PROGRESS REPORT

PROJECT TITLE: Value Added Materials from Corn
PROJECT NUMBER: 1063 - 16EU
REPORTING PERIOD: 07/01/2016-09/30/2016
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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.*)

This progress report contains intellectual property of a confidential nature that we ask not be shared outside of the MCGA.

The Hoye group has done further explorations of the Diels-Alder product readily derived from furfurol and itaconic anhydride (Pehere, A. D.; Xu, S.; Thompson, S. K.; Hillmyer, M. A.; Hoye, T. R. *Org. Lett.* **2016**, *18*, 2584–2587). As shown in panel A in Figure 1, we have found a new intermediate, the trifluoroacetate 2, which can be efficiently formed by simple treatment of 1 with trifluoroacetic acid. We are exploring ways to convert it to isochromanone (3). We are also preparing a more reactive catalyst (not shown) for the potential polymerization of this relatively stable lactone at very low temperature.

We have also initiated more extensive studies that are designed to capitalize on the complementary, dual electrophilic character of the molecule known as chloromethylfurfural [CMF, "5-(Chloromethyl)furfural is the new HMF: Functionally equivalent but more practical in terms of its production from biomass." Mascal, M. *ChemSusChem* **2015**, *8*, 3391–3395]. This compound is readily derived from six-carbon sugar-containing feedstocks, including the cellulosics and dextrose, the major constituent of corn sugar. We have learned how to carry out a number of transformations and a representative set is shown in Panel B. Various carboxylic acids, under basic conditions, will displace the primary chloride to give, for example, 4 when *N*-Boc-glycine is the acid. We have found high yielding conditions for oxidation of CMF to 1,5-diformylfuran (5). The chloride in CMF can also be displaced with phenols as shown for 4-nitrophenol to give 6. A number of condensation reactions of the aldehyde in CMF with ammonia derivatives have been studied as shown, for example, in the formation for the hydrazone 7. In situ NMR spectroscopic analysis of many of these reactions is proving to be very informative. All of these products are difunctional and we are gearing up to explore oligomerization with suitable reaction partners and/or activating agents.

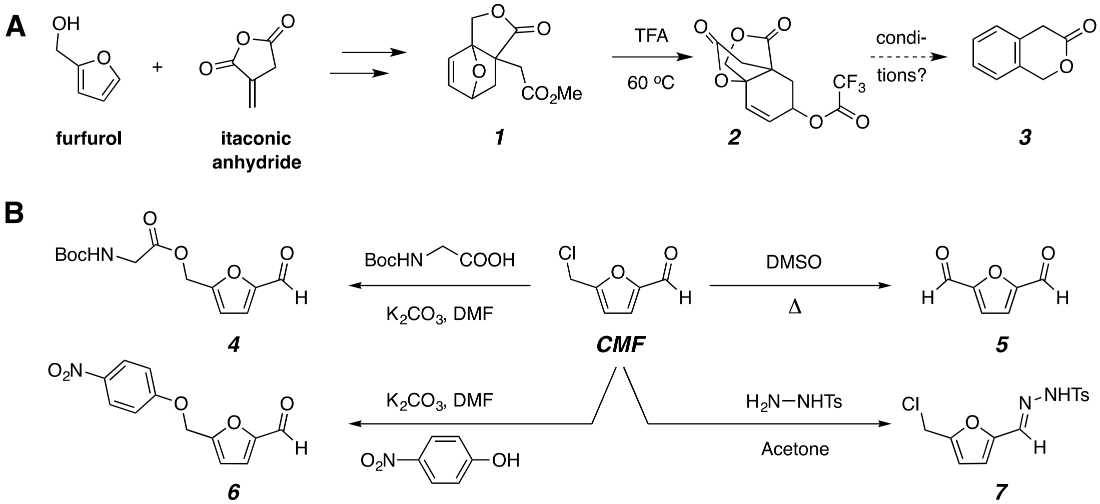


Figure 1. Exploration of chemical conversions of corn-based furans to new potential monomers for polymerization reactions.

The Tonks group has been continuing to work on optimizing hydroesterificative olefin polymerization (HOP) reaction conditions to generate new, higher molecular weight polyesters. During the previous quarter, we discovered 2nd generation catalyst conditions that removed all undesirable side products from our HOP reaction of 4-(hydroxymethyl)styrene, 8, and produced a polyester that had an intermediate molecular weight of approximately 3,000 g/mol. Our current work is focused on increasing the molecular weight of the polymers and on decreasing our catalyst loading. We have discovered that lowering the catalyst loading to 1% Pd and increasing the reaction concentration by a factor of 5 yields significantly higher conversion of 8 into a new polyester (>96% conversion) that has a significantly higher molecular weight than we previously observed (Figure 2). This material is extremely thermally robust we are currently working with the Hillmyer group to fully characterize this new polymer. We plan to file an invention disclosure and publish our initial results on this work within the calendar year.

