Molecular Recycling: Application of the Twelve Principles of Green Chemistry in the Diversion of Post-consumer Poly(lactic acid) Waste

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ABSTRACT

An increase in worldwide environmental consciousness has led to a movement to pursue methods of synthesis and reclamation that are environmentally friendly, or "green." Biodegradable, single-use, polylactic acid (PLA) cups, containers and utensils produced by Natureworks LLC from corn derived lactic acid are produced while generating water as the only byproduct. These plastic consumables, already a product of benign design, can be hydrolyzed into lactic acid (LA) using an acidic or basic hydrolysis procedure. The initial design and commercial manufacture of these PLA consumables currently provides an opportunity to discuss the Twelve Principles of Green Engineering in many educational settings. As described herein, the reclamation of lactic acid from these consumables provides a unique opportunity to involve students in the application of the Twelve Principles of Green Chemistry in theory and in practice. The procedures described herein can be applied to several laboratory based courses: General Organic Biochemistry, Molecular Biology, Introduction to Organic Chemistry for Allied Health Majors and a two-semester Organic Chemistry Course. An extension of this pedagogy to open-inquiry based laboratories or research experiences for the production of ethyl lactate will also be described.

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INTRODUCTION

Five of the "big-six" polymers including high and low density polyethylene (#4 HDPE and #2 LDPE), polyvinyl chloride (#3 PVC), polystyrene (#6 PS) and polypropylene (#5 PP) are not recycled in a closed-loop process, primarily due to the difficulty in breaking the carbon-carbon bond formed via the addition polymerization process. They are reclaimed but downcycled via a single cycle into lower value products that are themselves, not recyclable. For example, in 2003, 25 liter plastic drums made of HDPE were recycled into circuit boards used in metal finishing industries.[1] Furthermore, all of the big six polymers are derived solely from a petroleum-based feedstock.

Considering the bond enthalpy differences between carbon-carbon and carbon-hetero atom bonds, it is not difficult to understand why Nature's polymers are preferentially linked together via the latter. Amino acids, monosaccharides, fatty acids and alcohols are bound together to form proteins, carbohydrates and lipids via carbon-nitrogen or carbon-oxygen bonds. The carbon-hetero atom bonds are not only easily formed, but rapidly broken and reformed allowing consumed proteins, carbohydrates and lipids to serve as nutrient sources in the reformulation of needed building blocks for life.

The makings of a biodegradable polymer began in 1932 with Wallace Carothers at DuPont. Nature's polymer paradigm was at the forefront of Wallace Carothers' design when he first prepared nylon-6,6, a polyamide with carbon nitrogen bonds linking each monomer.[2] Evolution of nylon-6, prepared from the

seven membered cyclic amide, caprolactam, has resulted in a polymer that can also be reclaimed and transformed in a closed-loop recycling process to reform virgin nylon-6.

In 2003, Shaw Industries, Inc, was awarded the Presidential Green Chemistry Challenge, Designing Green Chemicals Award for the development of EcoWorx™, Carpet Tile: A Cradle–to-Cradle Product.[3] By replacing the bitumen, polyvinyl chloride or polyurethane carpet backing with a polyolefin resin, which is not only more environmentally friendly but also compatible with the nylon-6 depolymerization methods, Shaw Industries was able to develop a nylon-6 carpet tile that can be readily and cost-effectively collected and returned to the Ecoworx and nylon manufacturing processes. The cost of collection, transportation, elutriation and return to the manufacturing process proved to be less than using virgin raw materials. Rather than sell carpeting, Shaw's provides a "floor-covering" service, replacing worn with new carpet tiles, while recapturing the warn materials in a closed-loop process, not unlike how the proteins we eat are converted into proteins our body requires.

In addition to his work with Nylon 6,6, Carothers discovered polylactic acid (PLA) by heating lactic acid (LA) under a vacuum. More recently, NatureWorks LLC received the Presidential Green Chemistry Challenge Award for their development of a process to manufacture a more rigid form of PLA with a higher molecular weight.[4] PLA is an exceptional case study that incorporates the twelve principles of green engineering into various educational settings.[5] The twelve principles of green engineering[6] as enumerated by Anastas and Zimmerman can be found in Table I.[7] Current commercial applications of PLA include but are not limited to food packaging, synthetic fibers,[8] credit cards,[9] as a facial filler for HIV patients (Europe),[10] and for the microencapsulation of drugs.[11]

TABLE I. The Twelve Principles of Green Engineering.

