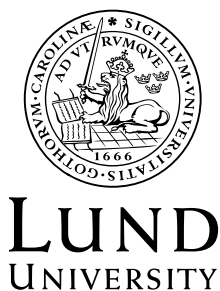


Synthesis and Investigation of Nitrile-Containing Polymers Inspired by Lignin

Master's Thesis



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Abstract

The lignin-inspired derivatives coniferyl aldehyde and sinapyl aldehyde were used to prepare nitrile-containing methacrylate monomers with the aim to synthesize bio-based polymers exhibiting high glass transition temperatures (T_g s). The aldehydes were initially transformed to the corresponding nitriles and then underwent methacrylation before being polymerised by free-radical polymerisation. The homopolymers displayed very low solubility in various solvents and did not exhibit any T_g s below the decomposition temperatures, indicating that the synthesized polymers were cross-linked.

Copolymers with styrene were also prepared with different compositions of the nitrile-containing methacrylate monomers. All the synthesized copolymers displayed very low solubility, similar to the homopolymers. Copolymers prepared with ≥ 25 mol% of the nitrile monomers did not exhibit any T_g , likely due to a significant degree of cross-linking. As the nitrile monomer content in the feed decreased to ≤ 5 mol%, the polymers exhibited T_g s ranging from 126 – 146 °C. This is attributed to a decrease in the degree of cross-linking in combination with reduced intermolecular interactions due to lower amounts of the highly polar nitrile group.

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1 Introduction

Plastics are some of the most versatile materials that have ever been developed and plays a crucial part in our daily life, as well as in the overall modern society that we live in today. Ever since the beginning of synthetic polymers, going all the way back to the development of celluloid in 1869, the advancement of new and already existing polymers has led to much more cost-efficient means of production. This has provided more affordable polymeric materials and has also increased its availability for more people regardless of income. The diversity of plastics has made it applicable in many different areas such as in the automotive industry, packaging, health care, construction and electronics [1].

Currently, polymers are mainly produced from fossil-based resources such as oil and natural gas, and accounts for around 5% of the total consumption of fossil resources [1]. The global production of plastics was 367 million tons in 2020, China being the major producer at 32% [2]. As the world population is still growing steadily, the need for plastics will not likely decrease in the near future [1].

The development of biobased polymers is becoming increasingly important to compete with the already existing and established fossil-based polymers, with the purpose of decreasing the carbon footprint and the overall dependence on fossil fuels. The challenge today is to effectively and sustainably produce biobased polymers which exhibits similar, or even better, properties compared to their fossil-based counterparts, at a reasonable price [3].

Among the properties of amorphous polymer materials, the glass transition temperature (T_g) is one of the most important. It indicates the temperature at which the polymer transitions from a hard glassy state to a soft rubbery state. This will also determine which temperatures the polymer can operate at, for a specific application. In general, there is a lack of biobased polymers that display a high T_g (> 100 °C). Incorporating rigid segments that act as barriers for conformational motions has been shown to increase T_g since higher temperatures will be required for the segments to start moving and transition into the rubbery state. Cyclic structures like aromatic or alicyclic rings as well as bulky side chains exhibit limited mobility and are such segments that impose conformational barriers [4].

Polymers are considered biobased when part of their carbon content originates from biomass. Biomass encompasses all renewable organic material that are produced by living organisms. Lignocellulosic biomass is the most abundant bio-renewable biomass available on earth and has shown great potential in the synthesis of sustainable fuels and chemicals [5]. The three main constituents of lignocellulosic biomass are cellulose, being the most abundant, followed by hemicellulose and lastly lignin which accounts for 15–30% of the biomass. Lignin is the second most abundant natural polymer, being essential for trees and plants to keep their structural integrity and acting as a barrier against pathogens and insects [6].

Lignin is of great interest as it is readily available, being a by-product from the refining in the pulp and paper industry. Lignin is also especially interesting as it is rich in aromatics, which have been demonstrated to be beneficial for synthesizing biobased polymers with high T_g [7]. Today, about 98% of the lignin being isolated by the pulp and paper industry is burned as fuel,

which highlights the immense underutilization of this material. Therefore, continued research and development in regards to effectively process and utilize lignin for various products is crucial to reach its full potential, and to increase its commercial value as a feedstock for the chemical industry [6], [8].

Besides rigid structures like aromatics, incorporating polar groups has also been shown to increase T_g since they can create strong intermolecular interactions such as dipole-dipole interactions and hydrogen bonding. These interactions will hinder the motion of the polymer, thus requiring more energy to transition into the rubbery state [4]. The nitrile group is one example of a polar group that can raise T_g . It has been used industrially to produce various acrylonitrile polymers or copolymers, like poly(styrene-co-acrylonitrile) (SAN), which possesses a higher T_g compared to pure polystyrene. An effective route for the synthesis of the polar nitrile group from aldehydes has been reported by Quinn et al. [9]. The mechanism has been proven to work for a large array of substrates including aliphatic, aromatic, and conjugated aldehydes, resulting in excellent yields. Due to its simplicity, mild conditions and its high efficiency, it offers a great opportunity for the development of nitrile containing biopolymers that possess high T_g [3].

By the incorporation of a nitrile group in accordance to the mentioned method, Bonjour et al. have reported that T_g increased substantially. The introduction of the nitrile function also provided good solvent resistance of several polymethacrylate biopolymers [3]. In this project, methacrylate monomers and polymers, inspired by lignin, containing the polar nitrile group will be further explored through synthesis and analysis of their properties.

2 Background

2.1 Biobased plastics

Biobased plastics are comprised completely (or partly) of renewable biobased resources such as starch, cellulose, lignin, vegetable oils, and proteins. Going back to the beginning of the 1900s, all the commercially available plastics were biobased since biomass feedstocks were, at the time, the only available resources to produce plastics. The first fully synthetic fossil-based polymer, Bakelite, was developed in 1907, and the interest in plastics has since increased substantially [1],[4].

This eventually led to an exponential growth in plastic consumption as the materials became cheaper and more accessible, especially after the Second World War. Due to the development of better and more cost-efficient production methods to make fossil-based plastics, which exhibited superior material properties compared to the biobased plastics, the latter were outmatched. Although, the concerns regarding the negative effects on climate, caused by the immense exploitation of fossil resources, hence the overall interest in bio-based plastics has risen tremendously in the past decades [1].

Poly(ethylene terephthalate) (PET) is one of the most commonly used synthetic plastics in the world today, mainly for the production of synthetic fibers and packaging for beverages and foods. In 2009, Coca-Cola introduced a partially bio-based PET bottle (Pet PlantBottle) containing 30% of renewable plant-based material. Further research and development have been made with the aim to increase the bio-content in bio-PET bottles from 30% to 100%. Coca-Cola announced in 2015 that a 100% bio-based prototype bottle had been produced. However it has not yet been applied at a commercial scale [10],[4].

The most widely used bio-based plastic in the world today, mainly used for packaging and fibres and entirely made from renewable resources, is poly(lactic acid) (PLA). Lactic acid is produced by fermentation of carbohydrates from sources such as sugarcane and corn starch [11].

PLA is a biodegradable polymer which degrades to lactic acid as it is metabolized in the human body. It has therefore found important uses within various biomedical applications such as wound clips and drug-delivery systems, but also in the agricultural industry as timed-release coatings for fertilizers [12]. Although, due to its relatively low T_g (~55 °C) and thermal stability, the applications are somewhat limited and several approaches to improve the T_g have been made by modifications of the molecular structure, resulting in T_g values ranging from 65–72 °C [4],[13].

2.2 Nitrile-containing polymethacrylates

The recent work reported by Bonjour and coworkers [3] presents the successful synthesis and polymerization of nitrile-containing methacrylate monomers based on the corresponding lignin-inspired aldehydes, namely 4-hydroxybenzaldehyde, vanillin and syringaldehyde. The three aldehydes were transformed into the corresponding nitrile compounds, which then underwent methacrylation and were eventually polymerised as shown in Figure 1.

The two steps were included in the preparation of the monomers, namely the nitrilation of the aldehyde group, followed by methacrylation of the hydroxyl group. Both resulted in high yields, 79–82% and 70–89%, respectively. The reported homopolymers were isolated in varying yields, ranging from 49–93%, being the lowest for the least substituted polymer. An increase in solubility in DMSO was observed as the degree of methoxylation increased in the monomer [3].

The homopolymers displayed high T_g values, 150, 164 and 238 °C, which increased with the number of methoxy groups on the aromatic ring. The flexibility of the repeating unit is likely reduced due to the presence of the methoxy group, hence affecting the segmental mobility of the polymer chain [3]. Homopolymers from the corresponding aldehydes reported by Emerson et al. displayed lower T_g values of 129 and 201 °C for the unsubstituted and disubstituted monomer respectively [14]. The difference in T_g between the polymethacrylates prepared by Bonjour et al. and Emerson et al. can be attributed to the presence of the highly polar nitrile group as it will increase the intermolecular interactions between the polymer chains. Copolymers consisting of various compositions of the nitrile-containing monomers copolymerized with styrene or methyl methacrylate (MMA) were also prepared, displaying a

similar trend with increasing T_g values as the content of the nitrile monomer increased. By the incorporation of nitrile monomers in methacrylic and styrenic polymers, the T_g can be tuned and controlled to be able to fit a specific application [3].

The three homopolymers displayed high decomposition temperatures at 5% weight loss ($T_{d,95\%}$), of 302, 303 and 319 °C. $T_{d,95\%}$ appeared to increase as the number of methoxy groups increased, similarly to what was observed for the measured T_g values [3]. Holmberg et al. have reported $T_{d,95\%}$ for the corresponding mono- and disubstituted aldehyde polymethacrylates of 264 and 303 °C respectively [7],[15]. This confirms that the incorporation of the nitrile group also improves the thermal stability of the polymers. The thermal window between T_g and $T_{d,95\%}$ ranged from 80–150 °C degrees which implies that the polymers could potentially be melt processable, although more difficult as the thermal window becomes narrower. These results reported by Bonjour et al. provide a promising strategy to synthesize biobased nitrile-containing methacrylate monomers for the preparation of high-performance polymers [3].

