

PROGRESS REPORT

PROJECT TITLE: Value added materials from corn
 PROJECT NUMBER: 1084-18EU
 REPORTING PERIOD: January 1 – March 31, 2019
 PRINCIPAL INVESTIGATOR: Marc A. Hillmyer
 ORGANIZATION: University of Minnesota
 PHONE NUMBER: 612-625-7834
 EMAIL: hillmyer@umn.edu

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

In the Tonks and Hillmyer groups, work was conducted toward the synthesis of co-polymers of undecenyl lactate and CO. One of the key issues identified with using hydroesterification as a polymerization method is the loss of end-group functionality via uncontrolled side reactions, with promiscuity of the alcohol group hypothesized to contribute significantly towards the loss of alcoholic end-groups. To circumvent this issue, we sought to explore the effects of a more tempered alcohol functional group, and hypothesized that a lactate group might serve this purpose. Furthermore, we had good success with using 10-undecenol as a suitable hydroxy-olefin for this chemistry, and suspected that undecenyl lactate might also react suitably in the hydroesterification reaction. Undecenyl lactate was successfully synthesized via acid catalyzed transesterification with lactide (Figure 1, middle).

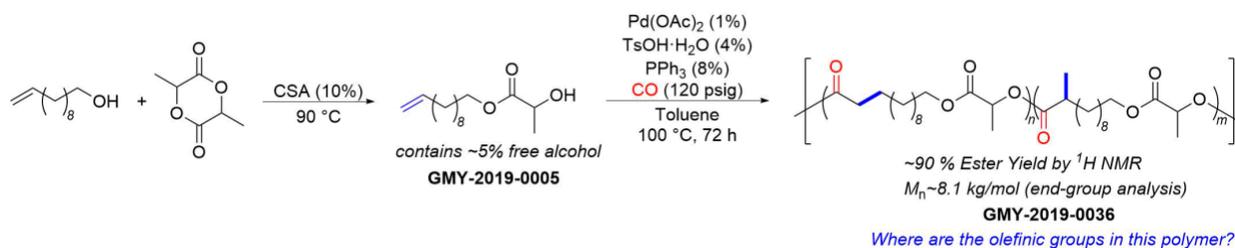


Figure 1. Synthesis of undecenyl-lactate and subsequent co-polymer with CO.

This route is advantageous in that it generates no condensation products such as water or alcohol that need to be removed. It does however require an excess of undecenol, which proved difficult to remove entirely, ultimately remaining in the final product as an impurity present in ~5%. Despite this, the hydroesterification of undecenyl lactate under the conditions shown below in Figure 1

gave a polymeric material, the molar mass of which was determined by SEC to be ~8-9 kg/mol. This was corroborated by ^1H NMR end-group analysis which gave $M_n \sim 8.1$ kg/mol. Interestingly, olefin end-groups could not be identified in the ^1H NMR spectrum, suggesting that at some point these are lost during the polymerization reaction. Also of note, this material did not precipitate from MeOH as did poly(dodecyloate), which was made via hydroesterification of 10-undecenol. Instead, poly(dodecenyllactate) had to be purified by dialysis, hinting at key differences in the microstructure of the lactate containing polymer compared to that made from pure 10-undecenol. Preliminary thermal analysis showed this material to be thermally robust, maintaining ~99% of its mass up to temperatures of ~295°C. Analysis by DSC gave a complicated thermogram, but seems to indicate a T_g at ~ -36 °C. Current efforts with this project are focused on 1) characterizing side reactions leading to loss of olefinic end-groups and 2) exploring the use of other olefin containing lactates such as those derived from 5-vinyl-2-hydroxymethylfuran, which can also potentially be derived from corn sugar.