Principle 1: Designers need to strive to ensure that all material and energy inputs and outputs are as inherently nonhazardous as possible.
Principle 2: It is better to prevent waste than to treat or clean up waste after it is formed.
Principle 3: Separation and purification operations should be designed to minimize energy consumption and materials use.
Principle 4: Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.
Principle 5: Products, processes, and systems should be "output pulled" rather than "input pushed" through the use of energy and materials.
Principle 6: Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.
Principle 7: Targeted durability, not immortality, should be a design goal.
Principle 8: Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw.
Principle 9: Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
Principle 10: Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.
Principle 11: Products, processes, and systems should be designed for performance in a commercial "afterlife".
Principle 12: Material and energy inputs should be renewable rather than depleting.

Molecular Recycling of PLA

Interestingly enough, PLA shares a similar molecular bonding structure to that of lipids or fats, which are routinely broken via acidic or basic hydrolysis (Fig. 1). Both processes have been successfully applied to post-consumer waste PLA, (Fig. 2) to depolymerize the PLA and reclaim the LA monomers, which can either be repolymerized or used as such.[12] The procedures for both the acidic and basic hydrolysis of post-consumer waste PLA were developed by students in an open-inquiry based laboratory. Consumer use of LA in the food industry is widespread,[a] for example as an antimicrobial spray for foods, however laboratory reclaimed LA by students is unsuitable for such a use. Convenient use of the LA students generate in the laboratory is as a green acidic cleaner, to remove soap scum and eliminate bacteria.

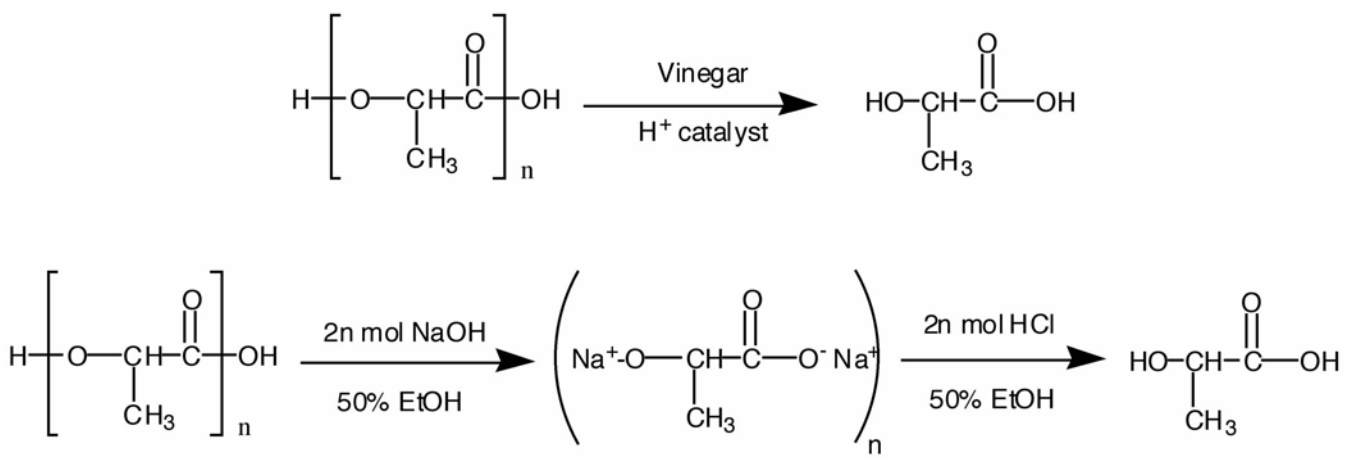

FIG. 1. Reaction equations for acid hydrolysis with vinegar (top) and base hydrolysis with NaOH (bottom).

FIG. 2. PLA cups are employed at many college cafeterias.

Base Hydrolysis

Add shredded PLA (5.0 g, 0.07 mol), NaOH (5.6 g, 0.14 mol) and a magnetic stir bar into a 250 mL Erlenmeyer flask. In order for the polymer to completely hydrolyze, a 2:1 molar ratio of the NaOH to the PLA is needed. Add enough 50% ethanol to cover the contents in the flask. Cover the mouth of the flask with a small watch glass and heat the reaction to a brisk boil with constant stirring for one hour to ensure complete hydrolysis of the PLA. Cool the reaction in an ice bath and acidify the resulting solution to a pH of 3.8 using concentrated HCl using pH meter. Filter the cold solution to remove any residual particulate matter. The filtrate is an aqueous solution of lactic acid and NaCl. Water, ethanol and NaCl can be removed by rotary evaporation followed by vacuum filtration.