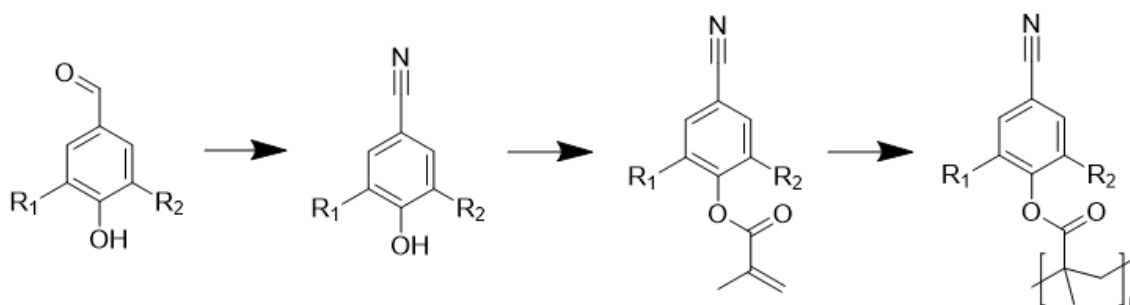


Figure 1: Synthetic pathway of the formation of nitrile-containing polymethacrylates starting from 4-hydroxybenzaldehyde ($R_1=H$, $R_2=H$), vanillin ($R_1=H$, $R_2=OCH_3$) and syringaldehyde ($R_1=OCH_3$, $R_2=OCH_3$).

2.3 High-performance and Engineering plastics

Commodity plastics are the most widely used polymers since they are cheap, produced in high volumes and are applied in areas where there are lower requirements on material properties. Such plastics include polystyrene (PS) and polyethylene (PE) which are commonly used as packaging products. Polymers that exhibit better properties compared to the commodity plastics are referred to as “engineering” and “high-performance” plastics. These properties can for instance comprise enhanced thermal stability, improved chemical resistance and superior mechanical properties, such as high tensile, impact and flexural strength. Engineering and high-performance plastics are generally more expensive compared to the commodity plastics and are produced in lower volumes. Due to the outstanding properties of some of these polymers, they can replace metals in certain areas, including aerospace and automotive applications where low weight and good mechanical properties are desired [16].

Some of the most common engineering plastics that possess enhanced properties are polyamides, polycarbonates and ABS. ABS is a copolymer that consist of acrylonitrile, butadiene and styrene and is widely used within the automotive industry. ABS was originally developed by modifying a styrene-acrylonitrile copolymer (SAN) with polybutadiene, which led to improved impact strength compared to SAN alone. SAN is a brittle polymer that is

optically transparent, similarly to PS, but exhibits enhanced thermal properties. The very polar acrylonitrile part of SAN is responsible for the increase in T_g , reaching temperatures above 100 °C which is the T_g solely for PS. Hence, the result is a material that is capable of withstanding boiling water without transitioning to its rubbery state [16],[17].

2.4 Lignin

Lignin is a natural three-dimensional polymer that is mainly composed of three crosslinked aromatic monomers (Figure 2), namely coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol. They are called monolignols and differ from each other based on the degree of methoxylation. These units are connected through ether and carbon-carbon linkages, resulting in the complex structure known as lignin [18].

The composition of lignin, as well as the content, varies depending on the plant source. For instance, hardwood lignin is mainly composed by equal amounts of coniferyl alcohol and sinapyl alcohol, while softwood lignin is mostly composed of coniferyl units. *p*-coumaryl alcohol is more common in lignin found in grass and herbaceous plants [19].

Depolymerization of lignin can be performed by different methods: hydrolysis, pyrolysis, catalytic cleavage, enzymatic- and oxidative degradation etc. These techniques are used to break down lignin into smaller aromatic molecules, such as alcohols, acids and aldehydes. These types of phenolics can subsequently be used as building blocks to synthesize various polymers, e.g. polyesters and epoxy resins. The most investigated compound that is obtainable from the depolymerisation of lignin, through oxidative degradation processes, is vanillin. Today, vanillin is the only aromatic molecule that is produced from lignin on a commercial scale, accounting for around 15% of the global production. It is used for many different applications, including being a flavouring agent and a precursor for polymer synthesis since it can be converted to a wide range of vanillin-derived monomers by modifications of the groups attached to the aromatic ring [18].

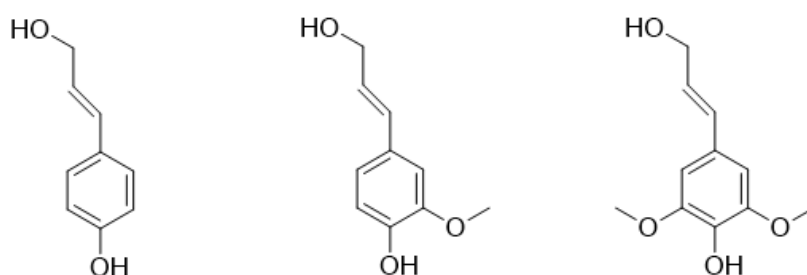


Figure 2: The three main monolignols, *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (read from left to right).

2.5 Project outline

This project includes the monomer synthesis displayed in Figure 3, starting from coniferyl aldehyde which has one methoxy group attached to the aromatic ring, and sinapyl aldehyde substituted with two methoxy groups.

These starting materials initially underwent a transformation of the aldehyde into a nitrile group according to the previously mentioned approach developed by Quinn et al. [9], followed by methacrylation of the hydroxyl group. In general, methacrylate monomers can easily undergo free radical polymerizations due to the reactive C-C double bond and will form a tertiary carbon radical, thus being more stabilized. Therefore, this will be the utilized polymerisation method in this work. This is a type of chain-growth polymerisation process, where high molecular weight polymers can be obtained very rapidly due to the highly reactive nature of radicals.

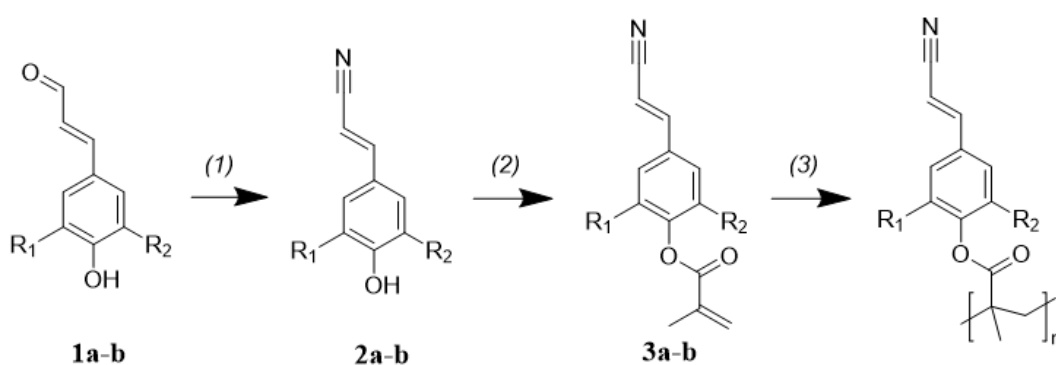


Figure 3: Synthetic pathway for the α,β -unsaturated nitrile-containing polymethacrylates including nitrilation (1), methacrylation (2) and polymerization (3). The letters, a and b, indicates the compound depending on the substituting groups R_1 and R_2 . a: $R_1=H$ and $R_2=OCH_3$. b: $R_1=OCH_3$ and $R_2=OCH_3$.

Attempts to selectively reduce the α,β -unsaturated monosubstituted nitrile (**2a**) (Figure 4) were made with the purpose to potentially study the difference between the saturated and the corresponding unsaturated polymethacrylates.

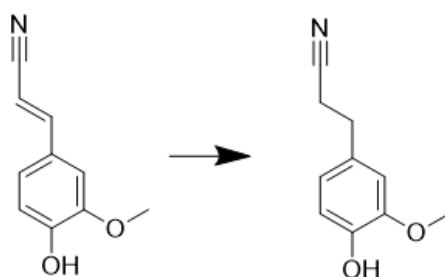


Figure 4: Reduction of the α,β -unsaturated nitrile (**2a**).

The synthesized monomers were also used in copolymerisation reactions in the presence of styrene to study the variation in properties of the polymers. As mentioned, T_g is a property that is influenced by the incorporation of different monomers in a polymer chain. Bonjour et al. have reported that the T_g of several copolymers synthesized from similar nitrile containing methacrylate monomers and styrene decreased as the molar ratio of styrene increased in the

feed. As the content of styrene is increased in the polymer chains, it will induce less steric hindrance and thus decrease the T_g . It is also affected by a lower amount of the polar nitrile group present in the polymer chains [3]. The utilization of different types of monomers is commonly performed to influence and control properties for certain applications.

The thermal properties of the synthesized polymers were examined through both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These methods will provide information regarding thermal transitions, that will include the determination of the glass transition temperature, as well as the thermal stability of the polymer.

3 Experimental Section

3.1 General procedure

The following section is a general procedure for the preparation of the monomers and polymers. The precise procedure for a specific compound can be found in section 3.5 *Synthesis of compounds*. All compounds and solvents were purchased from commercial suppliers and were directly used without any further purifications.

3.1.1 Nitration

A two- or three-necked round bottom flask was placed on a heating plate equipped with a magnetic stirrer. The respective aldehydes (1 eq.) were dissolved in water together with acetic acid (1.0 eq.) and hydroxylamine-*O*-sulfonic acid (1.01 eq.). One opening of the reaction flask was connected to a Schlenk line with the purpose of removing oxygen present in the flask using vacuum and refilling with inert N_2 , the other opening was sealed using a septum. The degassing procedure was performed several times to ensure complete removal of oxygen. Since the starting materials were sensitive to light, the flask was covered to prevent degradation. After purging was completed, the reaction was initiated by increasing the temperature to 50 °C under constant flow of N_2 . The reaction was run for 2.5 h until completion could be determined by 1H NMR spectroscopy combined with thin layer chromatography (TLC).

