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SUSTAINABLE APPROACHES TO RING-OPENING POLYMERIZATIONS AND POST-POLYMERIZATION MODIFICATION

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INTRODUCTION

Plastic as an Industrial Resource boomed into existence following the second World War. A period known as the Great Acceleration dawned, in which economic gain and resource consumption skyrocketed.¹ Plastic, an inexpensive, moldable, and lightweight material, changed the course of modern industry as a feedstock that could be applied to a wide variety of industrial markets. Although a good starting material for cheap production, synthetic plastics have been made historically from fossil fuel. Relying on a finite resource for infinite capabilities is expected to produce astronomical costs economically and environmentally.²

Green Polymers must be synthesized from non-hazardous, renewable materials, but also degrade swifter than their petroleum counterparts in order to support economic and environmental sustainability. Tulip, mint, citrus, and many other plant derivatives have provided unique and industry-scalable polymers with shorter post-consumer lifespans to petroleum plastics and no toxic secondary derivatives.³⁻⁵ Unfortunately, current processes typically require high energy inputs, complex synthesis methods, and expensive, nonabundant materials.

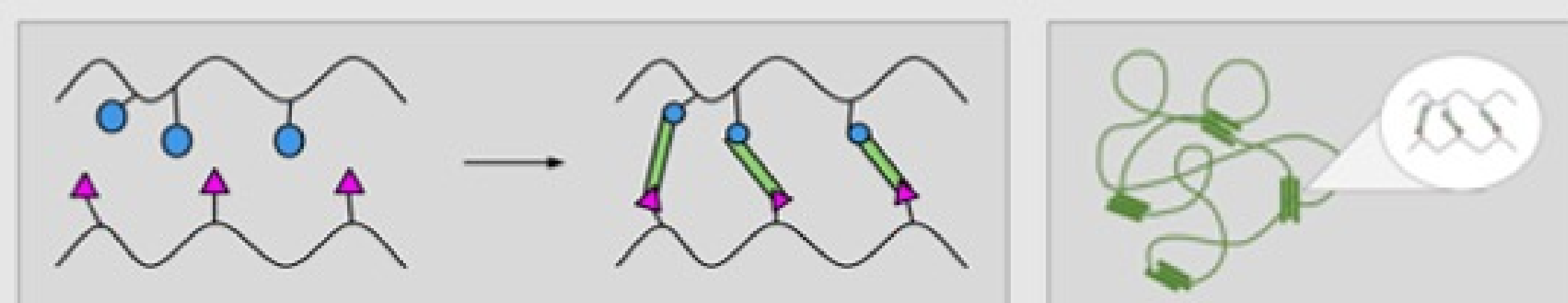
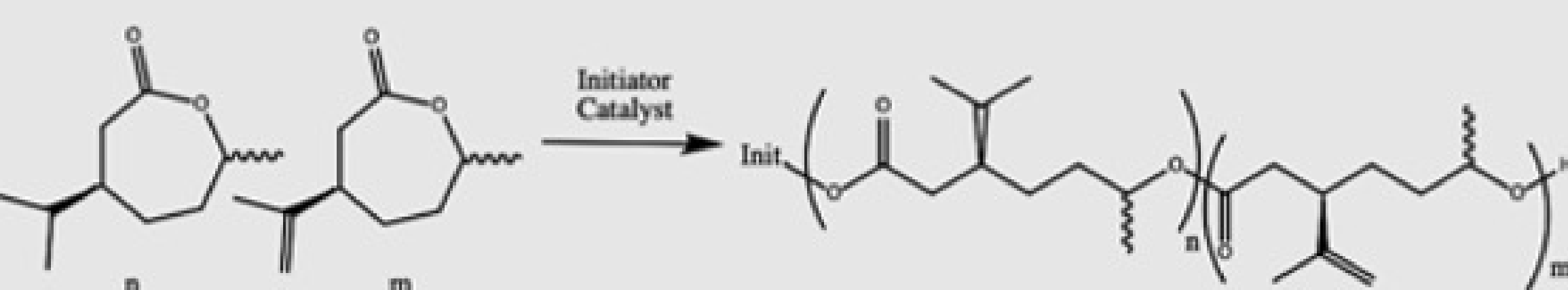


Figure 1: Chemical crosslinking

Figure 2: Cartoon of a polymer matrix with crystalline and amorphous regions (shown as bars and loops)