Acid Hydrolysis

Add shredded PLA (5.0 g, 0.07 mol) into a round bottom flask equipped with a reflux condenser. Add a magnetic stir bar and enough commercial *white vinegar* to cover the PLA. Wrap the round bottom flask with aluminum foil to ensure uniform and thorough heating. With constant stirring, heat the reaction mixture to reflux using a heating mantle. Hydrolysis of the PLA is complete once a completely transparent yellow solution forms. The reaction is typically complete in 65 hours. Water can be removed by rotary evaporation to afford a concentrated solution of LA with traces of acetic acid.

Application of the Twelve Principles of Green Chemistry

PLA can be hydrolyzed by using either the base or the acid procedure. The base hydrolysis requires the use of caustic sodium hydroxide and concentrated hydrochloric acid to convert the sodium lactate to lactic acid. Both reagents have associated hazards which increase the risk involved with their use. Conversely, the acid procedure requires only a solution of household vinegar which is extremely benign. The major difference between the basic and acidic hydrolysis procedures is the time it takes to hydrolyze the PLA into LA, the former is complete in 1 hour, while the latter can require up 65 hours with efficient heating. While the manufacture of PLA provides the opportunity to discuss the Twelve Principles of Green Engineering, comparing these two PLA hydrolysis procedures provides students with an excellent opportunity to compare and contrast the importance of each of the Twelve Principles of Green Chemistry, Table II.[13] Seven out of the twelve principles are relevant for both of the reactions and allow students to compare the two reactions to determine which procedure is more "green."

TABLE II. The Twelve Principles of Green Chemistry.

Principle 1: Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
Principle 2: Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
Priniple 3: Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
Principle 4: Use renewable feedstocks: Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
Principle 5: Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
Principle 6: Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
Principle 7: Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
Principle 8: Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
Principle 9: Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.
Principle 10: Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
Principle 11: Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
Principle 12: Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Principle 1 – Prevention

The E-Factor is defined as the g of byproduct divided by the g of product.[14] The lower the E-factor, the more efficient the process. The E-Factor provides a chemist with a measure of how many grams of waste is produced for every gram of product. Technically, the vinegar in the acid procedure can be reused, so the E-factor is 0. The E-factor for the base hydrolysis is dramatically higher because two moles of NaCl are produced for every mole of lactic acid product. The ethanol solvent and water can be reclaimed in both procedures but could be arguably considered for the E-factor calculation of each reaction.

Principle 2 - Atom Economy

Atom economy is measure of the efficiency of a planned reaction. To calculate atom economy, the molecular weight of the products are divided by the molecular weight of all of the reagents or starting materials used to produce the product. The calculation of atom economy of both of the

hydrolysis procedures indicates that the acidic hydrolysis is a far more atom economical procedure, as the acid is a catalyst (Fig. 3).

$$\left(\frac{MW_{products}}{\sum MW_{reagents}}\right)*100=\left(\frac{MW_{lacticacid}}{\sum MW_{NaOH+HCl+PLA}}\right)=\left(\frac{90}{40+36.45+72}\right)=60.6\%$$

$$\left(\frac{MW_{products}}{\sum MW_{reagents}}\right)*100=\left(\frac{MW_{lacticacid}}{\sum MW_{water+PLA}}\right)=\left(\frac{90}{18+72}\right)=100\%$$

FIG. 3. Calculation of the atom economy of the basic (top) and acidic (bottom) PLA hydrolysis procedures.

Principle 3 - Less Hazardous Chemical Syntheses & Principle 4 - Designing Safer Chemicals
Considering the hazards of solid NaOH and concentrated HCl as listed on the Materials Safety Data Sheets, with those of vinegar, it is clear that the acid hydrolysis procedure is a "less hazardous chemical synthesis." The active ingredient in most lime scale removers is muriatic acid, which is another name for HCl. LA is by far a "greener" safer chemical that is already used commercially for the same purpose.

Principle 5 - Safer Solvents and Auxiliaries
Basic hydrolysis of PLA in an aqueous solution of NaOH is facilitated with ethanol as a solvent. While ethanol can be reclaimed at the end of the process the basic hydrolysis procedure could be considered less "green" according to this principle as compared to the acid hydrolysis procedure which simply uses vinegar.

