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TITLE:

Designed for Molecular Recycling: A Lignin-Derived Semi-aromatic Biobased Polymer

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SUMMARY:

An example of a closed-loop approach towards a circular materials economy is described here. A whole sustainable cycle is presented where biobased semi-aromatic polyesters are designed by polymerization, depolymerization, and then re-polymerized with only slight changes in their yields or final properties.

ABSTRACT:

The development of chemically recyclable biopolymers offers opportunities within the pursuit of a circular economy. Chemically recyclable biopolymers make a positive effort to solve the issue of polymer materials in the disposal phase after the use phase. In this paper, the production of biobased semi-aromatic polyesters, which can be extracted entirely from biomass such as lignin, is described and visualized. The polymer poly-S described in this paper has thermal properties similar to certain commonly used plastics, such as PET. We developed a Green Knoevenagel reaction, which can efficiently produce monomers from aromatic aldehydes and malonic acid. This reaction has been proven to be scalable and has a remarkably low calculated E-factor. These polyesters with ligno-phytochemicals as a starting point show an efficient molecular recycling with minimal losses. The polyester poly(dihydrosinapinic acid) (poly-S) is presented as an example of these semi-aromatic polyesters, and the polymerization, depolymerization, and re-polymerization are described.

INTRODUCTION:

In contrast to the incineration of polymeric waste, chemical recycling offers the possibility to recover the monomers. Chemical recycling is a logical choice at the end of the technical life of polymeric materials since these polymeric materials are produced chemically¹. There are two

ways to recycle the polymeric material chemically, pyrolysis and molecular recycling². With pyrolysis, the polymeric material is transformed into products of higher value by using extreme conditions^{3,4}. Molecular recycling is an efficient method for recovering the starting materials using depolymerization. After depolymerization, the monomeric units can be repolymerized into virgin polymeric materials⁵. The availability of suitable monomers to apply molecular recycling on a larger scale is wanting. The current plastic problem dictates that society demands sturdy and robust polymeric materials. At the same time, it is also preferred that the same polymeric materials are easily recyclable and do not endure in the environment. Current polymeric materials with good thermal and mechanical properties do not depolymerize easily⁶.

Lignin, commonly found in vascular plants, is responsible for 30% of the world's natural carbon content and is the second most abundant biopolymer after cellulose. Lignin has a complex amorphous structure and appears to be a suitable alternative to replace aromatics extracted from fossil materials. The three-dimensional structure of lignin provides strength and stiffness to wood, as well as resistance to degradation. Chemically speaking, lignin is a very complex polyphenolic thermoset. It consists of varying composition of three different methoxylated phenylpropane structures. Syringyl, guaiacyl, and p-Hydroxyphenyl (often abbreviated as S, G, and H, respectively) are derived from the monolignols sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol⁷. The distribution of these units differs per biomass type, with softwood, for instance, consisting of mostly guaiacyl units and hardwood of guaiacyl and syringyl units^{8,9}. Renewable natural sources, such as trees and plants, are desirable for the production of redesigned monomers for innovative polymeric materials¹⁰. These monomers, isolated and synthesized from natural sources, are polymerized to so-called biobased polymers¹¹.

Aromatic carboxylic acids are several orders of magnitude less electrophilic than the equivalent aliphatic carboxylic acids for electronic reasons¹². Various commercial polyesters use aromatic carboxylic acids instead of aliphatic carboxylic acids. As a result, the fibers in polyester textiles made from poly(ethylene terephthalate) (PET) fibers are almost insensitive to hydrolysis during washing or, for example, rain¹³. When the molecular recycling of polyesters is wanted, it is advisable to use aliphatic esters in the build-up of the polymer.

For the reasons mentioned, we have investigated the possibilities of making polyesters from 4-hydroxy-3,5-dimethoxy-dihydrocinnamic acids¹⁴. Previous studies by Kricheldorf¹⁵, Meier¹⁶, and Miller^{17,18} show that it is challenging to build polymers using 4-hydroxy-3,5-dimethoxy-dihydrocinnamic acid. Decarboxylation and crosslinking hindered the polymerizations, and so limiting the success of these syntheses. Also, the mechanism of the polycondensation remained unclear. The presented paper describes the conditions in which the polyester poly-(dihydrosinapinic acid) can be synthesized regularly and in high yield, thus paving the way for using semi-aromatic polyesters that are molecularly recyclable.

We have developed a green and efficient way to synthesize sinapinic acid using a condensation reaction between syringaldehyde and malonic acid^{19,20}. After this Green Knoevenagel, hydrogenation produces dihydrosinapinic acid, which is suitable for reversible polycondensation. This publication visualizes the synthetic steps to the molecularly recyclable polymer

poly(dihydrosinapinic acid), referring to the base units of lignin, called poly-S. After analyzing the polymeric material, poly-S is depolymerized to the monomer dihydrosinapinic acid under relatively favorable conditions and repolymerized over and over again.

PROTOCOL:

1. Green Knoevenagel condensation of syringaldehyde towards sinapinic acid with 5 mol% ammonium bicarbonate

1.1. Add malonic acid (20.81 g, 200.0 mmol) together with syringaldehyde (36.4 g, 200.0 mmol) to a 250 mL round-bottom flask. Dissolve both constituents in 20.0 mL of ethyl acetate and add ammonium bicarbonate (790 mg, 10.0 mmol) to the flask.

NOTE: To ensure full completion of the condensation reaction, the rotary evaporator can be used to distill the ethyl acetate and concentrate the reaction mixture, resulting in a solvent-less reaction.

1.2. Keep the reaction mixture for 2 hours at 90 °C in the open flask without stirring for complete conversion to sinapinic acid.

NOTE: During this reaction, several morphological changes are observed. The reaction mixture changes from a dense grey mixture to a dissolved yellow mix due to the formation of water during the condensation step of the reaction. After evaporation of the condensate, the reaction mixture solidifies again, indicating full conversion.

1.3. In the work-up of the sinapinic acid product, dissolve the residue in 100 mL of a saturated aqueous NaHCO_3 -solution. Transfer the solution to a beaker and subsequently acidify it to a pH of 2 using 6 M HCl.

NOTE: While adding the saturated aqueous NaHCO_3 -solution, the crude product dissolves slowly and requires some time and manual scraping to dissolve fully. Once wholly dissolved and transferred to the beaker, the acidic solution of 6 M HCl is added drop-wise. Sinapinic acid will precipitate quickly, and the release of CO_2 gas will cause the product to foam.

1.4. Separate the resulting residue by vacuum filtration and wash it with demineralized water.

NOTE: At this point, the purity of the product can be analyzed by HPLC. If the product appears contaminated, the next purification step (e.g., recrystallization) must be applied.

1.5. After recrystallization in a mixture of water-ethanol (4:1, v/v), separate the crystals by filtration. Dry the residue at 60 °C in a vacuum oven, resulting in 42.56 g of pure sinapinic acid.

NOTE: The purity of sinapinic acid is measured by melting point analysis and HPLC.

2. Hydrogenation of sinapinic acid towards dihydrosinapinic acid with nickel.

2.1. Charge a 450 mL flask (using a hydrogenation apparatus) with sinapinic acid (33.6 g, 150 mmol). Dissolve the sinapinic acid in 300 mL of 2 M NaOH solution and add 1.5 g of nickel slurry (see **Table of Materials**) before fitting the flask to the apparatus.

NOTE: The color of the reaction mixture changes due to the addition of the alkaline solution. Sinapinic acid will be yellow in its crystalline form, but when deprotonated by the base, the color of the solution will change to red. The addition of nickel will turn the color black.

2.2. Pressurize the reactor with three bar of hydrogen gas and mechanically shake the reaction at 80 °C for three hours.

2.3. Cool the reactor to room temperature and depressurized slowly. Recover most of the nickel catalyst with a magnet and subsequently filter the solution under reduced pressure.

NOTE: The reaction mixture should change from red to green color, visible after filtration. The notable color change is because the conjugated system is interrupted by hydrogenation of the double bond.

2.4. Acidify the solution with a 4 M HCl solution towards a pH of 2. Subsequently, perform an extraction with ethyl acetate (4 times 50 mL). Remove the solvent under reduced pressure after drying over MgSO₄. Dry the solid product dihydrosinapinic acid at 60 °C in a vacuum oven.

NOTE: Theoretically, the polycondensation reaction can be processed on dihydrosinapinic acid, but there are some practical drawbacks. Due to the molecular structure, dihydrosinapinic acid sublimates above the melting point. An acetylation reaction can be performed to prevent sublimation and increase reactivity.

3. Acetylation of dihydrosinapinic acid towards acetylated monomers and oligomers (prepolymer).

3.1. Add dihydrosinapinic acid (22.6 g, 100 mmol) to a 250 mL round-bottom flask, followed by acetic anhydride (14.2 mL, 150 mmol) and sodium acetate (0.82 g, 10 mmol).

NOTE: The dihydrosinapinic acid does not fully dissolve in the acetic anhydride at room temperature.

3.2. Heat the solution to 90 °C while stirring for one hour for complete conversion of dihydrosinapinic acid towards 4-acetoxy-dihydrosinapinic acid and its acetylated oligomers.

NOTE: All the products remain dissolved in acetic anhydride. To increase the total precipitation of 4-acetoxy-dihydrosinapinic acid, add a small amount of water-soluble solvent in the next step.

3.3. Dissolve the solid in 25 mL of acetone, precipitate (solvent-non solvent) into 250 mL of 0.1 M HCl and filter under vacuum.

NOTE: The best result shows an entirely precipitated white, sticky solid. If the product solution is added to the HCl solution too quickly, the product remains as a brown liquid at the bottom of the acidic solution. In this situation, extract the entire product solution with ethyl acetate (4 times 50 mL). After drying over MgSO_4 , remove the ethyl acetate under reduced pressure. The product is 4-acetoxy-dihydrosinapinic acid and prepolymer.

