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Synthesis of bisvanillonitrile-based monomers and polymers

Bachelor's Thesis (12 ECTS)

Curriculum Science and Technology

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Tartu 2022

Resümee/Abstract

Synthesis of bisvanillonitrile-based monomers and polymers

The purpose of this work was to investigate the synthesis of bioderived bisvanillonitrile-based acrylic monomer and associated biobased polymer. Bisvanillin derivatives as the building blocks are appealing due to its rigid structure and the fact that it's generated from biomass. Firstly, this thesis presents the synthesis of the diacrylate of bisvanillonitrile. Secondly, the obtained diacrylic bisvanillonitrile and 1,6-hexanedithiol were used to prepare the corresponding biobased copolymer. Finally, the structural properties of the synthesized novel monomer and polymeric material were studied by NMR and IR techniques.

Keywords: *Biobased, sustainable, bisvanillonitrile, poly(β-thioester)*

CERCS: T390 Polymer technology, biopolymers; P390 Organic chemistry

Bisvanillonitriilil põhinevate monomeeride ja polümeeride süntees

Käesoleva töö eesmärgiks oli uurida bisvanillonitriilil põhineva akrülaat-monomeeri sünteesi ja vastava polümeeri valmistamist. Bisvanilliinist saadud struktuuriühikud on huvipakkuvad oma jäiga struktuuri ja biopõhistest lähteainetest pärinemise tõttu. Esmalt uuriti selles töös diakrülaadi sünteesi bisvanillonitriilist. Järgnevalt kasutati saadud diakrülaati ja 1,6-heksaanditiooli vastava biopõhise kopolümeeri sünteesimiseks. Sünteesitud uue monomeeri ja polümeeri struktuurid karakteriseeriti tuumamagnetresonantsspektroskoopia ja infrapunaspektroskoopia abil.

Võtmesõnad: *biomaterjalidel põhinev, jätkusuutlik, bisvanillonitriil, polü(β-tioester)*

CERCS: T390 Polümeeride tehnoloogia, biopolümeerid; P390 Orgaaniline keemia

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TERMS, ABBREVIATIONS AND NOTATIONS

BVN – bisvanillonitrile

DBU – 1,8-diazabicyclo[5.4.0]undec-7-ene

DMF – *N*,*N*-dimethylformamide

DMSO – dimethyl sulfoxide

Et_3N – triethylamine

EtOAc – ethyl acetate

IR – infrared spectroscopy

iSDA – isosorbide diacrylate

MeOH – methanol

NMR – nuclear magnetic resonance spectroscopy

PE – petroleum ether

PEF – polyethylene furanoate

PLA – polylactic acid

PET – polyethylene terepthalate

SEC – size exclusion chromatography

THF – tetrahydrofuran

TLC – thin layer chromatography

INTRODUCTION

Recent green chemistry research and development is based on biobased chemicals, which have the potential to significantly reduce the amount of petroleum consumed in the industry, as well as produce high-quality products from renewable sources. In general, vanillin is one of such biobased chemicals that has the potential to become a key-intermediate in the synthesis of biobased polymers (Fache *et al*., 2016). It can be easily derived from lignin-based biomass on large scale (Fache *et al*., 2016; Silva *et al*., 2009a).

Diverse methods of using vanillin derivatives as building blocks for novel polymers have attracted the curiosity of researchers(Fache *et al*., 2014). Additionally, the diderivative of vanilline-bisvanilline, is also an interesting biobased building block. In this work it was decided to use the rigidity of bisvanilline to prepare novel biobased high-performance polymers that can exhibit high glass transition temperature values (Bonjour *et al*., 2021). Generally, nitrile groups also add more rigidity to the molecular structure. Therefore, bisvanillonitrile was used as a starting material in this work to prepare novel biobased materials.

In short, the objectives of this work are as follows:

1. synthesis of diacrylate of bisvanillonitrile,
2. synthesis of biobased polymer from the obtained monomer.

Acrylation was chosen as the simple modification of the bisvanilline to introduce the polymerizable moiety into the polymer structure. Acrylates are highly reactive in the reaction with thiols, therefore the polymerization of diacrylate and dithiol was chosen as the method for obtaining the polymer. Thiols' broad reactivity, owing primarily to the presence of a highly reactive sulfur atom in their structure that modifies its valence state and the strong lability of the S-H bond, enables the production of a wide range of polymers (Glass, 2019; Koval, 2007).

This work gives first example of a copolymer synthesized from bisvanillonitrile-diacrylate and a dithiol.

1 LITERATURE REVIEW

1.1 Biobased polymers

Polymer chemistry has evolved from lab-scale studies to a massive plastic industry, supplying us with a wide range of useful materials ranging from lightweight packaging to long-lasting construction materials.

However, preparing synthetic polymers from fossil fuel is not a sustainable strategy. Since lignocellulosic biomass is the most plentiful raw material accessible at the moment, it could be used as an alternative to fossil carbon sources for polymer manufacturing (Delidovich *et al*., 2016; Isikgor & Becer, 2015). Lignocellulosic biomass is primarily composed of three components: cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%), all of which can serve as valuable building blocks for polymers (**Figure 1**) (Al-Naji *et al*., 2021; Delidovich *et al*., 2016; *Paper Hemicellulose Lignocellulosic Biomass Lignin, Plants, Text, Label, Logo Png | PNGWing*, n.d.). Cellulose is a semicrystalline polysaccharide made up of glucose units, whereas hemicellulose is an amorphous carbohydrate polymer made up mostly of xylose, and lignin is an amorphous heteropolymer with a variable structure and multiple aromatic sections. The feedstock determines the precise proportion of lignocellulosic biomass (Luterbacher *et al*., 2014).

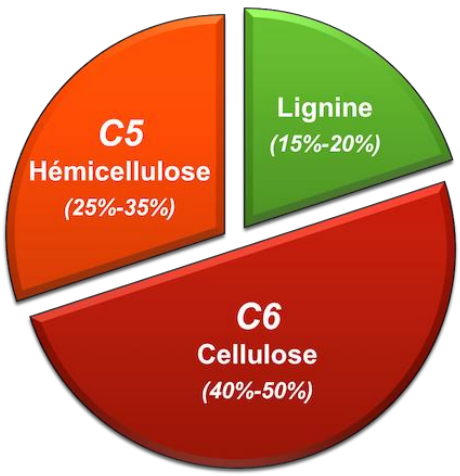


Figure 1. Lignocellulosic biomass (*Paper Hemicellulose Lignocellulosic Biomass Lignin, Plants, Text, Label, Logo Png | PNGWing*, n.d.).

Biobased compounds are chemical molecules generated from biomass, and biobased polymers are polymers manufactured from them (García-Depraect *et al*., 2021). In this thesis, biobased polymers refer to polymers made from biomass-derived monomers. Throughout the mid-twentieth century, the polymer industry relied entirely on petroleum-derived chemical, refining, and engineering processes (Zhu *et al*., 2016). Suddenly, biodegradable polymers such as polylactides, poly(hydroxy alkanoates), and succinate-derived polymers flourished in order to tackle the majority of difficulties in the agriculture and construction industries (Maiorana *et al*., 2015). Furthermore, the development of refinery operations has been greatly expedited as a result of advancements in the integration of chemical and biological pathways for the manufacture of various polymers. Alternatively, it is possible to convert biomass feedstock into raw materials for polymer synthesis, with the resulting polymers referred to as biobased polymers. Overall, economic studies have shown that biobased polymers can create new business prospects and long-term growth in new plastic industries (Rapeyko *et al*., 2017).

1.1.1 Applications of biobased polymers

Different industrial branches such as the paper, textile, packaging, food, and pharmaceuticals, utilize the most common natural sources derived from plant cell walls. Various strategies of impartion of thermoplastic processing capabilities to naturally non-thermoplastic polymers (**Figure 2**), are known to be testified and proven approaches (Wang *et al*., 2016). For instance, polylactic acid (PLA) has been used in the packaging sector as a result of improvements in its physical durability and processability (de Clercq *et al*., 2017). Furthermore, polyethylene furanoate (PEF) is employed in the food and beverage industry for bottles, films, and other packaging materials, due to its outstanding gas barrier qualities (Imre *et al*., 2019; Ng *et al*., 2017; Nguyen *et al*., 2018). As a result, biobased PEF is equivalent to petroleum-derived polyethylene terephthalate (PET), and its flexible chain, which allows for stretching and form recovery, is very appealing (Horvath *et al*., 2018; Nakajima *et al*., 2017; Rapeyko *et al*., 2017). A well-known succinate polymer – poly(butylene succinate) is made by direct polycondensation of succinic acis and butanediol (Vandekerkhove *et al*., 2018).

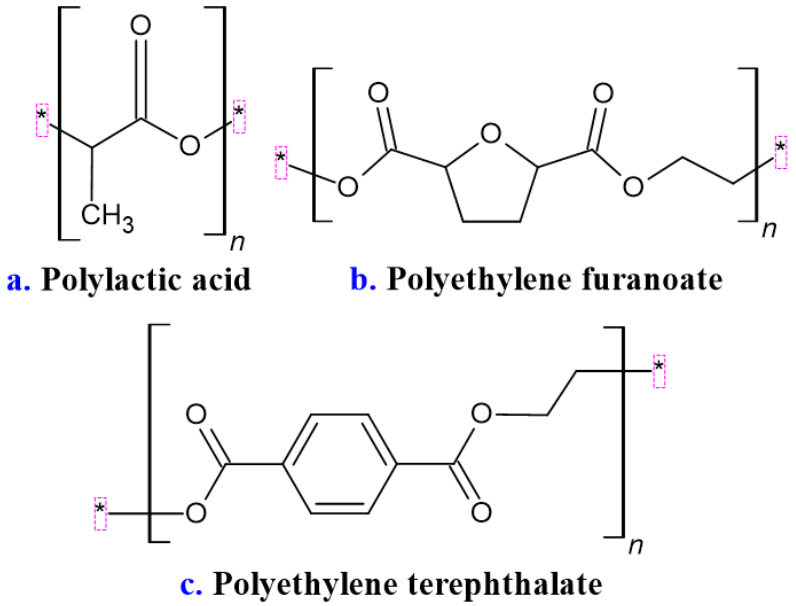


Figure 2. Examples of biobased polymers (a,b), structure of widely known oil-based polymer PET (c).

1.2 Polymerization methods

Polymerization is the process of connecting monomers together to form macromolecules of various sizes and forms. According to reaction mechanism, polymerization methods are divided into two major groups of chain-growth and step-growth polymerizations (Odian, 2004).

The two groups, principal differences are the species that react with each other and the molecular weight dependence on the level of conversion (**Table 1**) (Odian, 2004). In the instance of chain-growth polymerization, an initiator is used to activate the polymerization reaction, and the chain grows by adding one monomer at a time to the active species (Carraher, n.d.). As a result, the polymer's molecular weight rapidly increases to a very high value, and the reaction mixture always contains primarily monomers and polymers, but also minor amounts of developing chains.

