MinnesotaCorn RESEARCH & PROMOTION COUNCIL

2024 FINAL REPORT (project ongoing)

PROJECT TITLE: **Engineering Degradability into Corn-based Plastics**

PROJECT NUMBER: **6134-24DD**

PRINCIPAL INVESTIGATOR AND CO-INVESTIGATOR(S):

Professors Thomas R. Hoye (PI) and Ian A. Tonks (co-PI)

ABSTRACT

Researchers in the Hoye and Tonks laboratories in the Department of Chemistry (DOC) on the Twin Cities campus of the University of Minnesota (UMN) are investigating strategies for enhancing the post-use degradation of polylactic acid (PLA). PLA is a polyester that is derived from corn. It is widely recognized as the commercially most successful example of a widely used bio-derived polymer. In an effort to increase the degradability of PLA, various approaches are being pursued. Tonks group researchers has focused on doping small amounts (1-10%) of a CO_2-based monomer (EtVP) into PLA copolymers. The resulting polymers, *poly*(LA-co-EtVP) contain alkene sidechains that can be modified *via* thiol-ene click chemistry. The overall aim is to incorporate degradable functional groups that can be scrambled into the polymer backbones and provide degradation points to enhance PLA degradability. Currently, efforts have been on copolymer synthesis, post-polymerization modification, and optimization of ester scrambling. Hoye group researchers are exploring the design of novel lactone structures having a chemically degradable unit within the lactone ring. Copolymerization of these is envisioned to lead to more easily degradable analogs of PLA.

INTRODUCTION

As societal plastic production and use continues to increase at an enormous pace, there is a great need to develop sustainable materials that leverage renewable resources. It is also critical that new materials are potentially cost-competitive with current petroleum-based plastics. Biobased polyesters such as poly(lactic acid) (PLA) offer enormous opportunities in this regard.[1] For example, the starting materials can be agricultural waste products or inexpensively produced crops. The global biobased polyester market has already reached US$ 2.1 billion in 2022 and is projected to grow to US$ 9.6 billion by 2032.

Efficient waste plastic (polymer) decomposition/degradation remains an ongoing challenge in sustainable implementation of biobased plastics. Although PLA is compostable, that operation needs to be conducted in an industrial, high-temperature composting facility to proceed at a viable rate.[2] PLA does not degrade readily in the environment. As a consequence, individual uses of PLA-based plastics cannot compost these products in their own “backyard” composting set-up. Additionally, the biodegradation of PLA by microbes is challenging and can take years for complete degradation to occur.[3] Our aim is to install low levels of chemically degradable groups into PLA that will enhance subsequent microbial (and therefore, overall) degradation rates.

(OVERALL) OBJECTIVE AND GOAL STATEMENTS

In this proposed project, we have aimed to lay the groundwork for the development of a new strategy to incorporate degradable chemical entities into the backbones of polyesters, leading to more easily-degraded versions of poly(lactide) (PLA) and other bioderived polyesters. A main premise of this work is that we can design catalysts that can scramble polyester backbone ester linkages with sidechain esters, swapping the backbone linkage for the sidechain linkage in a process we have coined ***sidechain-backbone ester scrambling***. In principle, it should be possible to use simple chemistry to install many types of degradable linkers into the sidechain, which upon scrambling would then contain the degradable group along the backbone. This will allow cleavage of the plastic into smaller fragments of the polyesters following the degradation mediated by sunlight, moisture, or, even, fluoride in ocean water. The resulting smaller polyester fragments can then be more easily consumed by microbes in natural settings of soil and water (ocean) or in inoculated environments of sewage treatment plants and industrial composting facilities.

The overarching goal of this research is to engineer chemical degradation points into corn-based plastics (such as PLA) with the intent of developing polyester-based plastics that can more readily degrade in the environment.

MATERIALS AND METHODS

Both of the Hoye and Tonks laboratories in the DOC at the UMN are well-equipped for pursuing organic and polymer chemistries. Each of these Investigators has a well-established history of carrying out cutting-edge research at the intersection synthetic, structural, mechanistic, and catalytic chemistry. Both small molecule and polymer synthesis expertise is drawn upon to guide the investigations. Characterization of new chemical compounds and polymer materials made in the course of the studies is performed both in these two laboratories as well as in departmental spectroscopic facilities. There, nuclear magnetic resonance (NMR) and mass spectrometric (MS) measurements are routinely made on a nearly daily basis.