4. Polymerization of acetylated monomers and oligomers.

4.1. Add the monomers, dihydrosinapinic acid (20.8 g, 100 mmol), and prepolymer to a 100 mL round-bottom flask and add finely powdered NaOH (400 mg, 10.0 mmol). Heat the reaction mixture for three hours at a set temperature of 140 °C in the open flask while stirring at 100 rpm.

NOTE: During this reaction, water and acetic acid condense from the open flask. The pH of the vapor can be measured to confirm the condensation of acetic acid. The morphology of the reaction product changes from a molten state to a compact, light-brown product. The setup is subjected to a nitrogen flow to promote the evaporation of the condensate and prevent oxidation. Such reactions are usually stirred with a mechanical stirrer due to the high viscosity of the mixture. However, the use of a magnetical stirrer is sufficient, and the difference is negligible on this scale.

4.2. Set up a solvent assisted polymerization by adding zinc(II)acetate (180 mg, 1 mmol) and 25.0 mL of 1,2-xylene to the flask. Raise the set temperature to 160 °C.

NOTE: Raise the set temperature to 160 °C to ensure the reflux of 1,2-xylene and full reactivity of the polymerization. The temperature of the reaction itself remains at 144 °C, due to the boiling point of the 1,2-xylene.

4.3. Reflux the mixture at 144 °C for three hours with constant water and acetic acid removal using a Dean-Stark head.

NOTE: After adding the 1,2-xylene and heating the reaction flask to the required temperature, the reagents form a brown slurry with a lower viscosity. This lower viscosity is presumed to benefit the mobility of the end-groups of the polymer, promoting reactivity.

4.4. Cool the reaction mixture down and remove the 1,2-xylene by applying a vacuum (<10 mbar).

NOTE: The reaction mixture solidifies while evaporating the solvent and turns into an off-white solid.

4.5. Raise the temperature to 240 °C during the final stage of the polymerization and apply a

high vacuum <1 mbar for thirty minutes.

NOTE: Only a slight amount of condensate evaporates during this step because only a small amount of condensation is needed to boost the chain length substantially at this stage of polymerization.

4.6. Cool the polymer poly-S to room temperature and wash with methanol to eliminate dihydrosinapinic acid and prepolymers. The obtained product is a light-brown solid.

NOTE: After the process, the chain length and thermal properties of the polyester are investigated by GPC and DSC.

5. Representative procedure for the depolymerization of poly-S in 1 M NaOH:

5.1. Finely grind and sieve poly-S into particles smaller than 180 μm to measure hydrolytic degradation.

NOTE: To grind the particles to the required size, use a mortar and pestle with liquid nitrogen-cooled poly-S, followed by a mechanical sieving step.

5.2. Load several test tubes with 20 mg of poly-S and add 1.0 mL of 1 M NaOH solution. Incubate the tubes at three different temperatures (RT, 50, and 80 $^{\circ}\text{C}$), with an agitation of 500 rpm using a controlled environment incubator shaker.

NOTE: Use a heating-block/shaker with multiple entries for this reaction to ensure all the reactions take place in precisely the same (thermal) conditions.

5.3. Neutralize a test tube at regular time intervals with 1.0 mL of 0.5 M H_2SO_4 and add 2.0 mL of methanol after cooling.

NOTE: Small amounts of poly-S and only 1.0 mL of 1 M NaOH are used because these concentrations can, after the addition of methanol, be directly injected in HPLC and do not require any further dilution.

5.4. Filter all samples using 0.45 μm PTFE syringe filters and inject (20 μL) on HPLC using an autosampler. Monitor the absorbance at $\lambda = 254 \text{ nm}$, and calculate the concentrations from a calibration curve of known dihydrosinapinic acid standard solutions.

NOTE: The standard solutions of the calibration curve should be made in the same solvent mixture as the work-up after the depolymerization.

REPRESENTATIVE RESULTS:

Sinapinic acid was synthesized in high purity and high yield (> 95%) from syringaldehyde using the Green Knoevenagel condensation. (Supporting Information: **Figure S1**) The E-factor is an

indication of waste production where a higher number indicates more waste. The E-factor is calculated by taking the total material input, subtracting the amount of the desired end product, and dividing the whole by the amount of the end product. This Green Knoevenagel condensation has an E-factor of 1.0, which can be calculated: $(((29.81 \text{ g malonic acid} + 36.4 \text{ g syringaldehyde} + 0.790 \text{ g ammonium bicarbonate} + 18.04 \text{ g ethyl acetate}) - 42.56 \text{ g sinapinic acid}) / 42.56 \text{ g sinapinic acid})$. The sinapinic acid was hydrogenated with a high yield (>95%) to obtain the intended monomer dihydrosinapinic acid. (Supporting Information: **Figure S2**) This hydrogenation reaction has an E-factor of 0.84. Subsequently, dihydrosinapinic acid was acetylated to obtain 4-acetoxy-dihydrosinapinic acid and its prepolymer. The E-factor of this acetylation reaction was 0.45, assuming full conversion to 4-acetoxy-dihydrosinapinic acid (Supporting Information: **Figure S3**).

Usually, the E-factor of organic synthetic reactions of pharmaceuticals is between 5 and 100, and these reactions frequently use relatively harmful chemicals²¹. The E-factor, calculated for both the Green Knoevenagel and subsequent reactions, is remarkably low compared to these numbers. Yet, the E-factor exhibits some shortcomings. For example, the environmental hazard of a given waste component is not reflected by the E-factor. In principle, this can be compensated by the "environmental quotient" (Q) taking the "environmental unfriendliness" of a given waste into account. Because the catalyst ammonium bicarbonate is relatively harmless, the environmental unfriendliness quotient Q of the Green Knoevenagel is also stated as low. Still, additional research is essential to confirm this²². By applying the mentioned organic synthetic reactions, 4-acetoxy-dihydrosinapinic acid and its prepolymers are ready for the polycondensation to poly-S.

Figure 1 depicts the Proposed mechanism of the step-growth polymerization of 4-acetoxy-dihydrosinapinic acid. In step i, the added base starts the reaction and controls the reaction rate by deprotonating the acid group, thereby stimulating its reactivity²³. The formed carboxylate attacks the carbonyl of the acetoxy group and creates a tetrahedral. In this state, the phenoxide group connects to the other carbonyl through a phenoxide shift, which was initially the aliphatic carboxylic acid group. When the phenoxide shift has occurred, the acetate-ion leaves the intermediate, subtracts a proton from the original base and then leaves the reaction as acetic acid. In practice, this step is promoted by creating a vacuum in the reaction vessel²⁴. In each cycle, one novel molecule is added to the chain. During the progress of the polycondensation reaction, it turned out to be challenging to find the exact combination between increasing the molecular weight and degradation of the polymer chains. As the temperature was elevated with a gradient during the melt polymerization, growing amounts of degradation occurred as the viscosity of the polymer increased. A small amount of solvent was added during the second step of the polycondensation to decrease the viscosity. In this solvent-assisted poly-condensation, 1,2-xylene turns out to be a suitable agent for promoting the polycondensation²⁵.

Figure 2 represents three different ¹H NMR measurements during the polymerization process. The samples dissolved well and were measured in a mixture of CF₃COOD / CDCl₃. The ¹H NMR spectra were taken after the acetylation of sinapinic acid. The ¹H NMR spectrum in the middle is a sample taken from the same reaction. No specific compound was isolated, so acetylated sinapic

acid and its prepolymers are shown. The ^1H NMR spectrum above was taken from a sample after completion of the polycondensation. The areas of the acetyl end groups decrease during the polymerization process, and the number average degree of polymerization (DP_n) increases. After completing the reaction, the degree of polymerization was set at 43 repeating units as determined by ^1H NMR measurements.

GPC measurements were performed to investigate the chain length of poly-S, and various GPC-systems have been tested for the analysis. The initial step was to dissolve the polymeric material in several common organic solvents such as chloroform (CHCl_3), dimethylformamide (DMF), hexafluoro-2-propanol (HFIP), and tetrahydrofuran (THF). However, it appears that the highly crystalline material of poly-S, visible on DSC thermograms, was sparingly soluble in these solvents. Also, when the polymeric material was melted and then cooled very quickly in liquid nitrogen to increase the amorphicity of the polymer, only the short polymer chains dissolved in DMF. The value measured on GPC was only 1,900 up to 2,100 Da, which corresponds to approximately ten repeating units.

Another pretreatment method has been selected to perform a proper GPC measurement. Additional research²⁶ prescribes that a more amorphous polyester material can be formed when polystyrene in its atactic form is melt-mixed into the polyester. The two polymers (polyester and polystyrene) were placed together in a DSC pan, melted, and subsequently cooled in liquid nitrogen. Washing the quenched mixture with acetone removed the residual polystyrene, and after successfully dissolving in DMF, a high molecular weight polymer could be observed.

When poly-S was hydrolyzed in 1 M NaOH, the molecularly recyclable polyester yielded the starting material dihydrosinapinic acid in less than 10 minutes. HPLC, melting point analysis, and ^1H NMR confirmed this observation (Supporting information: **Figure S4**). Extended reaction times did not increase the yield, as shown in **Figure 3**.

The thermograms and GPC analysis of poly-S 1.0 and their successive generations poly-S 2.0 and poly-S 3.0 after forced amorphicity with atactic polystyrene are shown in **Figure 4** and **Table 1**, respectively. DSC analysis of poly-S shows a glass transition signal (T_g) at 113 °C and an endothermic melting signal (T_m) at 281 °C. The polymers from re-polymerized sinapinic acid 3a poly-S 2.0 up and poly-H 3.0 exhibit similar thermal properties (Supporting Information: **Figures S5-S7**). Poly-S is a semi-crystalline polymeric material because glass transition temperatures (T_g) and melting signals are present in the thermograms of poly-S and their successive generations. It can be stated GPC analysis after forced amorphicity with atactic polystyrene displays a constant length of polymeric material throughout the different generations (Supporting Information: **Figures S8-S10**).