Chain-growth polymerization takes place by repeated additions of monomers to the growing polymer chain. The most basic example includes the formation of polyethylene from ethylene molecules by the opening of a double bond, with two of the electrons initially in this link being used to form new carbon-carbon single bonds with two other ethylene molecules (Hadjichristidis *et al*., 2010). Commercially available chain-growth polymers in-

clude polyethylene (films, packaging, bottles), polypropylene (kitchenware, fibers, appliances) and polyvinyl chloride (pipe fittings, clear film for meat packaging).

On the other hand, step-growth polymerization takes place by reaction between monomers, oligomers, and polymers (Carraher, n.d.; Ito, 2016). Commercial step-growth polymers include polyurethanes, polyethylene terephthalate (a polyester) and nylon 6,6.

Table 1. Main differences between chain-growth and step-growth polymerizations.

Chain-Growth	Step-Growth
Only monomers react to the active site at the end of the growing chain, during propagation	All molecules present (monomer, oligomer, polymer) can react with any other molecule.
Monomers exist throughout the reaction; its concentration decreases steadily with time.	Monomers exist throughout the reaction, but large quantities of monomers are consumed early in the reaction.
There are two distinctive mechanisms during polymerization; these are initiation and propagation. In most cases there is also a termination step.	There is no termination step and the end groups of the oligomers and polymers are reactive throughout the polymerization process.
The reaction speed depends on the concentration of initiator (and co-initiator) and high-molecular weight polymers form throughout the duration of the reaction.	The reaction proceeds rapidly at the beginning but the molecular weight increases only slowly and high MW's are only attained at the end of the process by long oligomers reacting with each-other.
Long reaction times have high degrees of conversion but do not affect (much) the (average) molecular weight.	Long reaction times are needed for the synthesis of long (high molecular weight) polymers.
The mixture contains primarily monomers and polymers, and only small amounts of growing polymer chains;	Molecular species of any length (oligomers) exist throughout the reaction, with the length distribution broadening and shifting to higher MW with increasing reaction time.

Cross-linked polymers are a type of polymer in which the molecular chains are linked together. They are frequently thermosetting, meaning they cannot be melted or dissolved. To induce polymer cross-linking, the polymerization temperature can be raised. Many poly-

mers, including nylons, poly(vinyl alcohols), and cellulose, exhibit hydrogen bonding cross-linking. It is also possible that poly(vinyl chloride) is cross-linked in some fashion by hydrogen bonding via plasticizers such as tritolyl phosphate (Zhang *et al*., 2019). Additionally, diacrylic monomers can also be used as cross-linker units in different polymer structures.

1.2.1 Synthesis of poly(β-thioester)s

One interesting polymerization method in which diacrylates can be used is the synthesis of poly(β-thioester)s by Thiol-Michael mechanism. This polymerization type belongs to the step-growth polymerization methods. For the reaction to happen between SH-group and a double bond initiation by a base or a nucleophile is needed. The Thiol-Michael mechanism is demonstrated in **Figure 3** (Moon *et al*., 2018).

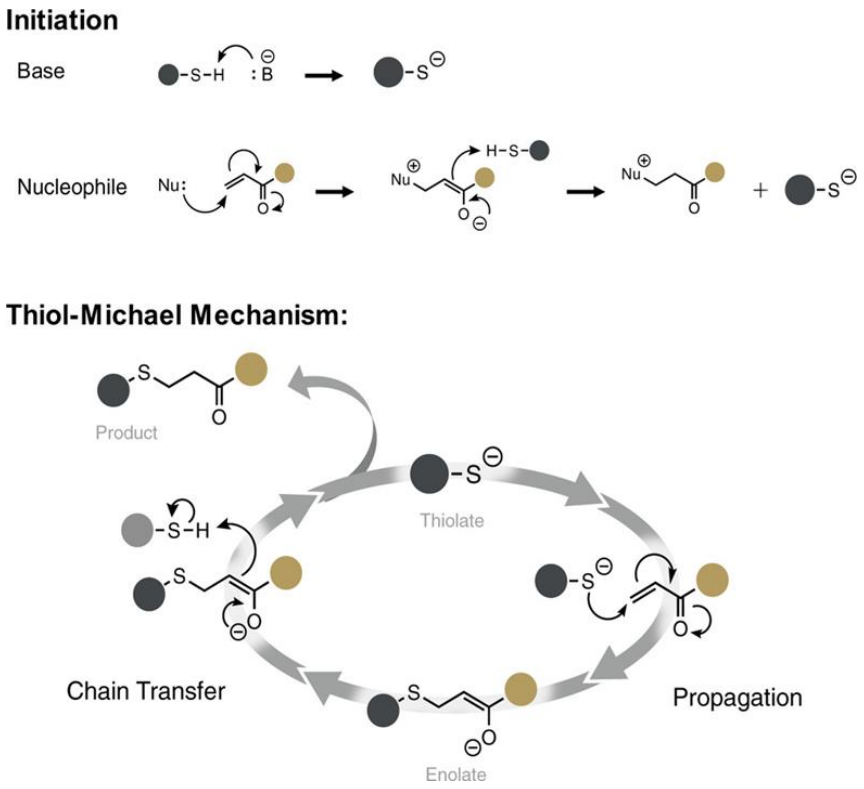


Figure 3. Initiation and the thiol-Michael mechanism (Moon *et al*., 2018).

In base-catalyzed reactions, a base abstracts hydrogen to form a thiolate anion, which then enters the thiol-Michael process. A nucleophile attacks the unsaturated -carbon of the

Michael acceptor in nucleophile-catalyzed reactions. The enolate formed then extracts hydrogen from a thiol to form the thiolate anion. An intrinsic side product of the catalyst's nucleophilic assault is the residual product. The thiolate anion attacks the Michael acceptor's unsaturated carbon, producing a negatively charged enolate. The enolate then extracts hydrogen from a fresh thiol, creating both the thiolate anion and the thioether product. In case of polymerization reaction, after many cycles, the product is then poly(β-thioester).

1.3 Vanillin

Vanillin (**Figure 4**) is a naturally occurring substance found in *Ficus erecta var. beecheyana, Pandanus utilis*, and other organisms. Vanillin appears as white or very slightly yellow needles. The molecule has a chemical formula $C_8H_8O_3$ and a molecular weight of 152.15 g mol^{-1}. The reported boiling point for vanillin is 285 °C (Boivin *et al*., 2021; *Vanillin - American Chemical Society*, n.d.).

Vanillin is a lignin-inspired building block that correlates to the guaiacyl lignin unit. The building block of this phenolic ring is substituted with one methoxy group, which optimizes chain rigidity (Fache *et al*., 2016).

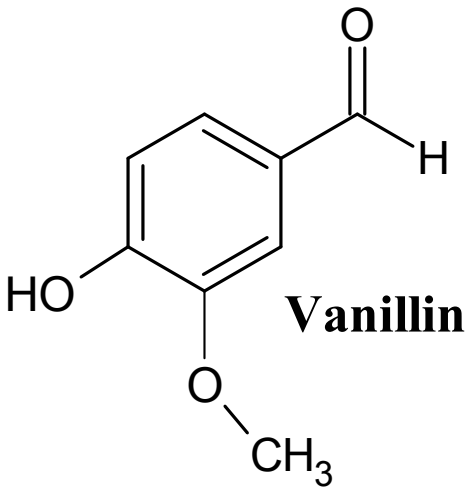


Figure 4. Structure of vanillin.

1.3.1 Manufacturing of vanillin

Converting lignocellulosic biomass into useful chemicals and fuels is now a viable technique for reducing energy depletion. Lignocellulosic biomass is the most abundant natural carbon source, and it is plentiful in the world of biomass (Norgren & Edlund, 2014). It has garnered extensive interest in producing chemicals using a variety of specialized processing systems. As a result, using lignocellulosic biomass as a feedstock may be the most efficient approach to achieving a future sustainable civilization (Boivin *et al*., 2021; Fache *et al*., 2016). Despite the fact that lignin from the sulfite pulping process accounts for less than 10% of the total lignin removed, it is used to make vanillin in the industrial world (Rodrigues Pinto *et al*., 2012). Nowadays, 15% of the overall vanillin production comes from lignosulfonates. The lignosulfonate-rich sulfite liquor is produced as a byproduct of the sulfite pulping of wood. **Figure 5** depicts the subsequent processing of this liquor (Belgacem *et al*., 2008).

Kraft lignins - a type of industrial lignin obtained from Kraft pulp, make up the vast bulk of lignins removed. They are often burned for energy to keep the pulping process viable (Silva *et al*., 2009b). However, an increasing number of studies are looking at the depolymerization of various lignins, including milled wood lignins, organosolv lignins, and lignins obtained through enzymatic procedures (C. Li *et al*., 2015; Zakzeski *et al*., 2010). This is in accordance with the biorefinery strategy, which uses lignins as a source of medium-to-high added-value aromatic building blocks rather than burning them (C. Li *et al*., 2015; Silva *et al*., 2009a). This is also the strategy chosen for this study, which aims to produce vanillin by depolymerizing various lignins under alkaline and oxidative conditions.

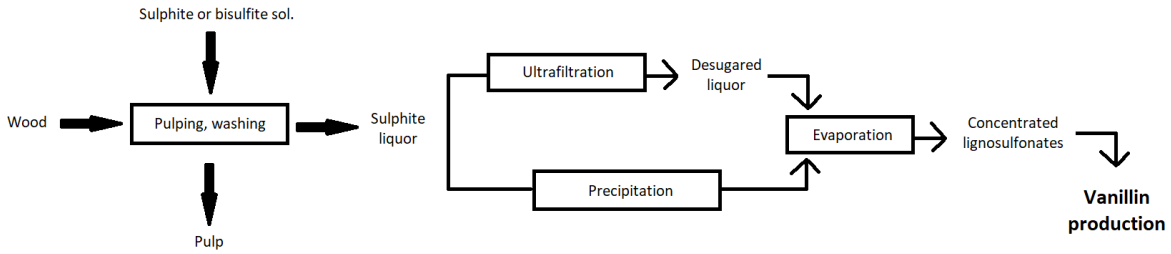


Figure 5. Production of vanillin from wood biomass.

1.3.2 Applications of vanillin

Vanillin is known to be used in flavorings, foods, fragrances, and medications. Almost all vanillin used in foods is synthetic, derived primarily from petrochemical feedstocks. It's a chemical, that can be intermediary utilized in the production of several key medications and other items. Vanillin has a poor bioaccumulation potential in aquatic species. It is widely acknowledged to be safe for use as a flavoring agent in foods and beverages (Boivin *et al*., 2021; Fache *et al*., 2016).