RESULTS AND DISCUSSION

Tonks Studies

Background and Introduction

Ethylvinylpyranone (EtVP, see Table 1) is derived from CO_2 and butadiene, two cheap and abundant waste feedstocks. Polymers synthesized from EtVP contain up to 28.5% by weight CO_2 content and were found to be biodegradable. Additionally, upon formation of *poly*(EtVP) pendent vinyl groups are present that enable post-polymerization modifications.[4] Doping PLA with EtVP would provide a vinyl handle for polymer modification while simultaneously increasing the amount of CO_2 incorporated compared to other possible comonomers for L-lactide (LLA).

Previously we have demonstrated the ability to synthesize random copolymers from EtVP and L-lactide.[5] Post polymerization scrambling was previous proven to be possible by Fahnhorst *et. al.* using poly(4-carbomethoxyvalerolactone), also known as *poly*(CMVL). The scrambling was performed using the Zn(II) catalyst,[6] and the reaction was shown to be achievable at room temperature. These conditions will provide a starting point for translation of this reaction to modified *poly*(L-*LA*-*co*-EtVP). Based on these two reports, we envisioned that a PLA-based copolymer with small amounts of EtVP doped in could be modified with ester side-chains containing degradable functional groups such as ketal, silaketal or photosensitive links. These side-chains could then undergo ester scrambling into the polymer backbone and act as degradation points to enhance the overall biodegradability and end-of-life options of PLA.

Objectives

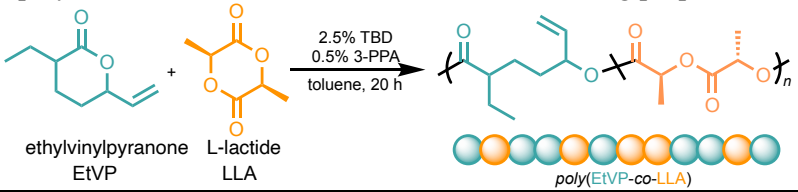
The overall objective is to synthesize a PLA with small amounts of EtVP doped in that has been functionalized and scrambled. This can be broken down into several aims:

1. Synthesize and characterize copolymers with 1-10% EtVP incorporation.
2. Modify EtVP sidechains *via* thiol-ene click chemistry.
3. Investigate and optimize ester scrambling into the polymer backbone.

Results

Copolymers with 1, 5, 10, and 20% EtVP were successfully synthesized and isolated using organo-catalyzed ring-opening polymerization (Table 1). These polymers exhibited moderate molar masses (M_n) and narrow dispersities. This reaction was able to be scaled all the way up to 10 grams.

Table 1. Random copolymerizations of EtVP and L-lactide and resulting properties[5]



EtVP %[b]	$M_{n,\,SEC}$ (kDa)[c]	$Đ$[c]
1	29.3	1.5
10	17.3	1.5
20	13.7	1.6

[a]Reaction conditions: 2.5 mol % TBD, 0.5 mol % 3-PPA, 3.24 M toluene (respective to LLA), 22 °C, 20 h. [b]Percentage of EtVP relative to LLA in monomer mixture.
[c]Determined by THF SEC using polystyrene standards.

Next, we used post-polymerization modification with thioesters to install sidechains on the EtVP units. The copolymers with 10% EtVP incorporation were dissolved in $CDCl_3$ and the desired thiol was added (x=1 or x=2) followed by a photo initiator (DMPA) (Figure 1). The reactions were then subjected to UV for 4-8 h. The reactions were monitored *via* ^{1}H NMR spectroscopy and the polymers were isolated by precipitation.

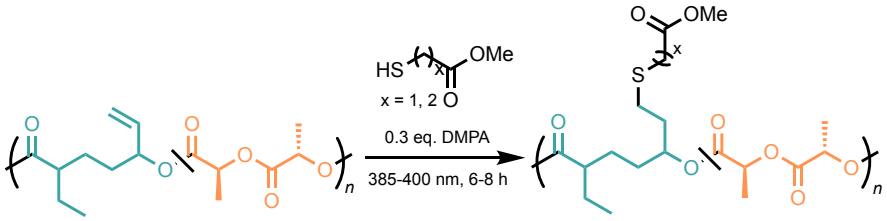


Figure 1: Post-polymerization modification of co-polymer with thioesters methyl thioglycolate (x = 1) and methyl 3-mercaptopropionate (x = 2)

