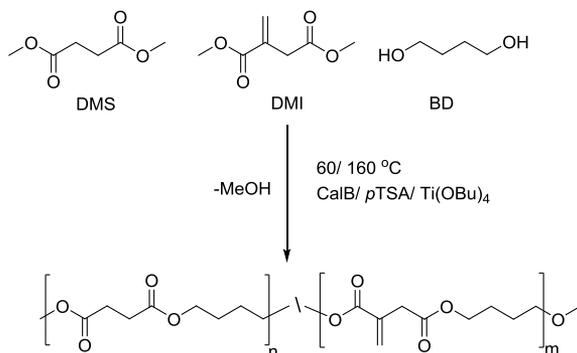


Table 2, Reaction conditions and molecular weights of polyesters synthesized with CalB and Ti(OBu)₄. (The monomers (DMI: DMS: BD) were used in a ratio of 1 : 1 : 1.5)

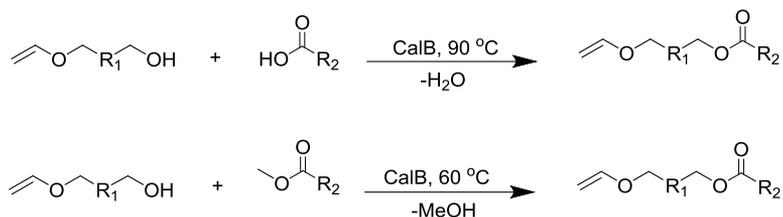
Polyester	Catalyst	Amount catalyst (%)	Inhibitor added	T (°C)	Time (h)	M _n ^[b] (g/mol)	M _w ^[b] (g/mol)
PISB-CalB	CalB	0.003 ^[a]	No	60	11	840	1500
PISB-Ti	Ti(OBu) ₄	0.7	Yes	160	4	880	2000

^[a]Actual concentration of active lipase when the weight of the acrylic carriers has been taken into account.^[b] Determined with THF-SEC.

Synthesis of vinyl ether ester monomers (PAPERS III, IV and V)

Alcohol vinyl ether was mixed with a fatty acid in a 1:1 molar ratio and placed in a round-bottom flask with molecular sieves and a magnetic stirrer (Scheme 3). The reaction was started by addition of 10 wt% immobilized CalB. Reactions were also performed at 90 °C in vacuum without molecular sieves. The structures of the synthesized VE esters with orthogonal functionality can be found in Figure 8. More details can be found in PAPER III.

Scheme 3. Synthesis of vinyl ether esters from different carboxylic acids/methyl esters and vinyl ether alcohol.



Difunctional vinyl ether esters were synthesized from different alcohol vinyl ethers and DMS (Figure 8). The alcohol vinyl ether was mixed with DMS in a 2:1 ratio and the synthesis was performed at 60 °C with a catalytic amount of CalB in bulk under reduced pressure. The formed methanol was distilled with a vacuum distillatory.

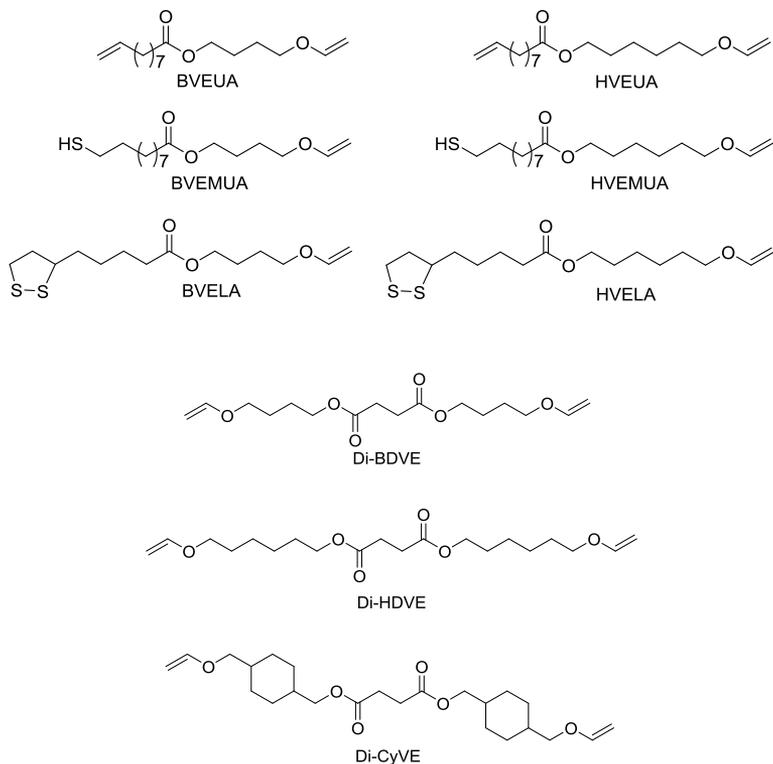


Figure 8. Vinyl ether ester monomers with orthogonal functionality that have been synthesized in PAPER III and difunctional vinyl ether esters that were synthesized in PAPER IV.

UV curing of unsaturated polyesters with free radical UV-polymerization

The polyesters were mixed together with 2 wt% irgacure 651 and heated to 70 °C under stirring to form a melt. The formulations were thereafter added onto glass substrates also heated to 70 °C followed by UV irradiation with a Fusion lamp, using a dosage of 6 J/cm².

Polymerization of monofunctional vinyl ether monomers with orthogonal functionality by cationic and radical UV polymerization

Initiator solutions were prepared from 10 mg initiator (Irgacure 651 as radical and UVAcure1600 as cationic) and 2 ml CDCl₃. Monomers (100 mg), were mixed with photoinitiator solution (corresponding to 1 wt% initiator) in vials and covered with aluminium foil. Polymerization was performed in vials with a magnetic stirrer, using a Hamamatsu L5662 UV-lamp (40 mW/cm²) and irradiated until VEs were consumed as confirmed with ¹H-NMR spectroscopy. Kinetics of the radical and cationic polymerizations were studied with real time-FTIR using a UV intensity of 17 mW/cm².

Crosslinking of difunctional vinyl ethers by cationic photopolymerization

Vinyl ether esters were mixed in different weight-ratios together in glass vials so that the total mass was 500 mg. Cationic UV initiator (UVAcure1600, 1 wt%) was added and the mixture was stirred. The mixture was added to a glass substrate and covered with a microscope slide followed by UV irradiation.

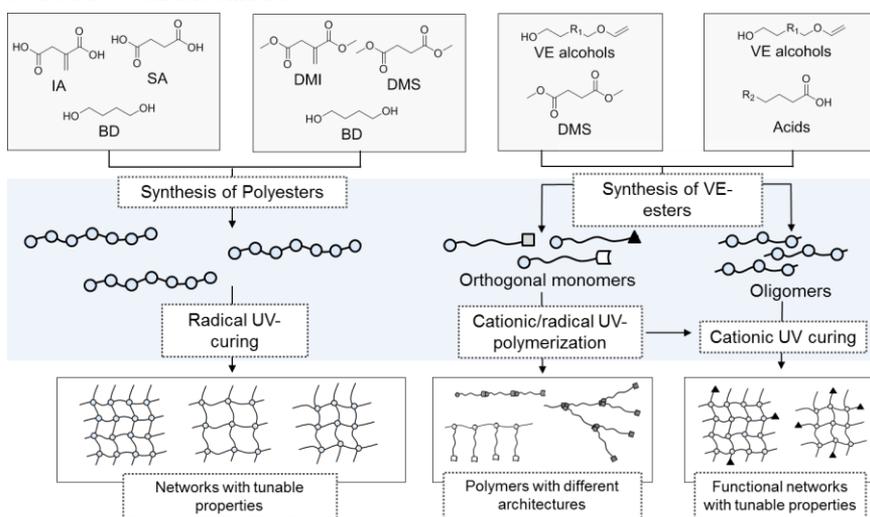
Postfunctionalization of networks

The vinyl ether monomer made from lipoic acid was first crosslinked with a difunctional vinyl ether ester by mixing with 1 wt % of the cationic UV initiator UVAcure 1600. The mixture was applied onto glass substrates and irradiated with UV light. The films were immersed in a solution containing Rhodamine-Vinyl ether and a catalytic amount of the radical UV initiator irgacure 651 in chloroform and the film was irradiated on both sides. The films were thereafter washed with methanol several times and incubated in methanol for 2 h to remove any non-bonded Rhodamine. More details can be found in PAPER V.

