

Improving Reaction Conditions for the Production of a Degradable Polyester

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Introduction:

Plastics have been integrated into nearly every aspect of our lives due to their versatility as a material. The major issue with this reliance is the amount of waste that is produced and the pollution that occurs resulting from its manufacturing and disposal.¹ Nearly 400 million tons of plastic waste is generated every year.² By the year 2030, it is estimated that some 53 million tons of plastic waste will exist within our oceans, rivers, and lakes alone.³

A possible solution to this issue is the implementation of degradable, environmentally-friendly plastics that come from biomass (Figure 1a). The naturally occurring small molecule *o*-hydroxycinnamic acid has shown promising results as a starting material for the production of a polymer (i.e., poly(*o*-hydroxycinnamic acid)) that is able to degrade in the presence of UV light (Figure 1b).⁴

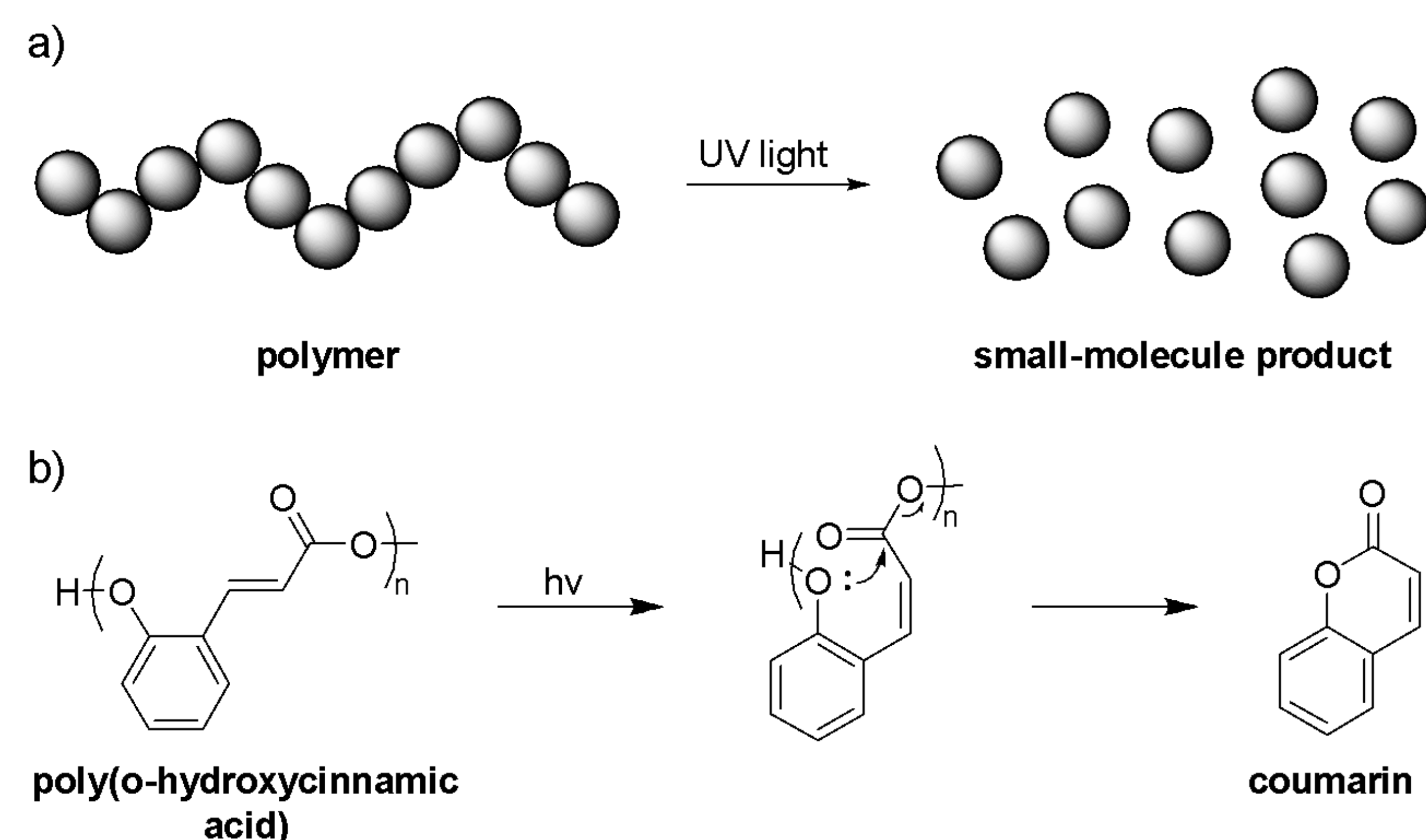


Figure 1: (a) General depiction of a depolymerization process in the presence of UV light. (b) Depiction of the photodegradation of poly(*o*-hydroxycinnamic acid).