The reaction mixtures were then quenched by the addition of sodium bicarbonate ($NaHCO_3$) until no further gas evolution could be observed. Depending on if the product had precipitated or not, it was either extracted with ethyl acetate (EtOAc) three times using a separatory funnel, or directly filtrated and washed several times with deionized water. When extraction was necessary, the organic phase was collected, and dried using magnesium sulfate ($MgSO_4$). A rotary evaporator was then used to concentrate the nitrated compound. The samples were then placed in a vacuum oven at 50 °C for at least 24 h.

3.1.2 Methacrylation

A two- or three necked round bottom flask equipped with a magnetic stirrer was placed on a heating plate. The respective nitrilated compounds (1 eq.) and 4-dimethylaminopyridine (DMAP, 0.02 eq.) were dissolved in EtOAc. The flask was sealed and purged in the same manner as for the nitrilation. Methacrylic anhydride was then added (1.01 eq.) and the reaction flask was purged again. The reaction was stirred at 55–65 °C for 26–28 h. Upon completion, the reaction was quenched using NaHCO₃ until no more gas was released. The organic phase was separated from the aqueous phase using a separatory funnel and washed two more times, once with additional NaHCO₃ and lastly with deionized water. The organic phase was then dried using MgSO₄, filtered and concentrated using a rotary evaporator. Column chromatography using basic aluminium oxide (Al₂O₃) with a mixture of EtOAc and toluene as eluent was then used to purify the methacrylated compounds. Lastly, one of the monomers were dissolved in acetone and further purified by precipitation in heptane.

3.1.3 Polymer synthesis

A two necked round bottom flask equipped with a magnetic stirrer was filled with dimethyl sulfoxide (DMSO), sealed with a septum, and degassed by purging the flask with several N₂/vacuum cycles, similar as for the monomer preparation. The respective monomers were then added to a Schlenk flask, equipped with a magnetic stirrer and dissolved in degassed DMSO. It was then placed on a heat plate and degassed again. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was dissolved in degassed DMSO, and a portion of this solution was added to the reaction mixture through the septum, to reach a quantity 0.4–1 mol%. The reaction flask was degassed again before increasing the temperature to 60 °C. The synthesis of the homopolymers and the copolymers using styrene followed the same procedure. The polymers were then precipitated in MeOH after reacting for 24 h. The samples were subsequently filtered, washed with MeOH, then dried in a vacuum oven at 50 °C for at least 24 h before thermal analysis measurements were performed.

3.2 Structural characterization

A Bruker DR X400 spectrometer was used for the nuclear magnetic resonance (NMR) spectroscopy measurements, both for proton (¹H) NMR and carbon (¹³C) NMR at 400 MHz and 101 MHz respectively.

3.3 Thermal analysis

The differential scanning calorimetry (DSC) measurements were performed using TA instruments DSC Q2000. The samples were first heated to 105–250 °C, depending on the sample, at 10 °C/min and remained at that temperature for 2 minutes, followed by a cooling cycle down to -50 °C and remained isothermal for 2 minutes. Lastly, the samples were heated again to the same temperature and with the same rate as the first heating cycle. Measurements

by thermogravimetric analysis (TGA) were performed using TA instruments TGA Q500. The samples were heated to 600 °C at 10 °C/min under nitrogen flow (60 ml/min).

3.4 Gel content estimation

The polymers (0.1–0.3 g) were added to separate centrifuge tubes with THF (12 ml) as solvent. The tubes were centrifuged for 20 min at 5000 rpm. The supernatants were collected and centrifuged again as before. The gels obtained from the first and the second centrifugation were collected and dried under vacuum at 50 °C. The results are compiled in Table 2, presented in section 4.2 *Polymerisations*.

3.5 Synthesis of compounds

3.5.1 3-(3-Methoxy-4-hydroxyphenyl) acrylonitrile (Coniferyl nitrile) **2a**

Coniferyl aldehyde **1a** (4.884 g, 27.4 mol, 1.0 eq.), hydroxylamine-*O*-sulfonic acid (3.434 g, 30 mmol, 1.1 eq.), water (195 ml) and acetic acid (1.57 ml, 27.4 mol, 1.0 eq.) was added to a 250 ml round bottom flask equipped with a magnetic stirrer. The flask was sealed and purged with N₂/vacuum cycles and. The mixture was then heated to 50 °C at 2.5 h under constant flow of N₂, the flask was covered to prevent exposure of light. To quench the reaction mixture, NaHCO₃ solution was added until no further release of gas was observed. The mixture was extracted with EtOAc (60 ml) three times. The organic phase was then collected separately and filtrated to remove solids, and then dried with MgSO₄. The organic phase was filtered again and concentrated with a rotary evaporator. The isolated product **2a** was dried in a vacuum oven at 50 °C to remove residual solvent. 3.996 g of brown powder was obtained (yield: 83%). ¹H NMR (400 MHz, DMSO-*d*) δ 9.75 (s, 1H), 7.49 (d, J = 16.6 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.2, 2.0 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.25 (d, J = 16.6 Hz, 1H), 3.80 (s, 3H).

3.5.2 3,5-Dimethoxy-4-hydroxy-cinnamonitrile (Sinapyl nitrile) **2b**

Sinapyl aldehyde **1b** (4.881 g, 23.4 mmol, 1.0 eq.), hydroxylamine-*O*-sulfonic acid (2.935 g, 25.7 mmol 1.1 eq.), water (130 ml) and acetic acid (1.34 ml, 23.4 mmol, 1.0 eq.) was added to a 250 ml round bottom flask equipped with a magnetic stirrer. The flask was sealed and purged with N₂/vacuum cycles and. The mixture was then heated to 50 °C at 2.5 h under constant flow of N₂, the flask was covered to prevent exposure of light. The product started to precipitate during the reaction. To quench the reaction mixture, NaHCO₃ solution was added until no further release of gas was observed. The precipitate was filtered and washed with deionized water. The isolated product **2b** was dried in a vacuum oven to remove residual solvent. 4.283 g of yellow powder was obtained (yield: 89%). ¹H NMR (400 MHz, DMSO-*d*) δ 9.08 (s, 1H), 7.47 (d, J = 16.6 Hz, 1H), 6.98 (s, 2H), 6.30 (d, J = 16.5 Hz, 1H), 3.79 (s, 6H).

3.5.3 4-(2-Cyanovinyl)-2-methoxyphenyl methacrylate (Coniferyl nitrile methacrylate) **CM 3a**

Coniferyl nitrile **2a** (5.930 g, 34 mmol, 1.0 eq.) and DMAP (0.092 g, 0.75 mmol, 0.02 eq.) was added to a 100 ml round bottom flask equipped with a magnetic stirrer and dissolved in EtOAc (50 ml). The flask was sealed and purged with N₂/vacuum cycles. Methacrylic anhydride (5.1 ml, 34.3 mmol, 1.01 eq.) was added to the reaction mixture and the flask was purged again as mentioned previously. The reaction was stirred for 28 h at 65 °C. After completion, NaHCO₃ was added until no further release of gas was observed. The mixture was then washed with NaHCO₃ (18 ml) and deionized water (18 ml). The organic phase was collected separately and dried using MgSO₄. The organic phase was then filtered and concentrated by rotary evaporation. The residue was purified by aluminium oxide column chromatography using a 1:2 mixture of EtOAc:toluene as eluent, and subsequently dried in a vacuum oven (50°C). 6.836 g of brown powder was obtained (yield: 83%). ¹H NMR (400 MHz, DMSO-*d*) δ 7.64 (d, J = 15.4 Hz, 1H), 7.47 (s, 1H), 7.30 – 7.18 (m, 2H), 6.53 (d, J = 15.3 Hz, 1H), 6.27 (s, 1H), 5.91 (s, 1H), 3.81 (s, 3H), 1.99 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*) δ 164.48, 151.24, 149.88, 141.57, 134.79, 132.78, 128.03, 123.33, 121.14, 118.67, 111.26, 97.01, 56.06, 17.97. HRMS *m/z* 266.0800 [M + Na]⁺ (calcd for C₁₄H₁₃NO₃Na, 266.0793).

3.5.4 4-(2-Cyanovinyl)-2,6-dimethoxyphenyl methacrylate (Sinapyl nitrile methacrylate) **SM 3b**

Sinapyl nitrile **2b** (4.276 g, 20.8 mmol, 1.0 eq.) and DMAP (0.053g, 0.42 mmol, 0.02 eq.) was added to a 100 ml round bottom flask equipped with a magnetic stirrer and dissolved in EtOAc (60 ml). The flask was sealed and purged with N₂/vacuum cycles. Methacrylic anhydride (3.13 ml, 21 mmol, 1.01 eq.) was added to the reaction mixture and the flask was purged again as mentioned previously. The reaction was stirred for 26h at 65 °C degrees. After completion, NaHCO₃ was added until no further release of gas was observed. The organic phase was then washed with NaHCO₃ (23 ml) and water (23 ml). The organic phase was collected separately and dried with MgSO₄. The organic phase was then filtered and concentrated by rotary evaporation. The residue was purified by basic aluminium oxide column chromatography using a 1:2 mixture of EtOAc:toluene as eluent. Lastly, the product **3b** was purified by being dissolved in acetone and precipitated in heptane. 3.227 g of white powder was obtained (yield: 58%). ¹H NMR (400 MHz, DMSO-*d*) δ 7.60 (d, J = 16.6 Hz, 1H), 7.11 (s, 2H), 6.57 (d, J = 16.7 Hz, 1H), 6.27 (s, 1H), 5.90 (s, 1H), 3.79 (s, 6H), 1.97 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*) δ 164.10, 152.08, 150.30, 134.59, 132.14, 130.09, 128.18, 118.67, 104.80, 97.21, 56.24, 18.03. HRMS *m/z* 296.0908 [M + Na]⁺ (calcd for C₁₅H₁₅NO₄Na, 296.0899).