3. Results and discussion

In this thesis, various binder resins have been synthesized by means of enzymatic catalysis as well as with other traditional catalysts. The resins were thereafter crosslinked by UV-initiated radical or cationic polymerization and the material properties have been evaluated. Monomers with orthogonal functionalities were also synthesized and used to develop polymer networks with functionalizable groups. Scheme 4 shows an overview of the work that has been performed.

Scheme 4. Schematic representation of the various starting materials that were utilized in this project to develop polymer/oligomers and monomers with orthogonal functionality that could be used as UV-curable binders.



3.1 Polyesters from bio-based monomers

Itaconic acid (IA) is a multifunctional bio-based monomer that is useful for the synthesis of cross-linkable polyesters. In PAPER I, polyesters were synthesized from IA, succinic acid (SA) and 1,4-butanediol (BD) which all can be produced from renewable feed-stocks while in PAPER II, the methyl esters dimethyl itaconate (DMI) and dimethyl succinate (DMS) were used instead of the acids. In PAPER I, the monomer composition was varied in order to tune the final material properties and synthesis was also performed to different conversions in order to compare the impact of molecular weight-difference of the polyesters on the final network properties. Characterization with FTIR

spectroscopy shows a significant shift of the absorption bands of the carbonyl group from 1700 cm^{-1} to 1737 cm^{-1} , corresponding to the carboxylic acid and ester, respectively (Figure 9). The two different esters from the IA-moiety give rise to two maxima since one carbonyl is conjugated. The C=C stretch of the conjugated double bond can also be observed after esterification, indicating that it is still intact (peaks at 1637 and 817 cm^{-1}).

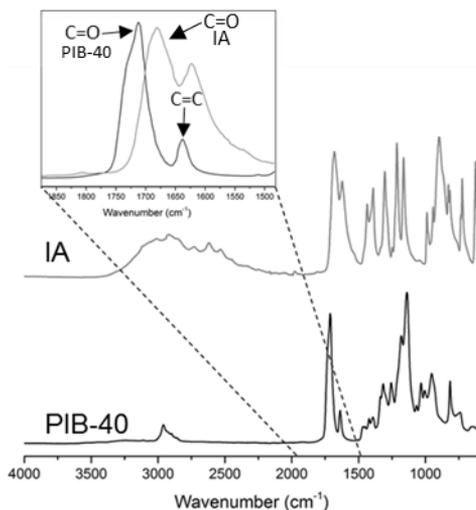


Figure 9. FTIR spectra of polyester IA and PIB-40 after polymerization. The carbonyl can be seen to shift from at 1700 to 1737 cm^{-1} as the ester is formed from the carboxylic acid.

$^1\text{H-NMR}$ spectra of the polyesters further confirm the polyester structures. Figure 10 shows the spectra for PIB-40 and PISB-50 that have similar conversions but different monomer composition. The synthesis was originally attempted with an acid to alcohol ratio of 1:1.02, however, in this case evaporation of BD made it difficult to obtain any polymers at all, and therefore the amount of diol was increased to compensate for the loss. In theory, when the molar ratio of carboxylic acid to alcohol is 1:1.2 and the conversion is as low as in this case (acid number 40), this should result in oligomers rather than polymers. But as can be seen in Figure 10, the number of end groups are low, indicating the formation of higher molecular weight material due to the evaporation of BD during the synthesis.⁹⁴ As the diol was in excess, evaporation of BD would decrease the stoichiometric imbalance and allowing for a higher molecular weight to be reached.

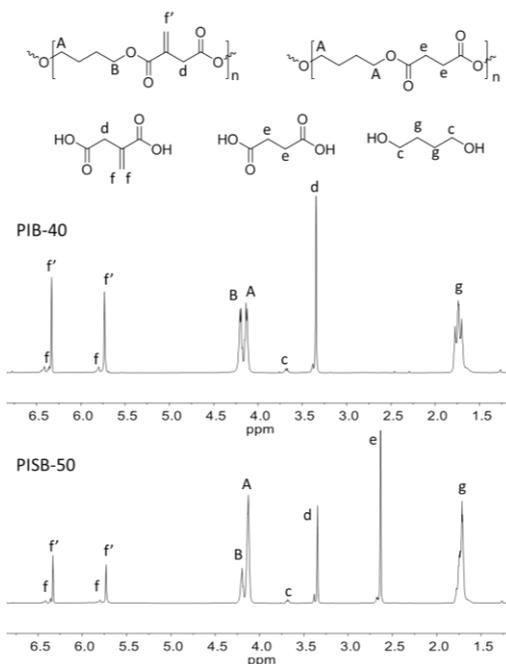
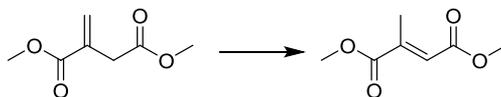


Figure 10. $^1\text{H-NMR}$ spectra in CDCl_3 of PIB (top) made from IA and BD and PISB (bottom) synthesized from IA, SA and BD. Small peaks around 5.4-6.6 ppm correspond to the unsaturations of IA where the conjugated carboxylic acid remains (labeled f in the spectra).

Another undesirable side-reaction that may take place is the rearrangement of the double bond in IA where it forms 2-methylfumarate (Scheme 5). This change in chemical shift would give a signal in the $^1\text{H-NMR}$ -spectra around 2.3 ppm and 6.8 ppm. There are some small peaks around 6.8 and 2.3 ppm, however, the signal from the methylene in IA is significantly larger which suggests that the extent of rearrangement is low.⁹⁵ All FTIR and $^1\text{H-NMR}$ spectra can be found in the supporting information (SI) of PAPER I.

Scheme 5. Rearrangement of the double bond in itaconate to 2-methylfumarate which may take place if the reaction conditions are not optimized.



SEC analysis confirmed that the molecular weights were indeed higher than the theoretical molecular weights that were calculated from the acid value. (Table 3). Even though the molecular weights are higher than the targeted values, the results still follow a trend - PIB synthesized to different conversions have different molecular weights, and PISBs that were synthesized to the same conversion but with different ratios of IA and SA had more similar molecular weights (M_n).

The thermal properties of the polyesters were analyzed with DSC and the results can be seen in Table 3. The majority of the polyesters have glass transition temperature of between -30 and -40 °C and also have some degree of crystallinity. Increasing amounts of SA increases the crystallinity, thus SA gives more crystalline polymers than IA, but molecular weight also appears to effect the crystallinity. This is reasonable since itaconic acid is less symmetric and more bulky, which makes it more difficult for the polymer to organize into a crystal lattice structure.

Table 3. Acid number (AN), molecular weights (M_n and M_w), dispersity (\mathfrak{D}), glass transition temperature (T_g), crystallization temperature (T_m) and crystal melting enthalpy of the synthesized polyesters (ΔH_m).

	AN (mg/g KOH)	M_n Theory ^{a)}	M_n ^{b)} (g/mol)	* M_w ^{c)} (g/mol)	* \mathfrak{D} ^{b)} (M_w/M_n)	T_g ^{c)} (°C)	T_m ^{c)} (°C)	ΔH_m ^{c)} (J/g)
PIB-90	90	430	1 800	4 500	2.5	-38	-	-
PIB-70	70	500	3 000	4 600	1.5	-32	45	7.1
PIB-60	60	540	4 400	32 000	7.3	-31	46	14
PIB-40	40	680	5 600	63 000	6.4	-31	45	33
PISB-85	40	670	4 700	19 000	4.1	-31	40	1.3
PISB-75	40	680	5 300	15 000	2.9	-33	44	11
PISB-50	40	680	5 400	11 000	2.0	-36	46	45

^{a)} Calculated from the acid number (AN).

^{b)} Determined with THF-SEC using polystyrene standards.

^{c)} Determined with DSC.

3.2 Comparing different catalysts for DMI based polyesters

During the esterification/transesterification of IA/DMI, there are a number of side reactions that may take place, including isomerization of the double bond leading to decreased reactivity during the crosslinking step, premature gelation, and BD may form THF by cyclization, that subsequently evaporates.

Therefore it was of interest to investigate whether different catalysts influence the side-reactions. The enzyme *Candida Antarctica* Lipase B (CalB) was proposed as a good candidate because it efficiently catalyzes esterification under mild reaction conditions which could minimize the number of side-reactions that may occur, in particular the rearrangement of the double bond and premature gelation. Therefore, the synthesis was performed with different common esterification catalysts (PAPER II) and their performance was compared. Six different catalysts, immobilized CalB, one organometallic catalyst ($\text{Ti}(\text{OBu})_4$) two acids (*p*TSA and H_2SO_4), and two organobase catalysts (DBU and TBD), were initially evaluated.