1.4 Vanillonitrile

Vanillonitrile (**Figure 6**), also known as 4-hydroxy-3-methoxybenzonitrile is a rigid chemical produced from vanilline. It has the formula of $C_8H_7NO_2$ and a molecular weight of 149.15 g mol^{-1}. The reported boiling point for bisvanillonitrile is 291 °C (760 mmHg). Additionally, vanillonitrile is an acutely toxic chemical compound (*4-Hydroxy-3-Methoxybenzonitrile | C8H7NO2 - PubChem*, n.d.; *Vanillonitrile, 4421-08-3*, n.d.).

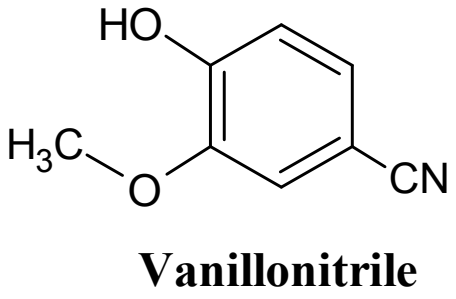


Figure 6. Structure of vanillonitrile.

1.4.1 Manufacturing of vanillonitrile

Vanillonitrile can be obtained directly from a commercial source. Alternatively, it is possible to produce it from vanillin by green catalysis or by directly converting the methyl group of 4-methylguaiacol through ammoxidation. Nitrilation is easily achieved in the-industrial environment utilizing ammonia, oxygen, and a vanadium or molybdenum oxide catalyst (Boivin *et al*., 2021).

2 THE AIMS OF THE THESIS

The main objective of the current thesis was to polymerize bisvanillonitrile derivatives into novel biobased materials. To accomplish this goal, the work was divided into two parts:

1. synthesis of diacrylate of bisvanillonitrile,
2. synthesis of biobased polymers from the obtained monomer.

3 EXPERIMENTAL PART

3.1 Characterization techniques

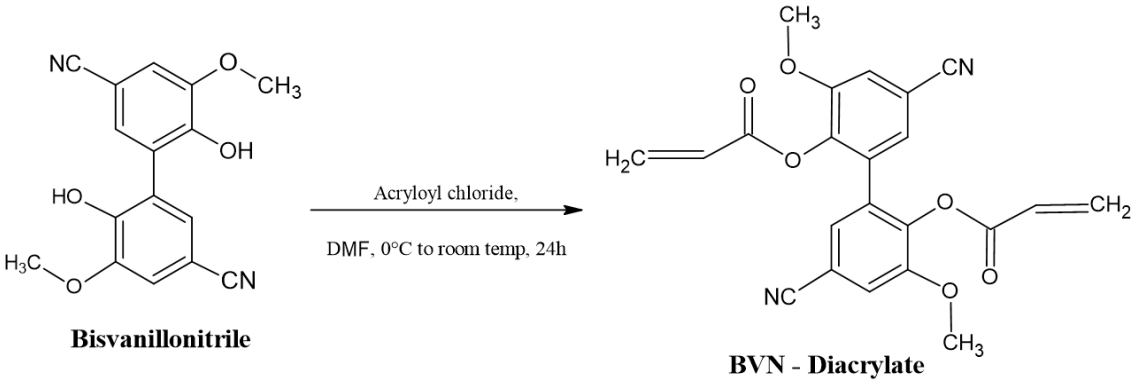
Nuclear magnetic resonance spectroscopy (NMR) was used to study the structures of the compounds; ^{1}H and ^{13}C spectra were acquired on a 400 MHz Bruker spectrometer at 400.1 and 100.6 MHz, respectively. For each compound, suitable deuterated solvents ($CDCl_3$, DMSO-d_6) were selected. Chemical shifts are expressed in parts per million (ppm). The following abbreviations are used for multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broadened singlet. Shimadzu IR Affinity-1 FTIR (ATR) spectrophotometer was used to record infrared spectra.

Size-exclusion chromatography (SEC) in THF was used to determine the molecular weights of the polymers. The SEC setup included three Shodex columns coupled in series (KF-805, 804, and -802.5) in a Shimadzu CTO-20A prominence column oven, a Shimadzu RID-20A refractive index detector, with Shimadzu Lab Solution software. All samples were run at 40 °C in THF and at an elution rate of 1 mL/min. Calibration was done by using poly (ethylene oxide) standards (M_n = 3 860, 21 160, 49 640, and 96 100 g mol^{-1}).

3.2 Synthesis of bisvanillonitrile diacrylate and its copolymer with dithiol

In this section the synthesis of diacrylate of bisvanillonitrile is demonstrated. Additionally, one polymerization attempt with 1,6-hexanedithiol is also explained.

3.2.1 Arylation of bisvanillonitrile with acryloyl chloride in DMF



Scheme 1. Synthesis of BVN-diacrylate.

BVN (202.4 mg, 0.68 mmol, 1 eq) was transferred into a 25 ml round-bottom flask fitted with a magnetic stirrer bar. A septum was then used to seal the flask. Degassing was done by replacing the air in the flask with Argon three times using a vacuum/argon cycle and then leaving it under an Ar-balloon connected via a syringe needle to generate an inert gas atmosphere. DMF (5 ml), followed by Et_3N (0.22 ml, 1.76 mmol, 2.5 eq) were taken with a syringe and added to the reaction flask. The flask was then left for continuous stirring and placed on an ice bath. For the following 30 minutes, acryloyl chloride (C_3H_3ClO) (142 µl, 1.76 mmol, 2.5 eq) was added dropwise to the reaction flask. After that, the ice bath was removed, and the mixture was left stirring overnight at room temperature. The next day, the reaction was stopped, and a small amount of sample was taken for the ^1H NMR measurement in $CDCl_3$. For further analysis, a TLC plate was prepared (10% $MeOH/CH_2Cl_2$). Several spots were seen from the TLC plate. After the obtained spectrum and the TLC results, a work-up was carried out. First, EtOAc (45 ml) was added to the crude mixture. Then, the organic phase was washed with aqueous NH_4Cl solution (10 ml, 3 times) and with distilled water (10 ml, 2 times) using a separatory funnel. After the separation, the organic phase was collected in the beaker. The following step was to dry the organic phase over $MgSO_4$. Next, the filtration was carried out using EtOAc for washing and the filtrate was later dried with rotary evaporator. The obtained product (140.2 mg) was a solid white powder. After the work-up TLC analysis and ^1H NMR measurement were carried out.

Purification of the product was performed with the help of column chromatography. Silica gel was used as a stationary phase, as for the mobile phase – different concentrations of

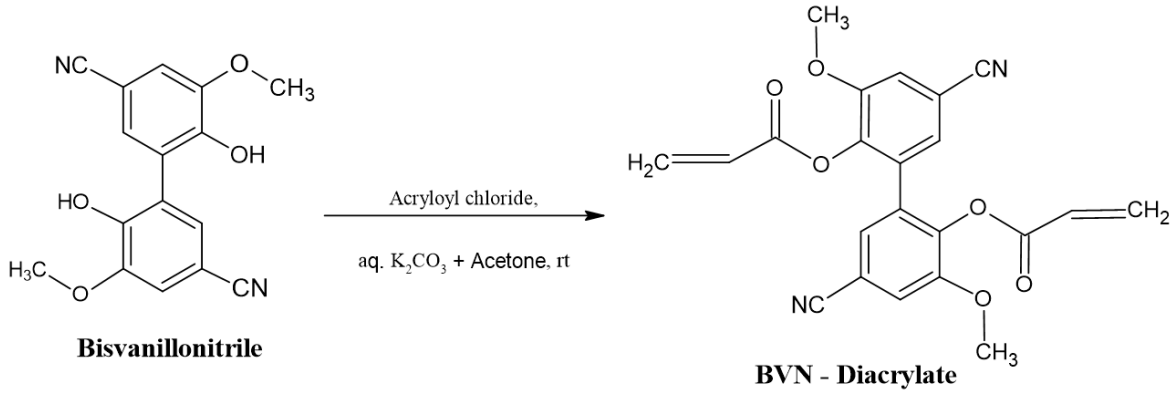
ethyl acetate in petroleum ether were used and refilled while collecting into test tubes. TLC analyses were performed for screening the product. The dissolved product came out while using a mobile phase of 30% EtOAc/PE. Based on the TLC results, contents from the reaction tubes (fractions 4-8) were collected into a flask. The flask was then placed under a rotary vacuum evaporator to remove the solvent. Afterward, the final weight of the product (115.8 mg, yield 42%) was obtained. Next, ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were measured, followed by IR analysis.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.24 (d, J = 1.8 Hz, 2H), 7.18 (d, J = 1.8 Hz, 2H), 6.48 (dd, J = 17.2, 1.1 Hz, 2H), 6.15 (dd, J = 17.2, 10.5 Hz, 2H), 5.96 (dd, J = 10.5, 1.1 Hz, 2H), 3.88 (s, 6H) ppm.; (**Figure 7**).

^{13}C NMR (100.6 MHz, $CDCl_3$) δ 162.6, 152.2, 141.4, 133.8, 131.0, 126.38, 126.35, 117.8, 115.6, 110.5, 56.8 ppm.; (**Figure 7**).

IR (ATR) ν_{max} (cm^{-1}): 2854.6-3089.9 (C-H), 2250 (C≡N), 1751.3 (C=O), 1589.34 (C=C stretch), 1134.1 (C-O-C asymm), 891.1 (C-O-C sym), 794.6 (C=C twist); (**Figure 8**).

3.2.2 Arylation of bisvanillonitrile in a mixture of aqueous K_2CO_3 and acetone



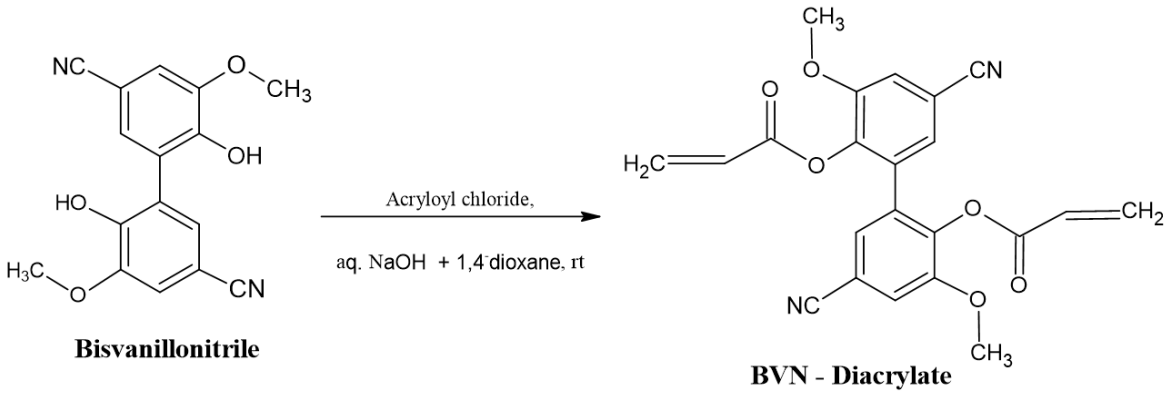
Bisvanillonitrile **BVN - Diacrylate**

Scheme 2. Acrylation of BVN in in a mixture of aq. K_2CO_3 and acetone.

