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**Progress Report**

PROJECT TITLE: Value added materials from corn

PROJECT NUMBER: 1063-16EU

REPORTING PERIOD: 02/01/2017 – 04/30/2017

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1.) PROJECT ACTIVITIES COMPLETED DURING THE REPORTING PERIOD. (*Describe project progress specific to goals, objectives, and deliverables identified in the project workplan.*)

The Tonks goup has been continuing our work on optimizing hydroesterificative olefin polymerization (HOP) reaction conditions to generate new, higher molecular weight polyesters. During the previous quarter, we found that lowering the catalyst loading to 1% Pd and increasing the reaction concentration by a factor of 5 yields significantly higher conversion of **9** into a new polyester (>96% conversion) that has a significantly higher molecular weight than we previously observed (Figure 1). However, attempts to further reduce the catalyst loading led to a significant problem: lowering the catalyst concentration resulted in slower productive HOP reactivity, and instead undesired polystyrene polymerization dominated, resulting in insoluble, uncharacterizable polymeric materials with limited potential value. During this quarter, we have focused on determining the kinetics of this reaction and designing methods to shut down unwanted polystyrene formation. Recently, we have found that adding radical inhibitors such as BHT to the HOP reactions completely inhibits polystyrene formation, resulting in high HOP conversions at low catalyst loadings with no observable sideproducts.



**Figure #1** New conditions have been developed for a fully-optimized HOP reaction that yields a robust and high molecular weight new polyester with no polystyrene sideproducts.

The Hoye group focused considerable effort on exploiting the difunctional molecule chloromethylfurfural (**CMF**), readily derived from glucose (see previous Progress Report). Displacement of the chloride with potassium methacrylate gave the monomer **1**. Upon radical initiated polymerization this reactive monomer led to a cross-linked thermoset. Control experiments suggest that the furan was participating in radical cross-linking events. Similar behavior was observed for the simple acrylate ester analog of **1**. Displacement of chloride from **CMF** by the potassium carboxylate of malonic acid monoethyl ester smoothly gave **2**, an A–B monomer. This compound undergoes efficient Knoevenagel condensation. We have recently discerned that the products **3** are cyclic oligomers; we have several ideas of how to overcome this limitation and exploit this otherwise promising chemistry for the production of higher molecular weight, linear polymers. The dialdehyde **4** is readily derived from **CMF**. We plan to copolymerize this bifunctional molecule with a bis-malonate ester like **5**, derived from bio-sourced diols **6**. Finally, we have synthesized the alcohol **7** and plan to reduce it to the diol **8** for incorporation into various polyesters and polyurethanes.

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**Figure 2**

The Hillmyer group has continued their work on the synthesis and polymerization of 7-methoxyoxepan-2-one (MOPO). One major hurdle in our work with cyclic hemiacetal esters has been their high degree of reactivity, resulting in autopolymerization of the monomers during purification and upon storage of purified material. We have worked to stabilize MOPO prior to and during purification via addition of base and/or radical inhibitors. We found that base successfully suppressed formation of linear poly(MOPO) during purification and storage. Thorough characterization of purified MOPO by liquid chromatography mass spectrometry (LCMS) revealed that, what we believed to be a monomeric substance, appears to be a distribution of MOPO and higher order cyclic oligomers of MOPO. Regardless, MOPO can be polymerized in the presence of diethylzinc or hydrochloric acid catalyst with or without exogenous initiator. Similar to 2-methyl-1,3-dioxan-4-one (MDO) we observe polymerization both by an active chain-end and an activated monomer mechanism. We are now working on establishing the kinetic parameters that will allow us to add MOPO at a rate that will effectively suppress the undesired active chain-end mechanism.

Furthermore, we have been working on the synthesis of 3-methyl-1,4-dioxepane-2,5-dione, a monomer that, upon ring-opening, yields a perfectly alternating copolymer of lactic and 3-hydroxypropionic acid, both biomass based molecules. Benzyl protection of methyl L-lactate followed by deprotection of the ester yields an acid that is subsequently esterified with ethyl 3-hydroxypropionate (Figure 3).



**Figure 3.** Progress in the synthesis of 3-methyl-1,4-dioxepane-2,5-dione.

We are currently screening hydrogenation conditions to remove the benzyl group. With the deprotected substance in hand we will cleave the ester to the acid and finally probe conditions to effect cyclization of the substrate to the cyclic diester monomer 3-methyl-1,4-dioxepane-2,5-dione (Figure 3).



**Figure 4.** Anticipated sequence of synthetic steps to obtain 3-methyl-1,4-dioxepane-2,5-dione.

2.) IDENTIFY ANY SIGNIFICANT FINDINGS AND RESULTS OF THE PROJECT TO DATE.

3.) CHALLENGES ENCOUNTERED. (*Describe any challenges that you encountered related to project progress specific to goals, objectives, and deliverables identified in the project workplan.*)

4.) FINANCIAL INFORMATION (*Describe any budget challenges and provide specific reasons for deviations from the projected project spending.*)

5.) EDUCATION AND OUTREACH ACTIVITES. *(Describe any conferences, workshops, field days, etc attended, number of contacts at each event, and/or publications developed to disseminate project results.)*

Anne Stevenson (UMN Extension), Laura Seifert (CSP Managing Director), and Jennifer Henderson (CSP Director of Education, Outreach, and Diversity) presented “Be a 4-H Scientist: New Physical Science Curriculum for Cloverbuds” as a workshop at the 2017 Youth and U conference for Minnesota 4-H Extension Educators on March 29, 2017.

Registration closed for the 2017 high school teacher workshop in Green Chemistry, and 31 high school chemistry teachers from across Minnesota have committed to attending the two-day workshop this summer.

Finally, a researcher in the Hoye group helped organize the UMN Chemistry Department’s participation in the March for Science, held April 22, 2017.