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

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Author Questionnaire

1. **Microscopy**: Does your protocol require the use of a dissecting or stereomicroscope for performing a complex dissection, microinjection technique, or something similar? **No**

2. **Software:** Does the part of your protocol being filmed include step-by-step descriptions of software usage? **No**

3. **Interview statements:** Considering the COVID-19-imposed mask-wearing and social distancing recommendations, which interview statement filming option is the most appropriate for your group? **Please select one**.

   ☒ Interviewees wear masks until videographer steps away (≥6 ft/2 m) and begins filming, then the interviewee removes the mask for line delivery only. When take is captured, the interviewee puts the mask back on. Statements can be filmed outside if weather permits.

4. **Filming location:** Will the filming need to take place in multiple locations? **No**

Current Protocol Length

Number of Steps: 16
Number of Shots: 47

Introduction

1. Introductory Interview Statements

REQUIRED:

1.1. **Dennis Molendijk:** The route of synthesis described in this paper provides a way to efficiently produce a new polymeric material specifically suitable for molecular recycling, which is a way of chemical recycling.

1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

1.2. **Dennis Molendijk:** The combination of depolymerization and repolymerization of the formed polymeric material poly-S creates a fully sustainable cycle and is presented as a proof of concept for the future of polymers.

1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

OPTIONAL:

1.3. **Koen van Beurden:** The polymer waste of the world accumulates, for instance, in the oceans as the plastic soup, which could be prevented by introducing molecularly recyclable polymers.

1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

1.4. **Koen van Beurden:** The polymer presented is an example of a polymeric material "Designed for Molecular Recycling," which should be implemented in other materials, in our opinion, to prevent accumulation in nature.

1.4.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

1.5. **Jack van Schijndel:** The Green Knoevenagel reaction and subsequent steps have been designed by and for our undergraduate students, so certain robustness has been already implemented into the reaction steps.

1.5.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

1.6. **Jack van Schijndel:** The COVID-19 pandemic has created a situation where online learning has become more important than ever. Visualization of these experiments helps us and others to deepen practical chemical education.

1.6.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

Protocol

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

2.1. Begin by adding 20.81 grams of malonic acid and 36.4 grams of syringaldehyde to a 250-milliliter round-bottom flask **[1]**. Dissolve both constituents in 20 milliliters of ethyl acetate **[2]** and add 790 milligrams of ammonium bicarbonate to the flask **[3]**. Distill the solvent with a rotavap **[4]**. *Videographer: This step is important!*

2.1.1. WIDE: Establishing shot of talent adding reagents to a flask.

2.1.2. Talent adding ethyl acetate to the flask.

2.1.3. Talent adding ammonium bicarbonate to the flask. **NOTE: Cut out the weight on the scale.**

2.1.4. Talent distilling solvent with rotavap

2.2. Keep the reaction mixture at 90 degrees Celsius for 2 hours in the open flask without stirring for complete conversion to sinapinic acid **[1]**.

2.2.1. Reaction incubating.

2.3. In the work-up of the sinapinic acid product, dissolve the residue in 100 milliliters of a saturated aqueous sodium bicarbonate solution **[1]**, then transfer the solution to a beaker **[2]** and acidify it to a pH of 2 using 6 molar hydrogen chloride **[3]**. Separate the resulting residue by vacuum filtration **[4]** and wash it with demineralized water **[5]**. *Videographer: This step is important!*

2.3.1. Talent dissolving the residue.

2.3.2. Talent transferring the solution to a beaker.

2.3.3. Talent adjusting the pH with hydrogen chloride.

2.3.4. Talent performing vacuum filtration.

2.3.5. Talent washing the residue.

3. Hydrogenation of sinapinic acid towards dihydrosinapinic acid with nickel

3.1. Charge a 450 milliliters flask with 33.6 grams sinapinic acid **[1]**. Dissolve the sinapinic acid in 300 milliliters of 2 molar sodium hydroxide solution **[2]** and add 1.5 grams of nickel slurry **[3]** before fitting the flask to the apparatus **[4]**.