In the first flask, K_2CO_3 (186.4 mg, 1.35 mmol, 2 eq) was mixed with H_2O (0.34 ml) and acetone (1.35 ml). The Argon flow was introduced to the system and the flask was left stirring in an ice bath. Afterward, acryloyl chloride (0.11 ml, 1.35 mmol, 2 eq) was added to the flask. Next, in the second flask, K_2CO_3 (2.76 mg, 0.35 mmol) was dissolved in H_2O (5 ml) and the mixture was then left stirring. Then BVN (202 mg, 0.68 mmol, 1 eq) was

added to this flask with aqueous K_2CO_3 Unfortunately, the BVN did not dissolve in this medium and therefore, this reaction was set aside.

3.2.3 Arylation of bisvanillonitrile in a mixture of aqueous NaOH and 1,4-dioxane

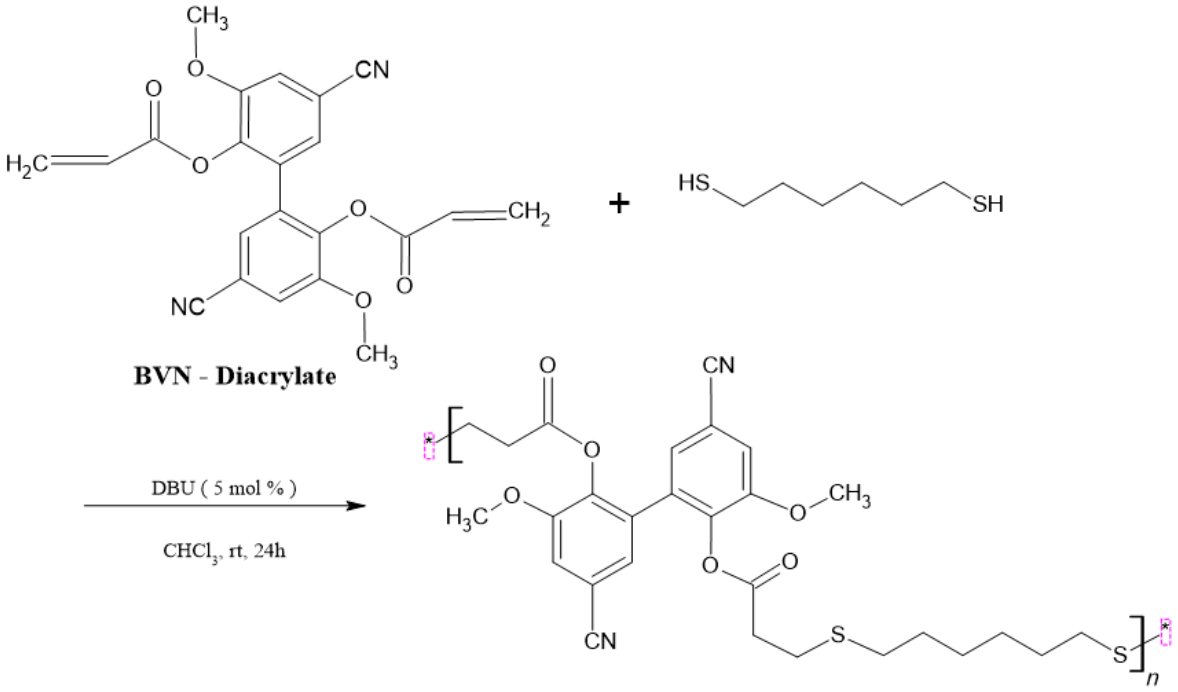


Bisvanillonitrile **BVN - Diacrylate**

Scheme 3. Acrylation of BVN in a mixture of aq, NaOH and 1,4-dioxane.

NaOH-water solution (1 mg in 1.2 ml, 0.02 M) and dioxane (0.4 ml) were added to the flask with bisvanillonitrile (99.6 mg, 0.34 mmol, 1 eq). When bisvanillonitrile was fully dissolved, the flask was purged with Argon, and finally the flask was left under an Ar-balloon connected via a syringe needle through a septum. Then, acryloyl chloride (61 µl, 0.75 mmol, 2.2 eq) was added to the solution. A small amount of sample was then taken for the NMR measurement (DMSO). The mixture was left stirring over the weekend. The NMR spectrum was measured again. In the following step, a separatory funnel was used for the separation of the organic and water phases of the mixture. The water layer was washed with $CHCl_3$ (10 ml, 3 times). Organic layers were collected, and dried over $MgSO_4$. After filtration, the organic layer was dried under rotary evaporator. The weight of the product was obtained – 44.3 mg. The NMR spectrum of the product was measured in $CDCl_3$.

3.2.4 Copolymerization of bissvanillonitrile-diacrylate with 1,6-hexanedithiol



Scheme 4. Copolymerization reaction of BVN-diacrylate with 1,6-hexanedithiol.

For the following polymerization reaction, bisvanillonitrile (58.8 mg, 0.14 mmol, 1 eq) was transferred to a 10 ml round-bottom flask with a magnetic stirrer bar inside. Argon was introduced into the system to create an inert environment for the reaction. The vacuum/Argon cycle was repeated three times. A needle was put through the septum to attach an Argon-filled balloon. Next, $CHCl_3$ (0.5 ml) and 1,6-hexanedithiol (22 µl, 0.14 mmol, 1 eq) were added with a syringe to the bisvanillonitrile. The flask was then cooled down in an ice bath. Next, $CHCl_3$ (20 µl) and DBU (1 µl, 0.0073 mmol, 0.05 eq) were mixed in the small vial and then, with a help of a syringe, transferred to the reaction flask with bisvanillonitrile at 0 °C. The reaction was left stirring overnight at room temperature. On the following day, the reaction was stopped by turning the stirring off, and a small amount of sample was taken for the NMR measurement. After the obtained crude ^1H NMR spectrum, which indicated the formation of a polymer, the reaction mixture was precipitated into Et_2O and allowed to stir overnight. By next morning the polymer had precipitated to the bottom of the beaker. The solvent was decanted, and the polymer residue was transferred to a small vial, while $CHCl_3$ was used as a solvent. Thereafter, the solvent was removed by rotavap, and the polymer was dried further in the vacuum oven at 40 °C for 16 h. The weight of the dried polymer was 34.4 mg (yield 43%). 5.5 mg of the dried polymer was

used for the SEC measurement in THF to determine the molecular mass of the polymer. ^{1}H NMR and IR measurements were also carried out to confirm the structure of the polymer.

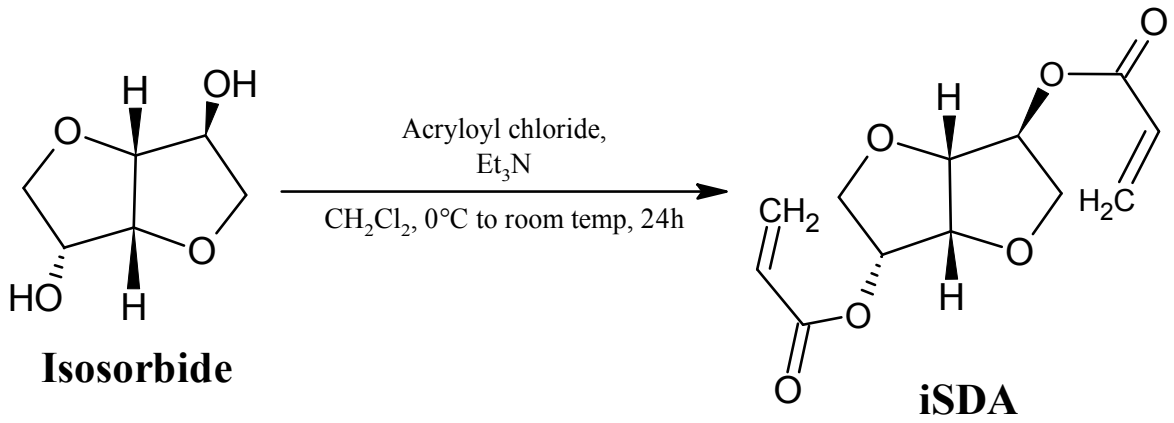
^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.16 (m, 2H), 3.89 (m, 6H), 2.68 (bs, 5H), 2.48 (m, 3H), 1.85-1.47 (m, 7H), 1.37 (m, 5H); (**Figure 10**).

IR (ATR) ν_{max} (cm^{-1}): 2854.6-3089.9 (C-H), 2360.8 (S-H), 2250 (C≡N), 1766.8 (C=O), 1589.34 (C=C stretch), 1284.5 (C-O-C asymm), 910.4 (C-O-C sym), 732.9 (C=C twist); (**Figure 11**).

3.3 Isosorbide diacrylate and its copolymers with dithiols

In this section, synthesis of isosorbide diacrylate (iSDA) and copolymerization reactions of iSDA with two different dithiols are described. The synthesis of iSDA has been reported before in scientific literature (Moon *et al*., 2018). Similar copolymerizations of iSDA and dithiols have also been demonstrated (Moon *et al*., 2018) In this thesis these polymerization reactions were carried out as a part of practice, and also for comparison purpose.

3.3.1 Synthesis of iSDA



Scheme 5. Synthesis of iSDA from isosorbide.

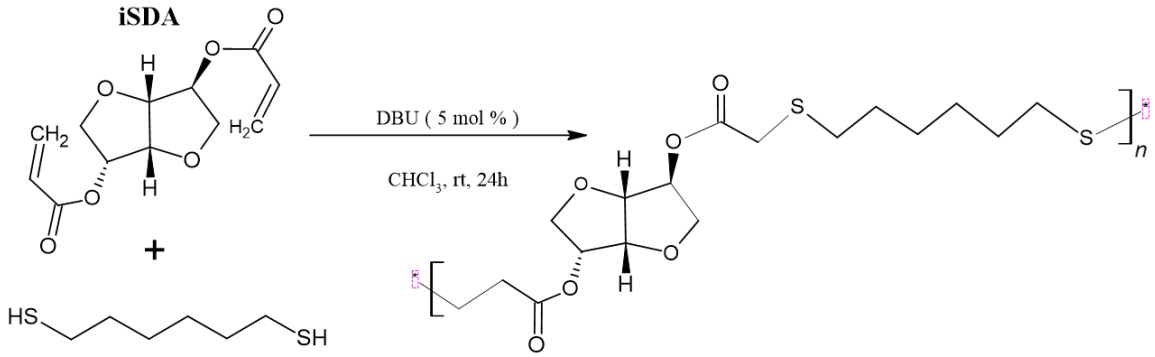
Isosorbide (2.55 g, 17.4 mmol, 1 eq) and DMAP (212.5 mg, 1.74 mmol, 0.1 eq) were added to a round-bottomed flask and dissolved in CH_2Cl_2 (2.3 ml). The flask was capped with a septum and the headspace was flushed with Ar. Et_3N (6.03 ml, 43.5 mmol, 2.5 eq) was added and the solution was cooled to 0 ºC in an ice bath. Acryloyl chloride (3.52 ml,

43.5 mmol, 2.5 eq) dissolved in 30 ml CH_2Cl_2 was added dropwise over 30 min to the reaction flask. The reaction was covered, allowed to warm to room temperature, and stir for 20 h. The sample changed its colour to yellowish. The reaction mixture was filtered to remove Et_3N * HCl and transferred to the separatory funnel. The organic layer was washed with 2x50 ml $NaHCO_3$, 1x50 ml dilute HCl, and 1x50 ml brine. The organic layer was dried with $MgSO_4$ and concentrated with rotary evaporator. The crude oil was purified by flash column chromatography using 1:4 to 1:2 EtOAc:PE to give the product as a white solid (2.08 g, 83.9% yield).