3.5.5 Poly[4-(2-cyanovinyl)-2-methoxyphenyl methacrylate] **PCM**

10 ml DMSO was added to a 25 ml round bottom flask equipped with a magnetic stirrer and was degassed at 40 °C with N₂/vacuum cycles. **CM** (0.500 g, 2.05 mmol, 1.0 eq.) and degassed DMSO (1.5 ml) were added to a 25 ml Schlenk flask equipped with a magnetic stirrer. The solution was degassed in the same procedure as before. AIBN (6 mg) was added to a vial and dissolved in degassed DMSO (2 ml). 0.45 ml of the AIBN solution was added to the Schlenk

flask and degassed again as before. The reaction was stirred for 24 h at 60 °C and then the product **PCM** precipitated in MeOH upon completion. The solids were washed with MeOH multiple times before drying in a vacuum oven at 50 °C (yield: 68%).

3.5.6 Poly[4-(2-cyanovinyl)-2,6-dimethoxyphenyl methacrylate] **PSM**

10 ml DMSO was added to a 25 ml round bottom flask equipped with a magnetic stirrer and was degassed at 40 °C with N₂/vacuum cycles. **SM** (0.248 g, 0.91 mmol, 1.0 eq.) and degassed DMSO (1.16 ml) were added to a 25 ml Schlenk flask equipped with a magnetic stirrer. The solution was degassed in the same procedure as before. AIBN (12 mg) was added to a vial and dissolved in degassed DMSO (2 ml). 0.2 ml of the AIBN solution was added to the Schlenk flask and degassed again as before. The reaction was stirred for 24 h at 60 °C and then the product **PSM** precipitated in MeOH upon completion. The solids were washed with MeOH multiple times before drying in a vacuum oven at 50 °C (yield: 69%).

3.5.7 Poly[styrene-co-(4-(2-cyanovinyl)-2-methoxyphenyl methacrylate)] **PSCM-x**

10 ml DMSO was added to a 25 ml round bottom flask equipped with a magnetic stirrer and was degassed at 40 °C with N₂/vacuum cycles. **CM** and styrene with a combined weight of approximately 0.5 g (x indicates the mol% of **CM** in the feed) and degassed DMSO (1.5 ml) were added to a 25 ml Schlenk flask equipped with a magnetic stirrer. The solution was degassed in the same procedure as before. AIBN (6 mg) was added to a vial and dissolved in degassed DMSO (2 ml). 0.45 ml of the AIBN solution was added to the Schlenk flask and degassed again as before. The reaction was stirred for 24 h at 60 °C and then the product **PSCM-x** precipitated in MeOH upon completion. The obtained yields can be found in Table 1.

3.5.8 Poly[styrene-co-(4-(2-cyanovinyl)-2,6-dimethoxyphenyl methacrylate)] **PSSM-x**

10 ml DMSO was added to a 25 ml round bottom flask equipped with a magnetic stirrer and was degassed at 40 °C with N₂/vacuum cycles. **SM** and styrene with a combined weight of around 0.5 g (x indicates the mol% of **SM** in the feed) and degassed DMSO (1.5 ml) were added to a 25 ml Schlenk flask equipped with a magnetic stirrer. The solution was degassed in the same procedure as before. AIBN (14 mg) was added to a vial and dissolved in degassed DMSO (2 ml). 0.45 ml of the AIBN solution was added to the Schlenk flask and degassed again as before. The reaction was stirred for 24 h at 60 °C and then the product **PSSM-x** precipitated in MeOH upon completion. The obtained yields are displayed in Table 1.

4 Results and Discussion

4.1 Monomer preparation

As displayed in Figure 3, sinapyl aldehyde **1a** and coniferyl aldehyde **1b** initially underwent nitrilation of the aldehyde group. Due to the light and oxygen sensitivity of these starting materials, the reaction vessels were covered and the reactions were performed under an inert nitrogen atmosphere to prevent degradation. NaHCO₃ was added to the reaction flask once the reaction had reached full conversion which was determined by TLC in combination with ¹H NMR spectroscopy. The ¹H NMR spectra for the compounds which are not presented in this section can be found in the Appendix. The addition of NaHCO₃ will neutralize the acids that are present in the mixture, forming salts which are soluble in the aqueous phase. Coniferyl nitrile **2a** could then easily be extracted using EtOAc without extracting too much of the unwanted species. Since sinapyl nitrile **2b** precipitated in the reaction mixture as it was formed, it did not require extraction. It was simply filtered and washed with deionized water. This approach to transform sinapyl aldehyde and coniferyl aldehyde to the corresponding nitriles proved to be very efficient and resulted in high yields, 83% and 89% respectively. Based on the spectra obtained from ¹H NMR analysis, **2a** and **2b** did not require further purification.

To obtain the corresponding α,β -saturated nitrile compound of **2a**, it had to be selectively hydrogenated. There are different methods that can be utilized to reduce α,β -unsaturated carbonyl compounds, although many of them include complex catalyst preparation and are limited to certain substrates, as well as the use of external hydrogen which often require elevated pressures. A simpler, faster, and less hazardous method has been developed using palladium catalysed (Pd/C) reduction system. Instead of external hydrogen gas, sodium borohydride is used as the reducing agent to generate hydrogen in situ. This approach has been proven to work for various compounds including an aromatic α,β -unsaturated nitrile, resulting in 100% yield [20]. Although several attempts to reduce **2a** were made, including longer reaction times, different solvents, and varying amounts of NaBH₄ and Pd/C, the reduced product could not be successfully obtained. The reactions resulted in very low conversions (< 5%).

Attempts to selectively reduce **1a** and **2a** were also performed using external H₂ and Pd/C as catalyst. The reaction did not appear to be selective towards the reduction of the α,β -unsaturated aldehyde since the formation of the completely reduced alcohol could be identified. The conversions were also observed to be very low. Thus, it was decided that the focus of the project would be put towards the unsaturated compounds.

2a and **2b** then underwent methacrylation of the hydroxyl group by utilizing methacrylic anhydride. As the methacrylic anhydride is reacted and cleaved, it will form methacrylic acid. Thus, NaHCO₃ is added to the reaction mixture upon completion which was determined by TLC and ¹H NMR. The salts that are formed can be easily removed by washing the organic mixture with deionized water. Coniferyl nitrile methacrylate **3a** and sinapyl nitrile methacrylate **3b** (**CM** and **SM**, respectively) both required further purification before polymerisation. To remove residual **2a**, **2b** and acid present in the respective mixtures, **CM** and **SM** were purified

by basic aluminium oxide column chromatography. Lastly, **SM** was purified by precipitation in heptane to remove residual impurities, obtaining a white powder (yield = 58%). ^1H NMR spectroscopy was used to get an estimate of the purity of the compounds throughout the purification steps. The ^1H NMR spectrum for the purified product **SM** is presented in Figure 5.

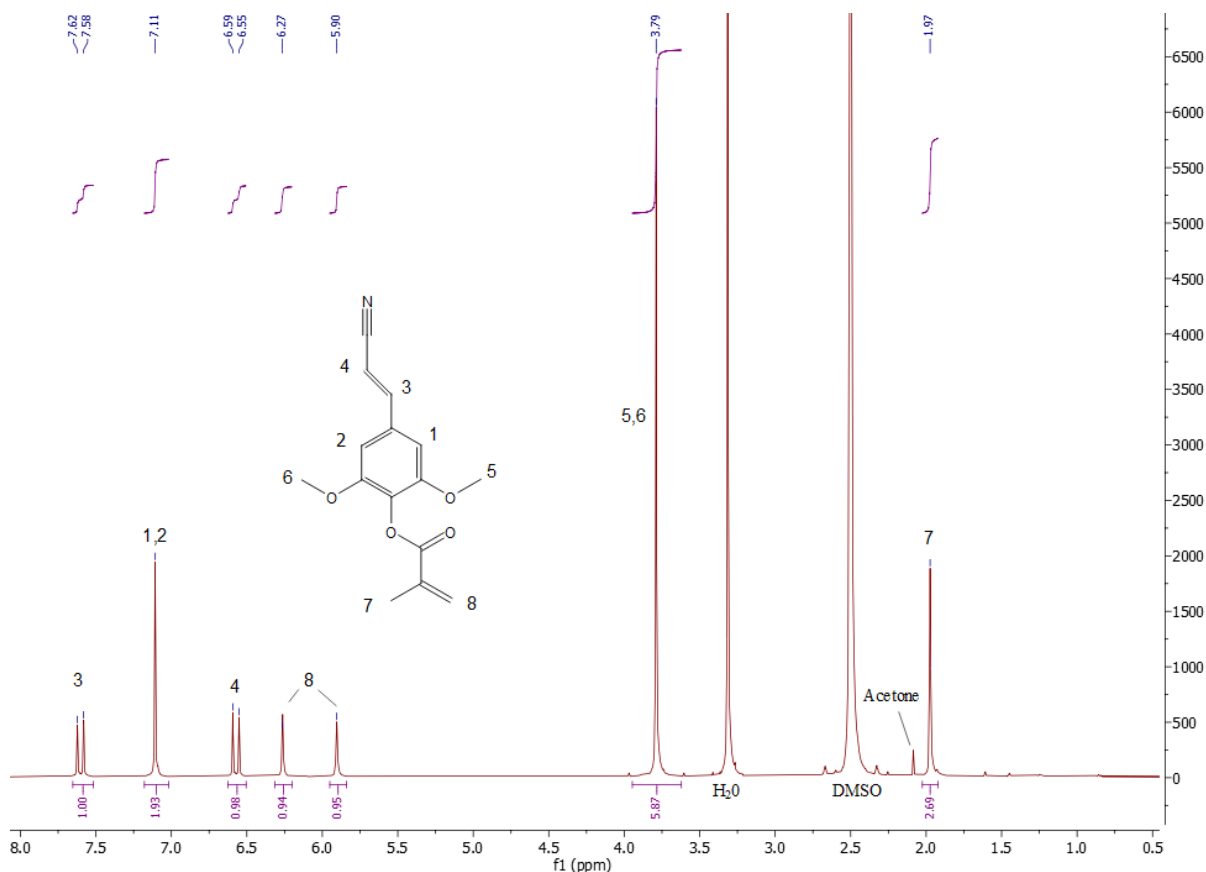


Figure 5: ^1H NMR spectrum for sinapyl nitrile methacrylate **SM**.