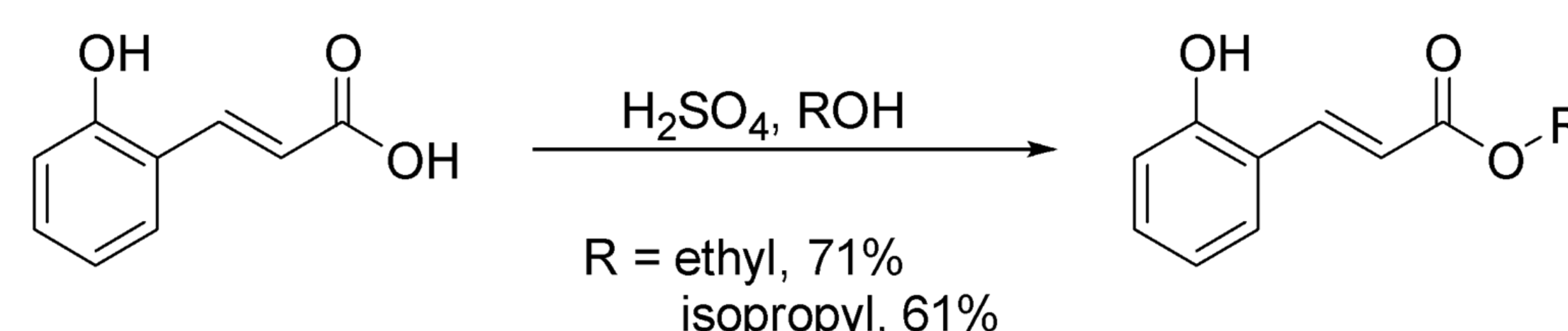
Our goal:

Previously, poly(*o*-hydroxycinnamic acid) was synthesized using thionyl chloride to form an acid chloride followed by condensation polymerization under reduced pressure. However, thionyl chloride is toxic and harmful to the environment. Our goal is to develop a strategy to synthesize poly(*o*-hydroxycinnamic acid) using greener reaction conditions. More specifically, we aim to use a process known as melt-polymerization in which our monomer is heated above its melting point in the presence of a catalyst, allowing it to undergo polymerization in the absence of solvent or harmful reagents.

Experimental:

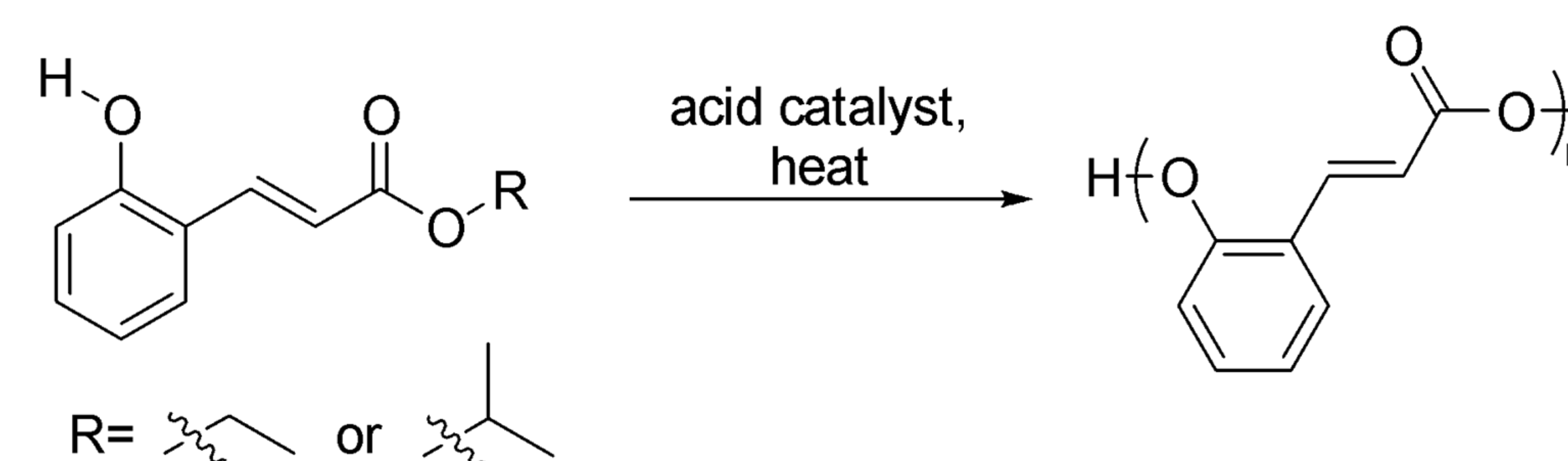
A limitation to polymerizing *o*-hydroxycinnamic acid via melt-polymerization is that it degrades at its melting point. As a result, it became critical to synthesize derivatives with lower melting points. However, these derivatives still needed to undergo condensation polymerization. To accomplish this, we synthesized ester derivatives of *o*-hydroxycinnamic acid. More specifically, we synthesized an ethyl ester derivative and an isopropyl derivative using acid-catalyzed esterification conditions (Scheme 1). These groups were targeted because they provided variation in melting point, boiling point, and reactivity. Both derivatives have a lower boiling point than the free acid precursor; however, the ethyl derivative is more reactive because it is less hindered, but the isopropyl group has a higher boiling point, allowing the temperature of the reaction to be increased further. Both of these attributes are important.