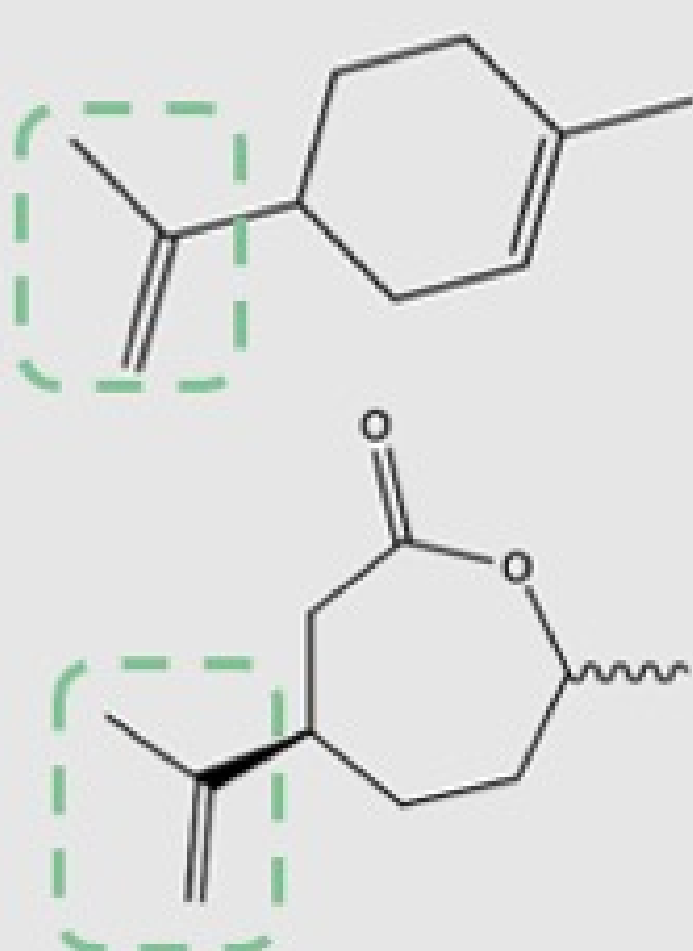
Simplifying Green Polymers is aided through a one-chain polymer matrix, creating one polymer and modifying it for chemical crosslinking (Figure 1). Chemical crosslinking leads to higher thermostability and tensile strength. The choice of crosslinks can establish separate crystalline and amorphous regions, enhancing both strength and flexibility (Figure 2). In this study, the principles of green chemistry were used in procedural modification, relying on more abundant chemicals, shorter stir periods, and less energy intensive methods.

OBJECTIVES AND APPLICATIONS



- I. Create a simple post-polymerization modification for tunable polymer matrixes through chemical crosslinking
- II. Design a method with the Principles of Green Chemistry, relying on renewable sources, simple processes, and minimal energy inputs
- III. Develop method to be applicable for a wide variety of monomers and modification agents

MODEL STUDIES WITH LIMONENE

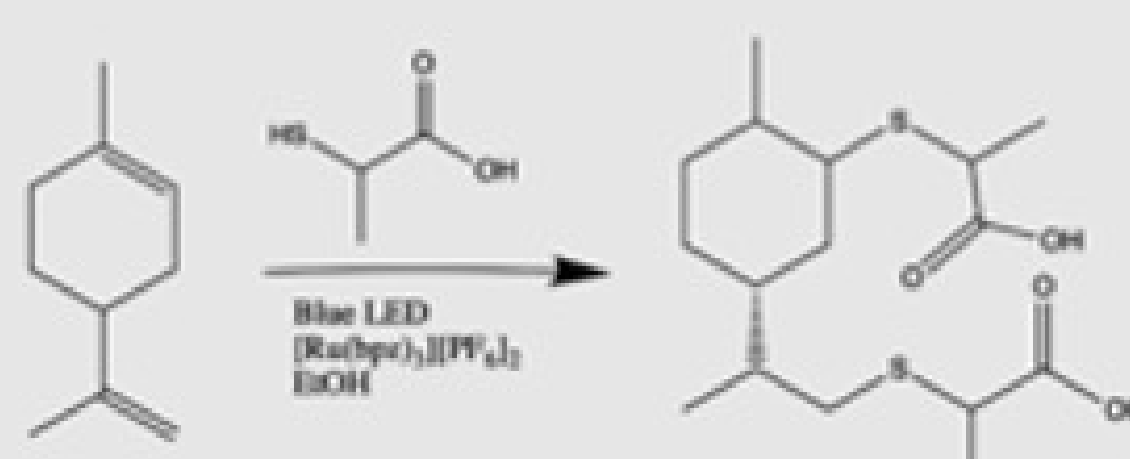


Limonene was used as the model for our copolymer modification. Limonene is a green compound deriving from citrus materials. This chemical could be harvested from citrus peels and similar biproducts.