Previously we have attempted the direct synthesis of β -methyl- δ -valerolactone via Pd-catalyzed hydroesterification of 3-methyl-3-buten-1-ol (Figure 2, left). However, after screening of various reaction conditions and supporting ligands, we could only achieve low yields of the desired product, along with a slew of other unidentified side products and incomplete conversions of the starting hydroxyolefin. We hypothesized that direct hydroesterification of 3-methyl-3-buten-1-ol is likely in competition with a number of other side reactions, and thus we either needed a way to suppress the side chemistry or enhance the rate of hydroesterification. Towards this latter approach, we hypothesized that a two-step route (Figure 2, right) could be feasible if instead we targeted the hydroxycarbonylation of 3-methyl-3-buten-1-ol to give the corresponding hydroxy acid and then attempted a ring-closing esterification. Drawing on previous reports of hydroxy carbonylation reactions, we attempted the first step of this two-step route using 5 equivalents of H_2O and 1,4-dioxane as a solvent. To our surprise, one of the major products of this reaction was the desired lactone, present in ~45% yield (according to GC-FID analysis). Also of note, the substrate was present in ~45% yield as well, indicating that the side chemistry observed in previous reactions was largely inhibited. In an effort to increase the yield of product as well as the conversion of substrate we tried to optimize this reaction, specifically by increasing the reaction time as well as the water to substrate ratio. However, these changes did not lead to significant improvements. Lastly, we tried doubling the catalyst loading, which to our surprise gave the desired product in ~91% yield and full conversion of substrate (by GC-FID). While these results are preliminary, we are hopeful that this result can be scaled up to give the desired lactone in high yields and quantity. Current efforts are focused on 1) scale up and 2) understanding if this reaction is indeed proceeding via the carboxylic acid as originally proposed, or if this solvent combination is simply leading to selective hydroesterification.

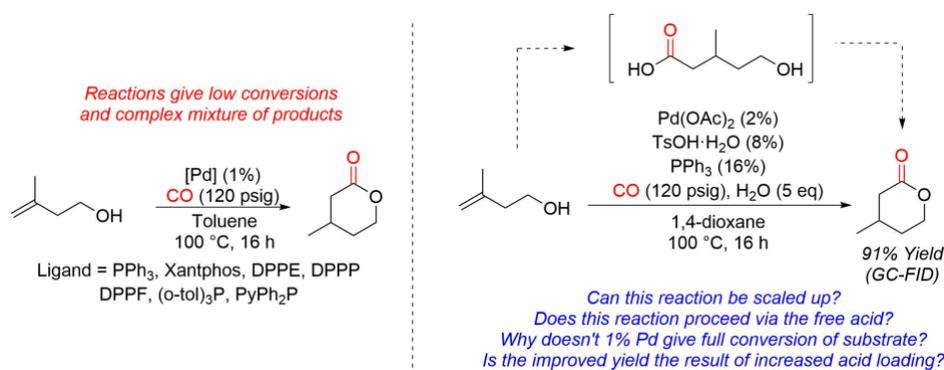


Figure 2. (Left) Direct hydroesterification of 3-methyl-3-buten-1-ol, which leads to a complex mixture of products, with low conversions of substrate and low yields of the desired product. (Right) Proposed hydroxycarbonylation of 3-methyl-3-buten-1-ol to give β -methyl- δ -valerolactone via the intermediacy of the hydroxy acid drawn up top in brackets.

Now that we have successfully completed our study of VBA as a monomer in HOP polymerization reactions, we have moved on to exploring more bioderived materials. A coumaric acid-based monomer has been prepared in a two-step synthesis (Figure 3). Here, we have modified the phenolic alcohol of coumaric acid into an aliphatic alcohol, anticipating that this will increase reactivity. An initial polymerization ran using this monomer resulted in polymerized styrene. Therefore, to prevent the polymerization of styrene, we will add 1% BHT to favor hydroesterificative polymerization, similar to our recently-published work using VBA as a monomer.