Principle 6 - Design for Energy Efficiency
The acidic hydrolysis procedure, thus has been "greener." However, with respect to energy considerations, the acidic procedure is by no means energy efficient. Even though the basic hydrolysis of PLA requires 1 hour of heating at reflux temperatures, this is dramatically less than the 65 hours of reflux time required by the acidic hydrolysis procedure. Additionally, the basic hydrolysis procedure can be completed in 15 minutes in a conventional microwave oven (650 W), while the acidic hydrolysis has remained incomplete even after 6 hours of heating in a research grade microwave oven (in 15 minute intervals at 1200 W).

Principle 7 - Use of a Renewable Feedstock
In both cases, PLA is obtained from post-consumer waste PLA cups which are derived from corn, which is currently considered a renewable resource.

Principle 9 – Catalysis
The acidic hydrolysis procedure utilizes vinegar as an acid catalyst while the basic hydrolysis procedure requires two moles of NaOH and HCl to afford the LA.

Principle 10 - Design for Degradation
Considering the end product LA as an acidic cleaner versus muriatic acid, microbes present in the waste water treatment plants naturally biodegrade LA into CO_2 and H_2O, while muriatic acid has been proven to destroy the microbe colonies.

Curricular Inclusion

The preparation of LA from post-consumer waste PLA is feasible at the middle or high school or undergraduate level and is a visual demonstration of molecular recycling in the laboratory. Full procedures, with pre-lab exercises and notes to instructors for four different experiments are included in the Appendix. A 20 minute, hands-on, "cooking-show" demonstration for members of the community that are not science oriented is also included. A brief description of each is provided below.

Brief Description of the Experiments

Introduction to Organic Chemistry Lab

Students will first determine the correct amount of base required to hydrolyzed a waste PLA cup into LA, which requires the discussion of how many moles of "LA residue" are in the weight of PLA measured (see Appendix A). Students then perform the basic hydrolysis followed by acidification to isolate a salt water solution of lactic acid. Students then compare the cleaning ability of the LA they prepared (without workup) versus water to remove synthetic soap scum (dried solutions of calcium hydroxide and sodium stearate sprayed alternately on the tile before drying with a heat gun) from a bathroom tile. Students finally isolate the crude lactic acid from the mixture through rotary evaporation of the water and subsequent filtration to remove the sodium chloride. The experiment can be adopted as a replacement for or in tandem to the standard "Saponification of Fatty Esters" experiment to generate soap.

Organic Chemistry Lab

This lab (see Appendix B) was performed exactly as above with full characterization as described herein. The ^{13}C and ^{1}H NMR (90 MHz) as well as the FT-IR spectra obtained on the final isolated lactic acid indicate that the lactic acid is clean enough for full characterization, (Fig. 4). The corresponding spectra of PLA are also easily obtained for comparison purposes, (Fig. 5). One final measure of the complete hydrolysis of PLA to LA can be determined by comparing the matrix-assisted, laser-desorption ionization, time-of-flight mass spectrometry (MALDI-TOF MS) before and after hydrolysis, (Fig. 6). This experiment also has the potential to introduce microwave accelerated reactions. Rather than heat the basic hydrolysis reaction on a hotplate for one-hour, the reaction can be completed in 4 five minute intervals on high heat in a 650 W standard household microwave oven with a turntable. As these microwaves tend to overheat by performing only one reaction at a time, multiple reactions can easily be completed depending only on the size of the microwave. The reaction has also been completed for up to 13 students at a time in CEM's Microwave Accelerated Reaction System (MARS). The opportunity also exists to compare the specific rotation of the starting PLA (acetone solvent) with that of the LA, to determine if the base hydrolysis affects the chirality of the resulting LA.

