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Ring-opening polymerization of lactones and lactides: An organic chemistry lab synthesis

Erin Wissler
College of Saint Benedict/Saint John's University

Ring-Opening Polymerization of Lactones and Lactides: An Organic Chemistry Lab Synthesis

Erin Wissler, Chris Schaller, PhD., Alicia Peterson, PhD., Nicholas Jones, PhD., Kate Graham, PhD., Bob Kirkley, M.S.

Chemistry and Biochemistry Department of the College of Saint Benedict and Saint John's University, St. Joseph, Minnesota 56374

This project analyzed the ring opening chemistry of D, L- lactide, γ – butyrolactone, valerolactone, dodecalactone and caprolactone. Starting with each of the above monomers, Sn(Oct)2,SnCl2, Zn(acac)2, ZnCL2, and AlCl3 were used as catalysts in the polymerization process. Initiators included benzyl alcohol, 2-phenylethanol and 1-butanol. The results of each reaction were analyzed by 1H-NMR and IR spectroscopy and dynamic light scattering (DLS). The results were collated to determine the most promising candidates for a student project in the teaching laboratory.

Introduction

Not only are polymers the backbone of a plethora of everyday products, but they also have a multitude of fascinating chemical properties that make them wonderful tools for learning important fundamentals of organic chemistry. Most polymerization procedures use toxic and hazardous reagents that make them difficult to prepare in teaching laboratory environments.[1] However, this procedure exemplifies green chemistry and produces polyesters which are biodegradable and originate with renewable monomers.

Green chemistry ensues that the use of reagents and products of an experiment utilize sustainable methods and reduce the production of hazardous substances. Polyesters are known for their non-toxic degradation products[2] and therefore are utilized heavily for green chemistry. Polylactide is an exemplary green polyester due to several key properties. Polylactide is easily obtainable from inexpensive raw materials[3] and the monomer, lactide, can be produced from lactic acid, a natural product of all animals and microorganisms. Because of its properties, polylactide has a wide range of applications that include both ecological and medical uses.[4] Polycaprolactone is also considered a biodegradable polymer and is used in various medical applications, most notably, delivery of steroids and vaccines.[5]

Because of the ring structure of the monomers, ring-opening polymerizations are extremely reactive. The ring strain of the initial monomer allows for a more amiable environment for the initiator to induce a nucleophilic attack. By using catalysts, this experiment is even more reactive. This procedure utilizes Lewis acids as catalysts in order to activate the carbonyl groups of the monomers. Several Lewis acids were tested all based on previous literature[6].

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[1] Schneiderman, D. K.; Gilmer, C.; Wentzel, M.T.; Martello, M.T.; Kubo, T.; Wissinger, J.E. *J. Chem. Educ.,* **2014**, *91* (1), 131–135.
[2] Kricheldorf, H.R. *Chemosphere*. **2001,** *43,* 49–54.
[3] Kricheldorf, H.R. *Chemosphere*. **2001,** *43,* 49–54.
[4] Ikada, Y.; Tsuji, H. *Macromol. Rapid Commun*. **2000,** *21*, 117–132.
[5] Coombes, A.G.A.; Rizzi, S.C.; Williamson, M.; Barralet, J.E.; Downes, S.; Wallace, W.A. *Biomaterials.* **2004,** *25,* 315–325.
[6] Hertler, W. R.; Sogah, D. Y.; Webster, O. W. *Macromolecules.* **1984,** *17,* 1415-1417.

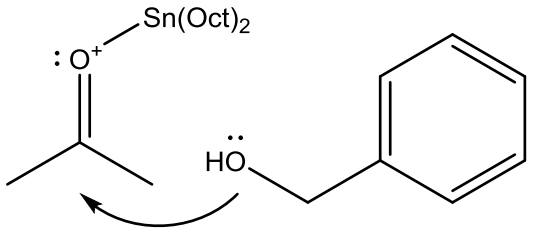


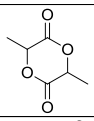
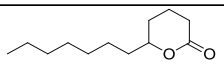
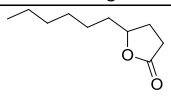
Fig. 1. Lewis acid catalyst coordinating to carbonyl group of monomer, allowing initiator to undergo nucleophilic attack.