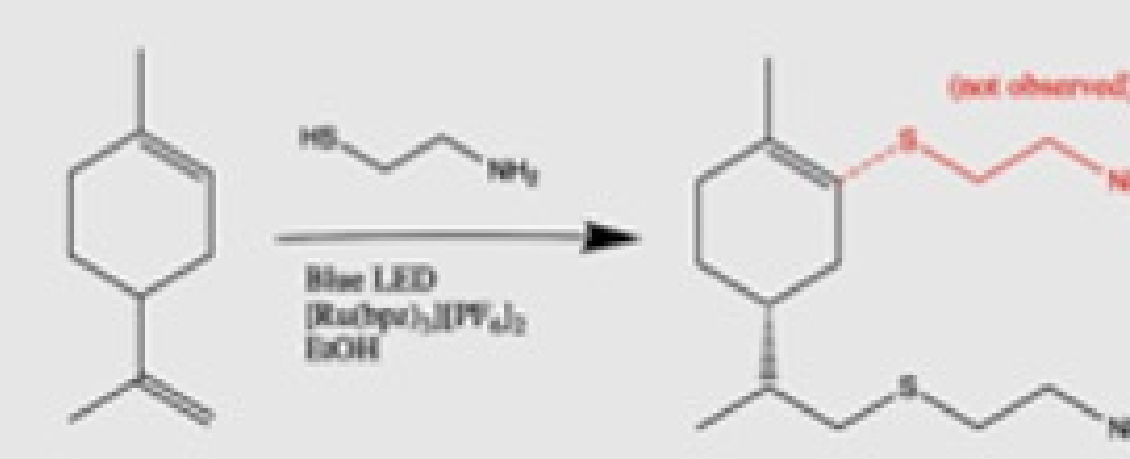
Our polymer monomers, dihydrocarvide and carvomenthene, can be synthesized from limonene. For this reason, limonene provides a good model, containing similar functional groups and overall structure as the monomers

METHODS FOR POST-POLYMERIZATION MODIFICATION

(1) Thiolactic Acid



(2) Cysteamine Hydrochloride



- I. 3 equivalents of functionalized thiol to limonene
- II. Blue LED light and Ruthenium catalyst for thiol-ene click reaction
 - i. Protocol from Firdaus et al.⁵ adapted catalyst methods from Tyson et al.⁷
- III. Minimal solvent volume (EtOH)
- IV. Stir time 12 hrs

CHARACTERIZATION

Preliminary H-NMR data was used to determine the efficacy of the thiol additions. With the effective modification, the double bonds on limonene will be eliminated.