The reaction temperatures were chosen based on common procedures taken from the literature, since the catalysts have different activation energies and are not all efficient at the same temperature. After initial screening, it was found that only *p*TSA, CalB and $\text{Ti}(\text{OBu})_4$ were suitable catalysts since they did not cause significant amount of side-reactions. *p*TSA did cause formation of THF from BD to some extent,⁹⁴ however, in the presence of other diols it is still a suitable catalyst since it did not cause any substantial amount of rearrangements or side reactions involving the itaconate. H_2SO_4 also resulted in the formation of THF, but a number of other by-products were also observed by $^1\text{H-NMR}$, while no significant amount of ester was formed. Therefore H_2SO_4 was considered unsuitable and not used further. The formation of THF was also observed previously when the synthesis was performed under more acidic conditions (PAPER I) however, because all polyesters in that study were synthesized with the same method, it was still possible to compare the materials to each other. In PAPER II, the initial reactivity was compared, but the evaporation of BD resulted in significant differences in molecular weight of the final polymers. This makes it difficult to compare the properties of the polymers of the crosslinked materials and therefore the use of *p*TSA was excluded from further comparison.

As DMI has two different ester groups, one being conjugated, it was also of interest to study the difference in reactivity of the two esters and to investigate whether the choice of catalyst would affect this. The formation of the ester from DMI with BD will give rise to different shifts in $^1\text{H-NMR}$ spectrum depending on which ester has reacted. In CDCl_3 the signal from the non-conjugated ester will result in peaks at 4.14 ppm, whereas the signal from the conjugated ester will give rise to peaks at 4.21 ppm (denoted A and B respectively in Figure 11). These peaks were studied in detail with samples analyzed consecutively from the beginning of the transesterification

reactions catalyzed by CalB, $\text{Ti}(\text{OBu})_4$ and *p*TSA. In Table 4, the selectivity of the different catalysts towards the different ester groups is presented as the reaction rate of the formation of ester B divided by the reaction rate of the formation of ester A. The results show that both CalB and *p*TSA are selective towards carbonyl A, the non-conjugated ester groups (For more details on reaction rates see the supporting information of PAPER II). The high selectivity of the enzyme was expected, since the reaction is dependent on the size of the molecules and how they fit in the catalytic site and the conjugated carbonyl in DMI is more sterically hindered than the non-conjugated. Furthermore, electronic effects due to the conjugated double bond have previously been seen in the cases of acrylates compared to saturated esters to decrease the reactivity of the carbonyl to nucleophilic attack, which makes it reasonable that the same applies to the carbonyls in DMI.⁹⁶ $\text{Ti}(\text{OBu})_4$ has a much lower selectivity and therefore catalyzes the reaction between both methyl esters with similar efficiency.

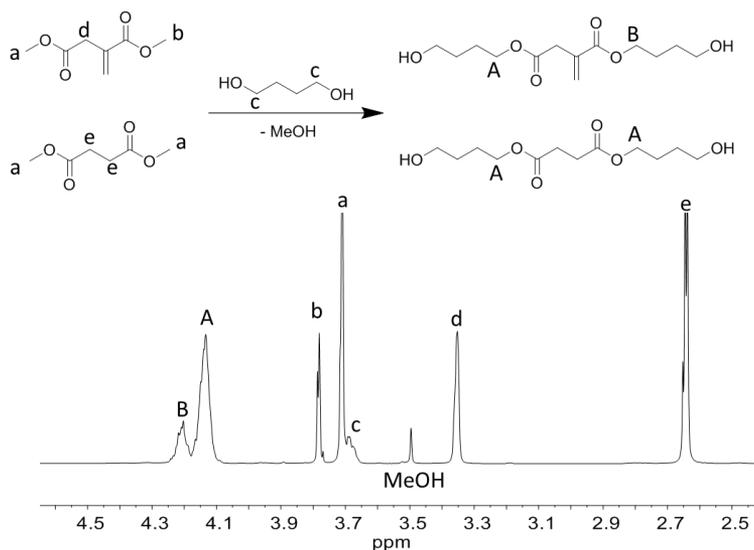


Figure 11. ^1H -NMR showing the formation of the conjugated ester bond at 4.20 (A) ppm and the non-conjugated ester at 4.14 (B). Spectrum was obtained in CDCl_3 .

This shows that there is not a large difference in reactivity between the methyl esters during catalysis with $\text{Ti}(\text{OBu})_4$, so when DMI and DMS are both present, the incorporation of DMI vs DMS in the final polymer will be random. On the other hand, when CalB or *p*TSA is used, DMI is more likely to be situated at the ends of the polymer. The methyl end groups can be seen in the

¹H-NMR spectra of the synthesized polyesters (Figure 12) and there is a noticeable difference between the amount of conjugated and non-conjugated end-groups that remain in the different spectra. The polyester synthesized with CalB has a higher number of conjugated end groups (b) than the polyester synthesized with Ti(OBu)₄, which corroborates with the selectivity of the catalyst under these conditions.

Table 4. Selectivity and reaction rate of the polymerization with different catalysts.

Catalyst	T (°C)	Selectivity (B/A)	Total initial rate ^[a]
CalB	60	13±3	250±50
Ti(OBu) ₄	160	2.5±0.2	17±3
<i>p</i> TSA	160	7.5±0.4	4.4±0.1

^[a] Initial reaction rate of total ester formation [$\mu\text{mol}_{\text{substrate}} / \mu\text{mol}_{\text{catalyst}} \cdot \text{min}$].

Some small signals at 6.7 and 2.3 ppm in the ¹H-NMR spectra of PISB-Ti in Figure 12 can also be observed, which indicate that some rearrangement of the double bond has occurred. This does not take place when CalB is used, most likely due to the lower reaction temperature. This rearrangement was also observed previously when polyesters were synthesized with acid catalysis (PAPER I).

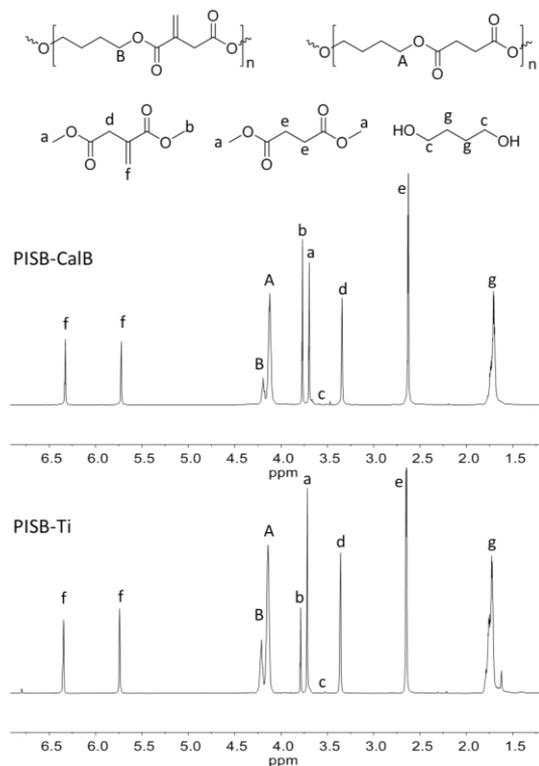


Figure 12. $^1\text{H-NMR}$ spectra of polyester synthesized from DMI, DMS and BD with CalB and with $\text{Ti}(\text{OBu})_4$.

Moreover, the difference in incorporation of DMI vs DMS was found to have an effect on the crystallinity of the resulting polyester (Figure 13). As was observed in PAPER I, the itaconate seems to decrease the crystallinity compared to succinate units. In this case, the formation of polyester catalyzed by $\text{Ti}(\text{OBu})_4$ does not show any significant amount of crystallinity. On the other hand, the polyester catalyzed by CalB has some degree of crystallinity, which supports the theory that the polyesters mainly have DMI at the chain ends and that longer segments without DMI in the middle of the chain would allow for a crystal structure.

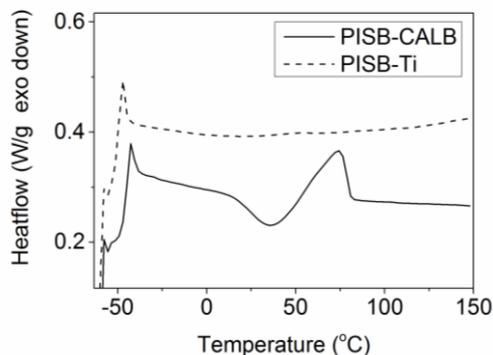


Figure 13. DSC thermograms of the polyesters synthesized with CalB (dashed line) and $\text{Ti}(\text{OBu})_4$ (solid line).