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 6.44 (ddd, J = 17.3, 15.4, 1.3 Hz, 2H), 6.14 (ddd, J = 27.8, 17.3, 10.4 Hz, 2H), 5.88 (ddd, J = 10.4, 6.4, 1.3 Hz, 2H), 5.28 (m, 1H), 5.23 (q, J = 5.4 Hz, 1H), 4.89 (t, J = 5.0 Hz, 1H), 4.54 (d, J = 4.6 Hz, 1H), 4.05-3.94 (m, 3H) 3.86 (dd, J = 9.3, 5.4 Hz, 1H).; (**Figure 13**).

The NMR data is consistent with previous literature report (Moon *et al*., 2018).

3.3.2 Copolymerization of iSDA and 1,6-hexanedithiol



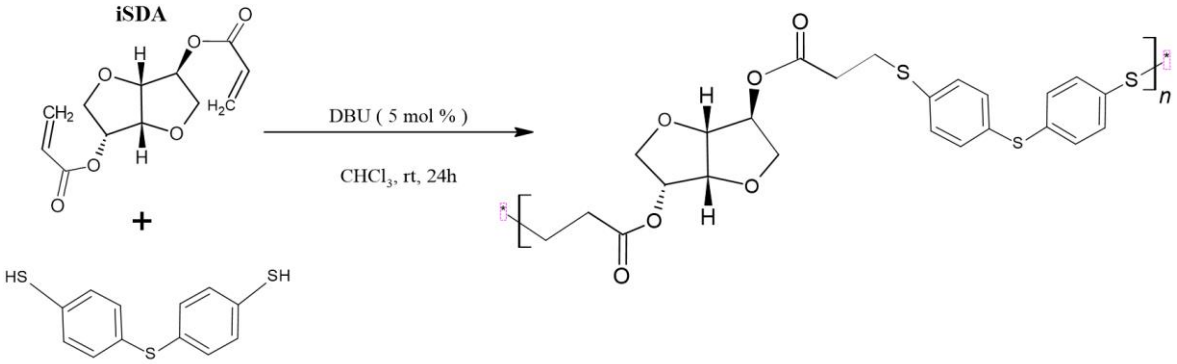
Scheme 6. Copolymerization of iSDA and 1,6-hexanedithiol.

In the following procedure, iSDA (100.3 mg, 0.39 mmol, 1 eq) and 1,6-hexanedithiol (61 µl, 0.39 mmol, 1 eq) were added to a round-bottomed flask and dissolved in $CHCl_3$ (2.3 ml). The flask was capped with a septum, the headspace was flushed with Ar, and the solution was cooled to 0 ºC in an ice bath. DBU (10 µl, 0.019 mmol, 0.05 eq) was added and the solution was allowed to slowly warm to room temperature and stir for 24 h. The sample changed its colour to yellowish. Measured the ^{1}H NMR spectrum of the reaction mixture. The polymer mixture was precipitated into Et_2O and allowed to stir overnight. By next morning the polymer had precipitated to the bottom of the beaker. The solvent was

decanted and the polymer residue was transferred to a small flask, while $CHCl_3$ was used as a solvent. Thereafter, the solvent was removed by rotavap, and the polymer was dried further in the vacuum oven at 40 °C for overnight. The final polymer was a white powder (66 mg, 41%). The ^1H NMR spectrum of the obtained polymer was measured. Small amount of polymer was taken for the SEC testing (11 mg/1 ml THF).

^1H NMR (400.1 MHz, $CDCl_3$) δ 5.4 (m, 2H), 4.85 (m, 1H), 4.50 (m, 1H), 3.97 (m, 3H), 3.82 (m, 1H), 2.77 (m, 3H), 2.64 (m, 4H), 2.52 (m, 3H), 1.65 (m, 2H), 1.57 (m, 4H), 1.38 (m, 4H) ppm.; (**Figure 14**).

3.3.3 Copolymerization of iSDA and 4,4'-thiobisbenzenethiol



Scheme 7. Copolymerization of iSDA and 4,4'-thiobisbenzenethiol.

For this method, iSDA (100 mg, 0.39 mmol, 1 eq) and 4,4-thiobisbenzenethiol (97.6 mg, 0.39 mmol, 1 eq) were added to a round-bottomed flask and dissolved in $CHCl_3$ (2.3 ml). The flask was sealed with a septum, the headspace was flushed with Ar, and the solution was cooled to 0 ºC in an ice bath. After adding DBU (10 µl, 0.019 mmol, 0.05 eq), the solution was left warming up to room temperature and stirring for 24 h. The sample turned a light-yellowish color. Measured the ^1H NMR spectrum of the reaction mixture. The polymer mixture was precipitated into Et_2O and allowed to stir overnight. By next morning the polymer had precipitated to the bottom of the beaker. The solvent was decanted and the polymer residue was transferred to a small flask, while $CHCl_3$ was used as a solvent. Thereafter, the solvent was removed by rotavap, and the polymer was dried further in the vacuum oven at 40 °C for overnight. The final polymer was a white powder (154.2 mg, 78%). The ^1H NMR spectrum was measured for the obtained polymer. Also, SEC analysis was carried out for the polymer in THF.

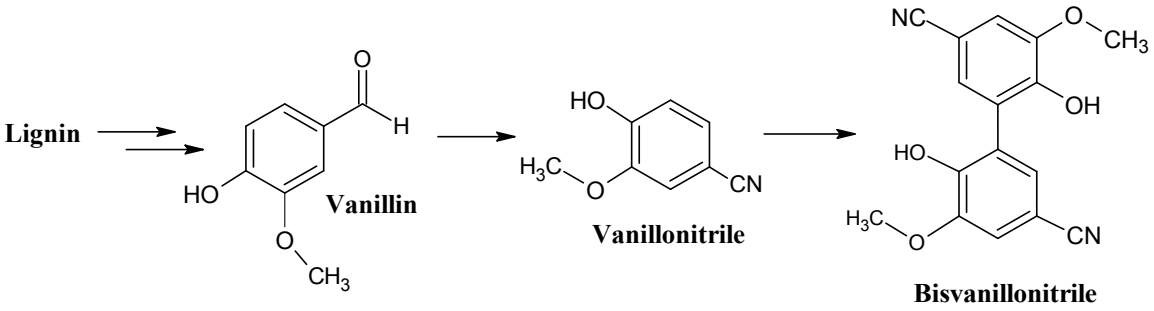
^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.25 (m, 8H), 5.17 (m, 2H), 4.81 (m, 1H), 4.45 (m, 1H), 3.93 (m, 3H), 3.79 (m, 1H), 3.14 (m, 4H), 2.66 (m, 4H) ppm.; (**Figure 15**).

4 RESULTS AND DISCUSSION

In this section of the thesis the results of the experiments are discussed. Firstly, the synthesis of diacrylate of BVN is presented. Then the synthesis of poly(β-thioester)s of the obtained monomer and isosorbide diacrylate are discussed.

4.1 Synthesis of bisvanillonitrile

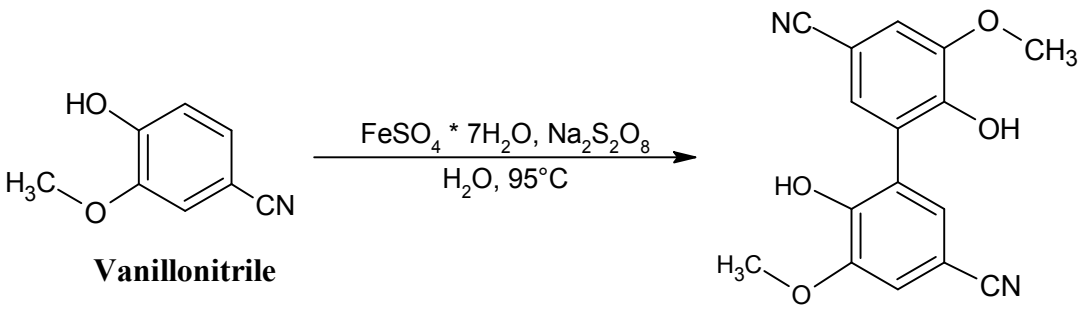
Bisvanillonitrile can be obtained from biosources, more precisely it can be synthesized from lignin units by the synthesis of vanillin and vanillonitrile (**Scheme 8**).



Scheme 8. General synthesis path for the preparation of bisvanillonitrile.

Bisvanillonitrile has already been synthesized before (Seynnaeve *et al*., 2021). According to the published article, bisvanillonitrile (BVN) was synthesized from vanillonitrile mixed in water, to which a solution of iron (III) chloride in water was added (Seynnaeve *et al*., 2021).

In the current work, the synthesis of bisvanillonitrile was done by Olivier Bonjour at Lund University, Sweden, according to the following scheme (**Scheme 9**) (Delomenède *et al*., 2008). In the reference article, the synthesis is reported for bisvanillin, but it also works for the synthesis of bisvanillonitrile when vanillonitrile is used as starting material (G. Li *et al*., 2020).



Vanillonitrile **Bisvanillonitrile**

Scheme 9. Synthesis of bisvanillonitrile from vanillonitrile with $FeSO_4*7H_2O$ and $Na_2S_2O_8$.

Bisvanillonitrile is a crystalline beige compound with a chemical formula $C_{16}H_{12}O_4N_2$ and a molecular weight of 296.28 g mol^{-1}.

4.2 Synthesis of bisvanillonitrile diacrylate

The purpose of this work was to synthesize the diacrylic monomer of bisvanillonitrile. It can be regarded as a fascinating and potentially valuable monomer due to its rigid structure and biomass-origin.

In order to select the right solvent for the acrylation of bisvanillonitrile, solubility testing was conducted by mixing bisvanillonitrile with different solvents. As a result of this testing, bisvanillonitrile happened to be soluble only in DMF, DMSO, and water. The results are summarized in **Table 2**.

Table 2. Solubility of bisvanillonitrile in different solvents.

Solvent	Solubility
DMSO	YES
DMF	YES
CH_2Cl_2	NO
H_2O	YES
1,4-Dioxane	NO
$CHCl_3$	NO
ACN	NO
50% H_2O + 50% Acetone	NO
Acetone	NO

The usage of DMF for the acrylation of bisvanillonitrile is very unfavorable due to the strong polarity and high boiling point of that solvent. More specifically, the high boiling point of a solvent makes it hard to remove it later from the product. Therefore, the author attempted to carry out the reaction in another solvent systems and compare the results of these experiments.