3.1.1. Talent charging the flask.

3.1.2. Talent dissolving the sinapinic acid.

3.1.3. Talent adding nickel slurry to the solution.

3.1.4. Talent fitting flask to reactor.

3.2. Pressurize the reactor with three bar of hydrogen gas **[1]** and mechanically shake the reaction at 80 degrees Celsius for three hours **[2]**. Cool the reactor to room temperature and depressurized slowly **[3]**. Recover most of the nickel catalyst with a magnet **[4]**, then filter the solution **[5]**. *Videographer: This step is important!*

3.2.1. Talent pressurizing the reactor.

3.2.2. Reaction shaking.

3.2.3. Reaction cooling.

3.2.4. Talent applying a magnet.

3.2.5. Talent filtering the solution.

3.3. Acidify the solution with a 4 molar hydrogen chloride solution to a pH of 2 **[1]**. Then, perform an extraction with ethyl acetate **[2-TXT]**. Remove the solvent under reduced pressure after drying over magnesium sulfate **[3]** and dry the dihydrosinapinic acid at 60 degrees Celsius in a vacuum oven **[4]**.

3.3.1. Talent adding HCl to the solution.

3.3.2. Talent adding ethyl acetate to the solution. **TEXT: 4 X 50 mL NOTE: Full extraction shot was filmed here, besides addition of the solvent.**

3.3.3. Talent removing the solvent.

3.3.4. Talent placing the product in the oven.

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

4.1. Add 22.6 grams dihydrosinapinic acid to a 250-milliliter round-bottom flask **[1]**, followed by 14.2 milliliters of acetic anhydride and 0.82 grams of sodium acetate **[2]**.

4.1.1. Talent adding the dihydrosinapinic acid to the flask.

4.1.2. Talent adding acetic anhydride and sodium acetate to the flask.

4.2. Heat the solution to 90 degrees Celsius while stirring for one hour for complete conversion of dihydrosinapinic acid to 4-acetoxy-dihydrosinapinic acid and its acetylated oligomers **[1]**.

4.2.1. Reaction stirring at 90 degrees.

4.3. Dissolve the solid in 25 milliliters of acetone **[1]**, precipitate it into 250 milliliters of 0.1 molar hydrogen chloride **[2]**, then filter it under vacuum **[3]**. *Videographer: This step is difficult and important!*

4.3.1. Talent diluting the mixture.

4.3.2. Talent precipitating the solution.

4.3.3. Talent filtering the solution.

5. Polymerization of acetylated monomers and oligomers

5.1. Add the monomers, 20.8 grams of 4-acetoxy-dihydrosinapinic acid and prepolymer to a 100-milliliter round-bottom flask **[1]**. Then, add 400 milligrams of finely powdered sodium hydroxide **[2]**. Heat the reaction mixture for three hours at a set temperature of 140 degrees Celsius in the open flask while stirring at 100 rpm **[3]**. *Videographer: This step is important!*

5.1.1. Talent adding the reagents to the flask.

5.1.2. Talent adding NaOH to the flask.

5.1.3. Reaction heating and stirring. **NOTE: Reaction itself takes place at the end of this shot, where the solid mixture melts into a liquid.**

5.2. Set up a solvent assisted polymerization by adding 180 milligrams of zinc(II)acetate *(pronounce 'zinc-2-acetate')* and 25.0 milliliters of 1,2-xylene to the flask **[1]**, then raise the set temperature to 160 degrees Celsius **[2]**. Reflux the mixture at 144 degrees Celsius for three hours with constant water and acetic acid removal using a Dean-Stark head **[3]**. *Videographer: This step is important!*

5.2.1. Talent adding the polymerization reagents to a flask.

5.2.2. Talent adjusting the temperature to 160 degrees.

5.2.3. Reaction refluxing.

5.3. Cool the reaction mixture down and remove the 1,2-xylene by applying a vacuum **[1]**. Raise the temperature to 240 degrees Celsius during the final stage of the polymerization **[2]** and apply a high vacuum for 30 minutes **[3]**.

5.3.1. Talent applying a vacuum to remove the xylene.

5.3.2. Talent raising the temperature.

5.3.3. Talent applying a vacuum.

5.4. Cool the polymer poly-S to room temperature and wash it with methanol to eliminate dihydrosinapinic acid and prepolymers **[1]**. The obtained product should be a light-brown solid **[2]**.