In summary, CalB, $\text{Ti}(\text{OBu})_4$ and *p*TSA can all be used to synthesize polyesters from IA or DMI. However, based on the findings in this study, it is best to avoid acid catalysts and use methyl esters instead of carboxylic acids when BD is used. If BD is exchanged for another diol, the carboxylic acids and acid catalyst may be used. The choice of catalyst may however affect the polymer composition and yield polymers with different properties such as varying degree of crystallinity.

3.3 UV-cured polyester networks

Photo-curing processes are attractive alternatives to thermal curing technologies. Some advantages of photo-polymerization include higher energy efficiency, spatial control and rapid curing. The polyesters in Paper I were crosslinked by UV-initiated radical polymerization and the materials were characterized with FTIR to determine the degree of curing, X , calculated according to Eq. 1. A is the area of the peaks corresponding to the carbonyl (1713 cm^{-1}) and the double bonds (1637 cm^{-1}) prior to curing ($t=0$) and after curing (t). The results can be found in Table 5. Peak intensities were normalized against the carbonyl peak.

$$X (\%) = \frac{(A_{1637}/A_{1713})_{t=0} - (A_{1637}/A_{1713})_t}{(A_{1637}/A_{1713})_{t=0}} \times 100\% \quad \text{Eq. 1}$$

A degree of curing as high as 75 % could be achieved without addition of any reactive diluents or reagents other than the radical initiator. It is reasonable that complete curing is not reached as the crosslinking will restrict the molecular mobility of the system.

Table 5. Degree of curing of films made from unsaturated polyesters synthesized from IA, SA and BD, as assessed by FTIR

Polyester	Degree of curing (%)
PIB-90	28
PIB-70	34
PIB-60	56
PIB-40	61
PISB-85	75
PISB-75	58
PISB-50	50

Unsaturated polyesters are commonly based on maleate or fumarate, that have 1,2-disubstituted unsaturations. These are relatively difficult to homopolymerize and therefore need to be copolymerized with other monomers, such as styrene, in order to achieve efficient curing.⁹⁷ IA has a 1,1-disubstituted unsaturation and as can be observed by the calculated degrees of curing, relatively high conversions can be reached. The disappearance of the alkene can be seen clearly in the FTIR spectra before and after curing of PISB-85 at 1637 cm⁻¹ (Figure 14). All the other FTIR spectra can be found in PAPER I.

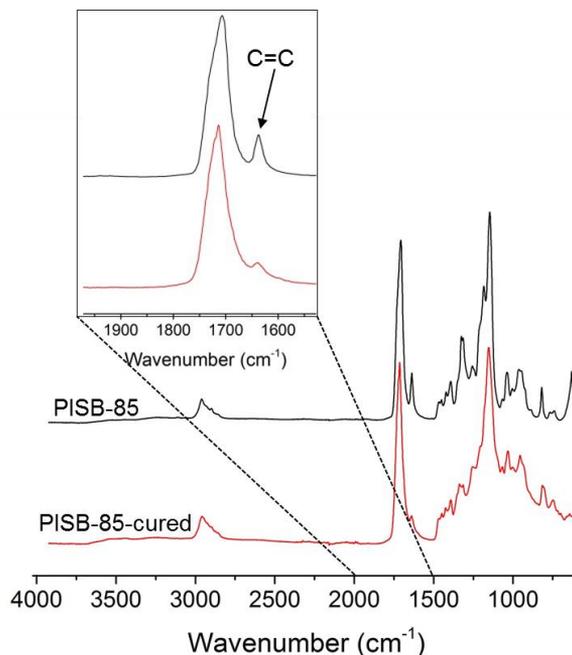


Figure 14. FTIR spectra before and after crosslinking of unsaturated polyesters based on itaconic acid. The alkene group can be seen at 1637 cm⁻¹ and shows a significant decrease after curing.

The thermo-mechanical properties of the crosslinked polyesters were studied with DMA and the results are shown in Figure 15. By varying the amount of SA in the polymer it was possible to tune the properties of the crosslinked polymer networks. Increasing the amount of SA decreases the T_g ($\text{Tan } \delta \text{ max}$) and the storage modulus becomes lower above the rubbery region. The $\text{Tan } \delta$ maximum is broader and lower for the networks with higher crosslinking densities and thus, more restricted mobility. Varying the molecular weights of the same polymer composition also gave an impact on the thermo-mechanical properties. As can be seen in Figure 15, there is a significant difference in storage modulus above the T_g for PIB-series; PIB-90 and 70 have moduli below 100 MPa whereas PIB-60 and 40 have moduli above 100 and a significantly higher T_g . This shows that the molecular weight has an impact on the mechanical properties, however, above a certain molecular weight the properties does not vary much. It is thus recommended to reach the same molecular weight as for PIB-60 or higher to have good mechanical stability.

PIB-90 and PIB-70 were furthermore very brittle and difficult to handle. Many of the materials also have a T_g above room temperature which indicates that vitrification may prevent full curing.

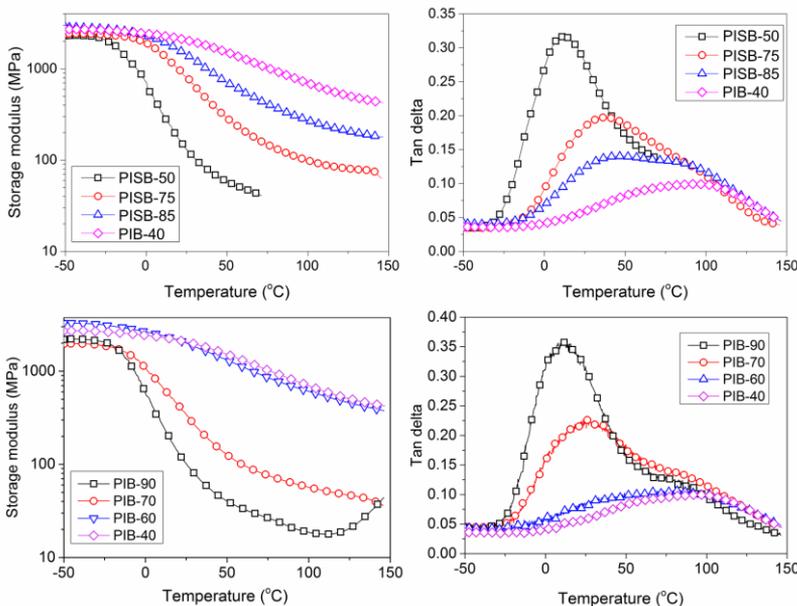


Figure 15. Storage modulus and Tan δ measured for the crosslinked polyesters based on IA, SA and BD PISB corresponds to polyesters from IA, SA and BD, with different ratios of IA and SA, while PIB corresponds to polyesters without SA synthesized to different conversions.

The thermo-mechanical properties of the crosslinked polyesters synthesized with $Ti(OBu)_4$ and CalB were also studied with DMA (Figure 16), with the networks exhibiting similar properties. The difference between $Ti(OBu)_4$ and CalB indicates that PISB-CalB has a slightly higher and broader T_g . This is likely to be due to the fact that PISB-Ti has more itaconate groups incorporated in the chain and thus it will have more dangling ends that can increase mobility. The polyester synthesized with *p*TSA and itaconic acid instead of DMI (PISB-50 in PAPER I) also has similar properties, despite having been synthesized from the acids instead of the methyl esters and also having a higher molecular weight.

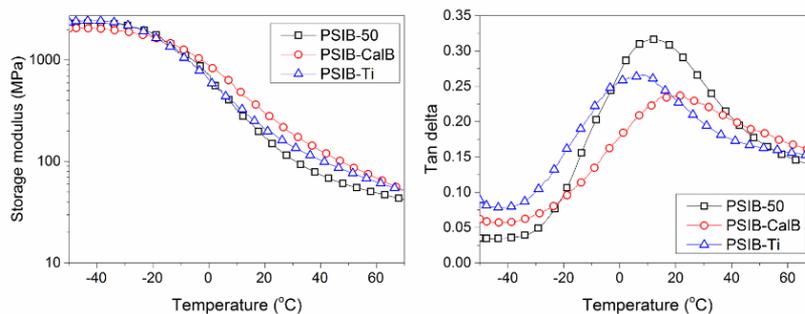


Figure 16. Storage modulus and Tan δ of the crosslinked polyesters that were synthesized with $\text{Ti}(\text{O}i\text{Bu})_4$ and CalB from DMI synthesized in PAPER II compared to the polyester PISB-50 synthesized in PAPER I with *p*TSA from IA.