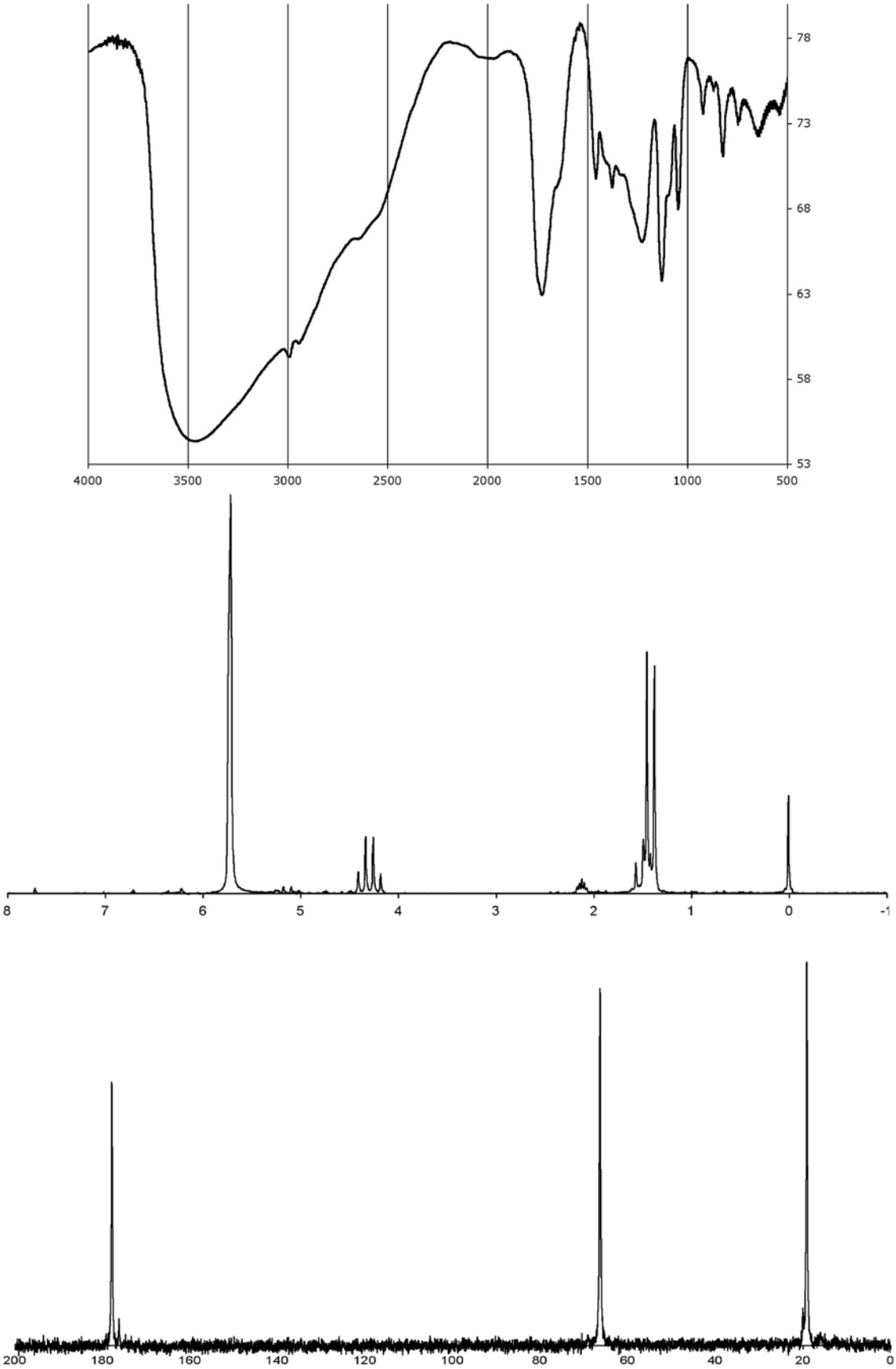

FIG. 4. Infra-red (neat-AgCl plates) (top), ^{1}H ($CDCl_3$ with TMS) (middle) and ^{13}C nuclear magnetic resonance (neat) (bottom) spectra of the crude LA isolated from the hydrolysis procedure.