For instance, for the sythesis of bisvanillonitrile-diacrylate (**Scheme 2**), the aqueous K_2CO_3 solution (4 M) was picked as a solvent (Chanthamath *et al*., 2013). Even though bisvanillonitrile was dissolving in water, it did not dissolve in this solution. Therefore, the reaction was stopped and no further analyses were carried out.

In another experiment, the synthesis of bisvanillonitrile-diacrylate was carried out in the mixture of aqueous NaOH (1.2 M) and 1,4-dioxane (**Scheme 3**) (*WO2019213588A1 - Polymerizable Monomers and Method of Polymerizing the Same - Google Patents*, n.d.). As a result of this reaction, the product was obtained. A small sample of the product was taken for the NMR testing and the ^{1}H NMR spectrum was measured. From the obtained spectrum of the product, it was seen that the crude mixture also contained solvent residues and some impurities and the proportion of product in the sample was very low. It was decided to not purify the product with column chromatography due to the small quantity.

Knowing that the most efficient solvent for dissolving the BVN was DMF, it was decided to perform the reaction in this solvent. The monomer, bisvanillonitrile diacrylate, was obtained through the reaction between BVN and Acryloyl chloride in DMF (Schultze *et al*., 2018). In this reaction, the acryoyl groups were attached to the hydroxyl groups of the BVN and this led to the formation of BVN-diacrylate. In order to get pure monomer, column chromatography was carried out. The suitable solvent for the flash column chromatography was selected through the TLC analysis (30% EtOAc/PE) and the product was purified. To confirm the structure of the obtained monomer, the ^{1}H and ^{13}C NMR ($CDCl_3$) spectra were measured (**Figure 7**). Followed by IR measurement (**Figure 8**). The chemical shifts in the region of 6.6-5.8 ppm in the ^{1}H NMR spectrum show the presence of acrylic protons. In the ^{13}C NMR spectrum, peak at 162.6 ppm indicates the carbonyl carbon (C=O) of the acrylic units in the obtained diacrylate. In the IR spectrum the absorption bands at 2250, 1751, 1589 and 794 cm^{-1} correspond to C≡N stretching, C=O stretching, C=C stretching and C=C twisting of acrylate, respectively. These findings prove the structure of BVN-diacrylate.

Nonetheless, to make the diacrylate of BVN a more appealing monomer the preparation of it necessitates replacing the purification step (column chromatography) to a more sustainable one and perhaps also, utilizing a less polar solvent in the synthesis.

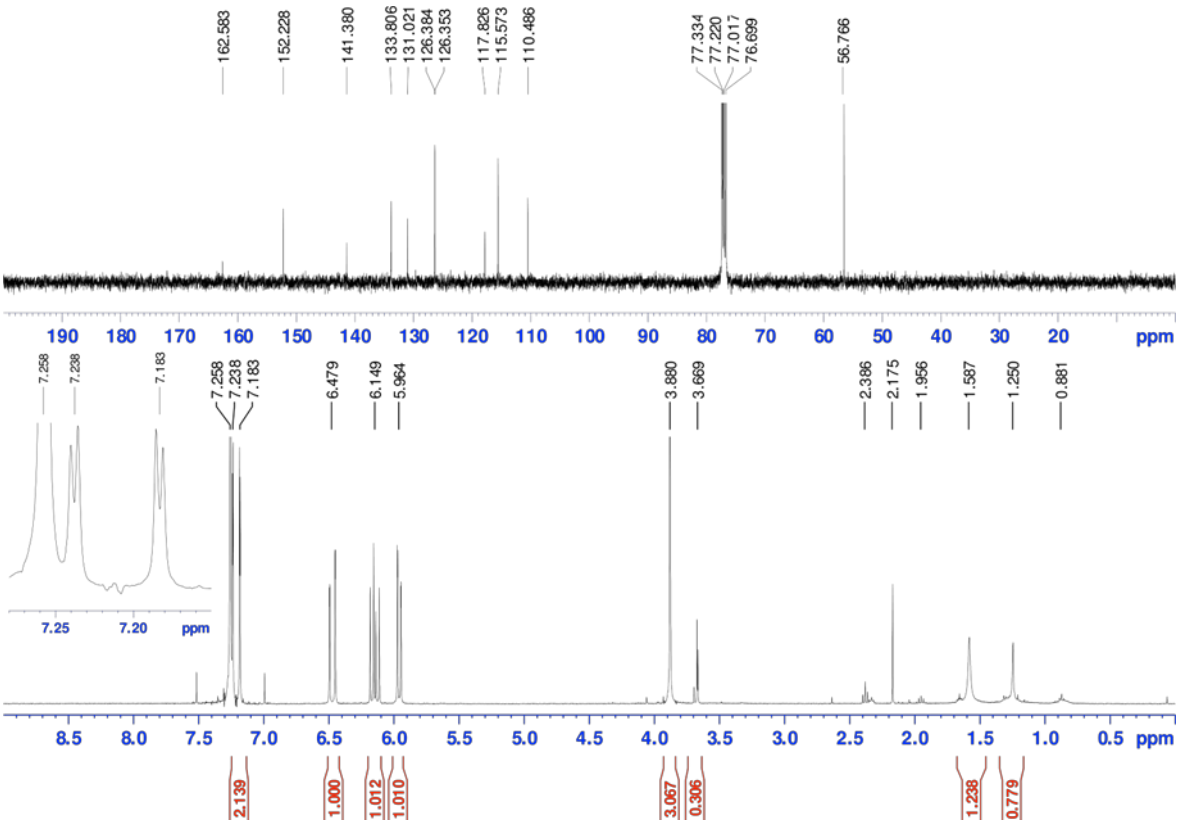


Figure 7. ^{13}C and ^{1}H NMR spectra of BVN-diacrylate in $CDCl_3$.

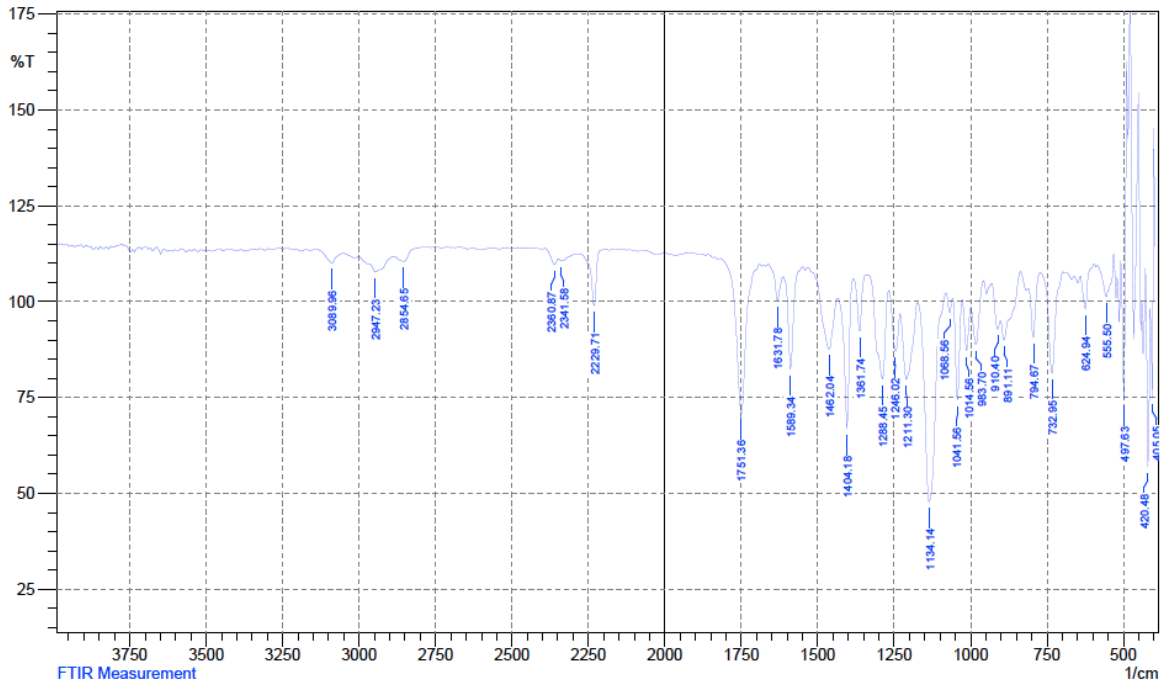
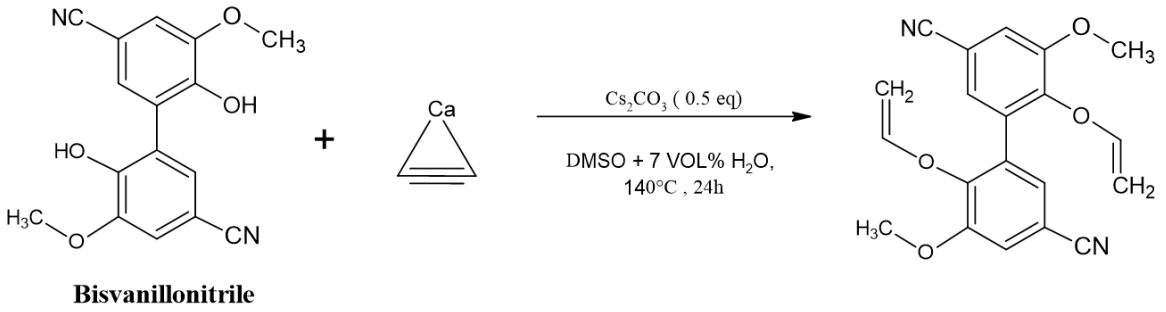


Figure 8. IR graph of BVN-diacrylate.

In addition to the obtained monomer, there was an attempt to synthesize another monomer, divinyl ether of BVN (Teong *et al*., 2017). In this reaction (**Scheme 10**), Cs_2CO_3 played a role of a catalyst and DMSO + 7 vol% H_2O was used as a reaction medium. The crude product was purified by flash column chromatography, however the ^1H NMR ($CDCl_3$) spectra of the collected fractions didn't show the wanted product. The synthesis of divinyl ether of BVN would be interesting to investigate further, because this compound could also be used as a building block in different polymers.



Scheme 10. Synthesis of monomer, divinyl ether of BVN.

4.3 Copolymerization of BVN-diacrylate

To show where this type of diacrylate could be used, an example polymerization reaction was carried out. A copolymerization with dithiols was chosen for the method. Dithiols can be successfully copolymerized with diacrylates to obtain poly(β-thioester)s.

The polymerization reaction between BVN diacrylate and 1,6-hexanedithiol was carried out in $CHCl_3$ overnight in the presence of DBU. The reaction conditions used successfully lead to polymerization. After the purification of the polymer **1** by precipitation and drying, the SEC analysis was carried out. The M_n of the polymer was 2 870 g mol^{-1} and the polydispersity index was 2.2 (**Figure 9**).