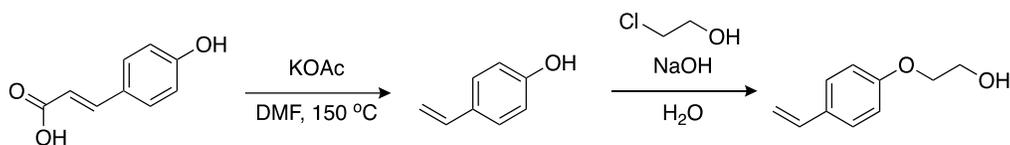
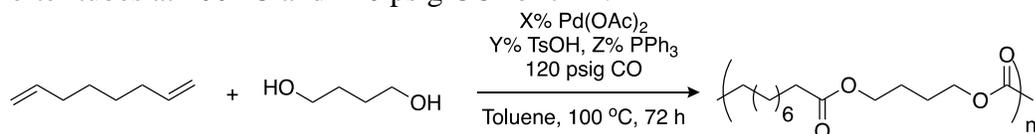


Figure 3. Synthesis of a new HOP monomer from bioderived coumaric acid.

Test polymerizations of butanediol and octadiene (Figure 4) have been done to determine ideal conditions for AABB polymerizations in comparison to previous our previously reported AB polymerizations with 10-undecenol.

Figure 4. Octadiene and butanediol carbonylative polymerizations. Reactions were carried out in Fisher-Porter tubes at 100 °C and 120 psig CO for 72 h.



Experiment	Catalyst Loading	Ester Yield from NMR	Expected MW (from nmr) (g/mol)	SEC data (g/mol)
1	1% Pd(OAc) ₂ , 4% TsOH·H ₂ O, 8% PPh ₃	69%	826	7352
2	1% Pd(OAc) ₂ , 4% TsOH·H ₂ O, 8% PPh ₃	78%	1,164	2812
3	2 % Pd(OAc) ₂ , 8% TsOH·H ₂ O, 16% PPh ₃	84%	1,600	-
4	5% Pd(OAc) ₂ , 20% TsOH·H ₂ O, 40% PPh ₃	88%	2,118	-
5	1% Pd(OAc) ₂ , 4% TsOH·H ₂ O, 8% PPh ₃ Addition of 5% TAB tosylate	85%	1,707	2293
6	1% Pd(OAc) ₂ , 4% TsOH·H ₂ O, 8% PPh ₃ Addition of 50% TAB tosylate	77%	1,107	-

From these preliminary results, it can be determined that a higher catalyst loading is needed than in the polymerization of 10-undecenol. When 5% Pd(OAc)₂ was used with corresponding increases in acid and ligand the expected molecular weight was 2,118 g/mol. This is an increase from 1,164 g/mol with 1% catalyst loadings. SEC data has been obtained for a few of the reactions, which confirms the presence of polymers and not just low molecular weight esters. Polymerization **1** with 1% catalyst loading showed polymers with 7352 g/mol molecular weights after the polymer was precipitated in methanol. Two polymerizations, **5** and **6**, were done with a phase transfer catalyst to overcome miscibility issues. However, this does not seem to have a large effect on the ester yield. Next, the solvent and ligands will be varied.

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

The synthesis of lactate containing co-polymers of CO and undecenyl lactate was shown to be possible using a hydroesterificative route. The resulting polymers are much more liquid like compared to poly(dodecyloate), which is synthesized from the pure undecenol monomer. Notably, end-group loss also proved to be present in the polymerization of undecenyl lactate, which we had hypothesized to be better suited towards end-group preservation.

We were able to achieve the direct synthesis of *β*-methyl-*δ*-valerolactone using what we hypothesize is a hydroxycarbonylative approach. This monomer, which has potential use in ring-opening polymerizations, was able to be synthesized in >90% yield according to GC-FID analysis.

The Hoye group has advanced its studies and understanding of the polymerization of 4-ketovalerolactone (**KVL**, Figure 5), a monomer available from levulinic acid. Levulinic acid is a commodity chemical available from six-carbon sugars (e.g., fructose). The resulting poly(4-ketovalerolactone) (**PKVL**) shows attractive thermal properties (high melting and low glass transition temperatures) that continue to drive the interest in this novel material. They have explored some copolymerization reactions of **KVL** with caprolactone. This should allow for tailoring of the thermal properties (and degradability, see below) of the resulting polymers.

Preparation of diblock and triblock polyesters, incorporating **PKVL** as a hard segment is now feasible. The triblock materials have potential for applications as thermoset plastics.