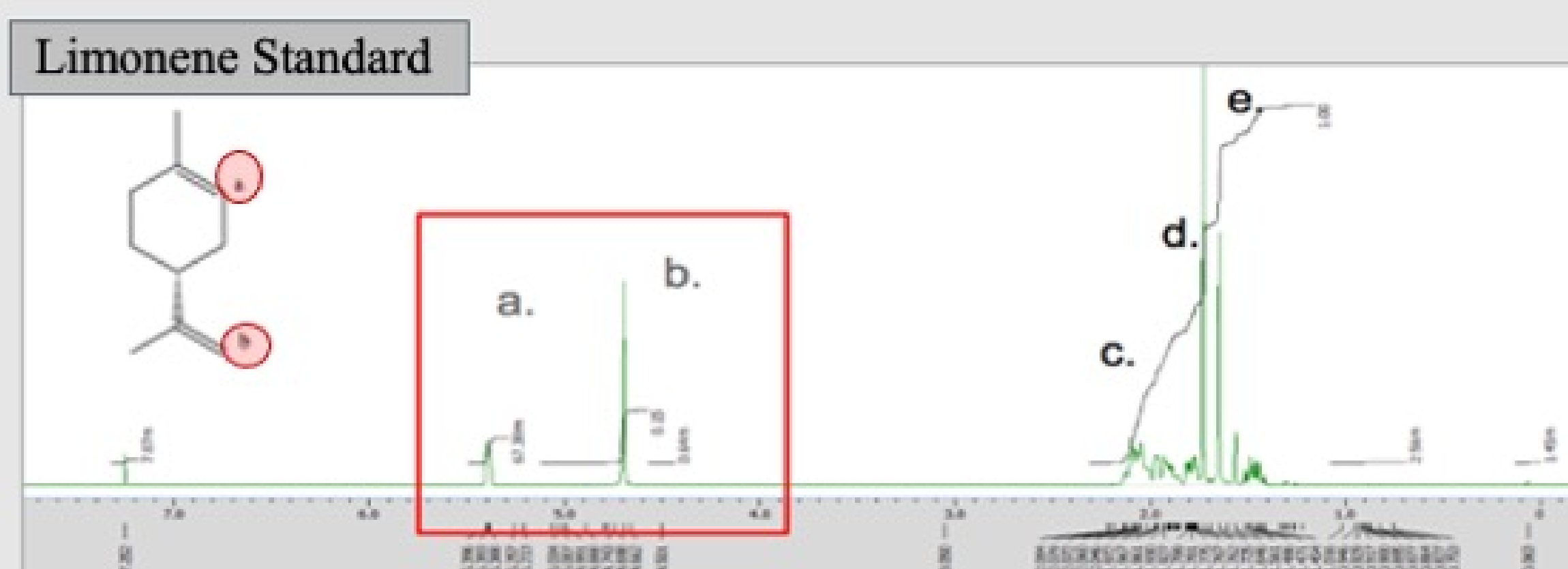


Figure 3: Peaks a (5.38 ppm) and b (4.69 ppm), represent the signal from double bonds present within the limonene

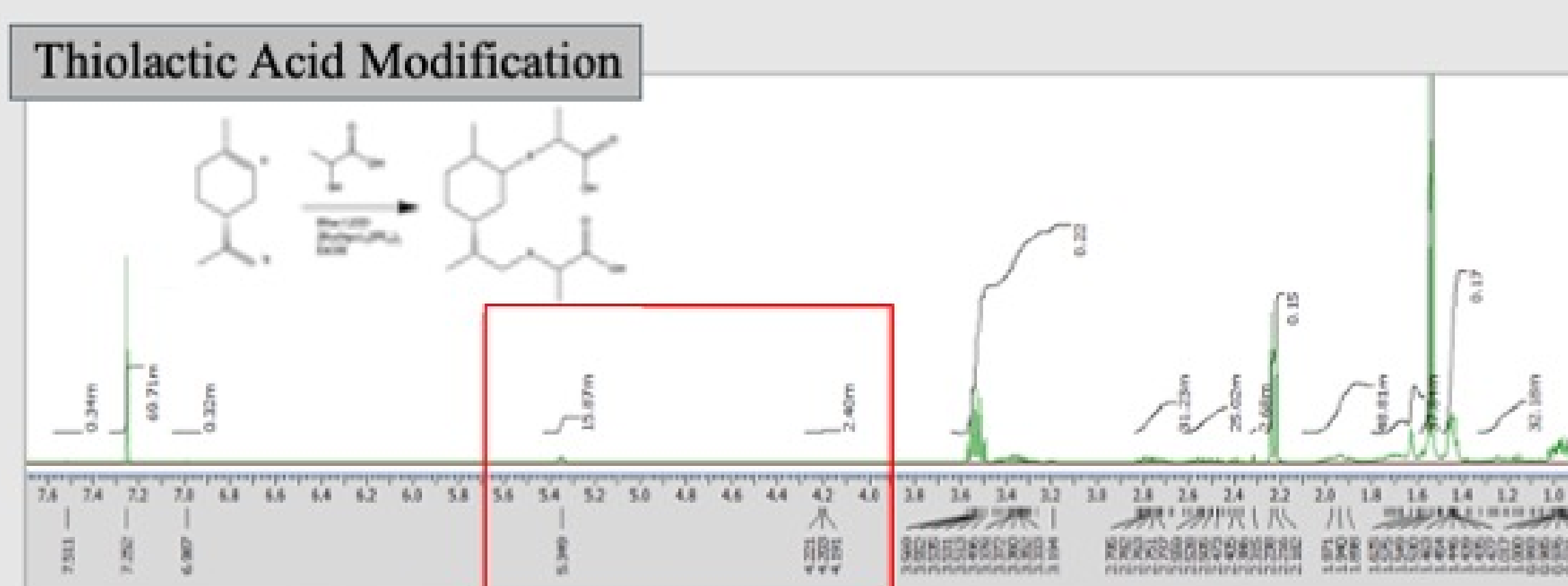


Figure 4: Peaks a and b now represent unreacted limonene double bonds, the decrease in integration indicates the effective replacement of double bonds with thiols