Even though there were no major differences in the material properties between the polymers synthesized with *p*TSA, $\text{Ti}(\text{O}i\text{Bu})_4$ or CalB after crosslinking, the $\text{Ti}(\text{O}i\text{Bu})_4$ -catalyst stains the polyester to a yellow color, whilst the CalB leaves no color. Furthermore, when CalB was used, the reaction could be run at 60 °C, rather than 160 °C for both *p*TSA and the $\text{Ti}(\text{O}i\text{Bu})_4$ catalyzed reactions. Therefore it was not necessary to add any radical inhibitors during the synthesis. An additional benefit of the enzyme catalysis is that the immobilized enzyme can be easily removed by filtration while the $\text{Ti}(\text{O}i\text{Bu})_4$ and the *p*TSA remain within the crosslinked polyester film. The long terms effect and potential leaching of these residues are unknown, however, comparing the visual differences between the crosslinked films (Figure 17) it can be seen that the enzymatically catalyzed polyester results in a network with no color which is a significant advantage for many applications.



Figure 17. Freestanding films made from PISB-CalB (left) and PISB-Ti (right) showing that the enzymatically synthesized polyester does not have any color.

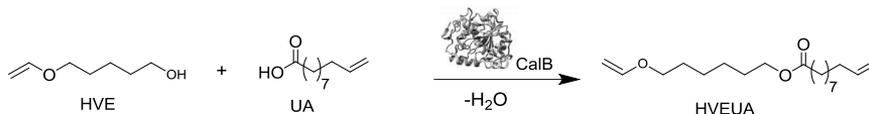
In conclusion, bio-based polyesters from IA, SA and BD or DMI, DMS and BD could be UV-cured. The monomer composition can be tailored to tune the properties the final polymer networks. Enzyme catalysis can have many advantages, some examples are the possibility to run reaction at a low temperature and that it does not discolor the final materials. However, using the enzyme will also require a different synthetic strategy from traditional polyester synthesis.

3.4 Vinyl ether esters and their polymerization

The potential for polyesters in the field of bio-based materials is promising,. However, developing polymeric materials that can be synthesized more efficiently is of interest. Synthesis of polyesters can be time-consuming in order to reach high monomer conversion and developing a system that can be synthesized and crosslinked in a shorter time-scale would be beneficial. Vinyl ethers (VE) are an interesting class of monomers that are reactive in cationic polymerization. As an alternative to polyesters, VE-ester monomers and oligomers are good alternatives. It is, however, not possible to synthesize VE-esters by traditional esterification procedures without deprotection and protection chemistry or multiple reaction steps because the VE-groups are sensitive to acids. In presence of acid VEs are converted to acetals or acid-acetals and this process occurs rapidly at elevated temperatures. CalB promotes the esterification and leads to consumption of the majority of the acid groups into esters and removes the possibility for acetal-formation.⁹⁸ Thus, the enzyme- catalyzed route provides a method for direct esterification without side-reactions that would otherwise not be possible.

The esterification between 10-undecenoic acid (UA) and hexane-diol vinyl ether (HVE) was studied (Scheme 6) as a model reaction in order to compare different reaction conditions for synthesis of vinyl ether esters with enzyme catalysis. Enzyme catalysis was also compared with the catalyst free reaction and to $Ti(OBu)_4$ in order to access the limitations of such alternative approaches.

Scheme 6. Experimental screening of the synthesis of VE-functional ester and comparison with uncatalyzed, enzyme catalyzed and $\text{Ti}(\text{O}i\text{Bu})_4$ -catalyzed reaction was performed for the reaction between 10-undecenoic acid (UA) and 1,6-hexanediol monovinylether (HVE).



When UA and HVE were combined at 90 °C, all VE functionality was consumed within minutes in the absence of catalyst. The $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst also yielded esters (c in Figure 18), but the vinyl ether still deteriorates. The acid can react with the VEs and form acetals (denoted f and g in the spectra) or the acidic conditions may catalyze the formation of acetals from vinyl ethers and alcohols. Both of these can be seen in Figure 18, but they also disappear after a few minutes which shows that these compounds are not stable under these reaction conditions. With the immobilized enzyme CalB on the other hand, the reaction can be performed at temperatures between 25-90 °C since the formation of esters is favored over the side reaction that degrades the vinyl ether functionality.

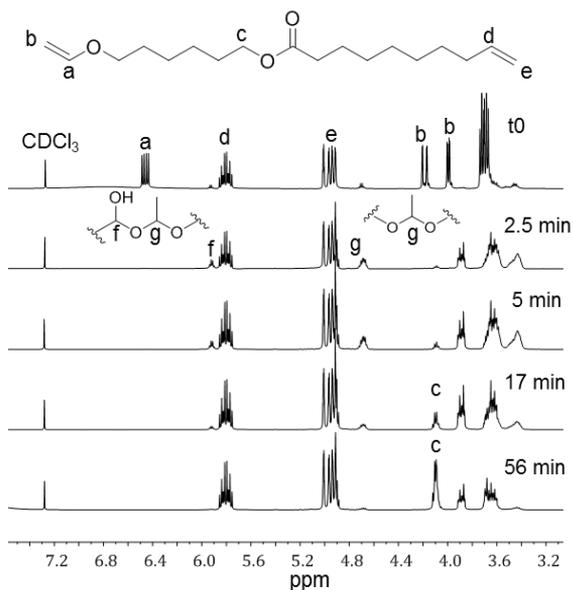


Figure 18. ^1H -NMR spectra of the reaction between HVE and UA as catalyzed by $\text{Ti}(\text{O}i\text{Bu})_4$ showing that all VE functionality (a and b) has deteriorated after only 2.5 min. Peaks formed at 5.9 ppm and 4.7 correspond to acetals.

The ester formation with CalB can be performed in various solvents as well as in bulk (Figure 19), and with a range of carboxylic acids, and is therefore a versatile method for synthesizing many new types of vinyl ether ester monomers and oligomers.

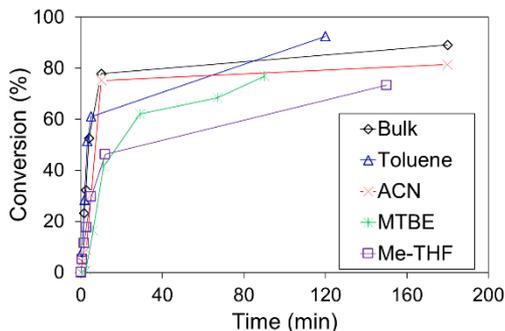


Figure 19. Conversion of ester formation from UA and HVE in different solvents for the reaction catalyzed by CalB in 22 °C with molecular sieves. Conversion was calculated from GC measurements.

In Paper III, three different types of functionalities were combined with vinyl ether to give new monomers with dual functionalities; a thiol (HVEMUA), an alkene (HVEUA) and a cyclic disulfide (HVELA). Because there are no intermediate steps, high yields are achieved for all products and the immobilized enzyme can be removed and potentially reused in a facile manner.

All VE monomers polymerized to some extent with radical and/or cationic UV-initiation. The structures of the resulting polymers depend on which type of initiator was used. Figure 20 shows the ¹H-NMR spectra of the monomer HVEUA before and after cationic polymerization. As can be observed the vinyl ether peaks at 6.48, 4.19 and 4.01 ppm have completely disappeared indicating full conversion of the VE groups. At the same time, the alkene at 5.7 and 4.9 ppm is still unreacted. Thus it can be assumed that the cationic polymerization of this monomer results in a linear polymer with pendant alkene groups. These alkenes could be suitable for further modifications with, for example, thiol-ene chemistry. No reaction could be observed when radical initiation was attempted. The vinyl ether functionality was unchanged, verifying that vinyl ethers do not homopolymerize radically and that the alkene in this case is also unable to undergo radical homopolymerization.