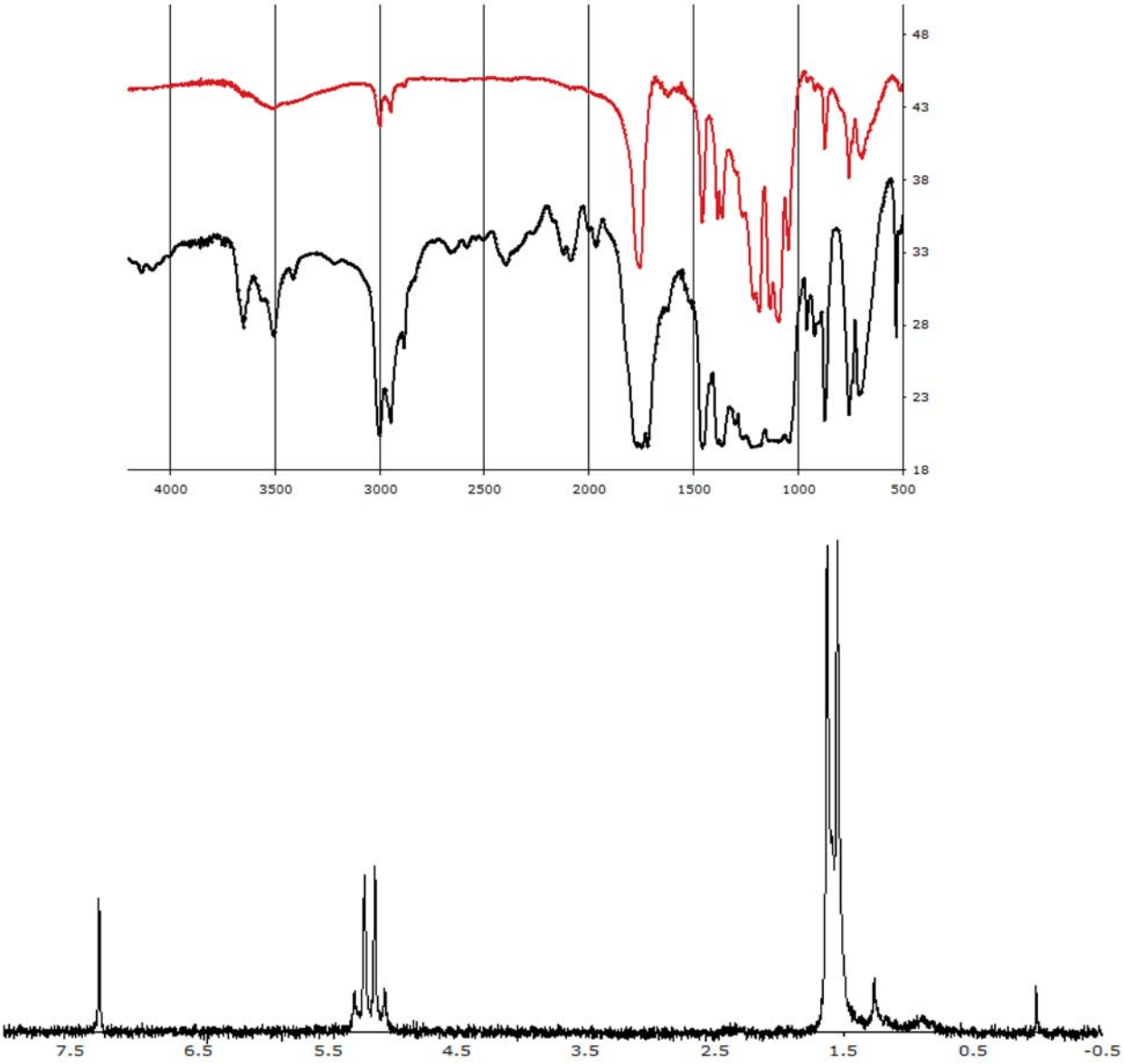

FIG. 5. Infra-red (thin polished film) (top-black), Infra-red ("partially-hydrolyzed" evaporated thin-film) (top-red) and ^{1}H ($CDCl_3$ with TMS) (bottom) spectra of post-consumer, waste PLA.