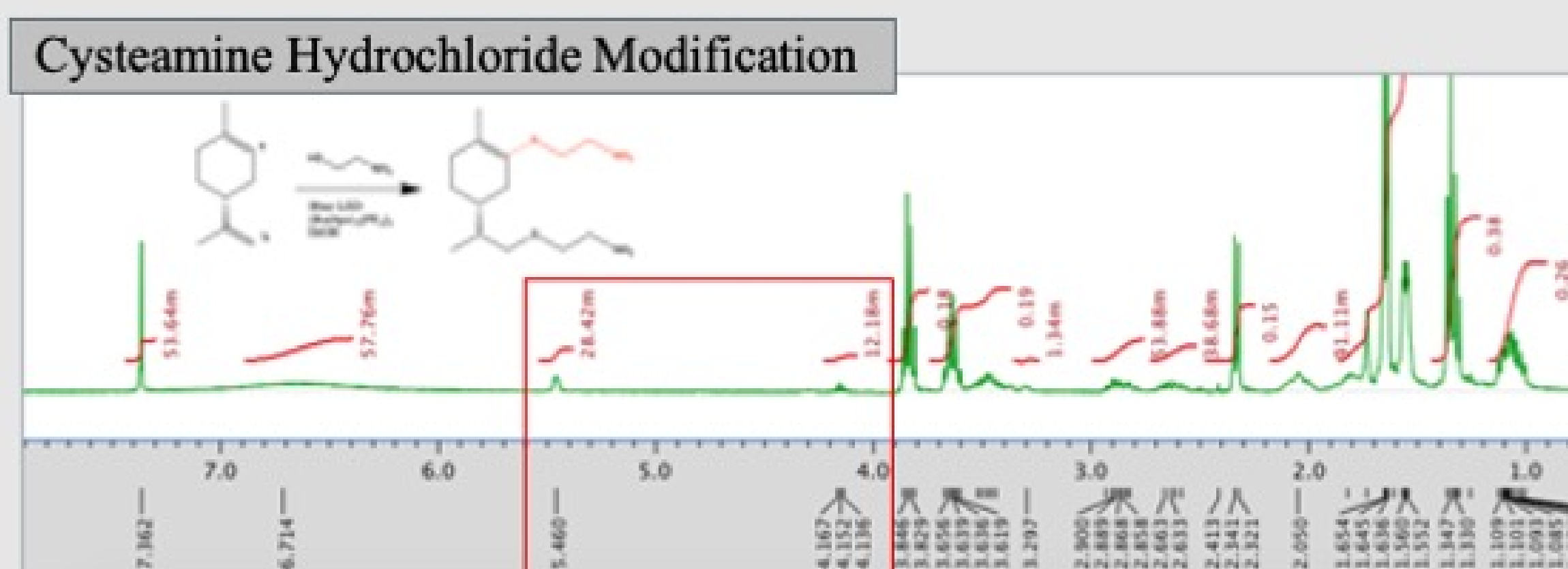


Figure 5: Peaks a and b still representing unreacted limonene in the presence of cysteamine hydrochloride

Table 1: NMR Results of Limonene Modification

Sample	Integration n, 5.39 ppm (a)	Similarity Integration	Integration , 4.70 ppm (b)	Similarity Integration
Unreacted Limonene	0.067	n/a	0.15	n/a
Thiolactate Trial	0.015	22.4%	0.0024	1.6%
Cysteamine Trial	.028	41.8%	0.012	8.0%