FIGURE AND TABLE LEGENDS:

Figure 1. Proposed mechanism of the step-growth polycondensation of 4-acetoxy-dihydrosinapinic acid.

Figure 2. Overlay of ^1H NMR spectra (25 °C, $\text{CF}_3\text{COOD}/\text{CDCl}_3$, with residual solvent peaks at

11.49 and 7.27 ppm for CF₃COOH and CHCl₃, respectively) of the isolated acetylation product of sinapinic acid (bottom); the prepolymer of poly-S (middle); poly-S after solid-state post condensation (240 °C, 30 min, vacuum) (top).

Figure 3. Alkaline hydrolysis (1 M NaOH solution, 80 °C) of poly-S over time, determined by dihydrosinapinic acid (DHSA) yield based on HPLC peak areas.

Figure 4. DSC thermogram of three generations poly-S.

Table 1. GPC measurements of poly-S generations.

DISCUSSION:

When dihydrosinapinic acid was heated in a reaction vessel, sublimation of the starting material occurred, and this effect was enhanced when a vacuum was applied. Acetylation has been performed on dihydrosinapinic acid to avoid sublimation. Kricheldorf et al.^{12,27} recognized that not only acetylation but similarly di- and oligomerization occurred. However, these esterified monomers and oligomers no longer sublime and are suitable as monomers for the melt polycondensation²⁸. Also, the formation of the prepolymers from 4-acetoxy-dihydrosinapinic acid confirms the hypothetical reaction mechanism²⁹.

¹H NMR measurements were used to determine the number average degree of polymerization, and GPC measurements were used to generate further chain length data. GPC measurements were always performed after forcing amorphicity by mixing polystyrene and quenching with liquid nitrogen.

The obtained results presented in **Table 1** show the GPC M_n values of the polymer samples correspond to about 670 repeating units of poly-S, on average, throughout the generations. These values are considerably higher than the corresponding values obtained with ¹H NMR measurements presented in **Figure 2** since these values are about 43 repeating units of poly-S. This variation is related to the trace impurities of the acetoxy-group containing compounds within the synthesized polymers, decreasing the number average degree of polymerization (DP_n) of poly-S, calculated with ¹H NMR measurements. Another explanation is related to the differences in hydrodynamic volumes of the polyesters and polystyrene standards used during the GPC measurements. The polydispersity PDI is below 2.0. This relatively low value can be attributed to high molecular polymer filtering out before GPC analysis.

Thermal characterization was carried out by using DSC and TGA techniques, whereby thermal properties were found comparable to PET. DSC analysis showed that the molecularly recyclable polymer poly-S has a melting temperature of 281 °C. This melting temperature is sixteen degrees higher related to PET³⁰. The glass-rubber transition temperatures of poly-S are also higher compared to PET, namely 113 °C versus 67 °C with PET. A higher glass-rubber transition temperature is often beneficial for many applications.

Finally, during the cooling cycle, poly-S has a lower crystallization temperature related to PET,

namely 151 °C versus 190 °C. The thermal gravimetrical analysis of poly-S indicated a decomposition temperature of 341 °C of poly-S. Compared to PET with a decomposition temperature of 470 °C, the decomposition temperature of poly-S is lower³¹ (Supporting Information: **Figure S11**).

The depolymerization of the formed polymeric material was observed for over two hours, at a temperature of 80 °C. HPLC-samples were taken to analyze the concentration of released dihydrosinapinic acid in a solution of 1 M NaOH. The samples were measured against a calibration curve of pure dihydrosinapinic acid to determine the HPLC yield. (Supporting Information: **Figure S12**)

A mass balance has been established to determine the loss of mass during a complete cycle of polymerization and depolymerization. An exact amount of 5.00 grams of dihydrosinapinic acid has been introduced into the polymerization process. After one cycle of polymerization, depolymerization to dihydrosinapinic acid, and work-up, 4.70 grams of dihydrosinapinic acid was produced, which corresponds to a yield of 94%. During the first cycle, most of the material was lost by manual handling (Supporting Information: **Figure S13-S14**). The loss of the monomer dihydrosinapinic acid was reasonably limited so that after three generations, approximately 85% of the initial amount of monomer remained.

This publication describes how a new polymeric material that is specifically suitable for molecular recycling has been designed. The combination of polymerization, depolymerization, in which the monomers are recovered, and repolymerization, has created an utterly sustainable cycle with only minimal losses. When the principles of Green Chemistry are applied further, it is possible to optimize the conditions of different steps. For example, subsequent studies can investigate hydrolysis under acidic conditions to prevent excessive salt-formation.

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DISCLOSURES:

The authors have nothing to disclose.

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Figures

Designed for Molecular Recycling: A lignin-derived semi-aromatic biobased polymer

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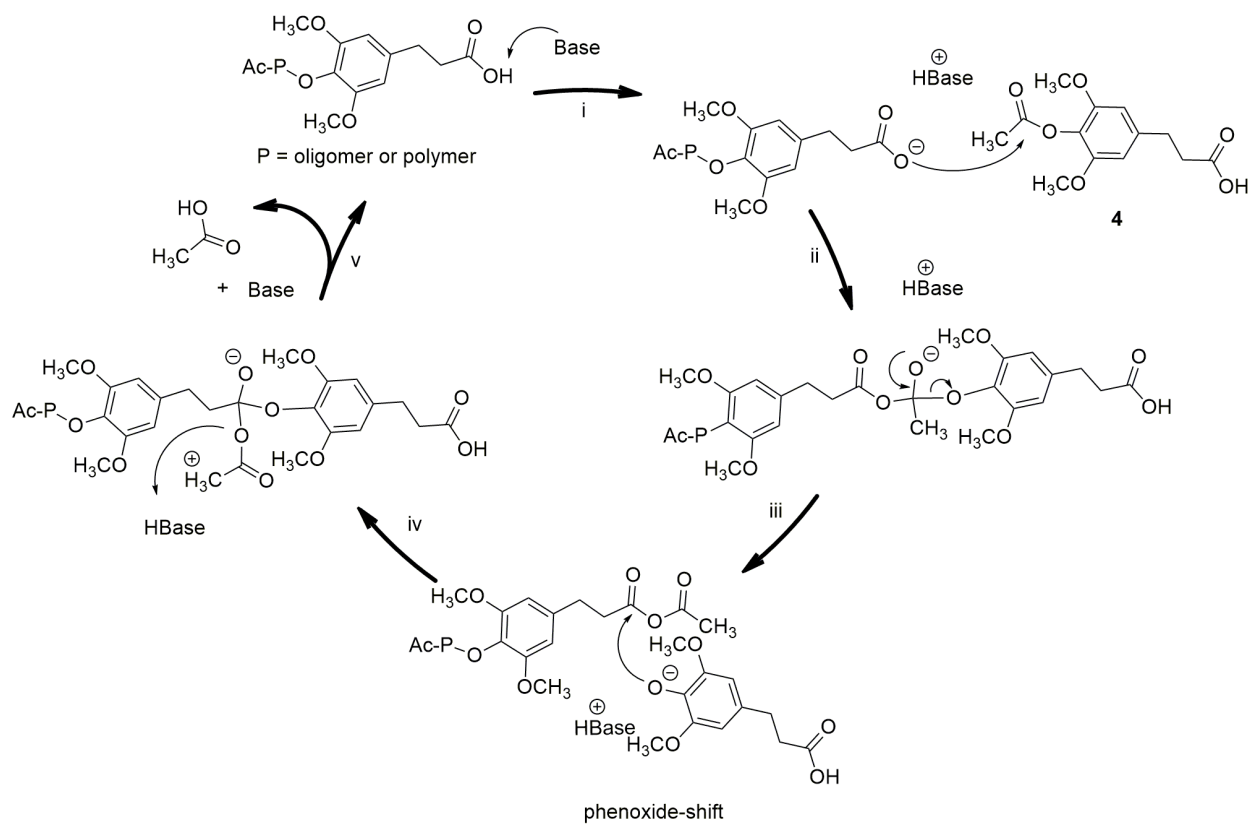