In this laboratory experiment, students synthesize polyesters using a Lewis acid catalyzed ring-opening polymerization. This procedure was designed to allow students to utilize their knowledge of basic mechanisms and chemical properties to synthesize polyesters. The product of the experiment then could be further investigated to practice molecule characterization, molecular weight calculations, and general data analysis.

Results/Discussion

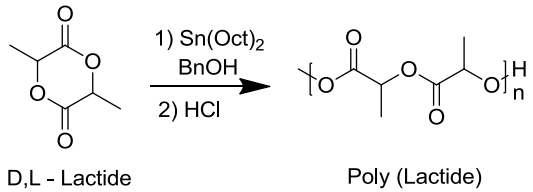
A group of six initial monomers were tested, along with five Lewis acid solutions. The monomers included D., L – lactide, Caprolactam, Γ- Butyrolactone, Δ- Dodecalactone, Δ- Valerolactone, ε- Caprolactone, and Γ- Decalactone. Lewis acid solutions tested were $Sn(Oct)_2$, $Zn(acac)_2$, $AlCl_3$, $SnCl_2$, and $ZnCl_2$.

Table 1. Chart of success of monomers and tested Lewis acid solutions. Success indicated by smiley faces and unsuccessful polymerizations indicated by "x"s.

	Structure	Sn(Oct)2	Zn(acac)2	AlCl3	SnCl2	ZnCl2
D,L-lactide		☺	☺	✖	✖	✖
Caprolactam		✖	✖	✖	✖	✖
Γ- Butyrolactone		☺	☺	☺	☺	☺
Δ- Dodecalactone		✖	✖	✖	✖	✖
Δ- Valerolactone		☺	☺	☺	☺	☺
E- Caprolactone		☺	☺	✖	✖	✖
Γ-Decalactone		✖	✖	✖	✖	✖

Polymerization of D, L – lactide

Scheme 1



^{1}H-NMR analysis of product showed additional peaks to starting material (ppm: q, 5.026; d, 1.640) from BnOH initiator (ppm: m, 7.333) and polymerized lactide (m, 5.133-5.205; m, 1.473-1.584). The shifts produced by the initiator give sign of attachment to starting monomer which allows for end group analysis. This will be further explained in analysis of Butyrolactone.

Both $Sn(Oct)_2$ and $Zn(acac)_2$ catalysts produced extremely successful polymerizations showing signs of success by polymer peaks on ^{1}H-NMR. Use of other catalysts illustrated possible signs of polymerization, but more likely produced oligomers of starting material. Similar results were observed when using ε-Caprolactone as initial monomer.