The thiolated polymers were then exposed to various reaction conditions in hopes of 'scrambling' the thioester and the EtVP unit (Figure 2). An EtVP incorporation of 10% was employed to increase ease of characterization of the copolymer before and after the scrambling reaction. The testing of these conditions to achieve successful exchange of the EtVP and thioester are currently in progress. Scrambling catalysts that have been tested include a Zn(II) complex (cat. 1) and TBD (Figure 2), with various alcohol added to help initiate the scrambling. Both catalysts have been tested on the methyl 3-mercaptopropionate (x=2) modified polymer at room temperature, employing PPA and BDM as alcohols (Figure 2). Additionally, cat. 1 has been tested at 80 °C with PPA. So far, no scrambling of the thioester and EtVP units has been observed.

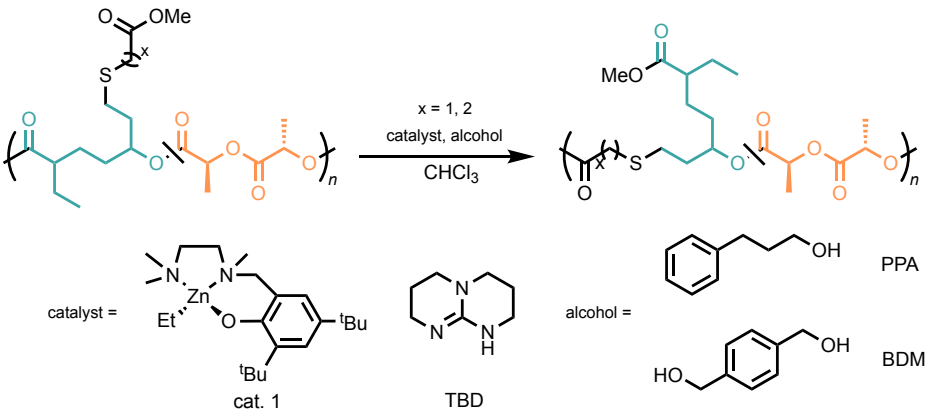


Figure 2: Current conditions tested for the transesterifications 'scrambling'

The next steps for optimization of this reaction will include variation of the catalyst loading, time of the reaction, reaction temperature, and alcohol employed. Additionally, the length of the carbon chain, x, will be varied to measure its effect on transesterification. Upon successful optimization of scrambling, reductions in the EtVP incorporation % of the copolymer will be performed and tested for transesterification using the optimized scrambling conditions. After successfully scrambling of multiple copolymers, degradable groups will be attached in place of the thioesters and transesterified into the polymer backbone. Copolymers with degradable groups will then be tested for their physical properties and biodegradability.

Hoye Studies

Objectives

Our goal is to copolymerize lactide with a small amount of a unique lactone, designed/engineered to introduce a (few) specific sites within the copolymer backbone that will enhance the chemical degradation of PLA. This should, in turn, speed up further microbial decomposition in the environment.

Results

The initial lactones we investigated is 4-ketovalerolactone (**1**, KVL, Figure 3a). Its synthesis follows a protocol previously reported by our lab, where levulinic acid, derived from corn-based products, is used as the starting material. We obtained **1** through a two-step process involving bromination and cyclization.[7]

Once the desired lactone **1** was synthesized, we studied its copolymerization with valerolactone (VL) and L-lactide (LLA) in an attempt to prepare the copolymer **3**. Initially, we explored the copolymerization of **1** and VL using the Brønsted acid diphenyl phosphate **(**DPP**)** as the catalyst. With optimized conditions, we then attempted the copolymerization of **1** and LLA, but found that LLA could not be polymerized to any significant extent using DPP as the catalyst. Switching to 1,5,7-triazabicyclo[4.4.0]dec-5-ene **(**TBD**)**, a catalyst effective for ring-opening trans-esterification polymerization (ROTEP) of LLA,[8] we now observed no incorporation of **1** into the PLA when attempting the copolymerization of **1** and LLA. This resulted in an atypical situation where the catalyst dependency of these two lactones was mutually exclusive – DPP polymerized **1** but not LLA, while TBD polymerized LLA but not **1** so we were unsuccessful in achieving the synthesis of either of the copolymers **3** or **4**.