Figure 1

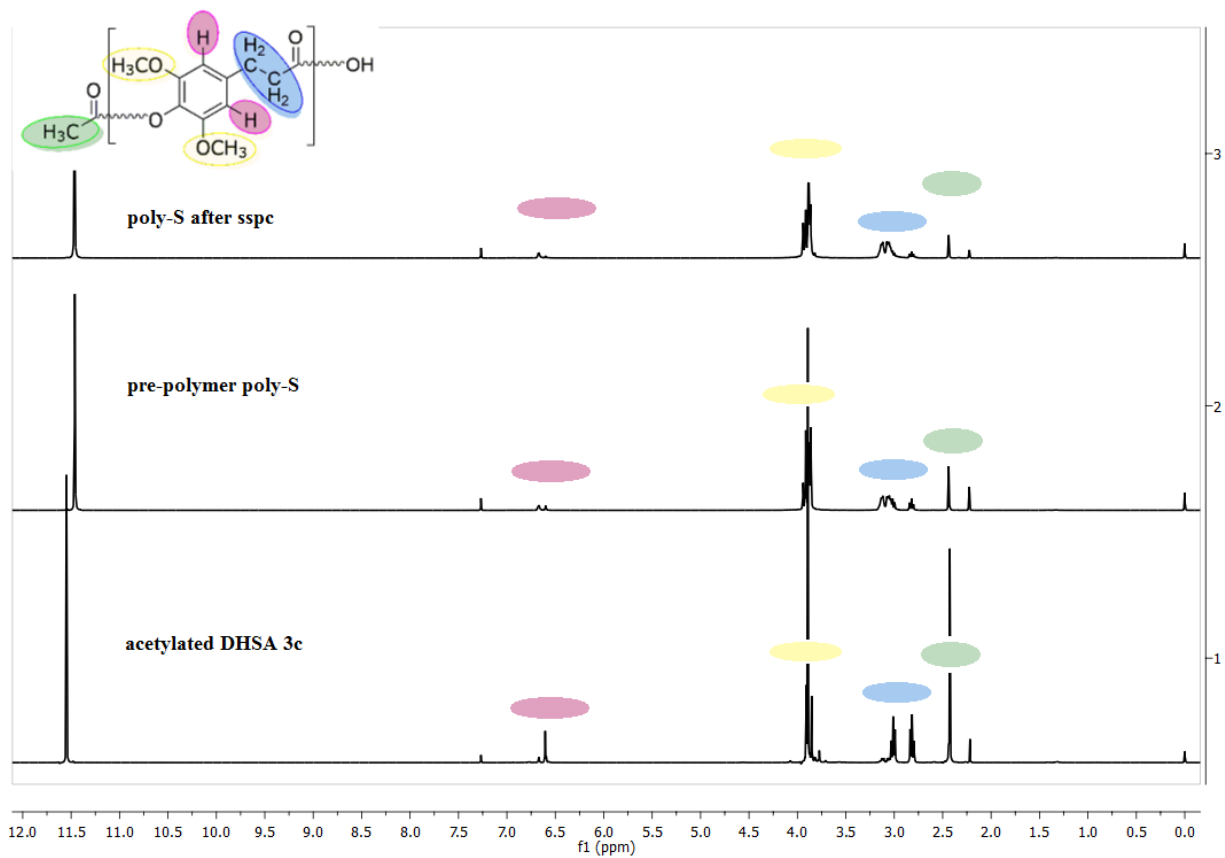
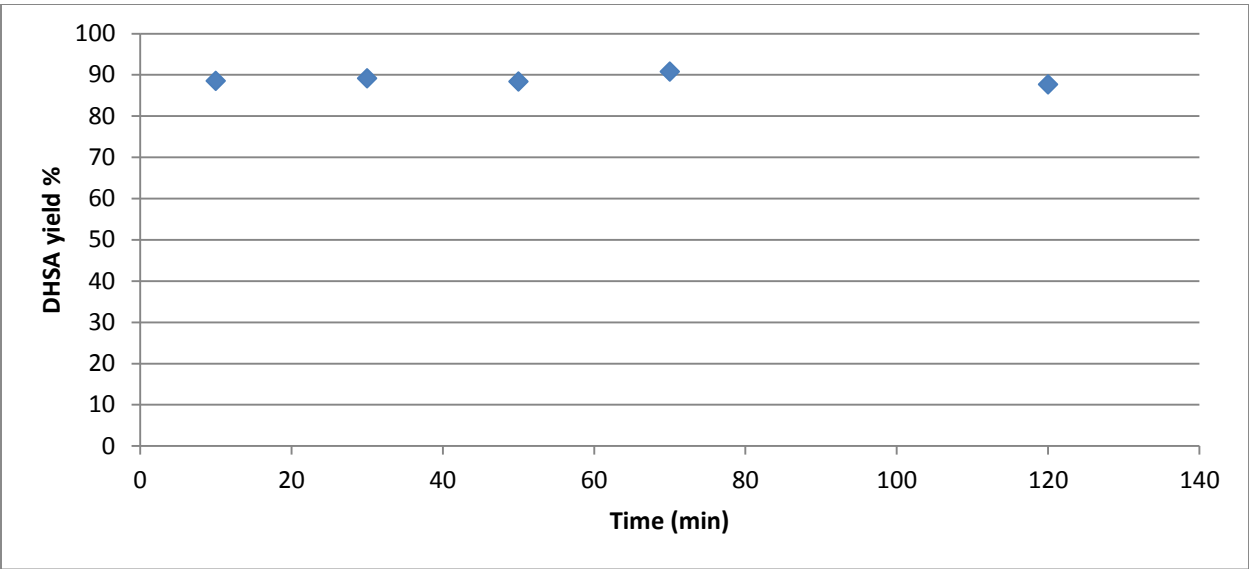


Figure 2

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48 **Figure 3**

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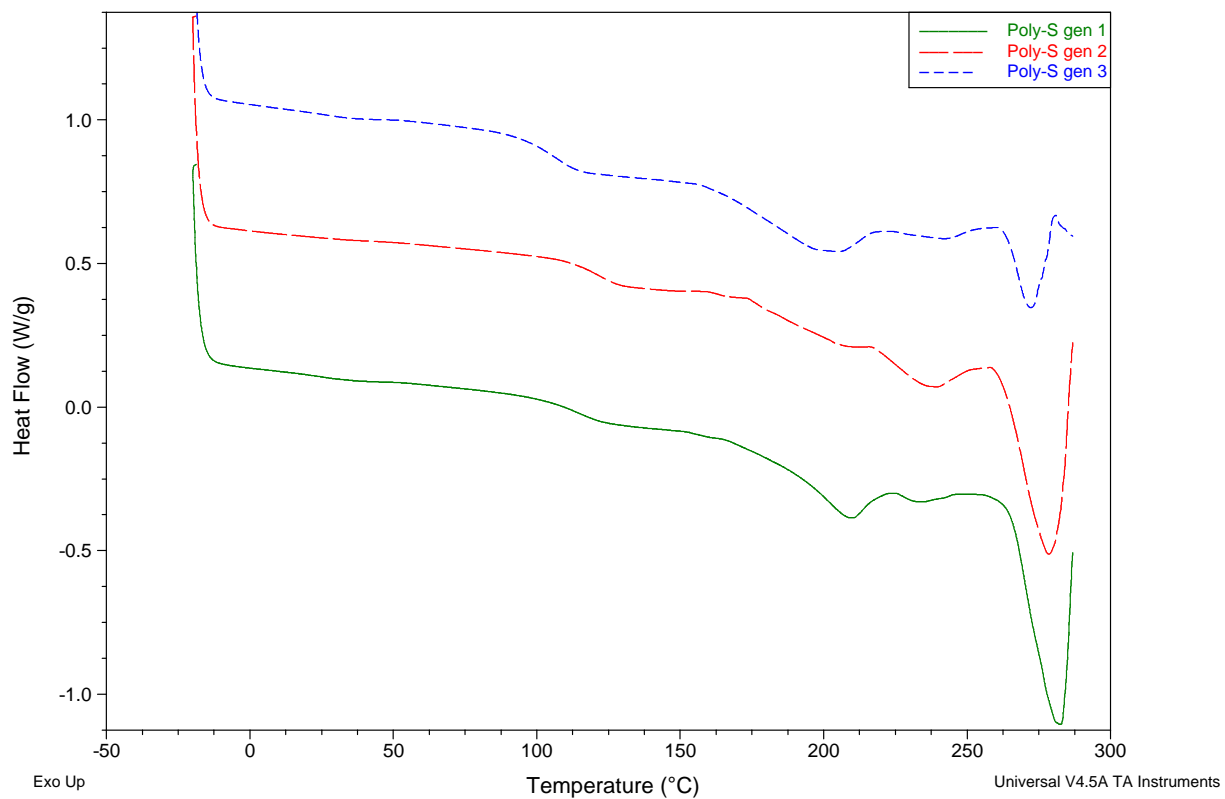


Figure 4

Generation	Poly-S (mg)	PS (mg)	M _n	M _w	PDI	DP
1.0	5.0	4.8	120030	193580	1.6	594
2.0	5.0	5.0	134740	194410	1.4	667
3.0	4.7	4.9	153620	237210	1.5	760

Table 1

Name	Company	Purity	Comments
Reaction 1: Green Knoevenagel condensation			
Ammonium bicarbonate	Sigma Aldrich	>99%	
Ethanol	Boom	Technical grade	
Ethyl acetate	Macron	99.8%	
Hydrochloric acid	Boom	37%	
Malonic acid	Sigma Aldrich	99%	used as received
Sodium bicarbonate	Sigma Aldrich	>99.7%	
Syngaldehyde	Sigma Aldrich	98%	used as received
Reaction 2: Hydrogenation			
Magnesium sulfate	Macron	99%	dried
Raney™ nickel	Sigma Aldrich	>89%	
Sodium hydroxide	Boom	Technical grade	dissolved
Reaction 3: Acetylation			
Acetic anhydride	Macron	>98%	
Acetone	Macron	>99.5%	
Sodium acetate	Sigma Aldrich	>99%	
Reaction 4A: Polymerisation			
1,2-xylene	Macron	>98%	
Sodium hydroxide	Boom	Technical grade	finely powdered
Zinc(II)acetate	Sigma Aldrich	99.99%	
Reaction 4B: Depolymerisation			
Sodium hydroxide	Boom	Technical grade	dissolved
Sulfuric acid	Macron	100%	
Analysis			
CDCl ₃	Cambride Isotope Laboratories, Inc.	99.5%	
CF ₃ COOD	Cambride Isotope Laboratories, Inc.	98%	
Dimethylformamide	Macron	>99.9%	
Hexafluoro-2-propanol	TCI Chemicals	>99%	
Methanol	Macron	>99.8%	

Tetrahydrofuran	Macron	>99.9%	
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After revising and uploading your submission, please also upload a separate rebuttal document that addresses each of the editorial and peer review comments individually.

Dear Editor and Reviewers,

Thank you for your careful review of our paper, and the comments, and suggestions. A significant revision of the paper has been carried out to take all of them into account. Moreover, in the process, we believe the paper improved significantly.

Editorial comments:

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Answer: We thoroughly proofread the manuscript and there are no spelling or grammar issues anymore.

2. Unfortunately, there are sections of the manuscript that show overlap with previously published work. Please revise the following lines: 388-395

Answer: We agree with this comment and following your recommendations, we have revised the lines 388-395

4. Please label the scheme as a Figure and number it accordingly.

Answer: We labeled the scheme as a Figure and numbered it accordingly.

5. Please remove the embedded figure(s) from the manuscript. All figures should be uploaded separately to your Editorial Manager account.

Answer: We removed all the embedded figures from the manuscript.

6. Please remove the embedded Table from the manuscript. All tables should be uploaded separately to your Editorial Manager account in the form of an .xls or .xlsx file.

Answer: We removed the embedded Table from the manuscript.

7. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol.