The formation of polymer **1** from the diacrylate of BVN and 1,6-hexanedithiol was also determined by the ^1H NMR spectrum (**Figure 10**). The IR spectrum of the obtained polymer was also measured and analyzed (**Figure 11**).

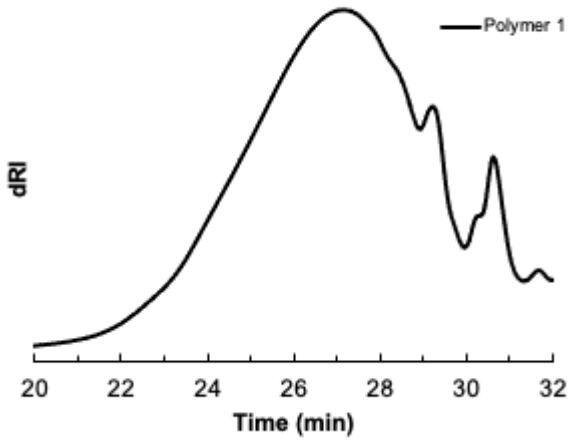


Figure 9. SEC curve of polymer **1**.

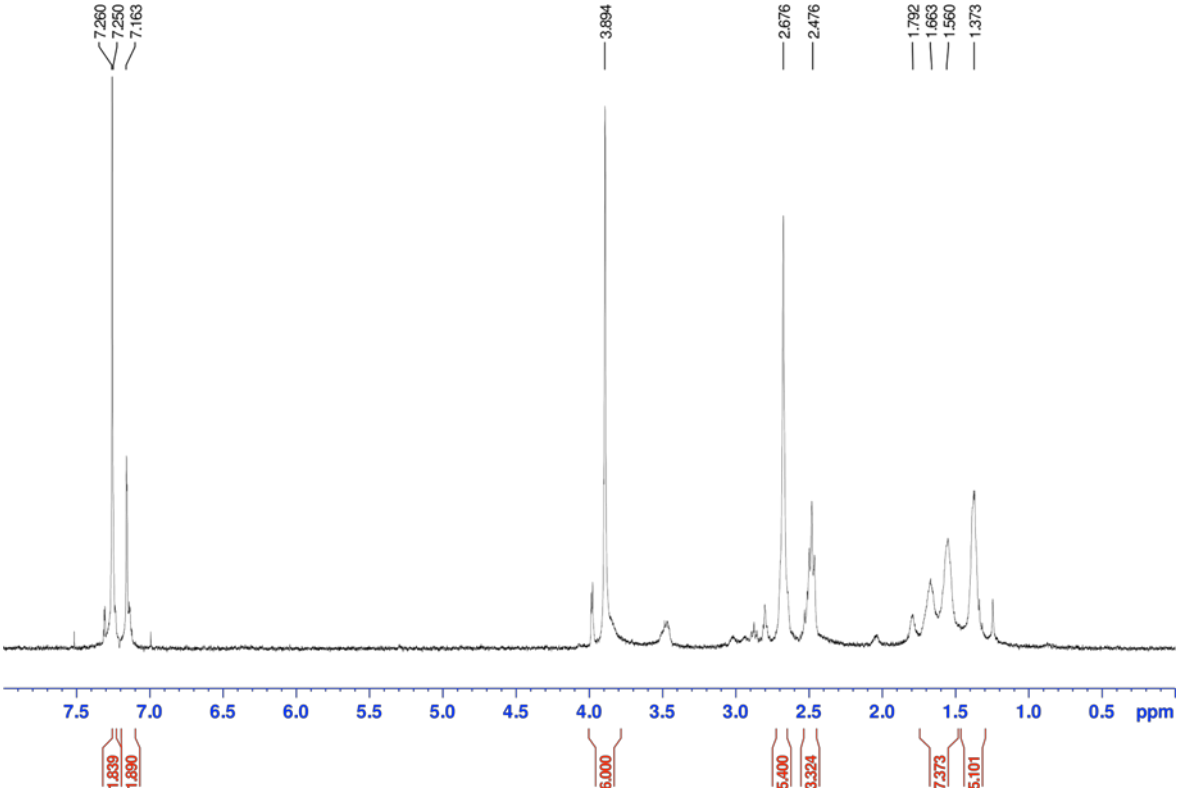


Figure 10. ^{1}H NMR spectra of polymer **1** in $CDCl_3$.

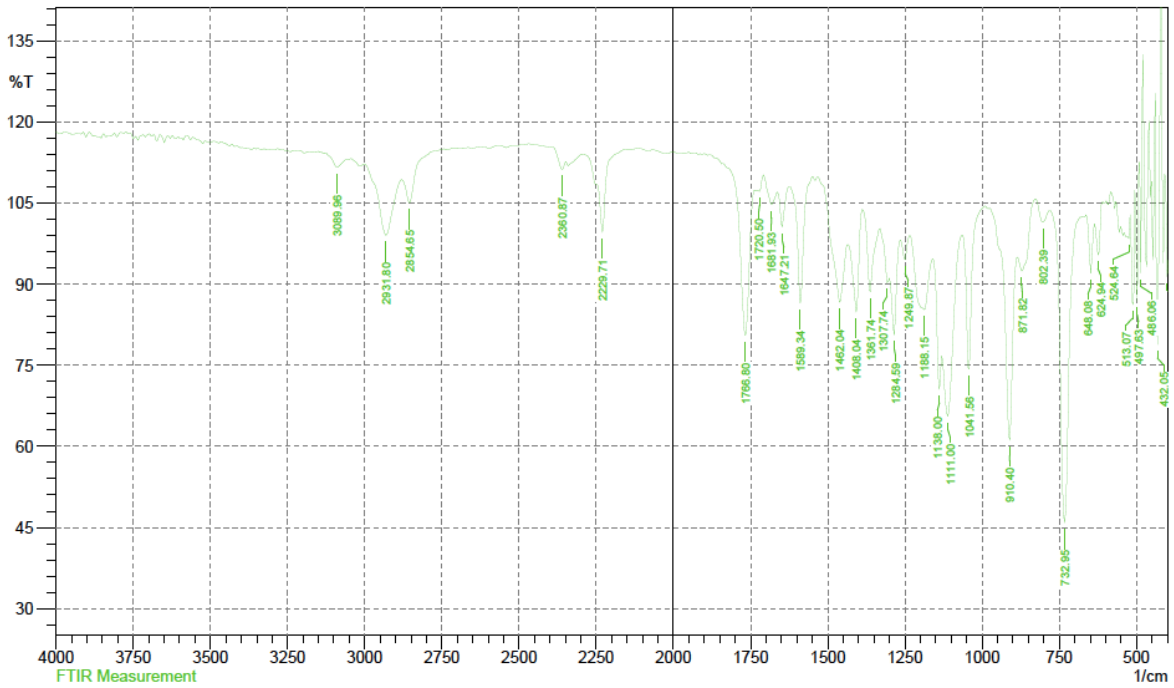


Figure 11. IR spectrum of polymer **1**.

In addition, copolymers of biobased isosorbide diacrylate and two dithiols were prepared. Polymer **2** was synthesized from 1,6-hexanedithiol and iSDA under the same conditions that were used for polymer **1**. The SEC analysis indicated that the number average molecular mass of polymer **2** (M_n = 2 523 g mol^{-1}) was comparative to the M_n of polymer **1** (see **Figure 12**). But the polydispersity index (1.3) was a bit lower for polymer **2**. In literature also a polymer of 1,6-hexanedithiol and iSDA has been synthesized (Moon *et al.*, 2018), but in this case the molecular weight was much higher (M_n = g mol^{-1}). The difference can be caused by the shorter reaction time or by the insufficient purging with argon. Also, in the ^{1}H NMR graph of polymer **2** some acrylate proton peaks can be seen between 6.6-5.8 ppm (see **Figure 14** in the appendix).

Furthermore, polymer **3** was synthesized of 4,4'-thiobisbenzenethiol and iSDA with the M_n of 8 475 g mol^{-1} and the polydispersity index of 2.1 (**Figure 12**). In this case, also some proton peaks corresponding to acrylate group can be seen between 6.6-5.8 ppm in the ^{1}H NMR of the polymer **3** (see **Figure 15** in the appendix).

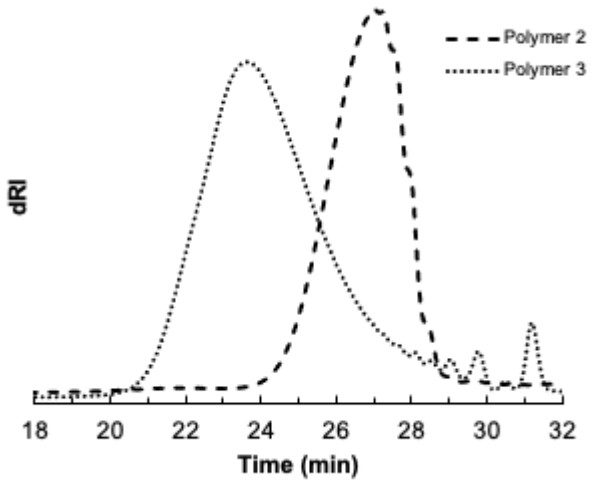


Figure 12. SEC curves of polymers **2** and **3**.

SUMMARY

In the present work, the goal was to prepare novel biobased monomers that include vanillin unit in their structure. Additionally, the aim was to show the polymerization of the obtained compounds.

Firstly, different methods were tried for the synthesis of nitrile-containing diacrylate of bisvanilline. The reaction between bisvanillonitrile and acryloyl chloride in DMF provided the wanted product. The obtained compound was purified by column chromatography and then the structure of this novel compound was confirmed by NMR and IR spectra.

The obtained diacrylate of bisvanillonitrile can be used in different polymerization structures. Poly(β-thioester) was chosen as the example polymer. Thus, diacrylate of bisvanillonitrile and 1,6-hexanedithiol were polymerized to a copolymer with M_n of 2 870 g mol^{-1}. The structure of the polymer was also confirmed by ^{1}H NMR spectrum.

Next, as a comparison, isosorbide diacrylate, which is also a biobased monomer, was synthesized and the copolymers of it with two different dithiols were prepared. The isosorbide diacrylate copolymer with 1,6-hexanedithiol exhibited similar number average molecular mass of 2 523 g mol^{-1} as the previous copolymer made from diacrylate of bisvanillonitrile and 1,6-hexanedithiol. The second copolymer of isosorbide diacrylate and 4,4'-thiobisbenzenethiol exhibited higher M_n of 8 475 g mol^{-1}.