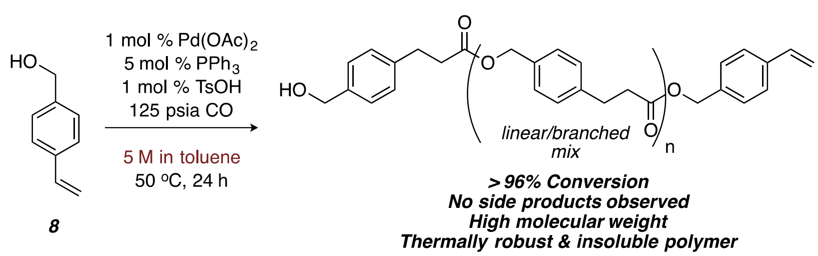


Figure 2. New conditions have been developed for a fully-optimized HOP reaction that yields a robust and high molecular weight new polyester.

The Hillmyer group has been working on new routes to degradable polyesters from commodity materials in a collaborative project within the Center for Sustainable Polymers. Unprecedented 7-membered cyclic hemiacetal ester monomers were synthesized for the preparation of hydrolytically and thermally degradable polyhemiacetal esters as shown in Figure 3. The monomer 1,3-dioxepan-4-one (DPO) was successfully polymerized in the presence of the organocatalyst diphenylphosphoric acid (DPP) and the alcohol initiator benzyl alcohol. The resultant poly(DPO) is a semicrystalline polymer with a glass transition temperature of T_g = −67 °C and a melting point of T_m = 47 °C. The related 2-methyl-1,3-dioxepan-4-one (MDPO) is extremely unstable and so far could not be isolated and stored without decomposition or spontaneous polymerization. We plan to investigate the copolymerization of DPO with 2-methyl-1,3-dioxan-4-one (MDO), a molecule that we have studied thoroughly, to suppress crystallization and thereby access a low T_g amorphous polyhemiacetal ester. We have begun the process of protecting these new chemical structures through an invention disclosure. Another effort in our laboratories is the synthesis of polyesters from ketene acetal monomers via free radical polymerization. Ketene acetal precursors 1 and 2 have been synthesized, purified, and characterized (Figure 4).

Figure 3. Synthesis of novel 7-membered cyclic hemiacetal ester monomers.

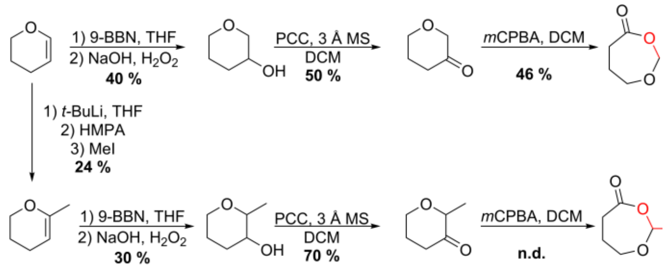
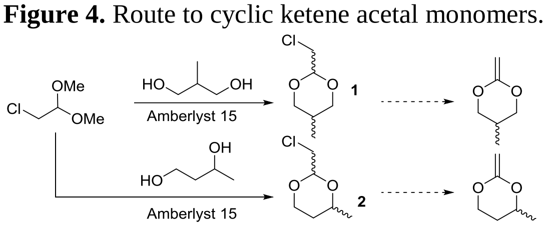


Figure 4. Route to cyclic ketene acetal monomers.



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

The Tonks group has discovered a new polyester that has a high molecular weight and is extremely thermally robust. These are all valuable properties, and currently, the Hillmyer group is characterizing the material. An invention disclosure has been filed with the University of Minnesota Office of Technology Commercialization.

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

Nothing to report

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

Nothing to report

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.)*

During this reporting period, members of the Hoye, Hillmyer, and Wissinger groups volunteered in the Center for Sustainable Polymers (CSP) exhibit at the Minnesota State Fair. This exhibit provides researchers with the opportunity to discuss their work and the importance of sustainable polymers with the general public. Approximately 275,000 people visit the EcoExperience building at the Minnesota State Fair annually, where this exhibit is located.

4-H youth in Anoka testing CSP developed modules

The 4-H modules for grades K-2 that are underdevelopment with the CSP and 4-H education professionals from the University of Minnesota, Cornell University, and University of California, Davis, went through pilot and field test stages in Minnesota, California, and New York, and were evaluated by the Center for Applied Research on Educational Improvement. The modules are now being revised based on the recommendations from the evaluation team.