In addition to our studies with **1** (KVL), we also explored a monothiodilactone as a potential monomer for incorporating (chemically labile) thioester linkages into PLA via ROTEP (cf. **5**). Monothiodilactone **2** was synthesized through a one-pot reaction between thiolactic acid and bromoacetyl bromide.[9] Using DPP as the catalyst for copolymerization of **2** with VL, we observed only limited oligomerization. Evidence suggested competitive ring-opening at the two different carbonyl groups in the monomer **2**, with termination by the thiol group, which prevented further chain growth (Figure 3b). Consequently, only low molecular weight oligomers of **6** were formed rather than the desired copolymer **5**.

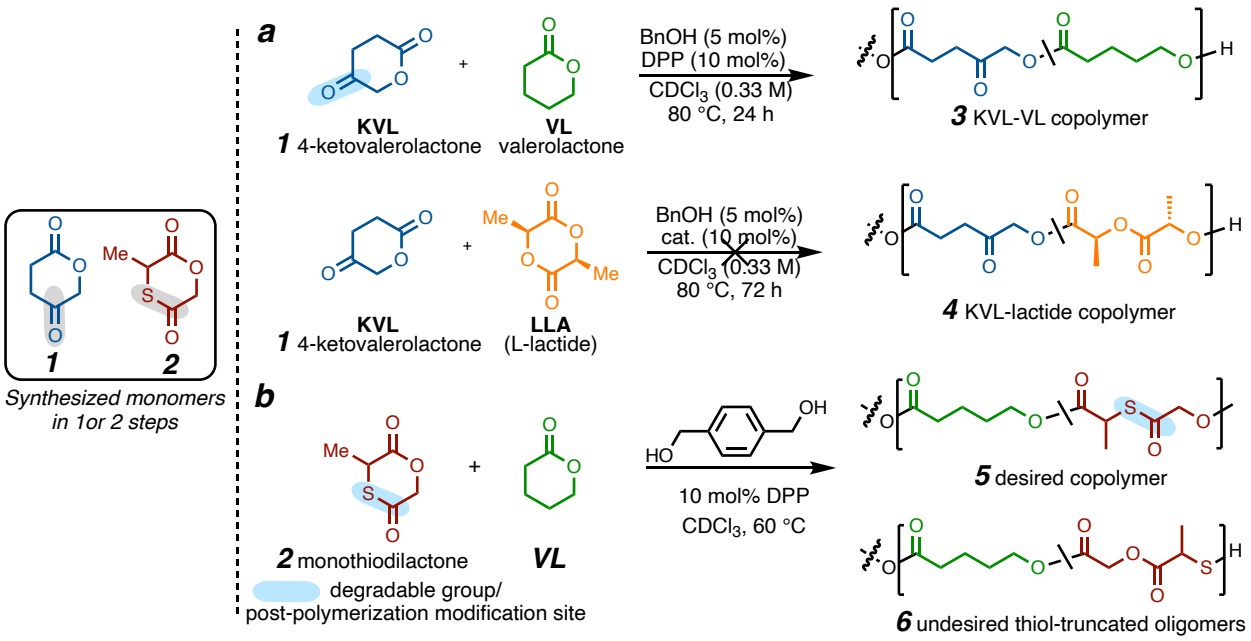


Figure 3. a) Attempts to identify a catalyst that copolymerizes **1** (KVL) with L-lactide (LLA) at comparable rates to allow formation of **3** (poly(KVL-*co*-VL). **b)** Study of the novel monothiodilactone **2** whose ROTEP with VL could give the polyester **5** containing a labile thioester linkage.

5-Ketocaprolactone (**7**, KCL) is a homolog (i.e., contains one more methylene group) of KVL that also comprises a lactone and ketone within the same ring, now seven-membered. KCL was synthesized from 1,4-cyclohexanedione by treatment with *meta*-chloroperoxybenzoic acid (*m*-CPBA) (Figure 4). Upon obtaining the crystalline material, we investigated the copolymerization of **7** and VL, using DPP as the catalyst. However, no copolymerization with VL was detected. Instead, we observed formation of oligomers **8**. Each oligomer was terminated by a vinyl ketone moiety, which arrested the further growth to higher molecular weight polymer.