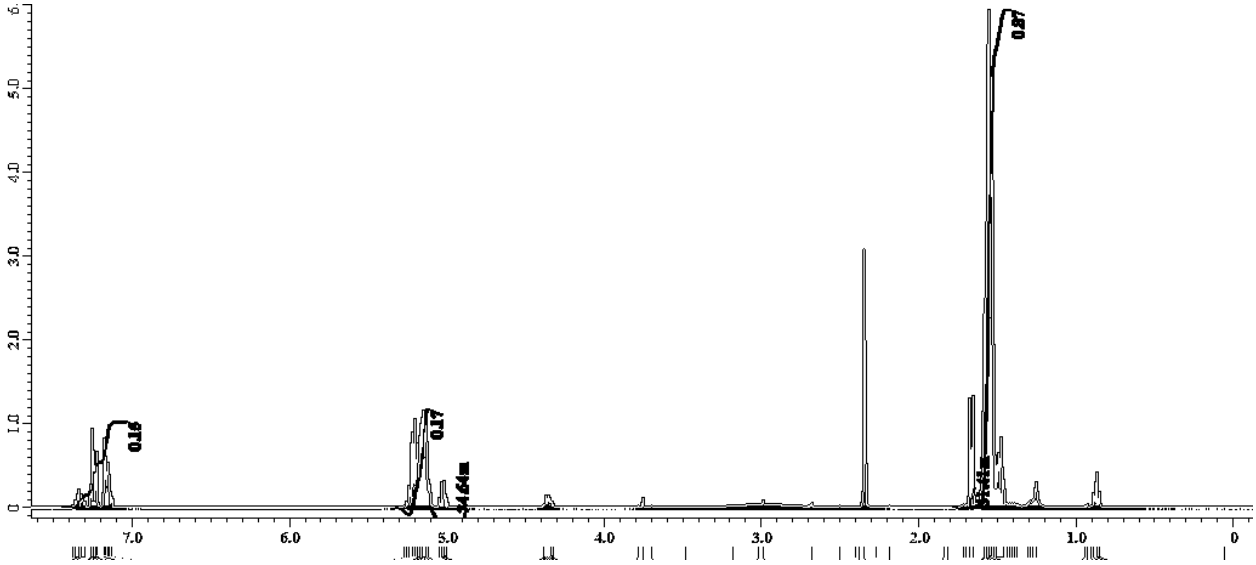


Fig. 2. ^{1}H-NMR of D,L-lactide product using $Sn(Oct)_2$.

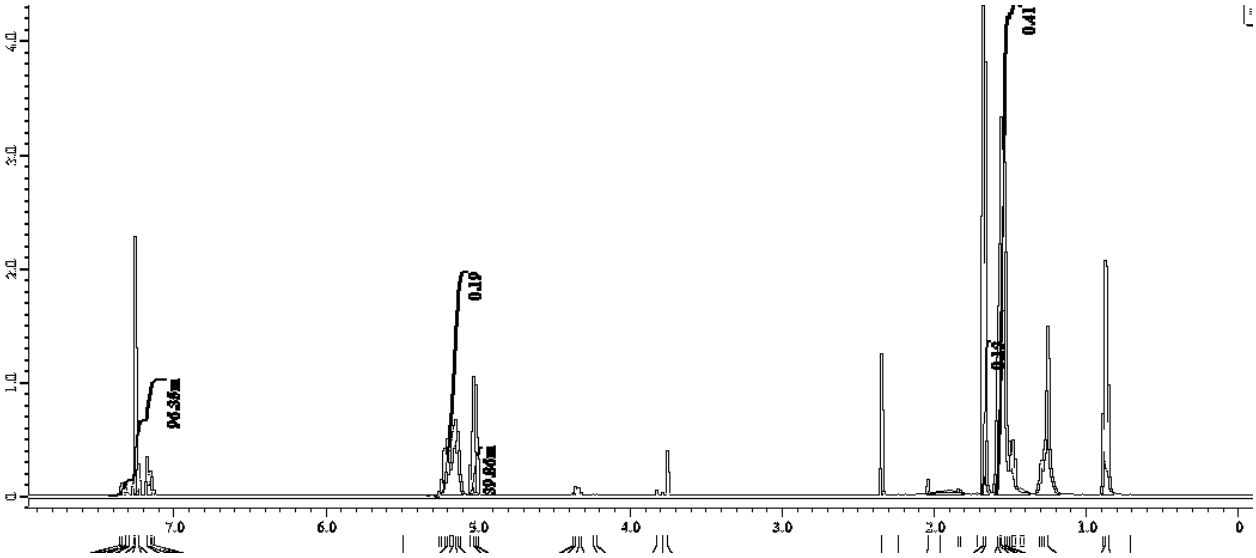
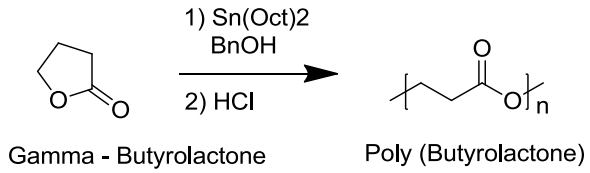


Fig. 3. ^{1}H-NMR of D,L-lactide product using $Zn(acac)_2$.