Answer: The protocol section is now written in the imperative tense.

8. How is the filtration done?

Answer: The filtration was done by vacuum filtration

9. Please highlight up to 3 pages of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol. Remember that non-highlighted Protocol steps will remain in the manuscript, and therefore will still be available to the reader.

Answer: We highlighted the essential steps of the protocol for the video.

10. Please ensure that the references appear as the following: [Lastname, F.I., LastName, F.I., LastName, F.I. Article Title. Source. Volume (Issue), FirstPage – LastPage (YEAR).] For more than 6 authors, list only the first author then et al.

Answer: We present the references following your recommendations

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The authors provided the protocol of a comprehensive polymerization, depolymerization and repolymerization of a type of lignin-derived "PET" type of polymer which demonstrated a very important example to the circular economy and green chemistry of plastic recycling process. The protocol is very well written and the results are adequately discussed. Very minor grammatically mistakes are suggested to be revised:

Minor Concerns:

Line 88: Subsequent to

Line 124: the purity of the product was usually checked by HPLC

Line 139: the color of the reaction mixture was changed due to

Line 151: the conjugated system was destroyed by

Line 161: An acetylation reaction was performed to ...

Line 176: All the products remain dissolved ...

Line 177: solvent was added in the next step

Line 197: The reaction morphologically change (no "will")

Line 183: remove "will"

Line 187: remove "will"

Generally, please revise all the future tense of the remaining text to present and passive tense.

Answer: We followed all these recommendations and made the necessary changes.

Reviewer #2:

Manuscript Summary:

this manuscript presented an interesting work about a method to obtain semi-aromatic polyester derived from lignin. In my opinion the protocol described by the authors is clear and the obtained results demonstrate that the method can be used to produce polymers from biomass. I suggest accept this work in the present form.

Major Concerns:

not applicable.

Minor Concerns:

not applicable.

Supporting Information

Designed for Molecular Recycling: A lignin-derived semi-aromatic biobased polymer