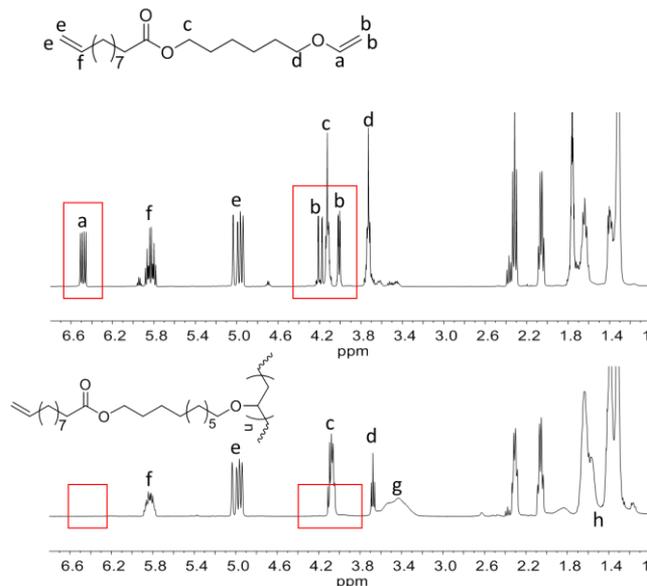
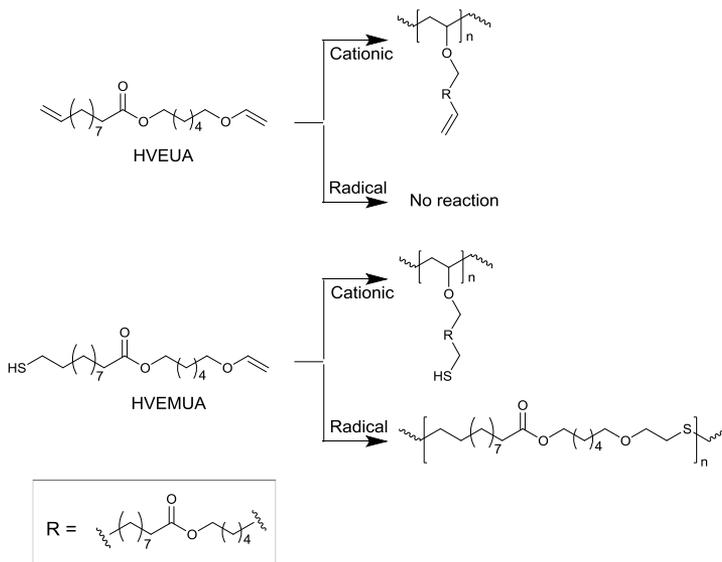


Figure 20. $^1\text{H-NMR}$ spectra of vinyl ether – alkene monomer HVEUA (top) and its product from cationic photopolymerization (bottom).

Conversely, the monomer that contained both vinyl ether and thiol (HVEMUA) could be polymerized both by cationic and radical initiation. Since VEs do not homopolymerize radically it can be assumed that the VE groups have reacted with the thiol in a step growth manner. Thus radical initiation yields a linear polymer with no pendant functional groups. When the polymerization is cationically initiated a polymer with pendant thiols is formed (Scheme 7). In addition, some other by products were also observed that are believed to be the product of thiol-ene reaction. Decomposition of the cationic initiator leads to some amount of radicals which may initiate the thiol-ene reaction.^{80, 99, 100} Some amount of acetal or thioacetal formation was also observed.

Scheme 7. Suggested intermediates of the radical and cationic polymerization products from HVEUA (top) and HVEMUA (bottom).



The cationic and radical polymer products of the vinyl ether-disulfide monomer (HVELA) were also studied with $^1\text{H-NMR}$ spectroscopy (Figure 21). The disulfide group remained unchanged during cationic polymerization and the vinyl ether has reacted completely, which indicates that the formed polymer is linear with pendant disulfide group. During radical polymerization the disulfide groups decreased by 50 % and all the VE had reacted. This was expected since the ratio of VE to sulfur atoms was 1:2 and consequently, this shows that all VE had reacted with one sulfur atom rendering 50 % of the disulfide groups unreacted. The results also indicate that the formed structure is branched since half the amount of disulfides still remains and have not formed thiols or thiol-radicals.

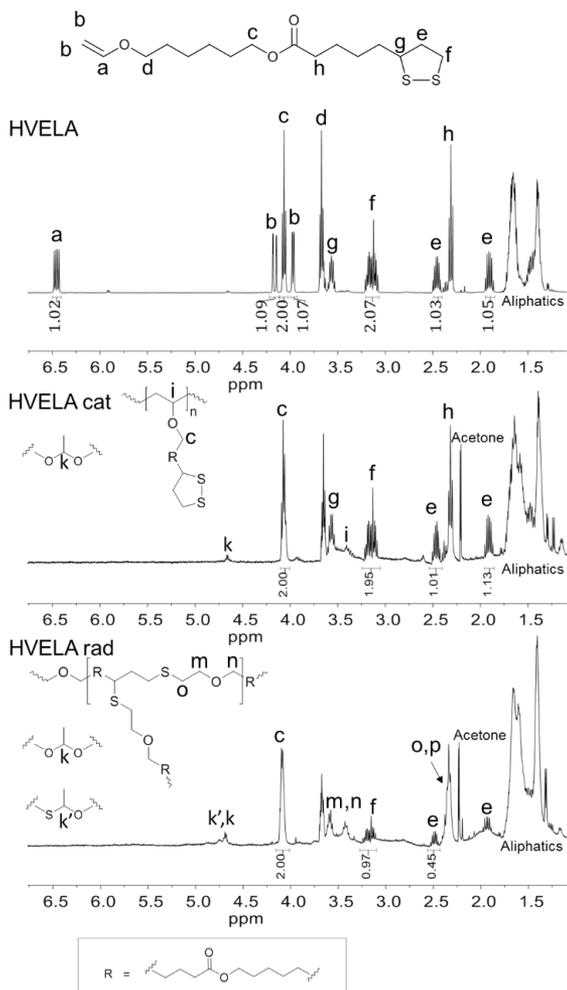


Figure 21. $^1\text{H-NMR}$ of HVELA (top) and the cationic (middle) and radical (bottom) polymerization products.

The reaction rate was also studied with RT-FTIR for both cationic and radical polymerization (Figure 22, top left and right) with different initiator concentrations. As can be observed, the reaction rate for cationic polymerization is significantly affected by the initiator concentration, however, for radical polymerization the range of 0.1 – 1 wt % initiator had little effect on the reaction rate. As discussed previously, the cationic initiation produces some degree of radicals which could potentially cause the disulfide to react with the vinyl ether, however, when 1 wt % initiator is used,

it can clearly be seen that the cationic polymerization is much faster. It is therefore more likely that the vinyl ethers are first consumed, thereafter if any thiyl-radicals are formed, thiol-ene reaction will still not take place. In Figure 22 the FTIR spectra time-lapse during cationic polymerization can be seen. From the spectra it is evident that the majority of the VE groups have reacted.

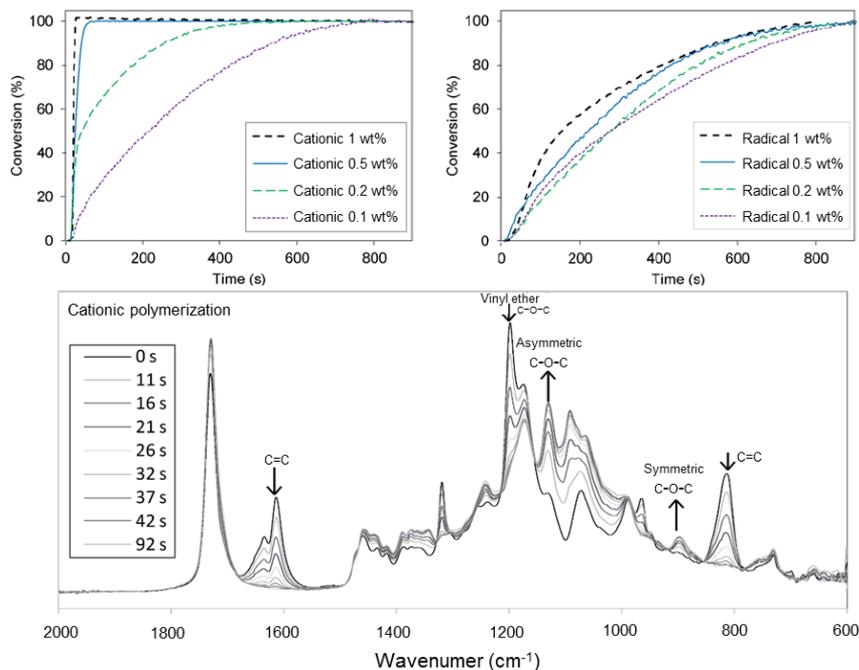


Figure 22. RT-FTIR of cationic (top left) and radical polymerization (top right) of HVELA. FTIR-time-lapse spectra for the cationic polymerization can be seen at bottom. All the spectra (before and after polymerization with different initiator contents) can be found in the SI for PAPER V.