Polymerization of γ-Butyrolactone

Scheme 2



Gamma - Butyrolactone Poly (Butyrolactone)

Analysis showed additional peaks to starting material (ppm: t, 4.181; t, 2.313; q, 2.093) from BnOH initiator (m, 7.107-7.289; s, 4.623) and polymerized Butyrolactone (t, 4.288; t, 2.419; q, 2.213). The slight shift of the three peaks from the monomers suggests polymerization due to the pull of the BnOH initiator. By utilizing end group analysis, a calculation is done to determine rate of polymerization. By looking at the integration of the three monomer peaks in comparison to that of the BnOH peak, a ratio of monomer to initiator is defined. In this case integration of 0.45 of monomer divided by 0.015 of initiator tells us that there is about 30 times as much monomer as there is initiator.

Use of all tested Lewis acid catalysts ($Zn(acac)_2$, $ZnCl_2$, $AlCl_3$, $Sn(Oct)_2$, and $SnCl_2$) elicited signs of polymerization as characterized by H^1-NMR data analysis. Δ-Valerolactone was tested using this procedure and showed similar results.

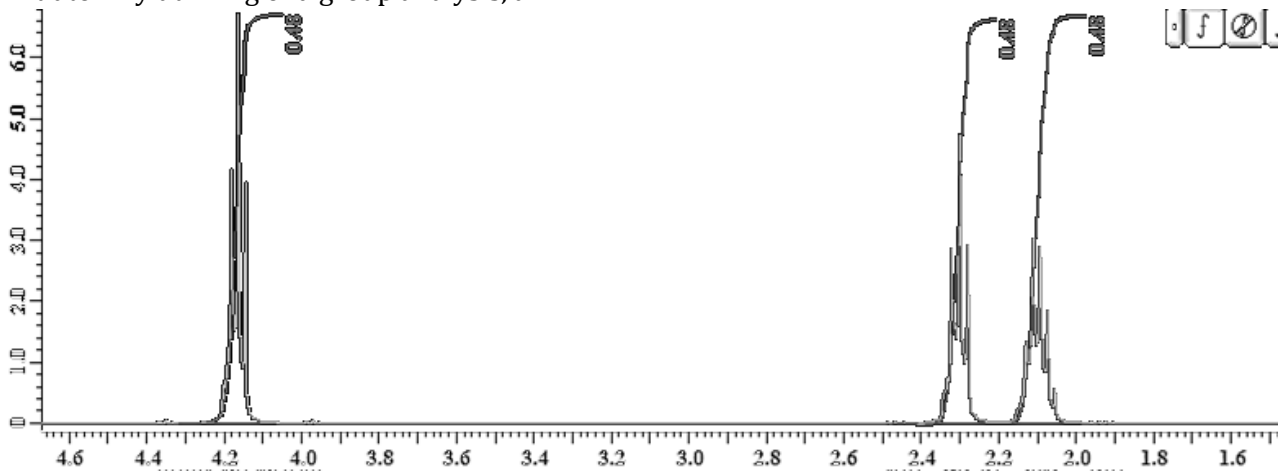


Fig. 4. ^{1}H-NMR of γ-Butyrolactone starting material.