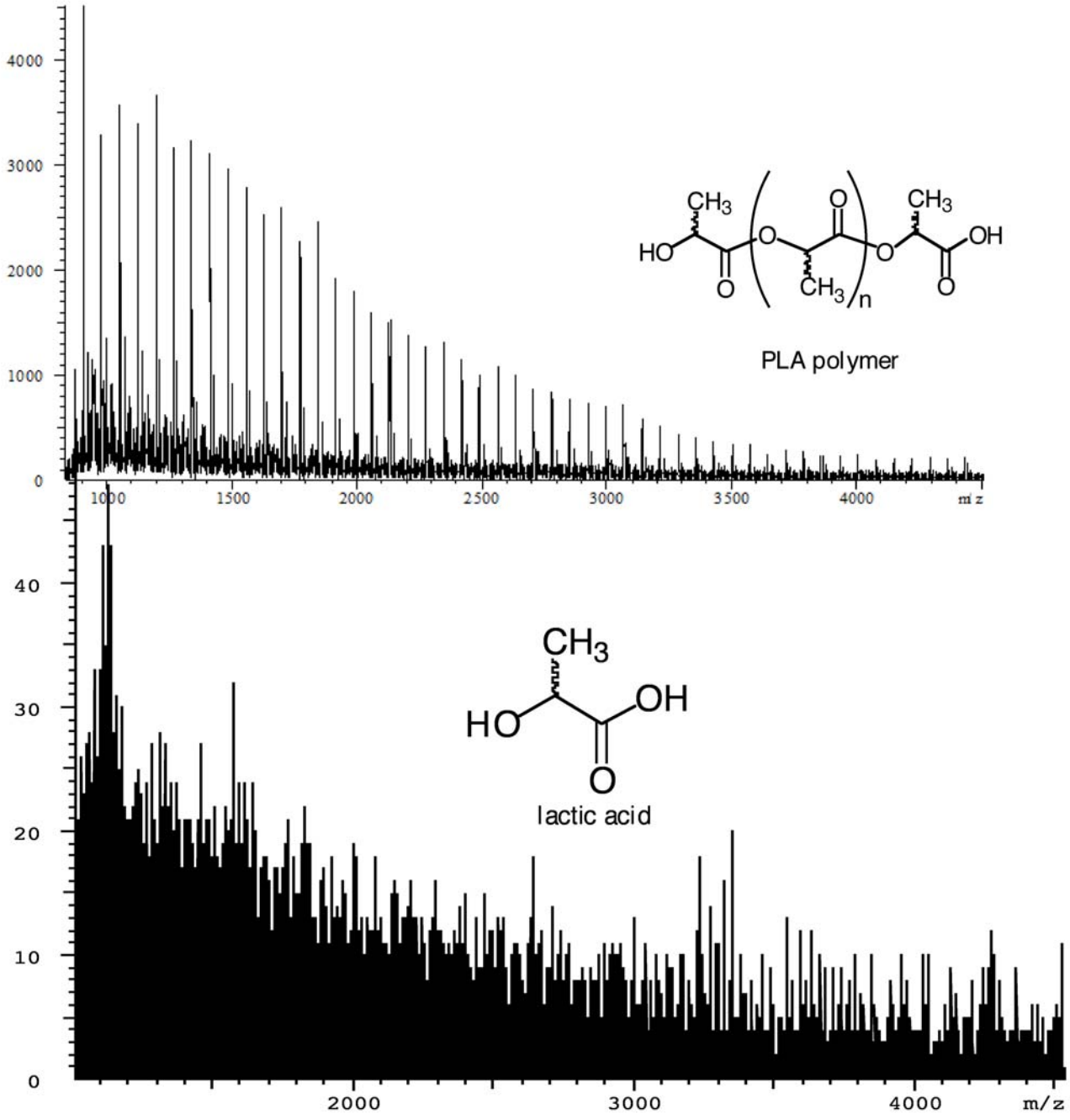

FIG. 6. Matrix-assisted, laser-desorption ionization, time-of-flight mass spectrometry (MALDI-TOF MS) before (top) (PLA) and after (bottom) (LA) hydrolysis. MALDI-TOF MS–Sample preparation: Solution **A**: 2 mg of PLA in 10µL of THF, Solution **B**: 20 mg of 2,5-dihydroxybenzoic acid in 100 µL of THF. Analyzed 1 µL of a mixture of a 1µL **A** with10 µL of **B**.

General, Organic and Biological (GOB) Chemistry

This laboratory activity (see Appendices C and D) is intended to help students determine the identity and quantity of the acid formed during hydrolysis by determining the pKA of the acid in solution. The first week, students perform the **Introduction to Organic Chemistry Lab** described above and the students then perform an acid-base titration. During the titration, students monitor pH as a solution containing base is gradually added to a small sample of the lactic acid. The way the pH changes with added base not only allows the determination of how much acid is present, but also will confirm its identity. The titration

provides data that can be examined and compared to the accepted behavior of lactic acid. Matching data support the assertion that the solution actually contains lactic acid.

Microbiology lab

It has been our experience that the majority of students enrolled in Introduction to Organic Chemistry are simultaneously enrolled in Microbiology. After completing the **Introduction to Organic Chemistry Lab** above students will compare the microbial properties of the synthesized LA to those of CLR and Lime-A-Way to determine which is the strongest antibacterial agent (see Appendix E). Students will discover that lactic acid is currently being phased in as the new commercial acidic cleaners because of its antibacterial properties.

