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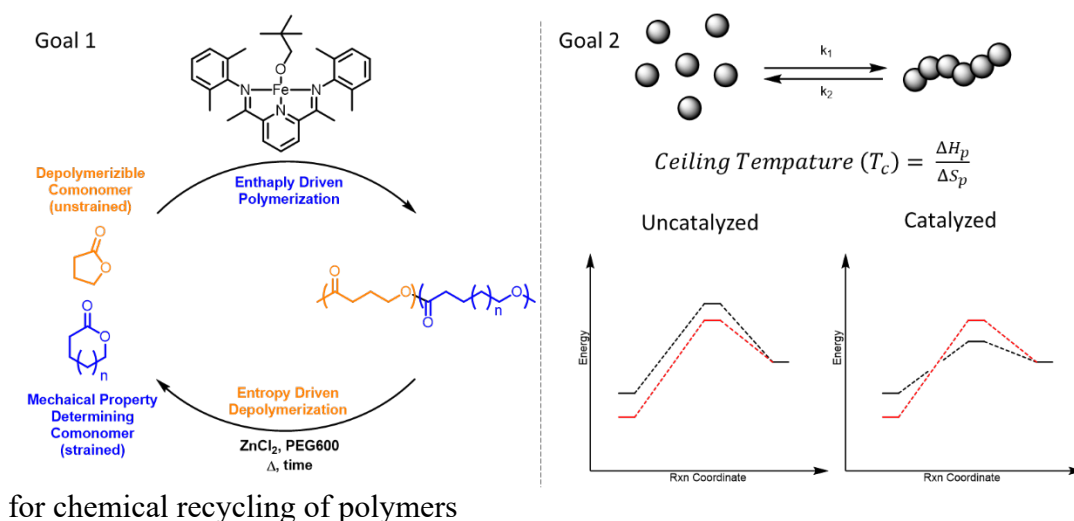
ARO report for W911NF-15-1-0454

This report was written by Mr. Connor Gallin, who is a 6-year doctoral candidate. He was advised by Prof. Byers until Prof. Byers' passing in August 2023. Prof. Wang, in his role as the department chair, is overseeing Mr. Gallin's thesis writing. He helped revise this report, although he was not involved in the project.

1. Accomplishments

a. What are the major goals of the projects?

- 1) The development of chemically recyclable polymers with tunable mechanical and recyclable properties through copolymerization of strained and unstrained cyclic monomers.
- 2) Development of selective, efficient, and robust ring closing depolymerization catalysts



b. What was accomplished under these goals?

- 1) A paper (Connor F. Gallin, Won-Woo Lee, Jeffery A. Byers "A Simple, Selective, and General Catalyst for Ring Closing Depolymerization of Polyesters and Polycarbonates for Chemical Recycling" *Angew. Chem.Int. Ed.* **2023**, 62, e202303762) was published detailing the development of a ring closing depolymerization catalyst for polylactones and polycarbonates
- 2) Copolymerization of unstrained gamma-butyrolactone (GBL) with strained caprolactone (ECL), valrolactone (DVL), and pentadecalactone (PDL) using a bis(imino)pyridine Fe (I) alkoxide ring opening polymerization catalyst
- 3) Creation of polymer films of GBL-PDL copolymers for mechanical testing of copolymers

Experimental Efforts during the most recent funding cycle (Jan 2022 to Dec 2023)

Pentadecalactone-co-Gammabutyrolactone Copolymerization Synthesis

Previously we have shown the ability to control the ECL and GBL in a copolymer by controlling initial monomer concentration and monomer ratios ranging from 0% GBL incorporation up to 44% GBL incorporation. Initial attempts to copolymerize pentadecalactone and gamma-butyrolactone proved unsuccessful. We discovered that the bis(imino)pyridine Fe (I) alkoxide complex was much more thermally robust than we have previously seen in the lab. Raising the temperature of the polymerization allowed for high conversion of the pentadecalactone and gamma-butyrolactone monomers using the following procedure.