The three impurity peaks that can be distinguished in Figure 6 at 6.19 ppm, 5.88 ppm, and 1.93 ppm appears to be originating from residual methacrylic anhydride. Two additional singlet peaks at 1.5 and 1.56 ppm, which do not correspond to the synthesized monomer, nor the methacrylic anhydride, could not be identified. Due to the difficulty to completely isolate **CM** at reasonable yields, it was decided nevertheless to proceed with the polymerisations.

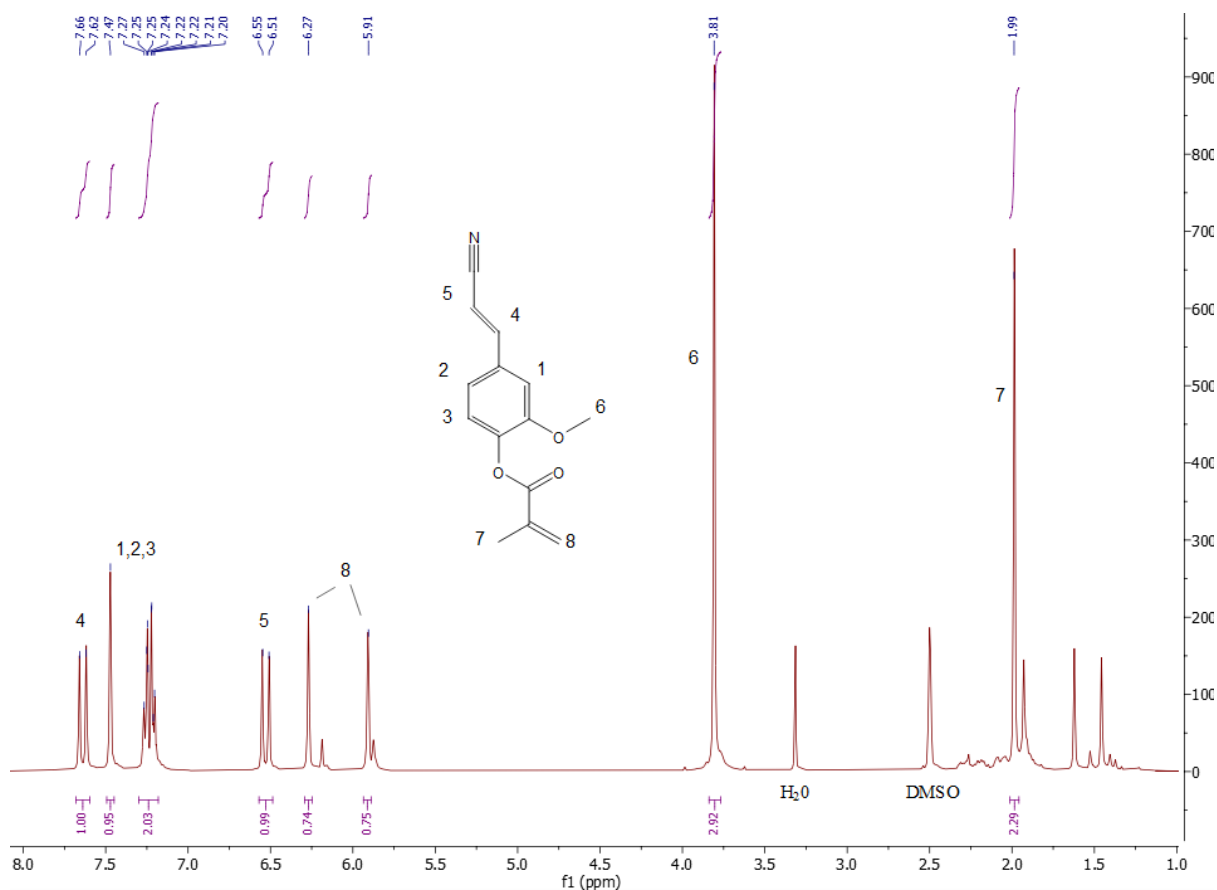


Figure 6: ¹H NMR spectrum of coniferyl nitrile methacrylate **CM**.

4.2 Polymerisations

Homopolymers of the synthesized monomers, **PCM** and **PSM** were prepared through free radical polymerisation in the presence of AIBN. This type of polymerisation is thermally initiated as the AIBN will start to decompose above 40 °C, forming radicals that react with the methacrylic part of the monomers and propagate to form longer chains.

As the monomers began to propagate the signals in the ¹H NMR spectra from the alkene part of the methacrylate were observed to decrease in intensity, thus confirming that the polymerisations took place. As the reaction proceeded, it was observed that gel-like lumps formed in the reaction vessel displaying low solubility, indicating that the synthesized polymer could potentially be cross-linked. Upon completion, the gel particles displayed little to no solubility in various solvents such as DMSO, DMF, acetone, chloroform and THF. Due to the difficulties in dissolving the polymers, the molecular weight for the respective homopolymers could not be determined by size-exclusion chromatography (SEC).

The thermal stability of the homopolymers, **PCM** and **PSM**, were analysed by studying the thermal decomposition at 5% weight loss ($T_{d,95\%}$) using TGA. The results obtained from TGA, found in Table 1, displayed a thermal decomposition at $T_{d,95\%} = 184$ °C and 307 °C respectively. **PSM** displayed a high thermal stability with a single decomposition step, comparable to what has been observed with similar polymethacrylates [3]. On the other hand, **PCM** displayed a

two-step decomposition where the polymer already began to decompose at 130 °C, losing about 26% of its weight before reaching the second decomposition step at around 308 °C (Figure A6 in Appendix). The temperature at which the second decomposition step for **PCM** begins is similar to the temperature of the single decomposition step for **PSM**. Since the two homopolymers are expected to display similar decomposition temperatures, as they have very similar molecular structure, this is likely due to the degradation of the backbone of the polymer chains which is connected by the methacrylic part of the monomers. Thus, the first decomposition step for **PCM** is likely attributed to degradations that are not part of the main polymer chain.

Table 1: Thermal data and isolated yields of the synthesized homopolymers and copolymers.

Sample	Nitrile monomer (mol%) in feed	$T_{d,95\%}$ (°C)	T_g (°C)	Yield (%)
PSM	100	307	-	70
PSSM-75	75	311	-	79
PSSM-50	50	324	-	81
PSSM-25	25	349	-	85
PSSM-5	5	315	142	51
PSSM-3	3	348	126	48
PCM	100	184	-	68
PSCM-50	50	194	-	84
PSCM-5	5	331	127	44
PSCM-3	3	301	124	41

It has been reported that the variation of T_g of polymers with different contents of similar nitrile-containing monomers follow a linear trend, with increasing T_g as the amount of the nitrile monomers increase [3]. To get an estimation of the T_g for the polymers that did not exhibit any transitions from the DSC measurements, the data points for 3 and 5mol% with respective T_g was plotted (Figure 7). Extrapolation was then used, with the assumption that it follows a linear trend, to obtain estimated T_g s for PSSM-25 and PSCM-50, 302 and 194.5 °C respectively. These estimated T_g s are above the temperatures of which the polymers started to degrade and could therefore not been identified by DSC analysis. It must be emphasized that there are only two data points for each series which increases the uncertainty surrounding these results.

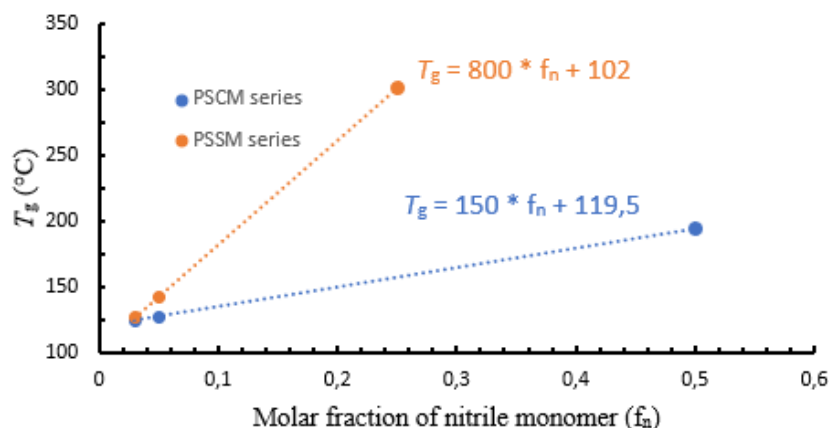


Figure 7: T_g of the copolymers containing 3 and 5 mol% of the nitrile monomers with respective T_g , and the estimated T_g values for **PSSM-25** and **PSCM-50**.

Neither **PCM** nor **PSM** displayed any thermal transitions when analysed by DSC, the polymers will therefore begin to degrade before reaching their T_g . These results, in combination with the very low solubility of the polymers, indicates that both homopolymers are cross-linked. This could potentially be caused by a [2+2] cycloaddition reaction of the α,β -unsaturated nitriles between two monomers, leading to the formation of a four membered ring that connects polymer chains shown in Figure 8, subsequently forming a cross-linked network.