In PAPER V, HVELA was used in networks to create functional networks that were postfunctionalized by using the disulfide group since these to a large extent remain unreacted after the cationic polymerization. Thus, it is more likely that if the disulfide bond is broken and forms a thiyl-radical it will either reform or form a new disulfide bond which can still be used for post-functionalization. The proposed structures of the polymer products from HVELA are presented in Scheme 8.

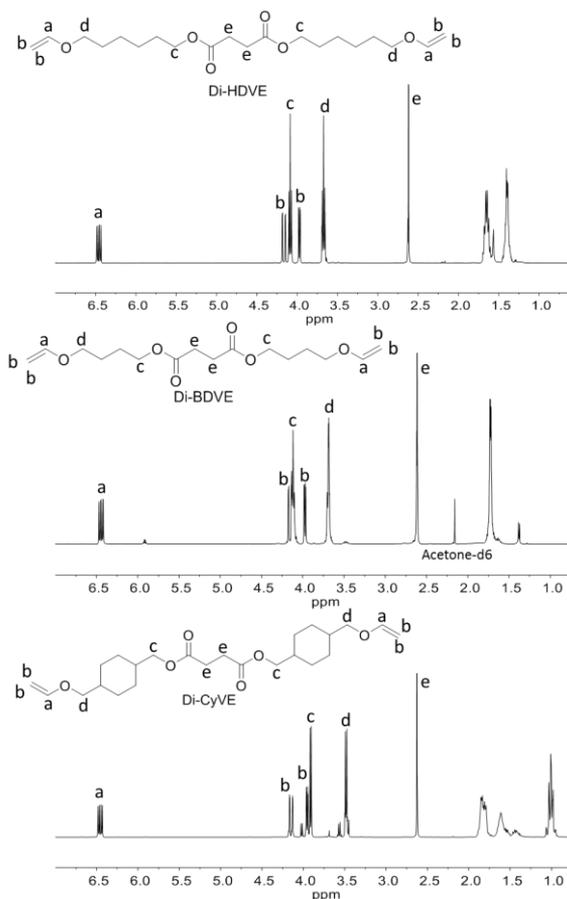


Figure 23. $^1\text{H-NMR}$ spectra of the synthesized difunctional VE oligomers. Measurements were performed in deuterated chloroform (CDCl_3).

The cationic polymerization of the difunctional oligomers was studied with RT-FTIR in order to investigate if there were reactivity differences between the oligomers as a result of their different structures (Figure 24). The cycloaliphatic oligomer reacted more slowly and appeared not to reach full conversion during the RT-FTIR experiment, but the low conversion is most likely due to vitrification. RT-FTIR was performed in transmission mode which meant that the films had to have a low thickness ($25\ \mu\text{m}$) in order to obtain spectra that were not saturated.

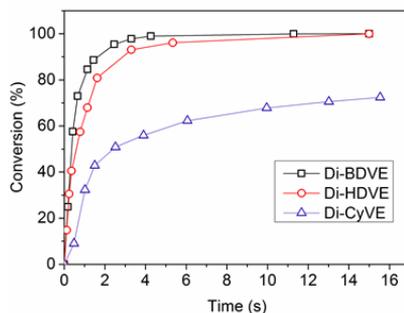


Figure 24. RT-FTIR of the difunctional VE oligomers showing the conversion of the VE peaks at 1613 cm^{-1} . The conversion was calculated by normalizing against the carbonyl peak.

All oligomers reached full conversion when films of approximately 200 μm were made to create free standing films for material characterization (Figure 25). This can be explained by the fact that the effect of vitrification observed in the kinetics study is decreased with increasing sample thickness since the heat produced during the reaction will dissipate more slowly. Furthermore, crosslinking was performed with a different UV source (Fusion system) with higher intensity that will also generate heat more rapidly than the spotlight source that was used for the kinetics study.

By varying the aliphatic and cycloaliphatic oligomers in different amounts, it was possible to develop clear free-standing films with T_g values ranging from -10 to 100 $^{\circ}\text{C}$ (Figure 26). The oligomer composition of the free standing films can be found in Table 6.

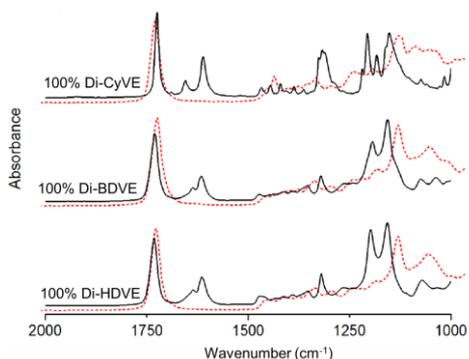


Figure 25. FTIR spectra before and after curing the difunctional VE oligomers. The VE peak can be observed at 1560-1690 cm^{-1} . Black line correspond to before curing and red dotted line corresponds to after UV-curing for 2 minutes.

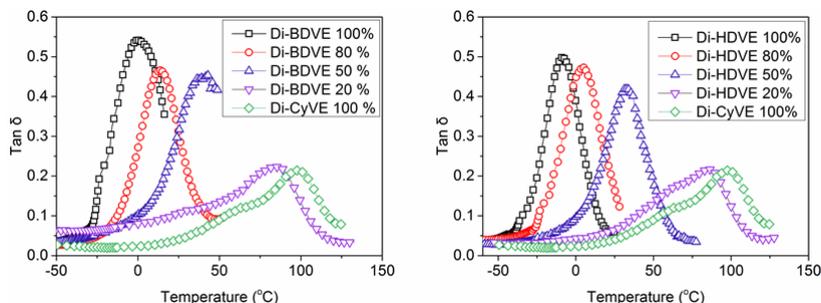


Figure 26. Tan δ as a function of temperature for the crosslinked films made from the difunctional VE oligomers in different compositions - from Di-CyVE and Di-BDVE and from Di-CyVE and Di-HDVE.

Figure 26 shows the Tan δ of the different networks where the T_g is taken as Tan δ maximum. Comparing these values with the Fox-Flory equation for determining the glass transition temperature of copolymers it is evident that these values correlate well with the theoretical ones (Table 6). The Fox-Flory equation is an estimate for polymers and not crosslinked polymer networks, however, this still indicates that the network is rather homogenous.

Table 6. Oligomer compositions of the crosslinked freestanding films. 1 wt% photo initiator was used for all combinations. T_g values for the different UV-cured formulations.

Name	Di-HDVE wt%	Di-BDVE wt%	Di-CyVE wt%	Theoretical T_g (°C) ^[a]	Measured T_g (°C) ^[b]
Di-HDVE-100	100	-	-	-10	-10
Di-HDVE-80	80	-	20	7	3
Di-HDVE-50	50	-	50	36	30
Di-HDVE-20	20	-	80	71	84
Di-BDVE-100	-	100	-	-1	-1
Di-BDVE-80	-	80	20	15	13
Di-BDVE-50	-	50	50	42	40
Di-BDVE-20	-	20	80	74	84
Di-CyVE-100	-	-	100	100	100

^[a] Calculated with the Fox-Flory equation; ^[b] Tan δ max assessed with DMTA

Interestingly, Di-CyVE-100 exhibited ductile behavior despite the high T_g and this made it possible to deform the crosslinked film at room temperature. A crosslinked film made of Di-CyVE-100 could be re-shaped the new shape could be preserved as long as it was kept in cold ice water. Upon removal from the water, it began to unfold at 22°C, finally regaining its original form in approximately 7 minutes (Figure 27) *i.e.* a shape-memory effect within this temperature range was observed. This effect can be explained by a change from a vitrified state at 0°C to a less restricted molecular mobility at room temperature.¹⁰¹ The transition range for Di-CyVE-100 begins above 0 °C. The other samples with lower T_g values are therefore not fully vitrified at this temperature. The rather broad transition range for Di-CyVE-100 also imply that the rate of shape recovery will be temperature dependent.