To conclude, in this study a novel diacrylic derivative of bisvanillonitrile was prepared. The synthesis of this biobased diacrylic bisvanillonitrile has not been reported before in scientific literature. The diacrylic bisvanillonitrile is a potential rigid building block that can be used in different polymeric structures, for example as comonomer in poly(β-thioester) s, and as a crosslinking unit in polyacrylates. Furthermore, synthesis of a copolymer of 1,6-hexanedithiol and the obtained novel diacrylate was demonstrated.

In short, one new interesting rigid compound was added to the field of bio-derived monomers, that can be used for the synthesis of biobased polymers which are nowadays very appealing as the components of high-performance plastics.

ACKNOWLEDGEMENTS

I would like to express my appreciation to my supervisor Lauri Vares, for giving me the opportunity to conduct my bachelors thesis in his research lab.

Thereafter, I want to express my deepest gratitude to my co-supervisor, Livia Matt. I have been extremely lucky to have a supervisor who cared so much about my work, and who responded to my questions and queries so promptly.

Special thanks to my program director Ilona Faustova, for her constant support and encouragement that helped me throughout the studies, research and writing of this thesis.

Also, I would like to thank Artemi Maljavin for the pivotal role he played while mentoring us during the studies.

I am thankful for my colleagues, in particular Alina Ismagilova and Siim Laanesoo, for their support while conducting the experiments.

I thank my coursemates, Mariia Novoshinskaia and Ekaterina Sedykh, for their constant support.

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APPENDICES

1. Characterization data of iSDA from isosorbide synthesis

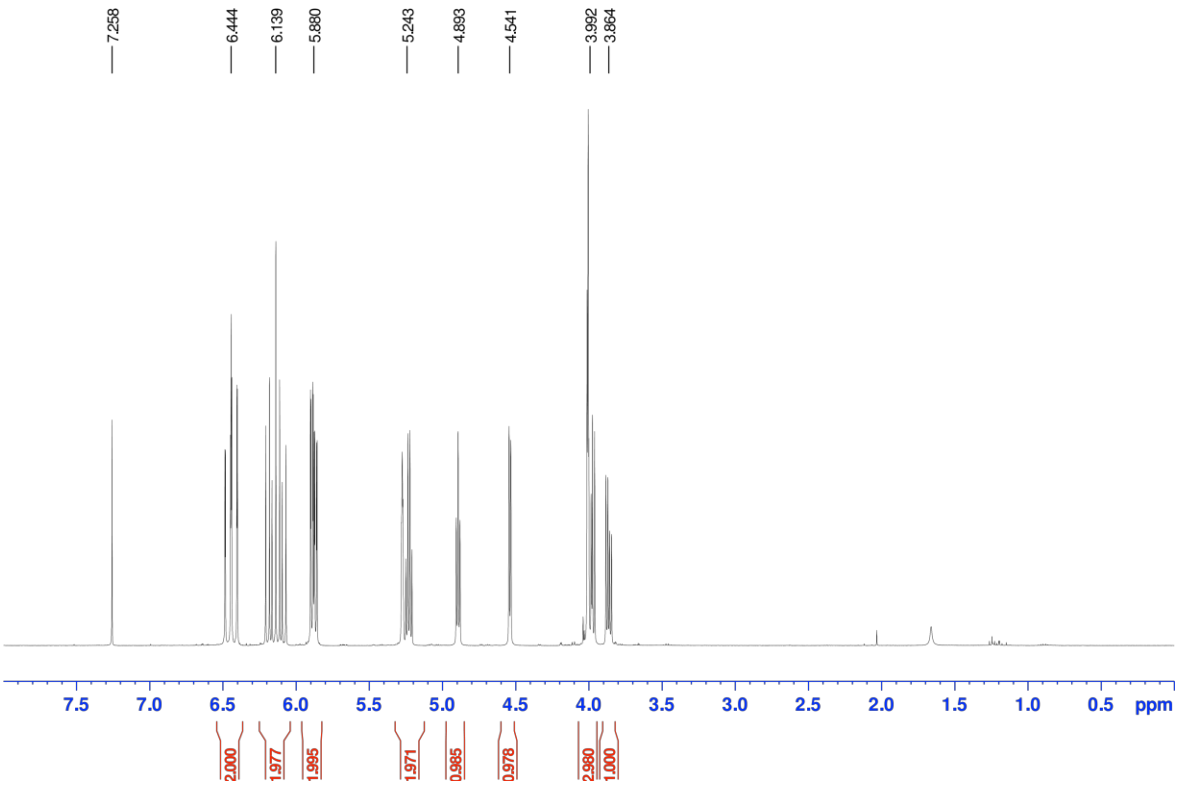

Figure 13. ^{1}H NMR of iSDA in $CDCl_3$.

2. Characterization data of polymer 2 of iSDA and 1,6-hexanedithiol

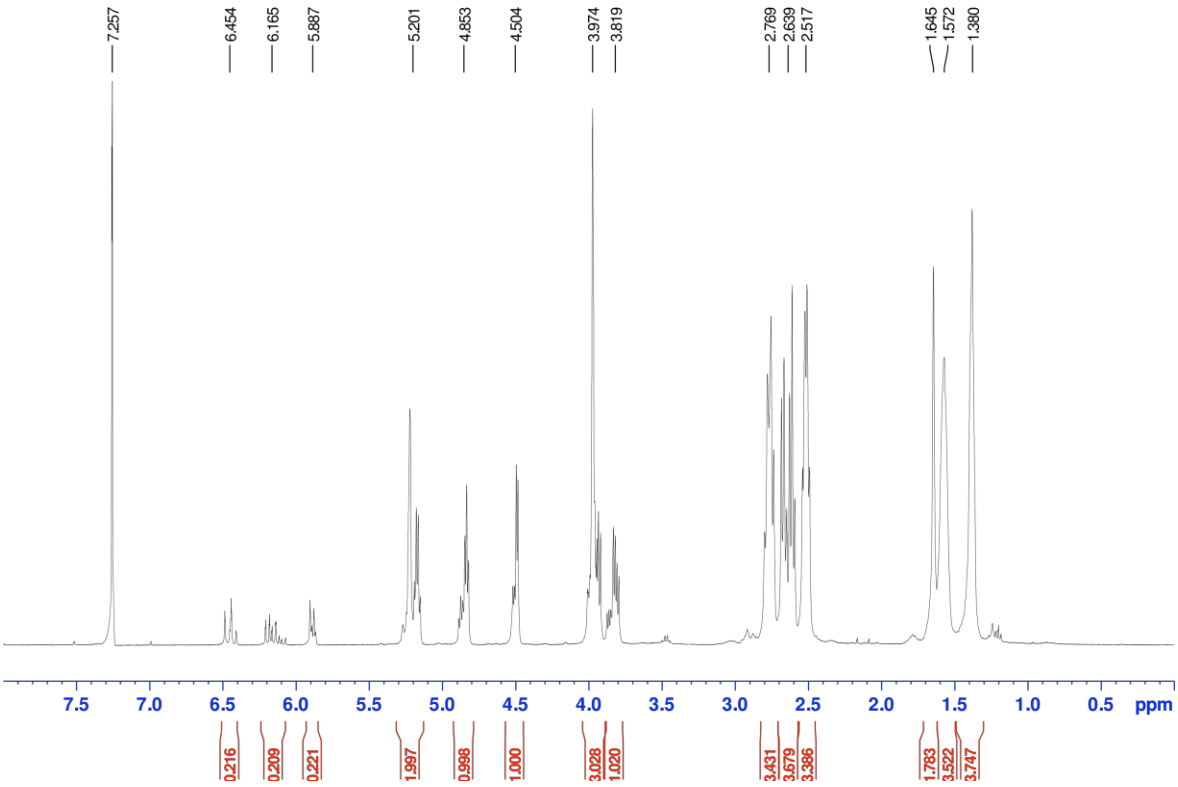

Figure 14. ^{1}H NMR of polymer **2** in $CDCl_3$.

3. Characterization data of polymer 3 of of iSDA and 4,4'-thiobisbenzenethiol

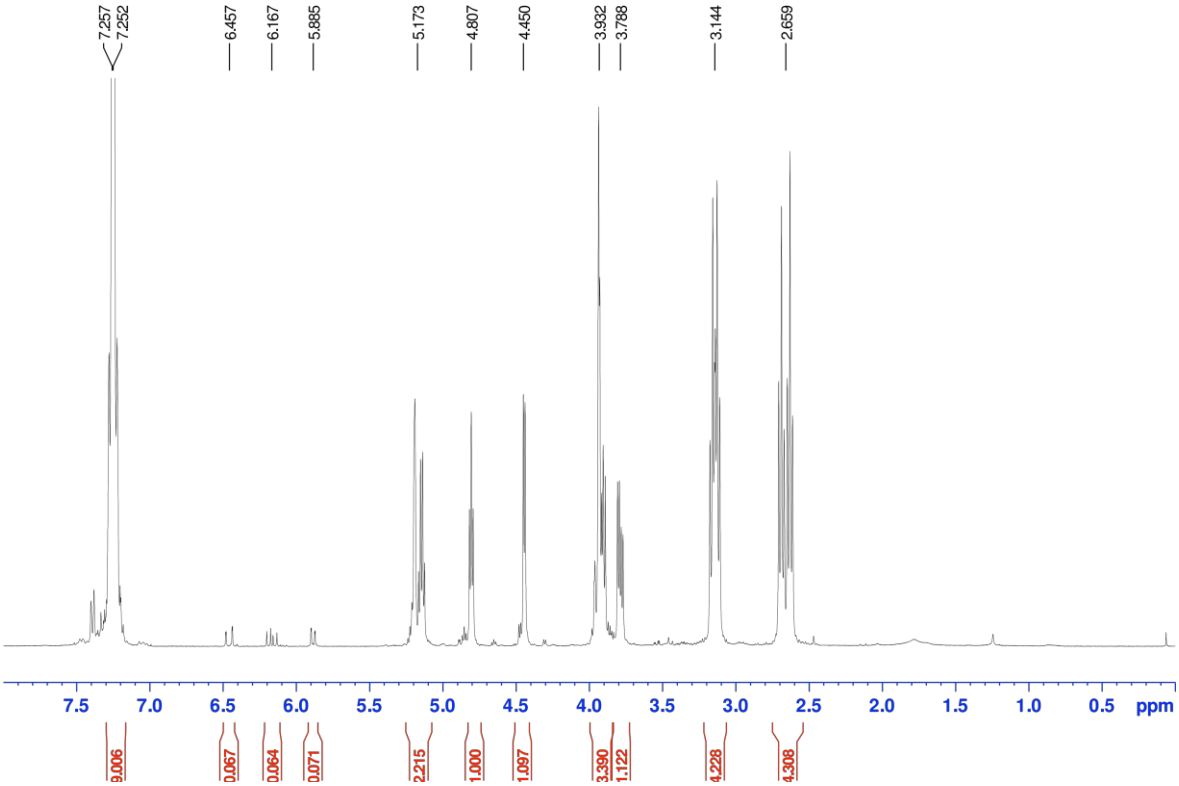

Figure 15. ^{1}H NMR of polymer **3** in $CDCl_3$.

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