It has been reported that various β -acrylic acids can undergo this type of cyclization reaction through the exposure of UV irradiation [21]. Cinnamic acid, being one of them, has been used in poly(methyl methacrylate) films to incorporate and control the amount of cross-linking by a photoinitiated free-radical polymerisation. This has also been shown to be reversible by exposing the cross-linked polymer with higher energy UV irradiation. This will cause a [2+2] cycloreversion reaction that disrupts the cross-linked network, generating separate polymer chains [22],[23]. Regarding this work, by examination of the ^1H NMR spectra, there is no indication of the presence of the cyclic dimer that could potentially be formed during the preparation of the monomers **CM** and **SM**. Therefore, if this dimer is the cause of the cross-linking, it is most likely formed during the radical polymerisation.

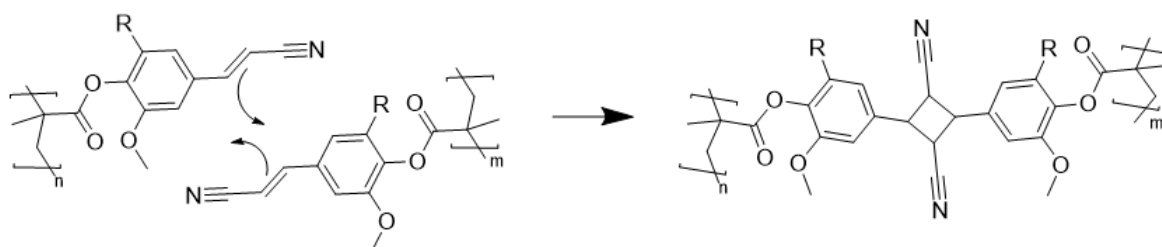


Figure 8: Formation of a four-membered ring between the α,β -unsaturated nitrile monomers, suggested to be one of the causes for the crosslinking. R = H or OCH_3 .

The crosslinking could also be formed through termination by combination between two radical nitrile monomers, since the double bond is susceptible to attacks by radicals (Figure 9). The nitrile compounds will then be connected by a C-C single bond between the α -carbons, depicted in Figure 9, but the β -carbons could also be involved in this type of reaction.

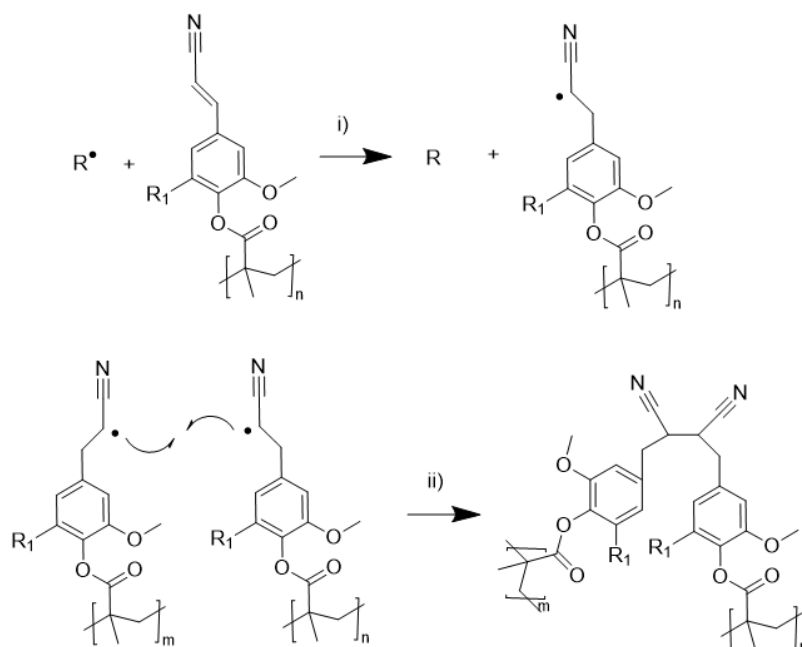


Figure 9: i) Chain transfer between R (arbitrary radical molecule) followed by ii) termination by combination between two radical nitrile monomers. A potential cause for the crosslinking. $R_1 = H$ or OCH_3 .

SM was copolymerized with styrene at different ratios, 25, 50 and 75 mol% of **SM**. These copolymers displayed low to no solubility, regardless of the ratio between styrene and **SM**. As the amount of **SM** was decreased from 75–25 mol%, no trend whether the copolymers displayed any change in solubility was observed. The reason for this is likely that the amount of **SM** is too high, resulting in a degree of cross-linking which remains high enough to not show significant differences in terms of solubility. Analysis of the molecular weight of the copolymers could not be performed by SEC due to the difficulty in dissolving the polymers.

The $T_{d,95\%}$ of **PSSM-75**, **PSSM-50**, **PSSM-25** ranged from 311–349 °C (Table 1) and did not display a clear trend whether the decomposition temperatures vary depending on content of the nitrile monomer in the feed. None of these copolymers displayed any thermal transition from the data obtained from the DSC, which implies that they will start to decompose before reaching their T_g , similar to the homopolymers.

As the content of the nitrile monomer in the feed was further decreased to 5 mol% (**PSSM-5**) and 3 mol% (**PSSM-3**), it was observed that the sizes of the insoluble gel-like lumps formed in the reaction vessel decreased. Although, it only appeared to be more dispersed since it still showed very low solubility. Hence, it was not possible to obtain 1H NMR spectra showing clear

signals at high intensities. **PSSM-5** and **PSSM-3** both displayed T_g s at 142 and 126 °C respectively. Thus, as the content of the nitrile monomer decreased, so did the T_g . A lower amount of **SM** in the polymer chain will lead to a reduced degree of cross-linking, decreasing T_g substantially since there is less hindrance for molecular motion, eventually resulting in polymers that do not decompose before transitioning to its rubbery state.

The T_g s for **PSCM-5** and **PSCM-3** were measured at 127 and 124 °C respectively, displaying a decrease in T_g as the amount of **CM** was reduced in the feed. Although, the difference is not as significant as for the **PSSM** series. As the content of **CM** decreased in the feed to ≤ 5 mol%, $T_{d,95\%}$ was observed to be above 300 °C, similarly to the **PSSM** series. The DSC traces for the polymers exhibiting T_g s below their decomposition temperatures are presented in Figure 10.

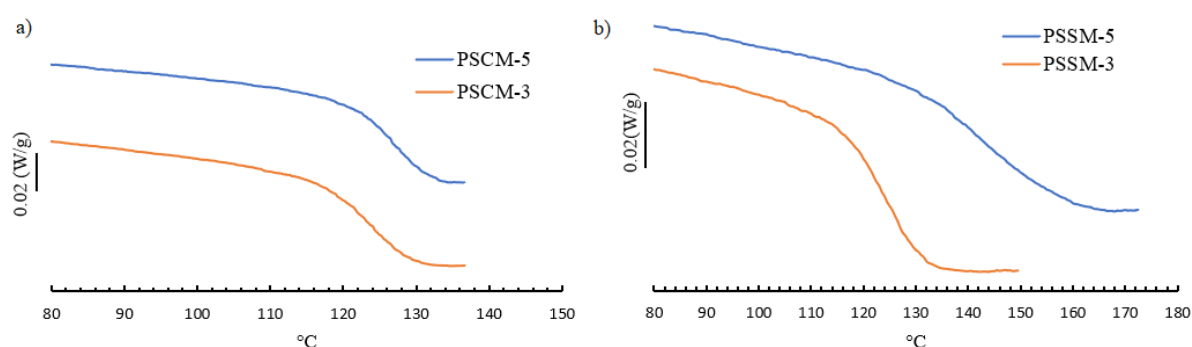


Figure 10: DSC traces (second heating cycle) of (a) **CM** copolymers, and (b) **SM** copolymers.

Compared to pure polystyrene, which possess a T_g of around 100 °C, it is evident that T_g is considerably affected by the incorporation of **CM** and **SM** in the copolymers. The significant increase in T_g is likely attributed to the crosslinking in combination with the presence of the polar nitrile group.

To get a rough estimation of the degree of crosslinking in the polymers, they were centrifuged with THF as the solvent. By measuring the difference in weight of the dry polymers, before and after centrifugation, it could be observed that there was a significant difference in weight as the content of the nitrile monomer decreased (Table 2). The polymers prepared from ≥ 50 mol% of **CM** and **SM** retained ≥ 93 wt% after centrifugation. As the content of **SM** decreased to 25 mol%, the obtained weight after centrifugation was 79 wt%. The polymers prepared with ≤ 5 mol% of the nitrile monomers were measured at 52–56 wt% after centrifugation. Thus, the amount of cross-links appears to decrease which could be expected. Although, the cross-linking is still significant considering the low contents of the nitrile monomers in the feeds.

Table 2: Retained weight after centrifugation of the synthesized polymers.

Sample	Retained weight after centrifugation (wt%)
PSM	98
PSSM-75	98
PSSM-50	94
PSSM-25	79
PSSM-5	55
PSSM-3	56
PCM	97
PSCM-50	93
PSCM-5	53
PSCM-3	52

5 Conclusion

Coniferyl aldehyde and sinapyl aldehyde were, as the first step in the monomer preparation, effectively transformed into the corresponding nitrile compounds using mild conditions, resulting in high yields and did not require further purification. The second step, and also the last step, of the preparation of the monomers included methacrylation of the hydroxyl group. The monomer which included two methoxy groups, **SM**, could be isolated at a moderate yield. Conversely, **CM** could not be fully isolated as the attempted methods of purifying the compound resulted in very low yields.

Attempts to selectively reduce an α,β -unsaturated nitrile to eventually synthesize the corresponding saturated nitrile monomer were performed, but were unfortunately unsuccessful. Thus, no comparisons could be made between polymers made from the saturated and unsaturated monomers.

The synthesized homopolymers and copolymers all appeared to be crosslinked, showing little to no solubility in various solvents. Therefore, the M_n and M_w could not be measured for any of the polymers. The thermal analysis of the two homopolymers displayed varying $T_{d,95\%}$, higher for the more substituted polymer and there were no indications whether they possessed a T_g lower than their decomposition temperatures. Thus, it appeared that the polymers contained a substantial number of crosslinks.