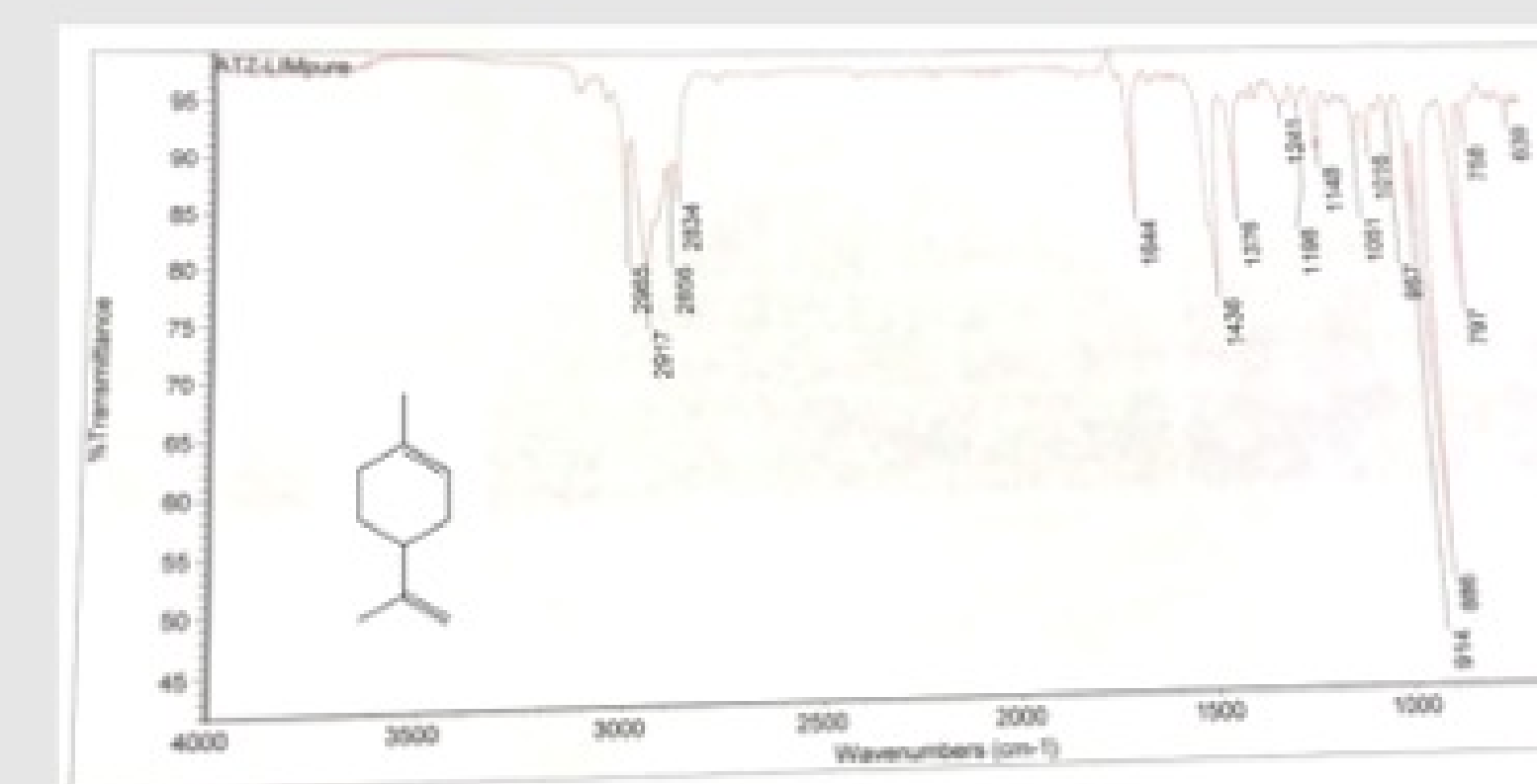


Table 2: IR data for Limonene Standard

Chemical Shift (cm ⁻¹)	Structure
3100	C-H (sp ²)
1436	C-H (sp ²)
888	C=C - H

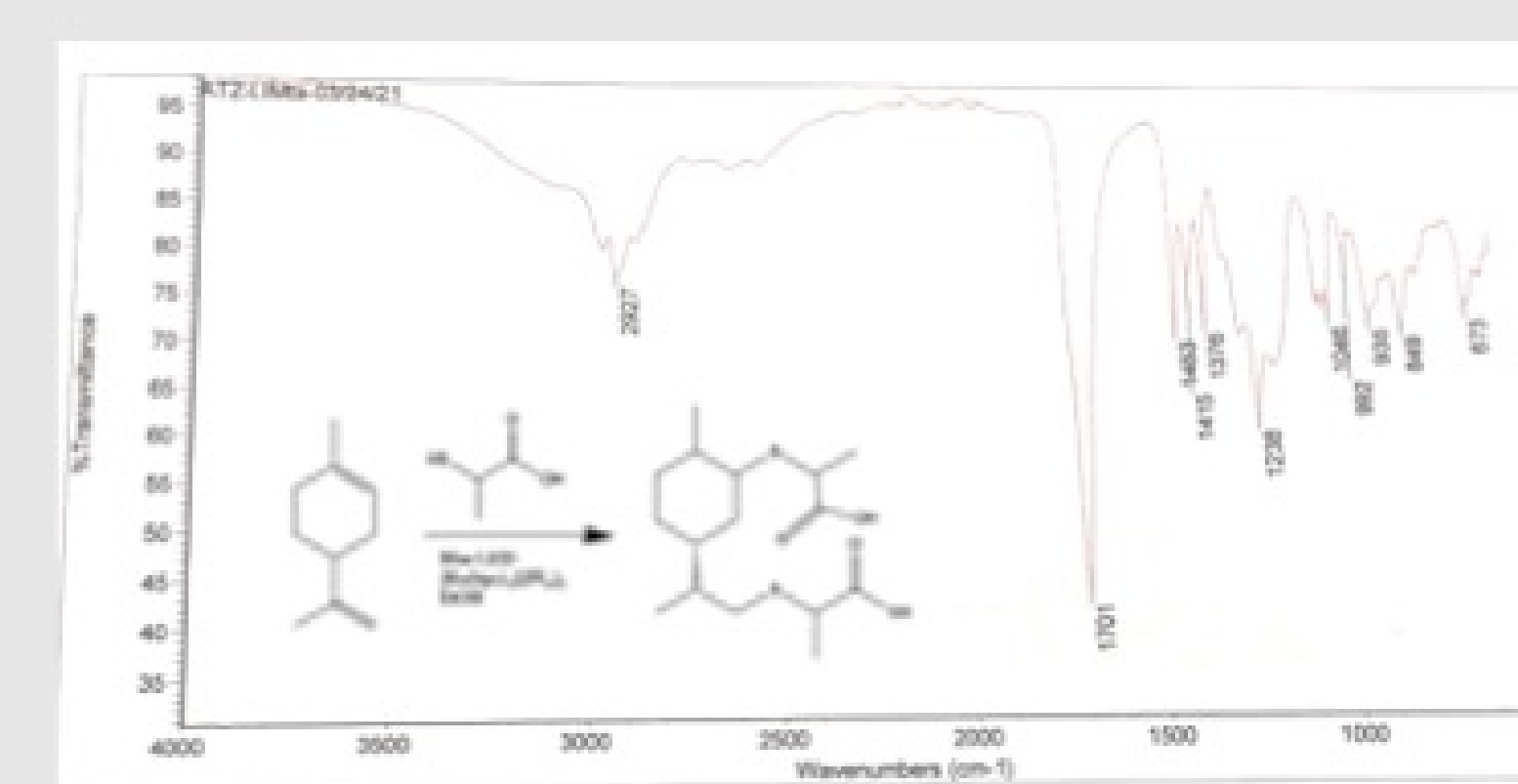


Table 3: IR data for Thiolactate-Modified Limonene

Chemical Shift (cm ⁻¹)	Structure
3400 - 2400	-COOH
1701	C=O
1463	C-H (sp ²)
1238	C-O

Preliminary IR data was used to determine the efficacy of the thiol additions. With the effective modification, a carboxylic acid (3400-2400, 1701 cm⁻¹) is present, and the C=C -H bonds (888 cm⁻¹) are minimized, confirming thiolactic acid is incorporated into the structure.

CONCLUSION

This model study provides a simple, green, synthetic route for modifying polymer chains for chemical crosslinking. Although the cysteamine modification presented some difficulty, the conditions used provided a 73% yield for the thiolactic acid modification using only 3 equivalents of reagent. ¹H-NMR analysis showed almost complete conversion of the double bond positions. Further this reaction took place within a 12 hour stir period under ambient temperature, with minimal solvent use, and under a Blue LED light source. This process aligns with the principles of green chemistry: minimizing hazardous materials, solvents, and energy usage.