Dennis Molendijk¹, Koen van Beurden¹, Jack van Schijndel¹

¹Research Group Green Chemistry, Avans University of Applied Science

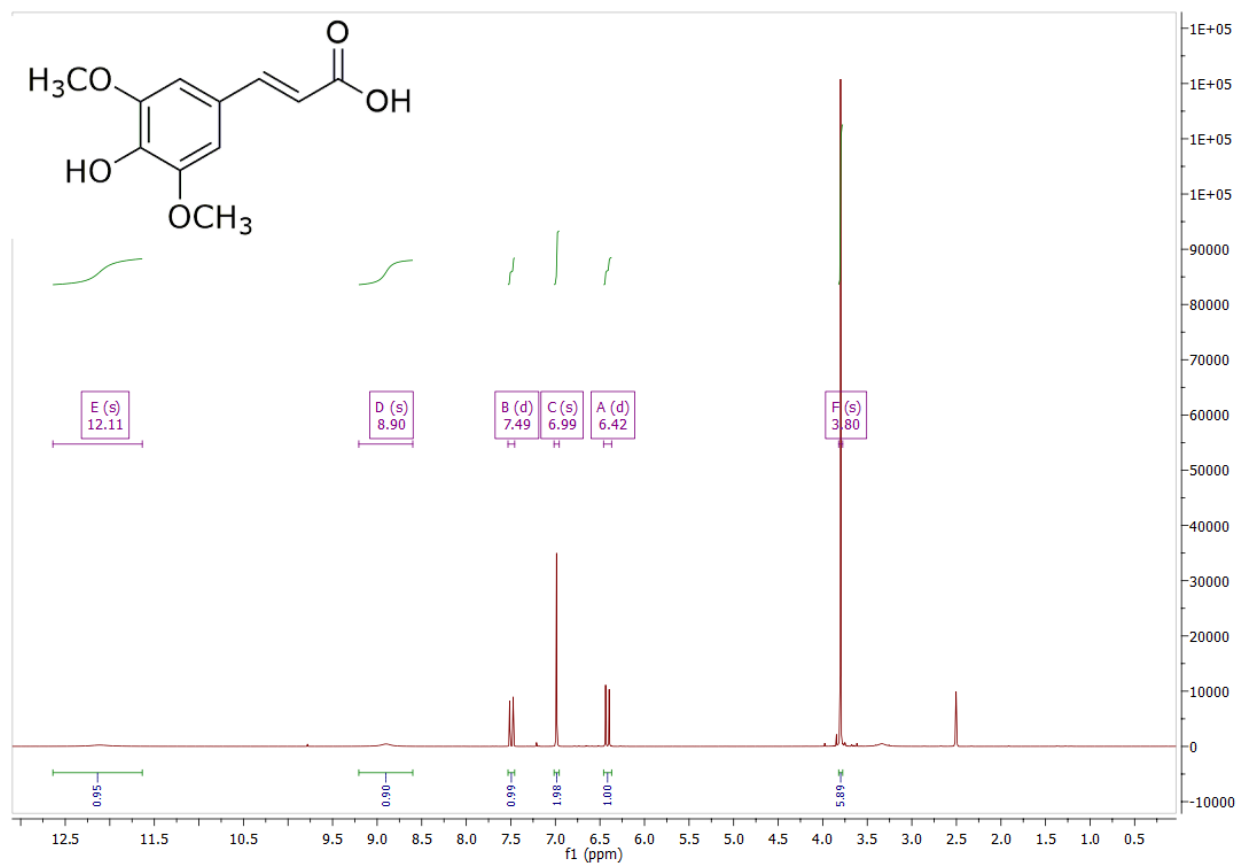


Figure S1: ^1H NMR spectrum of sinapinic acid

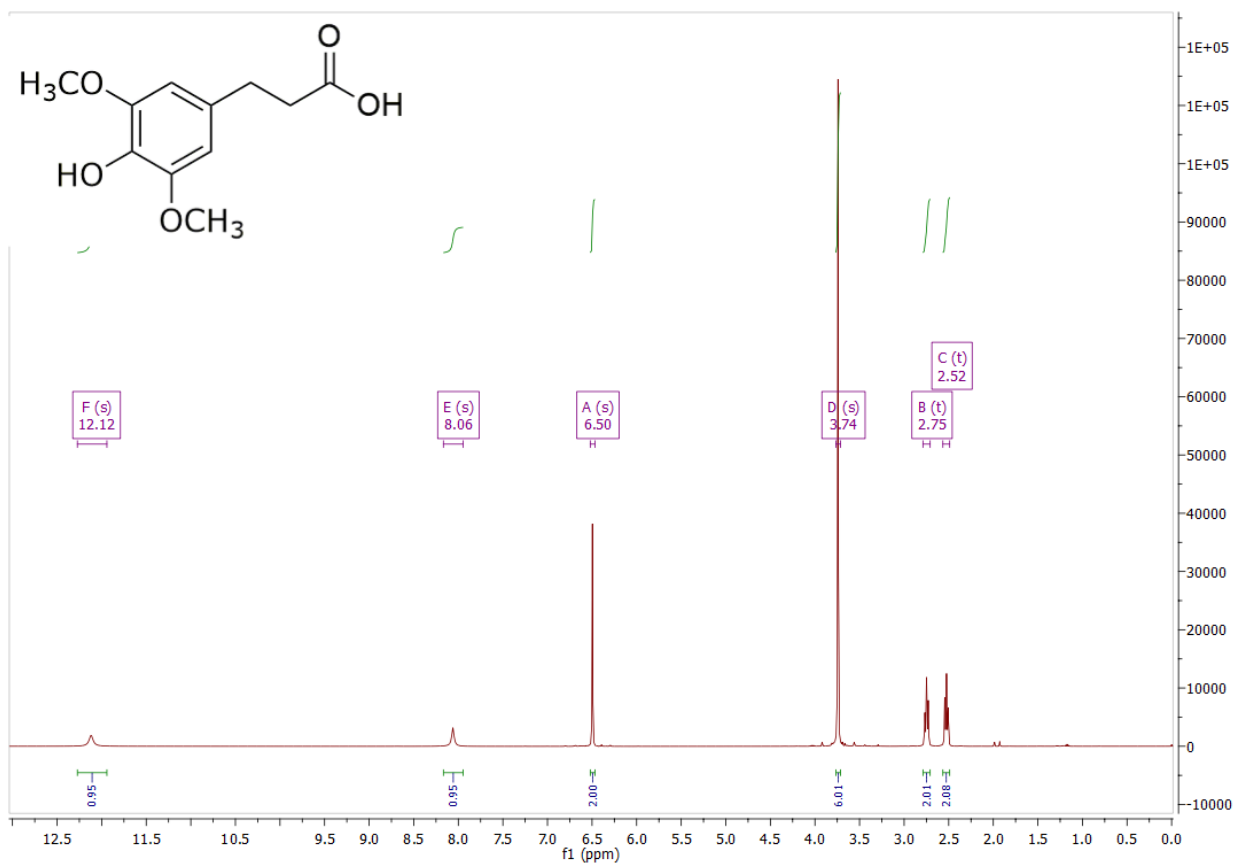


Figure S2: ¹H NMR spectrum of dihydrosinapinic acid

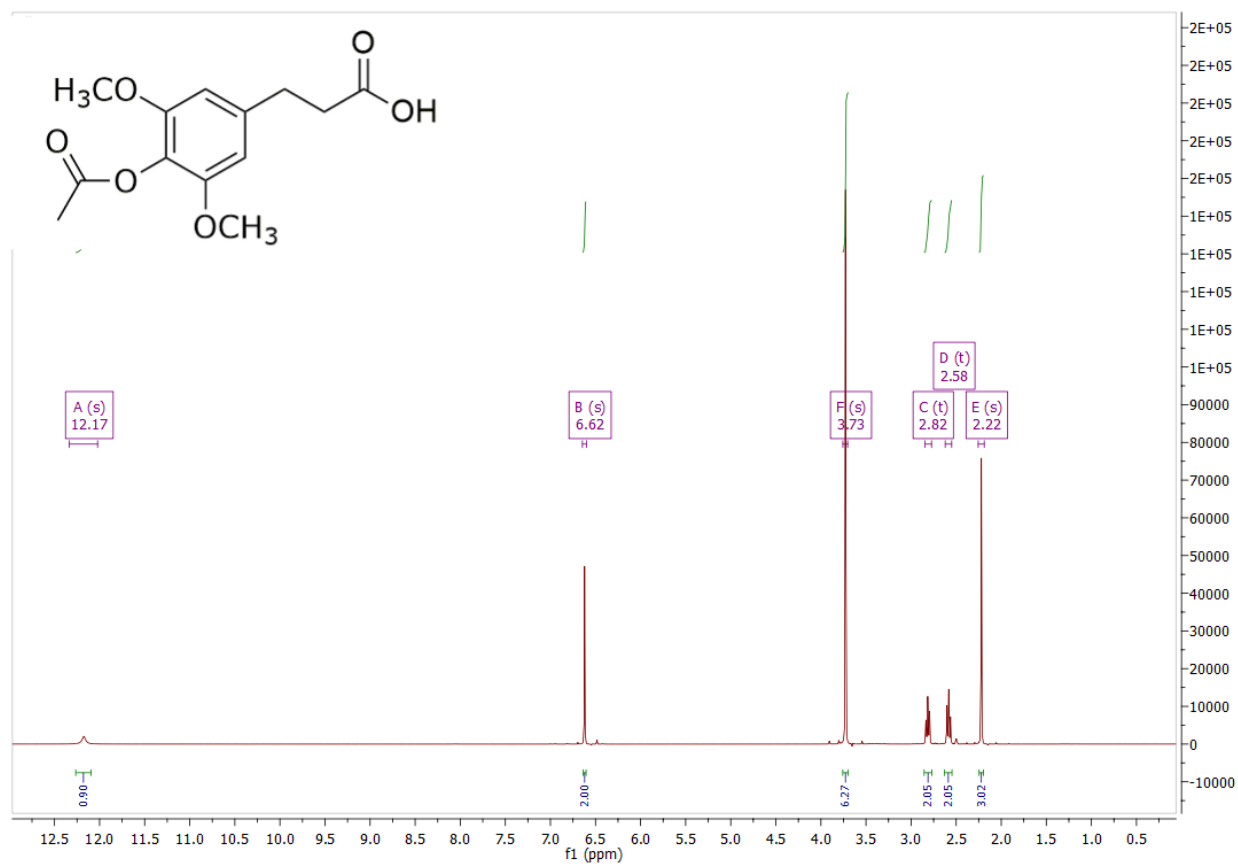


Figure S3: ¹H NMR spectrum of 4-acetoxy-dihydrosinapinic acid

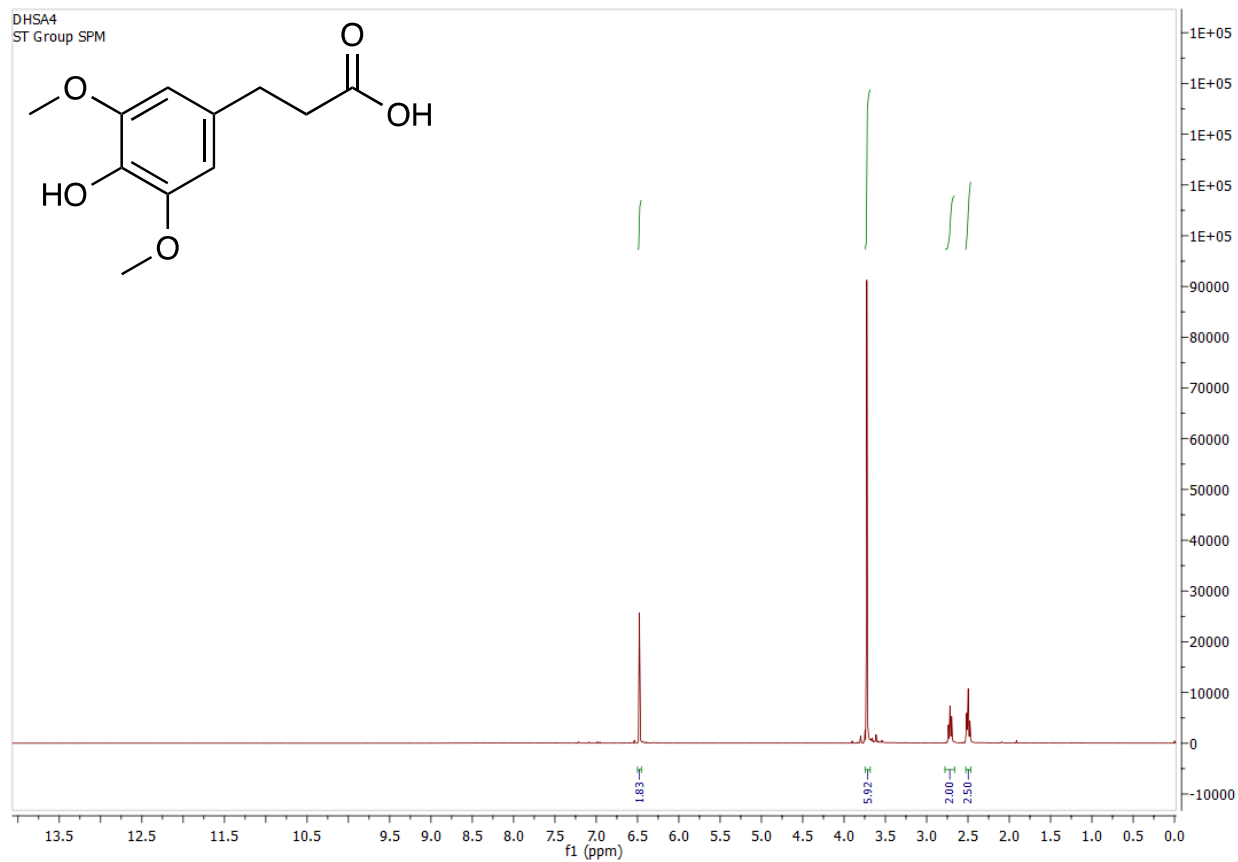


Figure S4: ¹H NMR spectrum of dihydrosinapinic acid, obtained after depolymerization of poly-

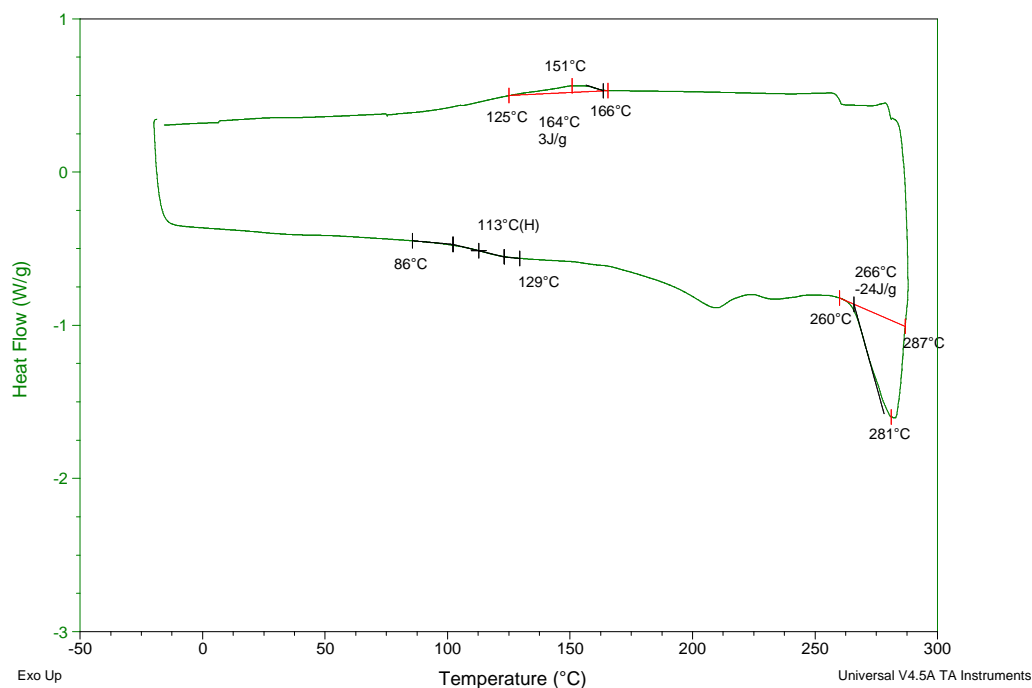


Figure S5: Full cycle DSC thermogram of Poly-S generation 1.0 in the third heating cycle

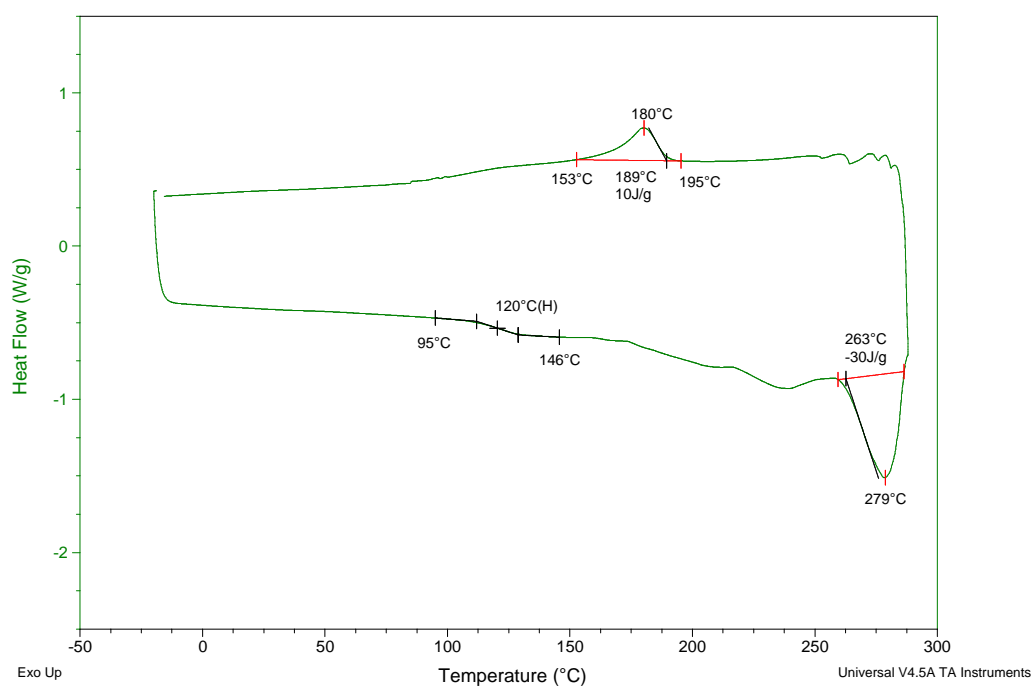


Figure S6: Full cycle DSC thermogram of Poly-S generation 2.0 in the third heating cycle