The copolymers that were synthesized with 25 mol% or more of the nitrile monomers in the feed did not display any T_g s from the DSC measurements. The decomposition temperatures varied, but no certain trend could be determined. A decrease of the nitrile monomer content in the feed (≤ 5 mol%) resulted in T_g s below the temperature at which they would begin to degrade. The significant changes in the T_g values are presumably attributed to the crosslinking of the polymers in combination with the increased intermolecular interactions induced by the highly polar nitrile group.

6 Future work

Regarding future work, it would be interesting to look further into the selective hydrogenation of the α,β -unsaturated compounds to eventually synthesize the corresponding saturated nitrile methacrylate monomers. These can then undergo polymerization reactions, both homopolymerizations as well as copolymerizations, for instance with styrene or MMA, to examine the differences in solubility and thermal properties.

As these polymers would not contain an α,β -unsaturated nitrile, which is the suggested cause of the cross-links, they could potentially be thermoplastics that exhibit enhanced thermal properties which are affected directly by the presence of the polar nitrile group as well as the substituted methoxy groups.

Further investigation regarding the proposed cause of the crosslinking could, for instance, be made by exposure of UV-light. It would be interesting to know whether the crosslinking can be controlled by exposing the polymers to certain wavelengths of UV-light, to form but also potentially break the crosslinks using different wavelengths.

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Appendix

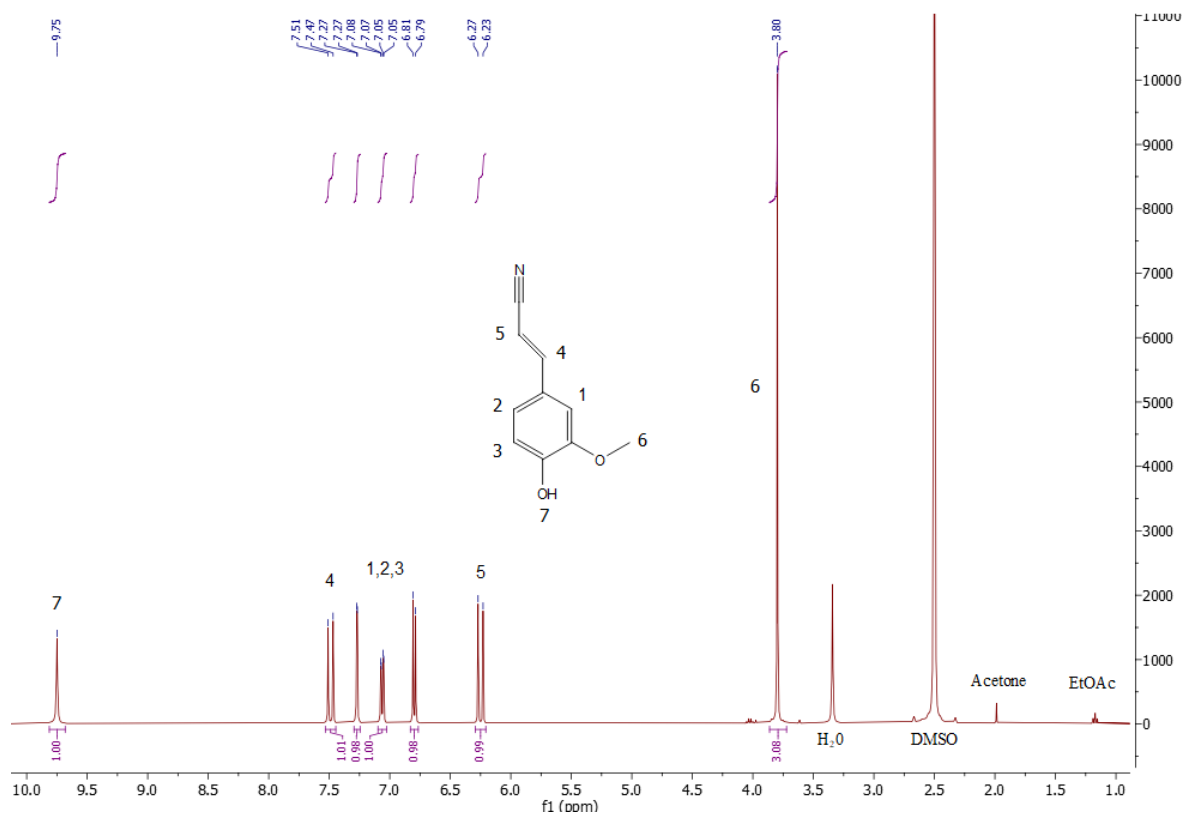


Figure A1: ¹H NMR spectrum for coniferyl nitrile (**2a**).

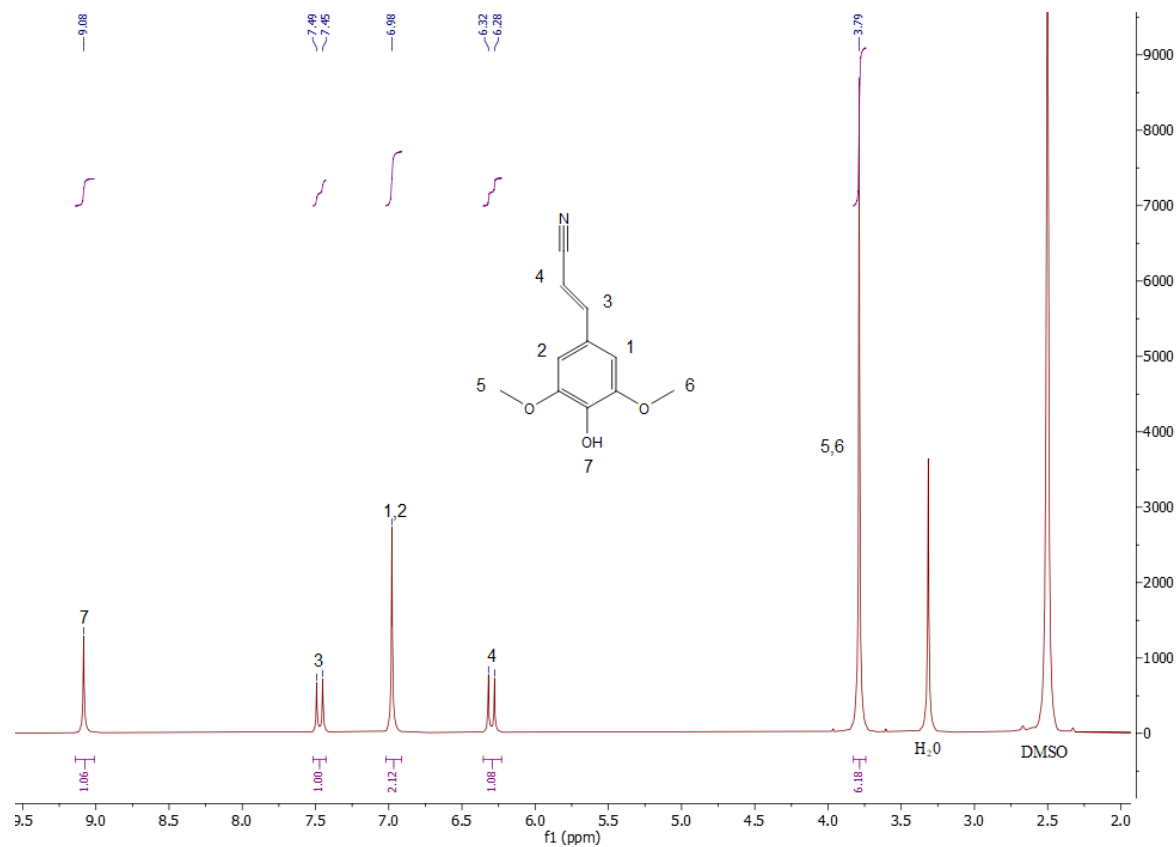


Figure A2: ¹H NMR spectrum for sinapyl nitrile (**2b**).

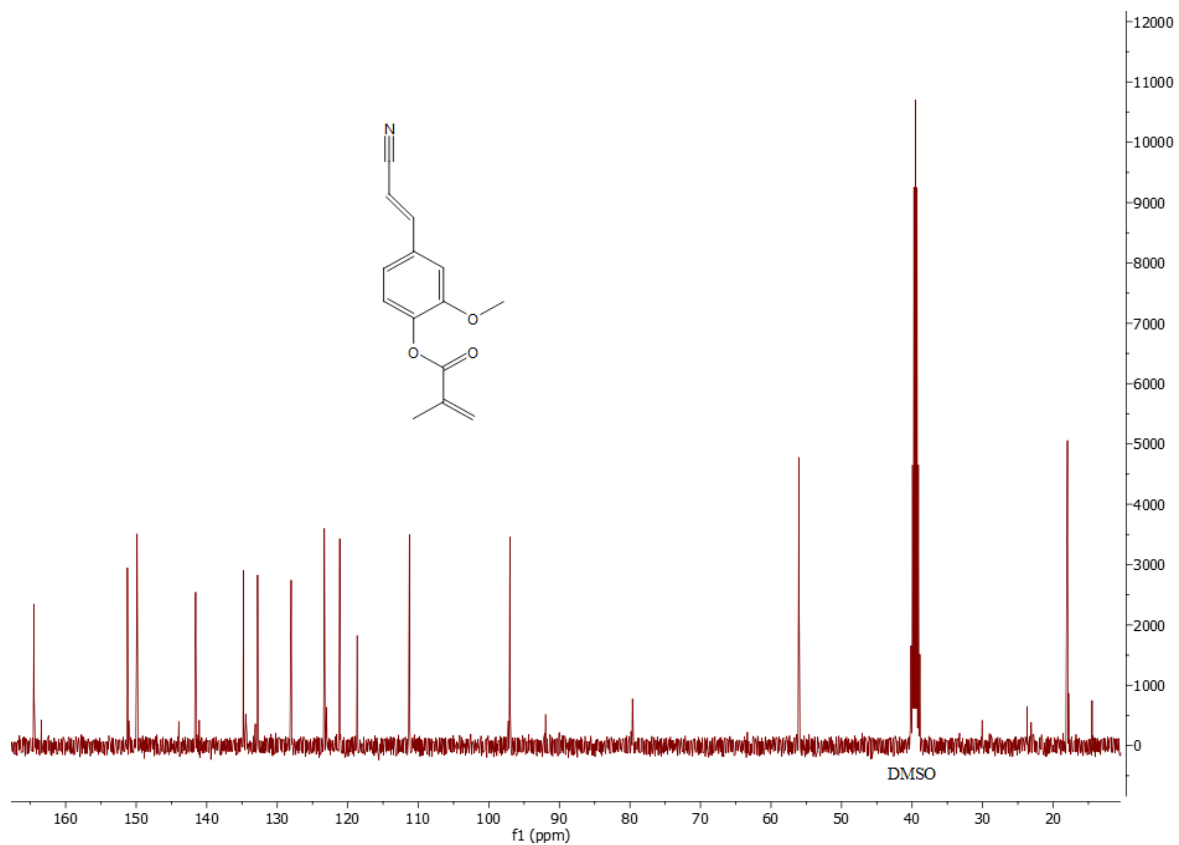


Figure A3: ¹³C NMR spectrum for coniferyl nitrile methacrylate (CM)

