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Synthesis and Potential Metal Absorption of Carbohydrate Polymer Derivatives

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ABSTRACT:
Clean and safe water supplies are always going to be in need. It is therefore necessary to ensure that our rivers and lakes remain unpolluted for our future generations. Unfortunately, the drive for inexpensive consumer goods has put a strain on our fresh water supply due to contamination from chemical byproducts.

Our investigation focused on finding an efficient way to detect heavy metal contaminants in polluted water resources. Ideally, the detector used should be comprised of a naturally occurring material that, with its presence in the system, will not add to the contamination problem. In past research environments sugars have been known to bond selectively to many elements including heavy metals. Our specific goal is to attach four sugars to a styrene base: beta-cyclodextrin, lactose, cellobiose, and inulin (shown below) with the hopes that these saccharides will bond selectively to certain heavy metals found in the water supply.

Chicory root, whose main component is inulin, has been used in the Netherlands for removal of heavy metals from contaminated water supplies. Chicory is grown across the polluted water and bonds to the heavy metals present in the water source. It is therefore our hope that inulin bound to styrene will have the same ability to bond to heavy metals in waste water to detect the presence of these impurities in the water. Beta-cyclodextrin, lactose, and cellobiose will be used as a comparison for this study to observe the efficiency of binding of these sugars to heavy metals.

Styrene, a conjugated pi-system, was incorporated in our system to provide a means of determining bonding affinity. The conjugated pi-system or alternating double bonds between two carbons is activated by light and the electrons present are promoted from their ground state to an excited state. As the electrons are relaxed back to their ground state the electrons release energy in the form of light. When heavy metals are attached to this substituted saccharide, light will once again be admitted, but because of the presence of the heavy metal the light emitted in the relaxation will change therefore providing data of the presence of a heavy metal. The absorbance and the wavelength will therefore show the presence and the concentration of any contaminants present in the wastewater. The substituted styrene will be polymerized with the water absorbing monomer acrylic acid. The polymerized saccharides will then again be tested using molecular recognition to observe the expected concurrent data as the unpolymerized styrene derivative saccharide.
Results:
The 4-O-(β-D-Galactopyranosyl)-N-((4-vinylbenzoyl)-β-D-glucopyranosylamine ((p-vinylbenzamido)-β-lactose) was synthesized with an overall yield of 37.4% yield based on lactose. The 4-O-(β-D-Galactopyranosyl)-N-((4-vinylbenzoyl)-β-D-glucopyranosylamine ((p-vinylbenzamido)-inulin) was synthesized and verified using 1H NMR. The β-Cyclodextrin has been synthesized to Per-6-azido-β-cyclodextrin, but difficulties in procedure have not allowed for the complete synthesis of the Per-o-amino-β-cyclodextrin. The progress shows that two out of the four proposed probes have been synthesized and will be tested as the other two probes will be synthesized. This synthesis will be completed in future work.

Methodology:
All 1H NMR spectra were obtained and recorded with a Nicolet 360 MHz. All IR spectra were obtained using a Perkin Elmer 1600 series FTIR. All chemicals were purchased from Aldrich Chemical Company in high purity and were used without further purification.

Vilsmeier-Haack Reagent:
Triphenylphosphine (14.0g, 53.3 mmol) was dissolved in dry DMF (40.0mL). Bromine (2.75mL, 53.3mmol) was added under nitrogen. The reaction was allowed to stir for 1hr. After the addition of the bromine the solution turned to an orange color. The product was then cooled in an ice bath. The product was filtered and washed with DMF to leave white solid. The weight of the product was 7.21g to give a yield of 56.4%.

Per-6-tosyl-β-cyclodextrin (a):
Reference: Matsui, Bulletin of Chemical Society of Japan 1978
Beta-Cyclodextrin (2.96g, 2.61 mmol) was dissolved in dry pyridine (20.0mL) at 0°C. P-toluenesulfonyl chloride (.365g, 1.91 mmol) in dry pyridine (3.0mL) was added and allowed to stir at 37°C for 20 hours. After the addition of the tosylate the reaction changed from clear to a pale yellow color and again to clear. The solvent was removed in high vacuum at 40°C. Water was added and the mixture was cooled to O°C to produce pink crystals. Crude weight of .17g to provide a yield of 76.2%. IR spectra for structural analysis.

Per-6-amino-β-cyclodextrin (c):
Synthesis of the Per-6-amino-β-Cyclodextrin is still in progress.

4-O-(β-D-Galactopyranosyl)-N-((4-vinylbenzoyl)-β-D-glucopyranosylamine ((p-vinylbenzamido)-β-lactose):
Reference: Kobayashi Macromolecules 1997

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Inulin (1.00g) from chicory root was dissolved in water (50.0 mL). Ammonium hydrogen carbonate (56.5g, .714 mols) was added over eight days. The reaction progress was monitored by thin-layer chromatography (4:3:3:2, ethyl acetate, acetic acid, methanol, and water). The TLC was stained using concentrated sulfuric acid (1mL), para-anisaldehyde (0.5mL), and concentrated acetic acid (50mL). The reaction was stirred at room temperature for 24 hours. The crude product was dissolved in water and then added to methanol (4.0mL, .0099 mols) THF (1mL) and sodium carbonate. The reaction was allowed to stir at O°C for 1 hour. p-vinylbenzoyl chloride (.57g, .00338mols) was then added to the reaction mixture and allowed to stir for 4 hours. The reaction progress was monitored using TLC (4:3:1:1, ethyl acetate, acetic acid, water). The product was then recrystallized three times from methanol and water. Recrystallized weight of the product was .28g to provide a yield of 37.4% based on lactose. 1H NMR in DMSO-d6 confirmed structural analysis of product.

Polymerization:
AIBN (.096 mmol, .15g) was dissolved in DMF (5.0 mL) and allowed to stir under nitrogen while styrene and acrylic acid were added dropwise to the solution. The reaction was allowed to stir above 56°C for 5 hours to yield off white polymers. Molar ratio of styrene and acrylic acid were manipulated in order to observe water absorption of individual polymers.
<table>
<thead>
<tr>
<th>Styrene</th>
<th>Acrylic Acid</th>
<th>Water Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>.010mols</td>
<td>.010mols</td>
<td>.005g</td>
</tr>
<tr>
<td>.010mols</td>
<td>.020mols</td>
<td>.02g</td>
</tr>
<tr>
<td>.010mols</td>
<td>.030mols</td>
<td>.02g</td>
</tr>
</tbody>
</table>

This acrylic acid styrene 2:1 polymer absorbed .02g of water. This will be the polymerization standard of choice for the styrene with the saccharide derivative.

**Future Work:**
Currently we are in the process of completing the synthesis of the saccharides to the styrene base. After the synthesis is complete we will begin testing the molecular recognition of the saccharides' ability to bond heavy metals in an aqueous solution. The styrene derivative saccharide will then be polymerized and tested again to see if the results remain concurrent with the results obtained from the unpolymerized styrene sugar.

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**Works Cited:**
1.) Kobayashi, K., Furuno, S., Matsuura, K. *Chemistry Letters* 1998