In a nitrogen filled glovebox, solid w-pentadecalactone (1 eq.) and liquid g-butyrolactone (1 eq.) were added to a 50 mL round bottom flask with a stir bar. The solution was allowed to stir until homogeneous. To the reaction vessel 2,6-bimethylphenyl bis(imino)pyridine iron (I) monoalkoxide complex (0.5 mol%) was added. Solution was allowed to stir until homogeneous. Reaction vessel was sealed with a 180 joint with Teflon stopcock and H-grease. The sealed reaction vessel was brought out of the glovebox and placed in a 100 °C oil bath for 24 hours. Once reaction was complete, the reaction vessel was unsealed and opened to the atmosphere to quench the reaction. The crude reaction mixture was dissolved in a minimal amount of chloroform and the polymer was precipitated in ice cold isopropanol. Isopropanol volume was approximately eight times the volume of chloroform used. The precipitation mixture was placed into large centrifuge containers and centrifuged to separate the copolymer from solution. After decanting the supernatant, the copolymer (pellet) was dissolved in a minimal amount of chloroform and transferred to an flask with stir bar. An EDTA solution was prepared using EDTA and brine solution EDTA solution was added to copolymer solution and allowed to stir for 48 hours (EDTA extraction of iron). After extraction the copolymer solution (organic layer) was separated using a separatory funnel (excess brine solution was added if layers were not clearly defined). Copolymer solution was filtered through a glass filter frit to remove excess EDTA. Chloroform in solution was evaporated off under reduced pressure. Resulting copolymer was allowed to dry under vacuum overnight. Different initial monomer ratios were used to control the PDL-GBL copolymer makeup.

Results

1. Controlling GBL Incorporation in PDL-GBL copolymers

<i>Entry</i>	<i>Initial Monomer Ratio</i>	<i>%PDL Incorp</i>	<i>%GBL Incorp</i>
<i>1</i>	<i>1:1</i>	<i>94</i>	<i>6</i>
<i>2</i>	<i>1:2</i>	<i>76</i>	<i>24</i>
<i>3</i>	<i>1:4</i>	<i>74</i>	<i>26</i>
<i>4</i>	<i>1:8</i>	<i>68</i>	<i>32</i>

Table 1: 200 mg of pentadecalactone, 0.5 mol% bis(imino)pyridine Fe (I) neopentanol catalyst, 100 °C, N₂, 24 hour

2. PDL-GBL Copolymerization Over Time

Entry	Time (h)	%PDL Conversion	%GBL Conversion	%GBL Incorp.
1	1	7.3	5.8	41.4
2	2	8.9	6.4	41.8
3	3	12.1	5.9	30.4
4	6	16.1	8	27.7
5	18	35.4	11.6	23.3
6	24	43.3	13.6	25

Table 2: 500 mg of pentadecalactone, 1:4 PDL:GBL initial monomer ratio, 0.5 mol% bis(imino)pyridine Fe (I) neopentanol catalyst, 100 °C, N₂, 24 hour

3. Scale up of PDL-GBL Copolymer Synthesis for Mechanical Testing

Entry	PDL (g)	GBL (g)	%PDL conv.	%GBL conv.	%PDL incorp.	%GBL incorp.
1	10	3.5800	81.3	18.3	83.9	16.1
2	8	2.8700	56.2	18.4	79.1	20.9
3	2	0.0286	>99%	37.8	97.0	3.0

Table 3: 500 mg of pentadecalactone, 1:4 PDL:GBL initial monomer ratio, 0.5 mol% bis(imino)pyridine Fe (I) neopentanol catalyst, 100 °C, N₂, 24 hour

Summary

We have reported the discovery of a simple, selective, and general catalyst for the ring closing depolymerization of polylactones and polycarbonates. Our current work is looking at the copolymerization of strained cyclic monomers with unstrained cyclic monomers to produce polymers that have tunable mechanical and recyclable properties. The strained monomer will

provide for an enthalpy driven polymerization while the unstrained monomer will provide for an entropy driven depolymerization of the copolymer. This will allow for tuning the mechanical properties of the polymer based on the strained monomer and lower the energy requirement for depolymerization based on the content of the unstrained monomer.

c. What opportunities for training and professional development has the project provided?

One graduate student, Connor Gallin, and one undergraduate student Won-Woo Lee has worked on this project.

d. How have the results been disseminated to communities of interest?

Connor F. Gallin, Won-Woo Lee, Jeffery A. Byers “A Simple, Selective, and General Catalyst for Ring Closing Depolymerization of Polyesters and Polycarbonates for Chemical Recycling” *Angew. Chem.Int. Ed.* **2023**, 62, e202303762

Connor Gallin, Won-Woo Lee, and Jeffery Byers, “Tuning mechanical and recyclable properties of polyethylene-like polymers through copolymerization” Gordon Research Conference Polymers 2023, South Hadley, Mass., June 2023, Poster Presentation