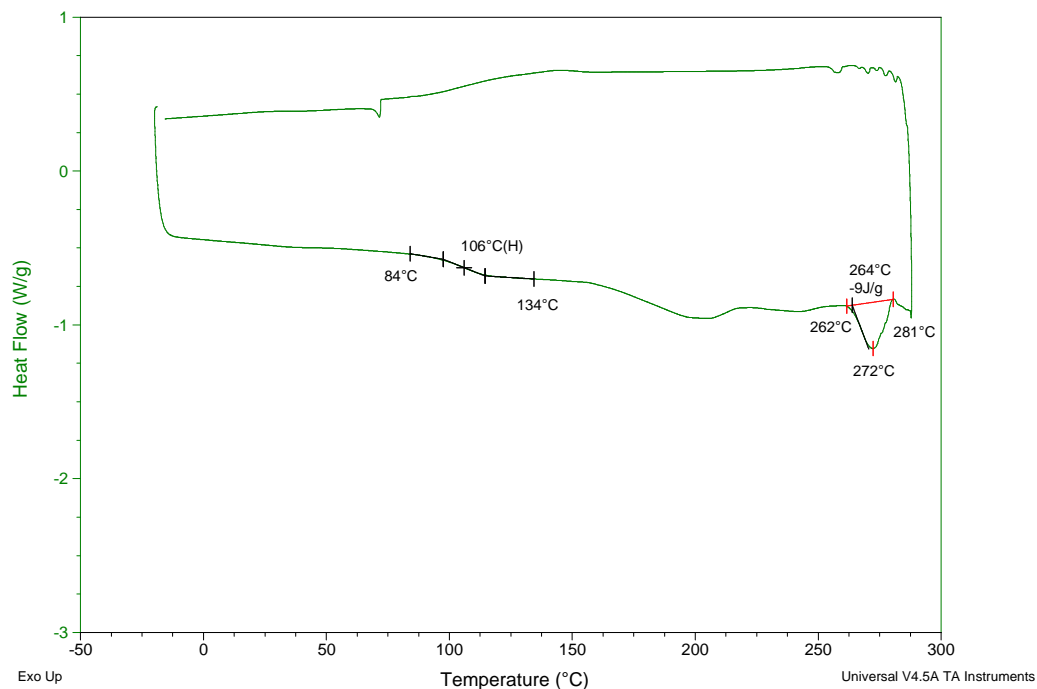


Figure S7: Full cycle DSC thermogram of Poly-S generation 3.0 in the third heating cycle

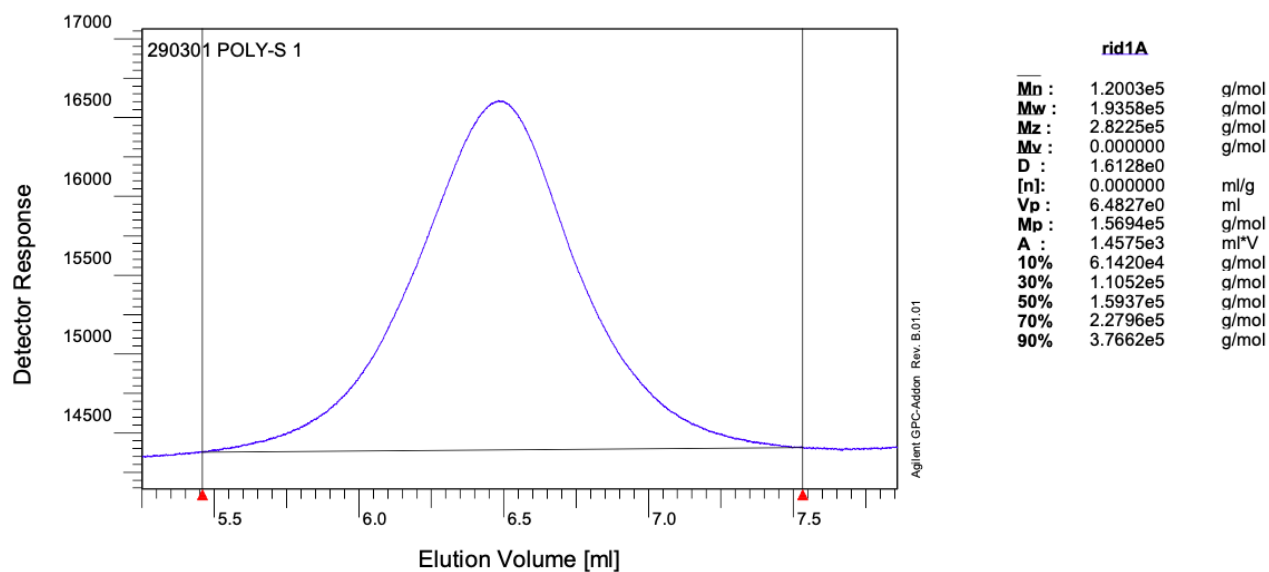
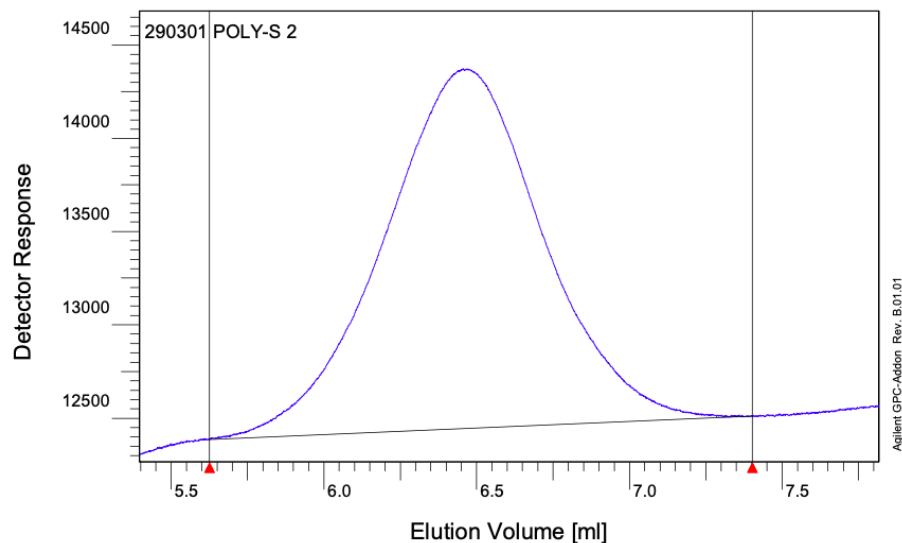
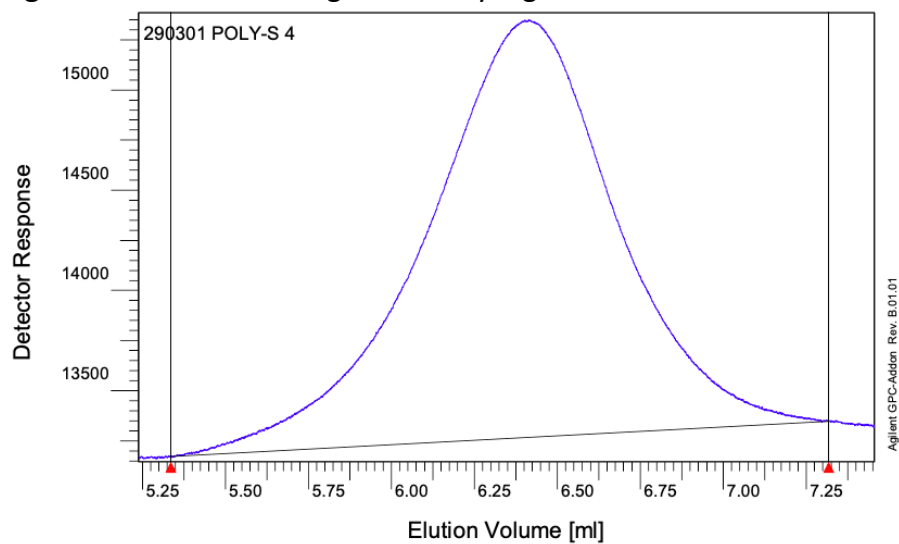


Figure S8: GPC chromatogram of Poly-S generation 1.0



rid1A		
Mn :	1.3474e5	g/mol
Mw :	1.9441e5	g/mol
Mz :	2.6259e5	g/mol
Mv :	0.000000	g/mol
D :	1.4429e0	
[n] :	0.000000	ml/g
Vp :	6.4560e0	ml
Mp :	1.6819e5	g/mol
A :	1.1562e3	ml*V
10%	7.2424e4	g/mol
30%	1.2040e5	g/mol
50%	1.6764e5	g/mol
70%	2.3107e5	g/mol
90%	3.5675e5	g/mol