FUTURE WORK

- I. Apply conditions to modification of polymer side chains⁶
- II. Experiment with conditions to convert pendant carboxylic acids into acid chlorides.
- III. Crosslink copolymer chains with the functionalized thiol post-polymerization modification (Figure 6)
 - i. The carboxylic acids can be converted easily into strong nucleophiles or electrophiles to facilitate this process

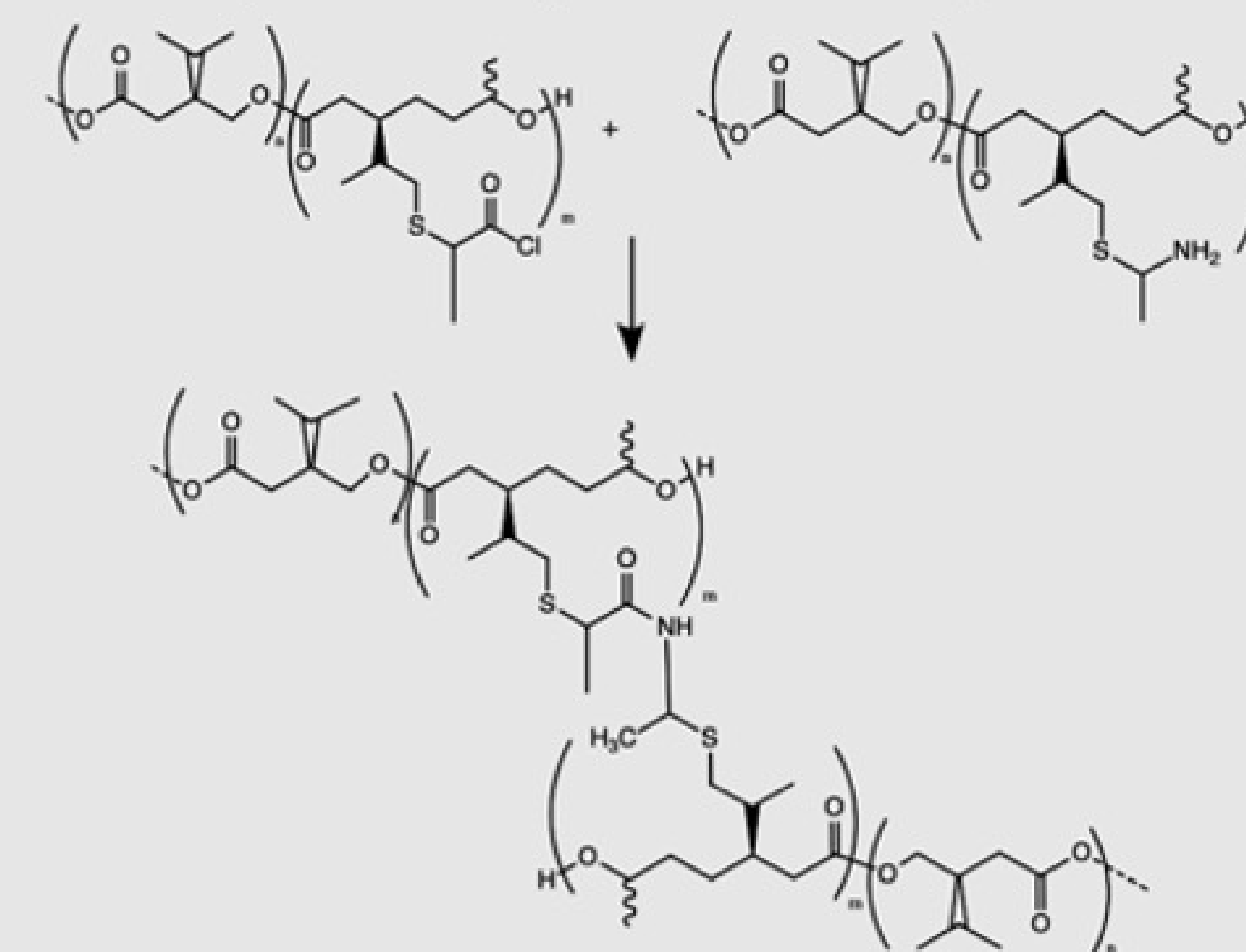


Figure 6: Potential crosslinking pathway following post-polymerization modification

ACKNOWLEDGEMENTS

I would like to acknowledge the support of the CSB/SJU Undergraduate Research Office for the grant supporting this research, and summer research stipend. Thank you to Alex Messner and Mikayla DuFresne for their previous work which supplied significant contributions in modifying the photocatalytic reaction.

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