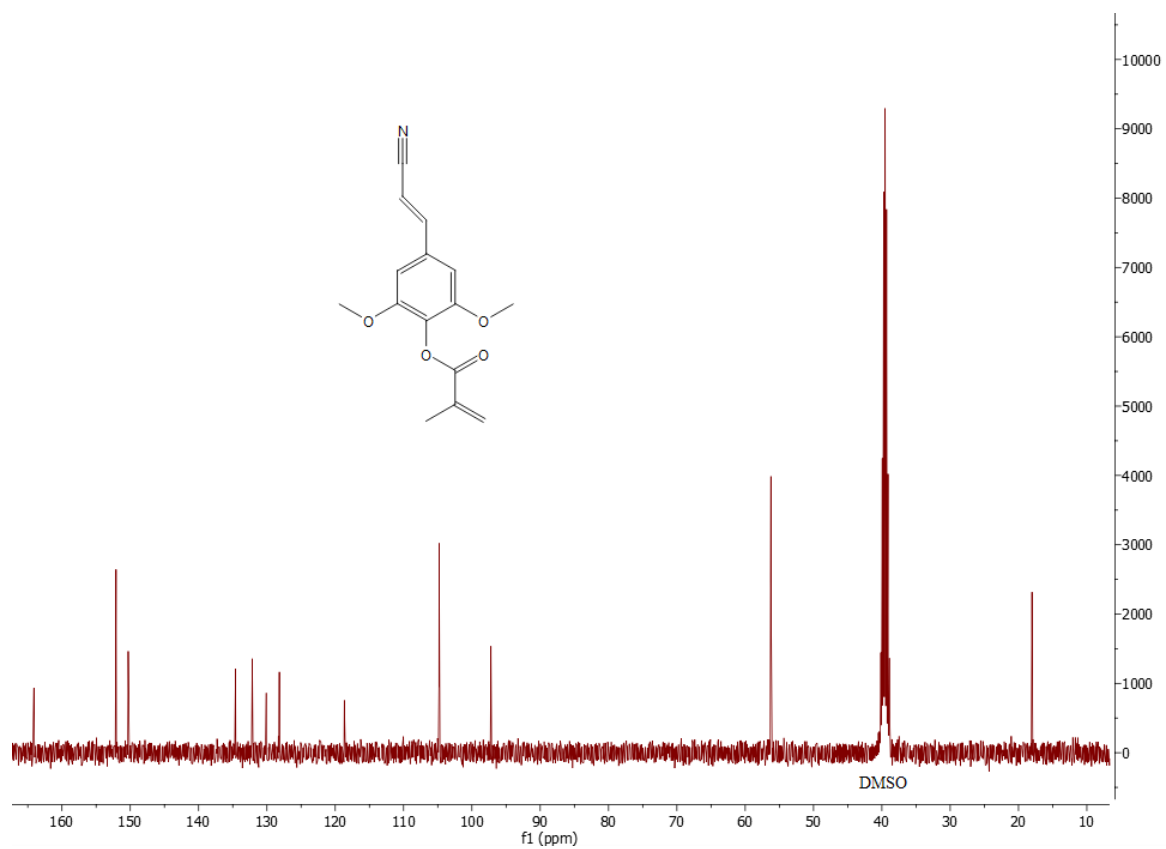


Figure A4: ¹³C NMR spectrum for sinapyl nitrile methacrylate (SM)

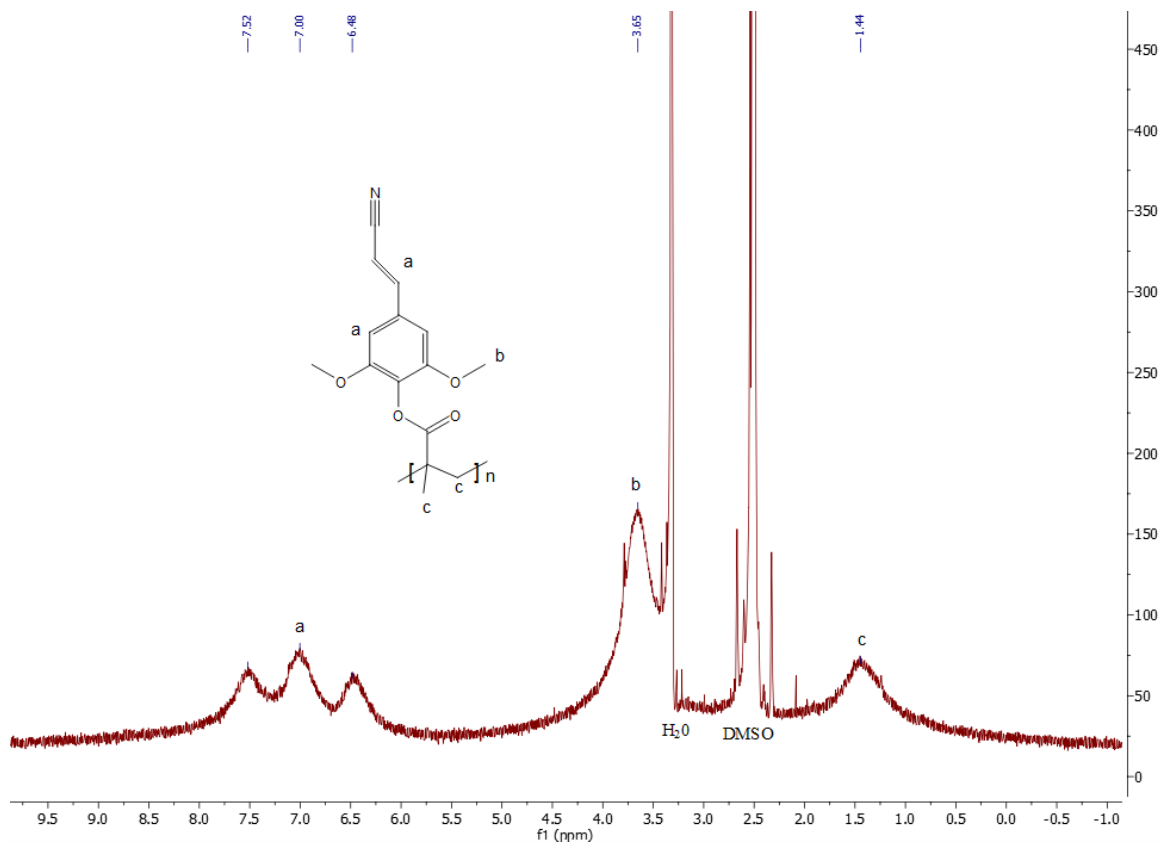


Figure A5: ¹H NMR spectrum for poly[4-(2-cyanovinyl)-2,6-dimethoxyphenyl methacrylate] (**PSM**)

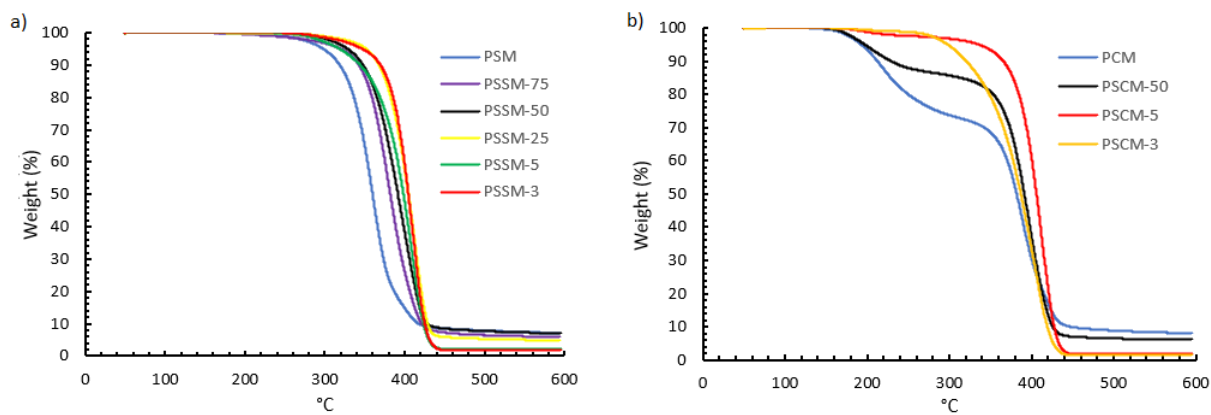


Figure A6: TGA traces of (a) **PSM** and the **PSSM** series, and (b) **PCM** and the **PSCM** series.