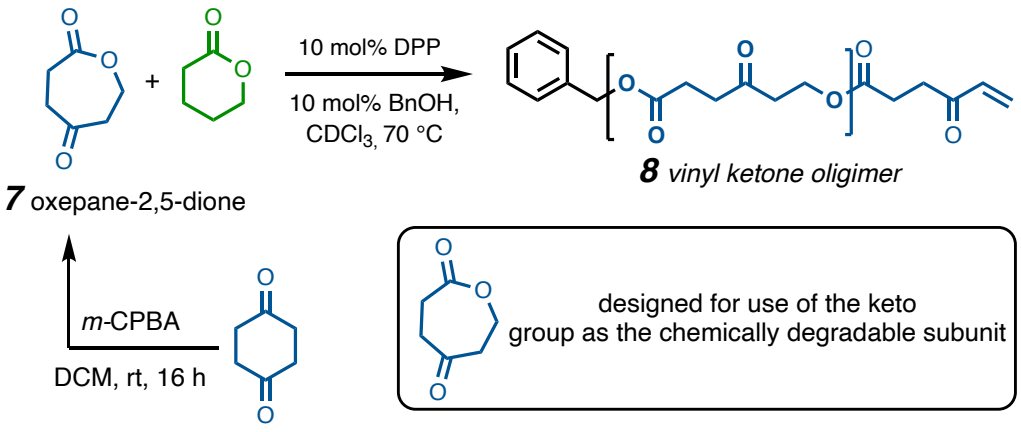


Figure 4. Study of the copolymerization of 5-ketocaprolactone (**7**, KCL) with VL could give a polyester having a labile keto moiety embedded in its backbone. However, elimination events led to the production of only oligomeric materials **8** containing an alkene.

In the fourth quarter, of year one, we have focused on producing degradable polymers containing acetal (or ketal) units as the potentially degradable (i.e., weak) link in the polyester. We hypothesized that

incorporating various small molecule substituents at the acetal position would enable the controlled rate of degradation in various settings (e.g., compost vs. waste sediment vs. ocean). Additionally, the rates of degradation could also be tuned through post-polymerization modifications.

Toward this end goal, we are working toward synthesizing the acetal- or ketal-containing lactone monomers **9** or **11**, respectively, from commercially available, inexpensive sources (Figure 5). In principle, these can be derived from glycolic acid, which we reacted with propargyl bromide or allyl bromide in the presence of Cs_2CO_3, leading to esterification. Further cyclization is being explored using either mercuric sulfate or $PdCl_2/KI$[10] with the goal of producing the lactone ketal **9**. The enol ether lactone **10** potentially can be obtained by an epoxidation/cyclization/elimination sequence. In an approach to the acetal lactone **11** we treated glycolaldehyde diethyl acetal with catalytic pyridinium *p*-toluenesulfonate (PPTS) at 80 °C, which produced a separable cis/trans diethoxy-1,4-dioxane derivative in a 1:1 ratio.[11] The final desired lactone acetal monomer **11** can then be obtained by treating this intermediate with *m*-CPBA in the presence of BF_3•OEt_2.