5.4.1. Talent washing the poly-S with methanol.

5.4.2. Light-brown product.

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

6.1. Finely grind and sieve the poly-S into particles smaller than 180 micrometers to measure hydrolytic degradation **[1]**. Load several test tubes with 20 milligrams of poly-S **[2]** and add 1 milliliter of 1 molar sodium hydroxide solution **[3]**. Incubate the tubes at three different temperatures with an agitation of 500 rpm **[4-TXT]**.

6.1.1. Talent grinding the poly-S.

6.1.2. Talent loading the test tubes.

6.1.3. Talent adding NaOH to a few tubes.

6.1.4. Talent placing the tubes in a shaker-incubator. **TEXT: RT, 50, and 80 °C**

6.2. Neutralize the test tubes at regular time intervals with 1 milliliter of 0.5 molar sulfuric acid **[1]** and add 2 milliliters of methanol after cooling **[2]**.

6.2.1. Talent neutralizing a test tube.

6.2.2. Talent adding methanol to a test tube.

6.3. Filter all samples using 0.45-micrometer PTFE syringe filters **[1]** and inject 20 microliters into HPLC using an autosampler **[2]**. Monitor the absorbance at 254 nanometers and calculate the concentrations from a calibration curve of known dihydrosinapinic acid standard solutions **[3]**.

6.3.1. Talent filtering a sample.

6.3.2. Talent adding a sample to HPLC.

6.3.3. Talent at the computer, looking at a calibration curve. **NOTE: Multiple screens of the HPLC were shot, but use the 3D rainbow colored screen.**

Results

7. Results: Step-growth polycondensation of 4-acetoxy-dihydrosinapinic acid

7.1. Sinapinic acid was synthesized in high purity and a greater than 95% yield from syringaldehyde using the Green Knoevenagel condensation **[1]**. The proposed mechanism of the step-growth polymerization of 4-acetoxy-dihydrosinapinic acid is shown here **[2]**.

7.1.1. LAB MEDIA: Figure S1.

7.1.2. LAB MEDIA: Figure 1.

7.2. Hydrogen-1 NMR measurements were taken during the polymerization process **[1]**.

7.2.1. LAB MEDIA: Figure 2.

7.3. When poly-S was hydrolyzed in sodium hydroxide, the molecularly recyclable polyester yielded the starting material dihydrosinapinic acid in less than 10 minutes as confirmed by HPLC, melting point analysis, and hydrogen-1 NMR **[1]**. Extended reaction times did not increase the yield **[2]**.

7.3.1. LAB MEDIA: Figure S4.

7.3.2. LAB MEDIA: Figure 3.

7.4. 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 here **[1]**.

7.4.1. LAB MEDIA: Figure 4 and Table 1.

7.5. DSC analysis of poly-S shows a glass transition signal at 113 degrees Celsius and an endothermic melting signal at 281 degrees Celsius. The polymers from re-polymerized sinapinic acid 3a poly-S 2.0 up and poly-H 3.0 exhibit similar thermal properties **[1]**.

7.5.1. LAB MEDIA: Figure S5, S6, and S7.

7.6. Poly-S is a semi-crystalline polymeric material because glass transition temperatures and melting signals are present in the thermograms of poly-S and their successive generations. GPC analysis after forced amorphicity with atactic polystyrene displays a constant length of polymeric material throughout the different generations **[1]**.

7.6.1. LAB MEDIA: Figure S8, S9, and S10.

Conclusion

8. Conclusion Interview Statements

8.1. **Dennis Molendijk:** When attempting this protocol, keep in mind that a correct temperature is crucial for the Green Knoevenagel reaction. A slightly higher temperature can lead to different side-reactions.

8.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera. *Suggested B-roll: 2.1, 2.2.*

8.2. **Koen van Beurden:** We have explored an example for a Molecularly Recyclable polyester, but closely related building-blocks can follow the same procedure, all while maintaining specific thermal and mechanical properties of the polymer.

8.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

8.3. **Jack van Schijndel:** This method can be used in organocatalysis through the claim of the Green Knoevenagel reaction and demonstration of the catalytic intermediates, as well as in the still reasonably unexploited area of molecular recycling.

8.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.