Scheme 1. Synthesis of *o*-Hydroxycinnamic Acid Derivatives.



Once we synthesized, purified, and characterized our monomers, we turned our attention to polymerization conditions. To accomplish this goal, we melted our monomers in the presence of an acid catalyst (Scheme 2). Ultimately, we tested two different acid catalysts in an effort to synthesize the desired polymer. One set of conditions utilized Bronsted-Lowry acid (BLA) catalysts, and the second set used Lewis acid (LA) catalysts. Under both sets of reaction conditions, the monomer was heated above the melting point in the presence of the catalyst overnight. While at this elevated temperature, reduced pressure was used to remove the corresponding alcohol byproduct being produced, allowing a transesterification polymerization reaction to occur.

Scheme 2. Synthesis of Poly(*o*-Hydroxycinnamic Acid) from *o*-Hydroxycinnamic Acid derivatives via Melt Polymerization.



Results:

Entry	R Group	Conditions	Outcome
1	ethyl	TsOH, heated to 110°C	oligomers
2	ethyl	TsOH, heated to 140°C	short polymers
3	isopropyl	TsOH, heated to 110°C	no reaction
4	isopropyl	DBSA, heated to 140°C	oligomers
5	ethyl	DBSA, heated to 100°C for 3 hours & then 130°C	short polymers
6	ethyl	Dowex, heated to 140°C	oligomers
7	ethyl	Fe(acac) ₃ , heated to 100°C	oligomers
8	ethyl	AlCl ₃ , heated to 140°C	no reaction
9	ethyl	Al(acac) ₃ , heat to 100 °C	oligomers
10	isopropyl	Zinc acetate, 100°C	no reaction
11	isopropyl	Sn(Oct) ₂ , heat to 100 °C	no reaction

Within these experiments we primarily tested three factors, the impact of the ester group, the acid catalyst, and the temperature of the reaction. Initially we tested BLA catalysts. Under a variety of temperatures we saw modest results with the ethyl group and poor results with the isopropyl group. We believe this may be due to steric hindrance resulting from the bulkier group. Simultaneously we tested LA catalysts under similar conditions. However, ultimately, the Lewis acid catalysts were less effective than the BLA's.

Conclusion:

While progress was made in our goal to synthesize the desired polymer under greener conditions, we were not able to reach the efficiency seen using thionyl chloride. However, we will continue to explore alternative green reaction conditions for this polymerization.

References:

- 1) Huang, A., et. al., *Int. J. Environ. Res. Public Health*, **2022**, *19*, 4556
- 2) Chamas, A., et. al., *ACS Sustain. Chem & Engin.*, **2020**, 3493-3511
- 3) Borrelle, S., et. al., *Science*, **2020**, 1515-1518
- 4) Baker, M. S., et. al., *Mater. Today Commun.*, **2022**, *31*, 103280