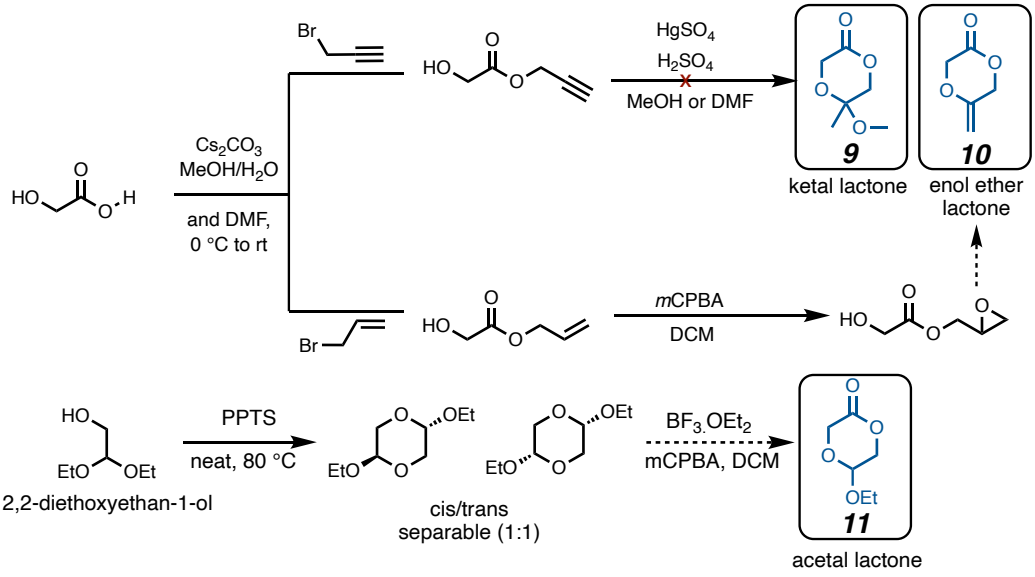


Figure 5. Approaches to the synthesis of the ketal or acetal lactones **9** or **11** and of the enol ether lactone **10** in short sequences from commercially available sources.

In our second year, our focus will be on improving the synthesis of these acetal monomers. So that their copolymerizations with VL and LLA can be explored (Figure 6). This will allow us to then explore the rates of hydrolytic degradation of the resulting ketal-, acetal-, and enol ether-containing polymers **12** and **13**.

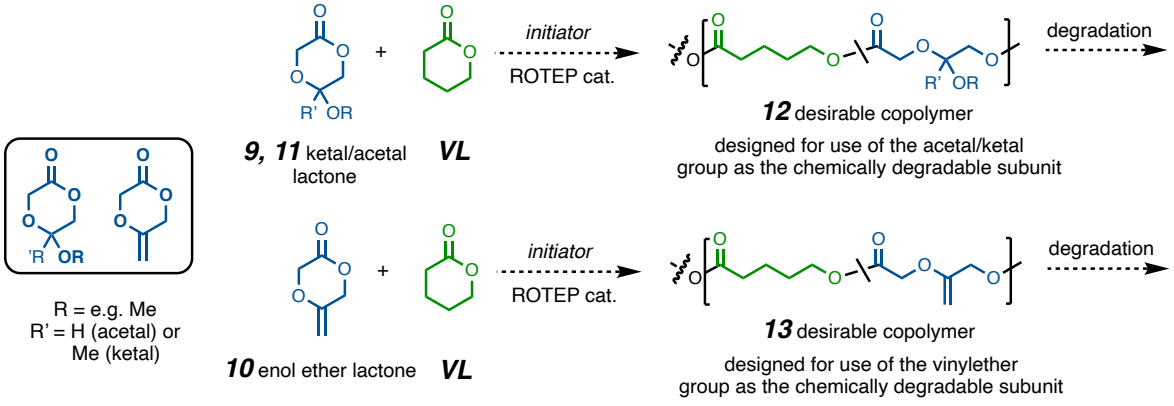


Figure 6. Future studies on the ROTEP of the designer lactone monomers **9**-**11** with VL to yield polyesters **12** and **13**, featuring hydrolytically labile units embedded in their backbone.

CONCLUSIONS

Thanks to the funding provided by MCGA, we have been able to lay the groundwork for significant advances in year 2 of the overall project.

EDUCATION, OUTREACH, AND PUBLICATIONS

Professor Tonks presented an annual research update to the Minnesota Corn Research & Promotion Council on December 12, 2024, sharing research progress from the Hoye and Tonks research group's collaborations investigating new strategies for synthesizing degradable PLAs. In the presentation, Professor Tonks detailed the progress toward "doped" PLA materials containing specialty small-molecule additives that will ultimately serve as environmentally-triggerable degradation points. Additionally, Professor Tonks delivered an invited research presentation at an international conference, the Gordon Conference for Inorganic Reaction Mechanisms, that highlighted this same work. Finally, Mr. Ryan Anderson, a PhD student in the Tonks group who has been supported by past MCRPC to work on degradable plastics, accepted a job offer to work in degradable plastic development at Dow Chemical upon graduation this coming May.

Professor Hoye and two of research collaborators (Sangjun Lee and Trinadh Kaicharla) attended the "Minnesota Corn Growers Reception" held in McNamara Hall on September 4, 2024. This was sponsored by the University of Minnesota Foundation in recognition of the long-standing and much-appreciated support that the MCRPC has provided to collaborators at the UMN. A poster was presented there describing a portion of the year 1 efforts in both the Hoye and Tonks groups on this project.

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