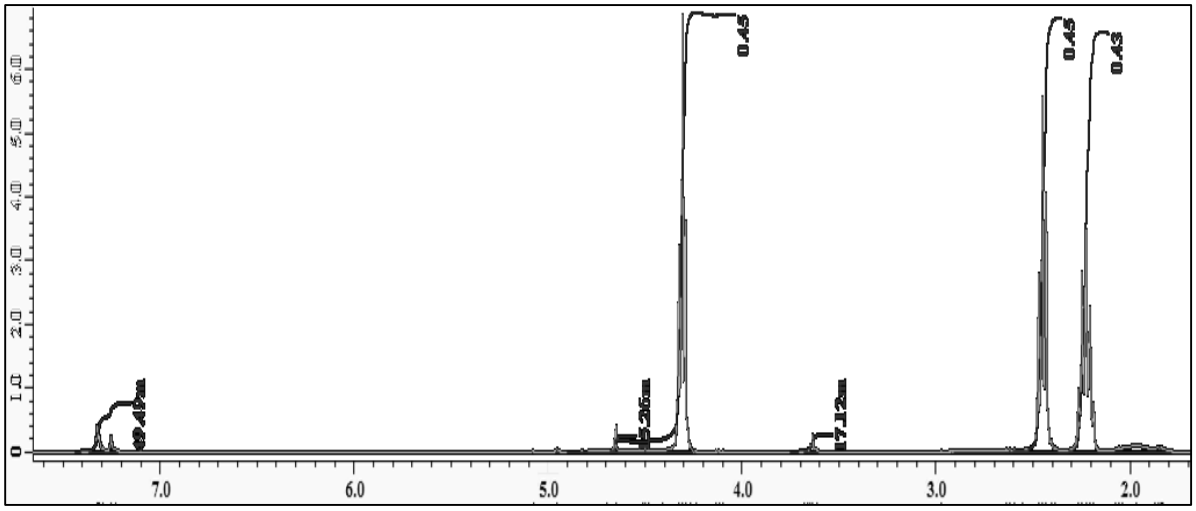
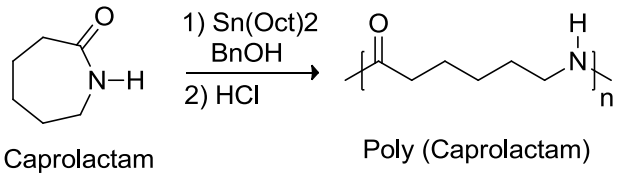


Fig. 5. ^{1}H-NMR of γ-Butyrolactone product using $ZnCl_2$.

Polymerization of Caprolactam

Scheme 5



Caprolactam Poly (Caprolactam)

Though shifts were observed on H^1-NMR that initially struck hope of polymerization, no polymerization was observed using any of the five tested Lewis acid solutions.

Use of Other Monomers

Caprolactam, Δ- Dodecalactone, and Γ-Decalactone showed no signs of polymerization after NMR analysis with any of the five Lewis acid solutions.

Conclusion

The most successful Lewis acid solutions were $Sn(Oct)_2$ and $Zn(acac)_2$ for this ring-opening procedure. The best results were incurred with D, L -lactide, γ-Butyrolactone, Δ-Valerolactone, ε-Caprolactone as initial monomers. Though Caprolactam, Δ-Dodecalactone, and Γ-Decalactone were tested using this procedure, successful polymerization was not observed with these monomers. This procedure was devised to be completed within a 4 hour lab and with organization and correct preparation, can be done in about 3 hours. Future work includes analyzing products with DLS instruments to examine the size of particles in solution to calculate molecular weight and rate of polymerization.

Experimental

Sn(Oct)2 (4mL x 0.035 M), toluene (1.5mL) and BnOH (1mL x 0.070 M) were loaded into an oven-dried 25mL round bottom flask containing lactide (500mg). Solution was refluxed (110° C) for two hours and allowed to cool to room temperature. After HCl (0.20mL x 1 M) was added to flask, solution was transferred by glass pipette to beaker containing heptane (100mL) and cooled in an ice bath for 20 minutes. Heptane was decanted off to obtain precipitate. When necessary, precipitate was further dried via N2 gas and ROTA-vap.

Acknowledgements

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