Figure S9: GPC chromatogram of Poly-S generation 2.0



rid1A		
Mn :	1.5362e5	g/mol
Mw :	2.3721e5	g/mol
Mz :	3.3285e5	g/mol
Mv :	0.000000	g/mol
D :	1.5442e0	
[n] :	0.000000	ml/g
Vp :	6.4142e0	ml
Mp :	1.8725e5	g/mol
A :	1.3735e3	ml*V
10%	7.9808e4	g/mol
30%	1.3956e5	g/mol
50%	1.9903e5	g/mol
70%	2.8204e5	g/mol
90%	4.5827e5	g/mol

Figure S10: GPC chromatogram of Poly-S generation 3.0

Sample: Poly S 29 juni SSPC 260C
Size: 5.1010 mg
Method: Ramp

TGA

File: C:\...\Poly S 29 juni SSPC 260C.001
Operator: Dennis
Run Date: 29-Jun-2018 15:57
Instrument: TGA Q500 V20.13 Build 39

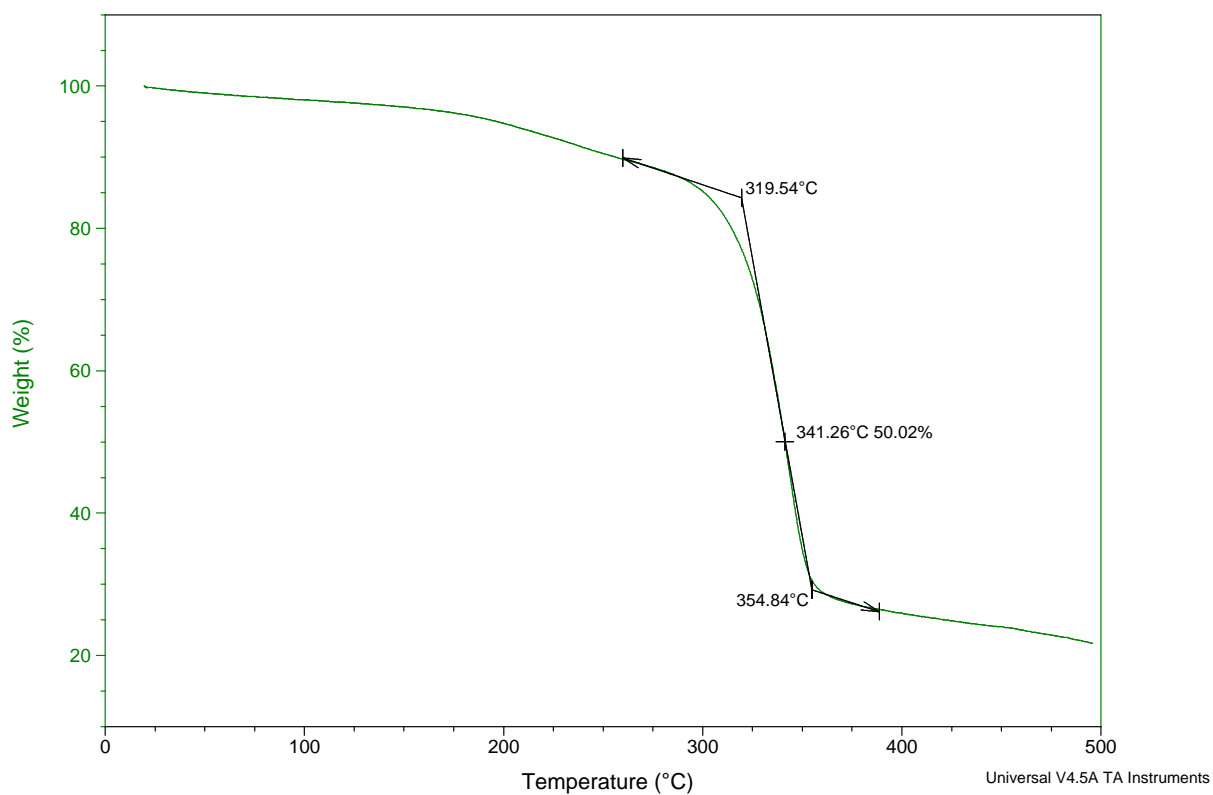


Figure S11: TGA thermogram of Poly-S generation 1.0

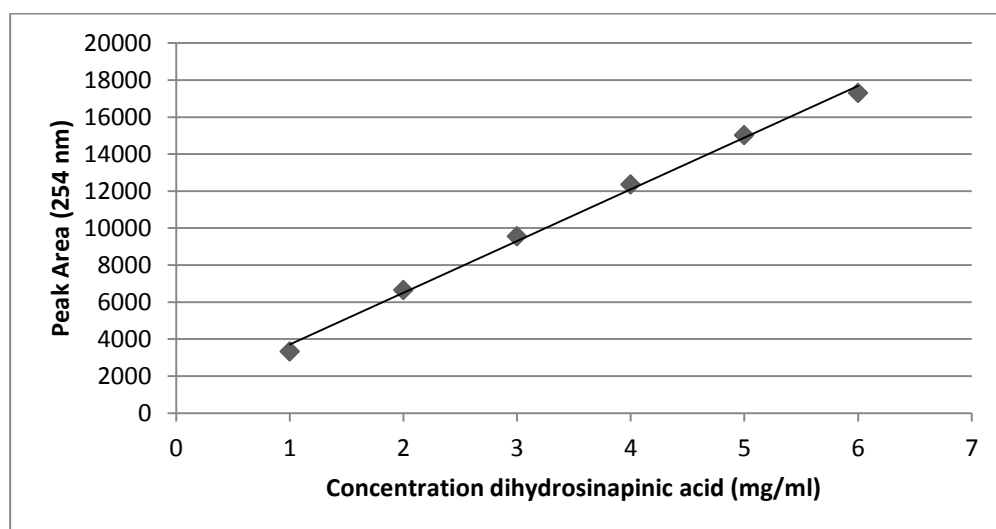


Figure S12: HPLC calibration curve of dihydrosinapinic acid

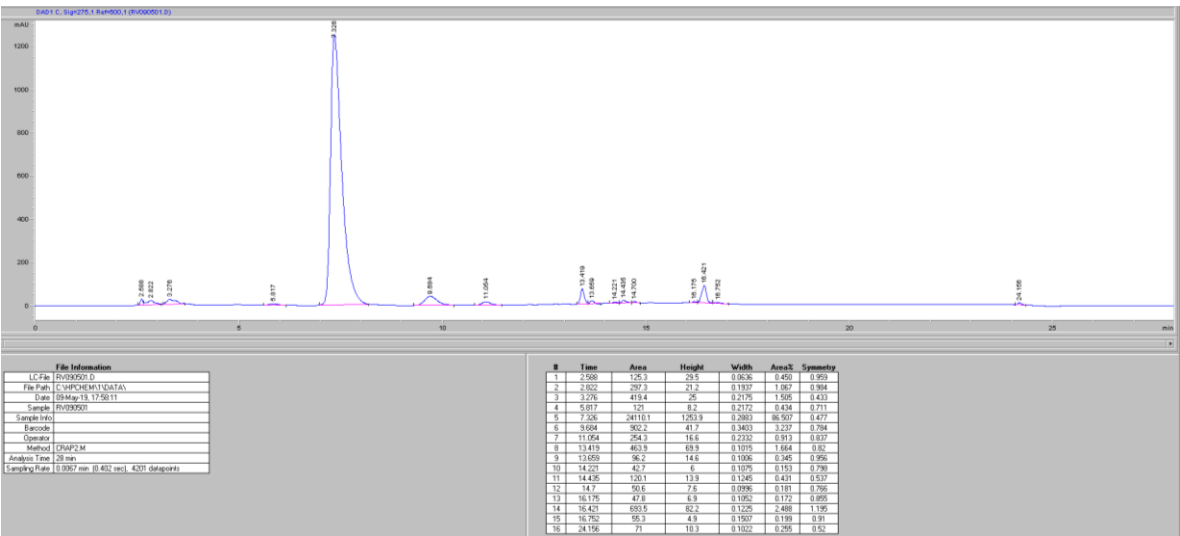


Figure S13: HPLC chromatogram of dihydrosinapinic acid, obtained after depolymerization of poly-S

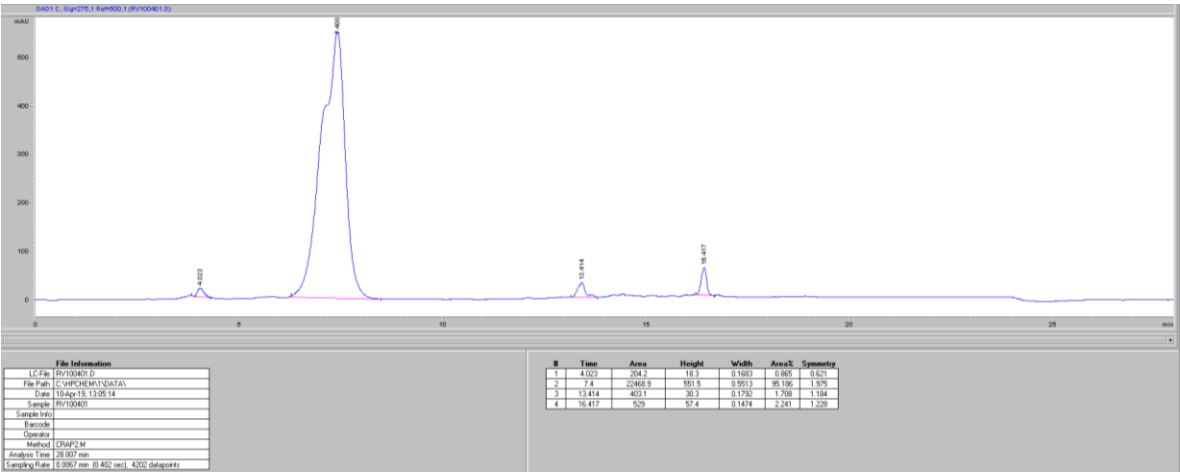


Figure S14: HPLC chromatogram of dihydrosinapinic acid reference