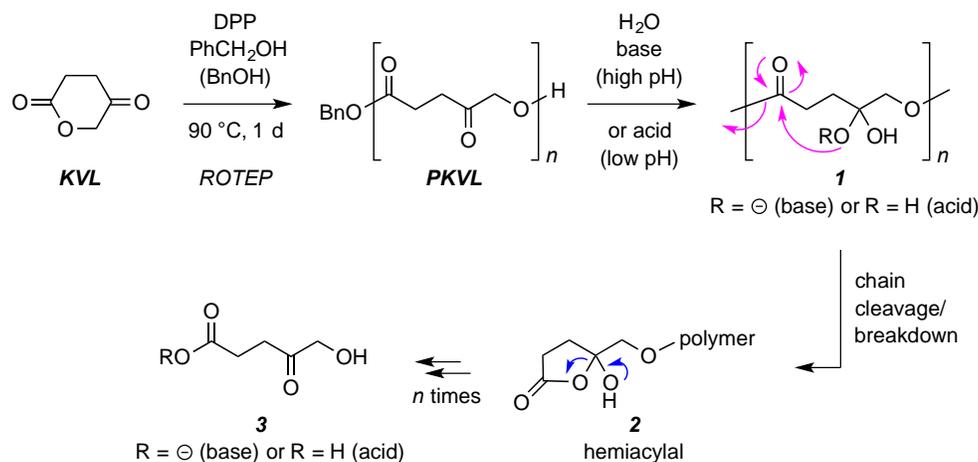


Figure 5. Synthesis of **PKVL** from **KVL** by ring-opening transesterification (ROTEP) provides a polyester that is easily cleaved by hydrolysis under either basic or acidic conditions.

Polymer/plastic decomposition/degradation is a growing theme in overall efforts of the Center for Sustainable Polymers. In a new thrust for this project, Hoyer researchers have explored aspects of the hydrolytic degradation of **PKVL**. Rapid chemical decomposition is seen in both acidic and basic aqueous media, the latter being especially fast. While this might limit some of the potential for application of **KVL**-containing polymers (i.e., decomposition prior to the end of the useful lifetime of the polymer-containing product), breakdown upon disposal of a polymer-based product is a desirable feature. Both chemical and enzymatic cleavages impact the compostability of polymers and plastics. Thus, understanding the rates of such (hydrolytic) processes (for polyesters) is important. The facile hydrolysis of **PKVL** back to 5-hydroxylevulinic acid (**3**, Figure 5) can be attributed to the presence of the ketone carbonyl group in the **PKVL** backbone. More specifically, the equilibrium amount of ketone hydrate (cf. **1**) enables an intramolecular attack to the ester carbonyl (cf. magenta arrows in **1**) to produce the chain-cleaved, transient hemiacetal **2**, which then rapidly isomerizes (blue arrows) to the isomeric ketoacid **3**.

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

The loss of end-groups and presence of side reactions is still a key problem in achieving the synthesis of high-molar mass polymers in the synthesis of co-polymers of undecenylactate and CO. We are currently trying to tackle this using both a monomer and catalyst design approach.

While we were successful in achieving the direct synthesis of *β*-methyl-*δ*-valerolactone, the long-term goal is to be able to apply this chemistry to the synthesis of other cyclic esters/anhydrides, which will test the regioselectivity of this chemistry. Scale up is another challenge that we hope to overcome in the near future.

The biggest challenge still facing the **PKVL** project is the efficiency of the synthesis of the **KVL** monomer, currently done by the direct bromination of levulinic acid. This gives a mixture of the 3-bromo- and 5-bromolevulinic acids. We plan to study the bromination of the ethylene ketal of levulinic acid to learn if that will improve the selectivity of this key reaction. More efficient access to **KVL** would enable larger scale preparations of **PKVL**, allowing for more detailed studies of polymer properties.

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

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

The 2019 Summer Undergrad Research Participants have been recruited into the Center for Sustainable Polymers. The program received 105 applications and 11 students have accepted research positions across the center for summer 2019. Melissa Barrera from New York University was selected as the Corn Growers Fellowship recipient. Melissa will work with Professor Tom Hoye during summer 2019.