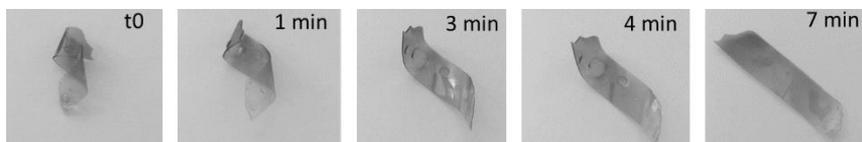


Figure 27. A crosslinked film of 100% Di-CyVE exhibiting shape memory effect in room temperature after having been deformed and “locked” in ice water.

In conclusion, the VE-ester oligomers can be synthesized rapidly by enzyme catalysis with little to no side reactions and no purification steps necessary. At the same time, oligomers with different structures can be combined in different ratios and cationically crosslinked in a few seconds to yield polymer networks with fine-tuned properties.

3.6 Functional polymer networks based on vinyl ethers

Since HVELA can be polymerized with cationic initiation without affecting the amount of disulfides to any significant extent, this monomer was copolymerized with the difunctional VE oligomer Di-CyVE by cationic polymerization to give polymer networks that can be post-functionalized. The formed films had different thermo-mechanical properties depending on the ratio of HVELA to Di-CyVE (Figure 28). Increasing amount of HVELA resulted in softer materials with lower T_g which is reasonable since the crosslinking density becomes lower.

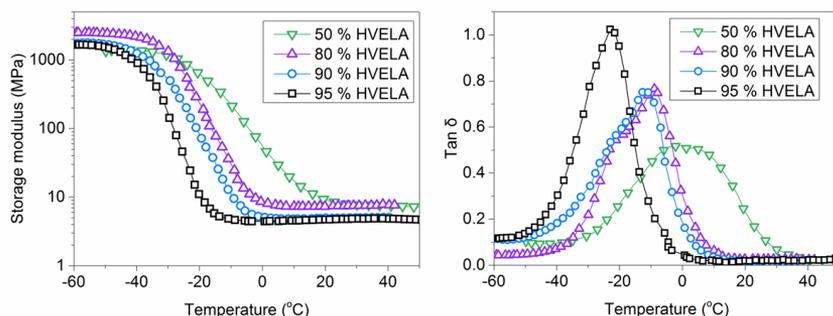
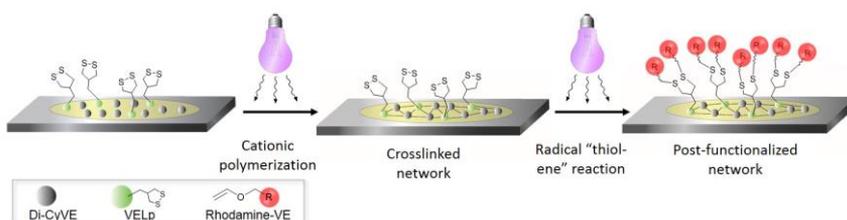


Figure 28. Thermo-mechanical properties of films made from different compositions of HVELA and Di-CyVE, assessed with DMA.

The crosslinked films were immersed in a solution containing radical photoinitiator and VE functionalized Rhodamine and subsequently irradiated with UV light on both sides (Scheme 9). Since VEs do not homopolymerize radically, but do react with the cyclic disulfide, the only possibility for Rhodamine-VE to react by radical initiation would be to form a covalent bond to one of the sulfurs in the disulfide ring which is part of the crosslinked network.

Scheme 9. Crosslinking and postfunctionalization of networks containing Lipic acid moieties.



After washing in methanol multiple times and soaking the films in methanol for several hours to leach any unbound Rhodamine, the dye was still present on the films (Figure 29). The difference in HVELA content of the films also becomes evident since increasing amount of HVELA resulted in films that had a stronger intensity of the remaining dye (Figure 29). As a reference, one of the networks was composed of 50% HVEUA and 50 % Di-CyVE in order to show that the dye would not attach without the presence of disulfide groups, even though the film was treated the same way as the other films (sample to the furthest left in Figure 29).

In summary, utilizing enzyme catalysis it was possible to synthesize vinyl ether-ester monomers with dual functionality in an efficient and benign way. These can be used to develop polymers with different architectures as well as used to develop polymer networks that may be post- functionalizable.

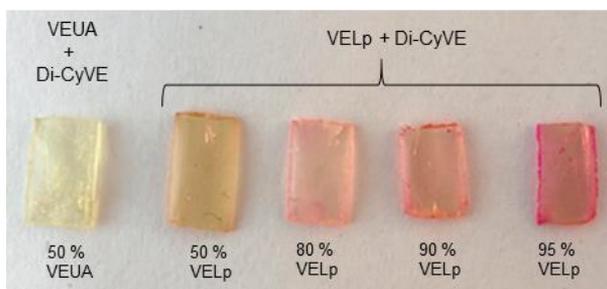


Figure 29. Crosslinked films made from HVELA and Di-CyVE in different ratios that have been post-functionalized with Rhodamine-VE and thereafter washed and incubated in methanol. Sample on the far left is unmodified despite having been treated identically to the others because it did not contain any HVELA.

4. Conclusions

The aim of this work has been to develop polymer networks from bio-based resources *via* sustainable chemistry, and to demonstrate the possibility to tune the final mechanical properties of the networks. The work herein shows that itaconate based polyesters can be synthesized in bulk and UV-cured efficiently and that the material properties can be tuned by varying the monomer composition. However, it is important that the synthetic strategy is chosen with care as different side-reactions takes place if the conditions are not optimized. Ti(OBu)₄, *p*TSA and CalB can be used as catalysts for itaconic acid/dimethyl itaconate based polyesters, but if 1,4-butanediol is used, all forms of acid should preferably be avoided. Compared to other traditional catalysts, such as metal catalysts and acid catalysts, the CalB was a good choice as it can give the same result of the final crosslinked network properties while also decreasing the number of side reactions that may take place. The synthesis was performed at lower temperature which reduces the energy consumption of the synthesis. Furthermore, it is possible to remove and recycle the enzyme after the reaction, the enzyme is non-toxic, efficient and does not discolor the products which is an important factor in many applications.

It was also demonstrated that the immobilized CalB enables the synthesis of new vinyl ether monomers. These monomers can also have orthogonal functionality which can be useful in a range of different materials applications. One example of an application is coating primers where a remaining functional group can be useful to bind the next layer of coating. It could also be interesting in biomedical applications when for example the binding of a target ligand into different kinds of drug delivery systems is desirable. With the herein developed synthetic methods, a wide range of new vinyl ether monomers can be developed for the design of new polymers and polymer networks.

Considering the principles of green chemistry, the materials synthesized in this work fulfill many of these principles: during the synthesis the majority of the by-products has only been water or methanol which can be distilled off and potentially recycled, thereby preventing excessive waste. By utilizing enzyme catalysis, the direct esterification of vinyl ether esters was possible thus avoiding several reaction steps and number of reaction intermediates. None of the produced oligomers/polymers are hazardous and the majority of

the syntheses are performed in solvent-free conditions. Furthermore, the combination of enzyme catalysis and photopolymerization with bio-based raw materials creates a sustainable and energy efficient process.

In conclusion, there are already a wide range of bio-based monomers available and new monomers are continuously developed. Many of these monomers as well as fatty acids are promising for use in polymer applications to replace fossil based polymers. Combining these bio-based starting materials together with enzymatic catalysis and photopolymerization provides new synthetic pathways for the development of polymeric materials in more sustainable ways. This thesis demonstrates some of the possibilities for these classes of materials.

5. Future work

The use of lipase catalysis with CalB provides an opportunity to create new monomers and oligomers with multiple functionalities. It would be interesting to continue the development of new orthogonal molecules that can be used in material applications such as drug delivery systems or polymer grafting. The enzyme gives an opportunity to develop new kinds of materials in reaction conditions that are benign. For example, a lot of work has been done on self-healing materials based on disulfide networks, but commonly synthesis of these materials presented in literature use many different toxic compounds which could be avoided by using immobilized CalB instead.

Comparing the work performed in this thesis with an industrial level of resin synthesis, there is a long way to go with scale up. During this work, the first synthesis of VE-esters were performed on 1 g scale and towards the end scales up to 20 g were made of the products. To see how the synthesis works on a larger scale and development of more efficient recycling of the enzyme would be of great interest in order to save resources and decrease the cost so that it could be applied on an industrial level.

Moreover, while many of the principles of green chemistry has been fulfilled in this work, it would be attractive to develop polymer networks that are stable in their area of application, but that are able to degrade after their end-use. This could for example be performed by enzymatic degradation, degradation by active microorganisms or certain type of reactions with reversible covalent bonds.

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