DISCUSSION

Typical arguments about adopting new course materials focus upon the notion of an already full curriculum. The benefits of the experiments described herein are that they need not stand alone as they can be easily performed in tandem with existing experiments. The traditional concepts that can be discussed with this suite of experiments include ester hydrolysis, saponification, acid-base titrations, pKa, solubility of calcium salts, the difference between soap and acidic cleaners, household chemistry and various methods of spectrometry and spectroscopy. However, as compared to the traditional experiments this suite offers several opportunities to update the curriculum by fostering discussions of green engineering and green chemistry topics such as the use of safer solvents/reaction conditions, green polymers, use of a renewable feedstock, alternative energy sources (microwave heat), the E-factor, atom-economy, designing safer chemicals, energy efficiency, catalysis, design for degradation. Students will also learn first hand how to investigate the toxicity of chemicals by being introduced to methods for locating and interpreting the Materials Safety Data Sheets.

As a “cooking show” demonstration (see Appendix F), the saponification portion of the lab has been presented to a group of 50 in a non-laboratory environment (seminar room) during a 30 minute workshop. The lab has also been successfully performed by non-science alumnae, faculty, students and trustees and many members of the Admissions and Alumni Relations offices. Participants cut-up a PLA cup and mix it into an ethanol/water solution of sodium hydroxide. After heating the reaction in the microwave for 10 – 15 minutes, participants notice the digestion of all of the PLA. From another sample prepared and cooled earlier, participants then acidify the solution to convert the sodium lactate into lactic acid. Participants can use their “acidic cleaner” solution of lactic acid to remove synthetic soap scum from a bathroom tile. The effectiveness of LA as compared to that of LimeAway, CLR and water to dissolve synthetic soap scum can also be measured, time permitting.

The majority of the experiments described herein have been developed through open-inquiry based laboratory experiments in our research integrated laboratory curriculum. Two extensions that are currently being investigated that are worthy of further development also focus on the diversion of post-consumer PLA waste: the preparation of ethyl lactate and ethyl pyruvate. We are currently investigating the success of substituting ethyl lactate as a replacement for more toxic, flammable and hazardous solvents currently used in the undergraduate teaching laboratories. The more benign nature can be discussed by considering the current commercial applications of ethyl lactate which include perfumes (stabilizer), facial cleansers (alpha-hydroxy acid) and food additives/flavorings (slightly sweet with hints of coconut). More challenging yet potentially exciting prospect to energize students in an open-inquiry based laboratory would be to consider whether enantiomerically pure ethyl lactate could be prepared from enantiomerically-pure, commercial, post-consumer waste.

CONCULSION

The increase of worldwide environmental consciousness is driving the student demand for curricula that more fully describes the greener materials that are being created. These products of benign design are the direct result of the application of the principles of both green engineering and green chemistry. The initial design and commercial manufacture of PLA consumables currently provides an opportunity to discuss the Twelve Principles of Green Engineering in many educational settings. As described herein, the reclamation of lactic acid from these consumables provides a unique opportunity to involve students in the application of the Twelve Principles of Green Chemistry both in theory and in practice within several laboratory based courses: General Organic and Biochemistry, Molecular Biology, Introduction to Organic Chemistry for Allied Health Majors and a two-semester Organic Chemistry Course. As proposed, the pedagogical model presented here for the open-inquiry based laboratory can be readily extended to the preparation of ethyl lactate as an additional diversion for post-consumer PLA.

ACKNOWLEDGEMENTS

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APPENDIX A

Cups to Cleaners, Trash to Treasure: Converting a PLA cup to LA soap an Introductory Organic Chemistry Laboratory

In the Saponification lab, you prepared soap through the basic hydrolysis of fatty esters. In this accompanying experiment you can isolate lactic acid (an acidic cleaner) through the acid or basic hydrolysis of post-consumer waste polylactic acid cups (Fig. A1).

Applications of PLA in the food industry include food packaging products such as salad trays, grocery bags, and cold drinking cups. PLA is great for safely packaging food because it is resistant to heat and oil, resilient to mild heat, and biodegradable as waste.[†a] PLA has other, non-food related applications such as a new type of fiber called Ingeo™ Fibers. Instead of stemming from a petrochemical resource like traditional synthetic fibers, Ingeo™ Fibers are created from a source of natural feedstocks such as corn and have many applications ranging from apparel such as t-shirts, jeans, and jackets to home textiles like pillows, mattresses, and carpeting. Even the production of the fiber is environmentally preferred because the process uses 68% less fossil fuels than the process for creating conventional synthetic fibers.[†b] Along with NatureWorks, Perfect Plastic Printing is now manufacturing PLA credit cards, replacing cards commonly made with PVC (polyvinyl chloride).[†c]

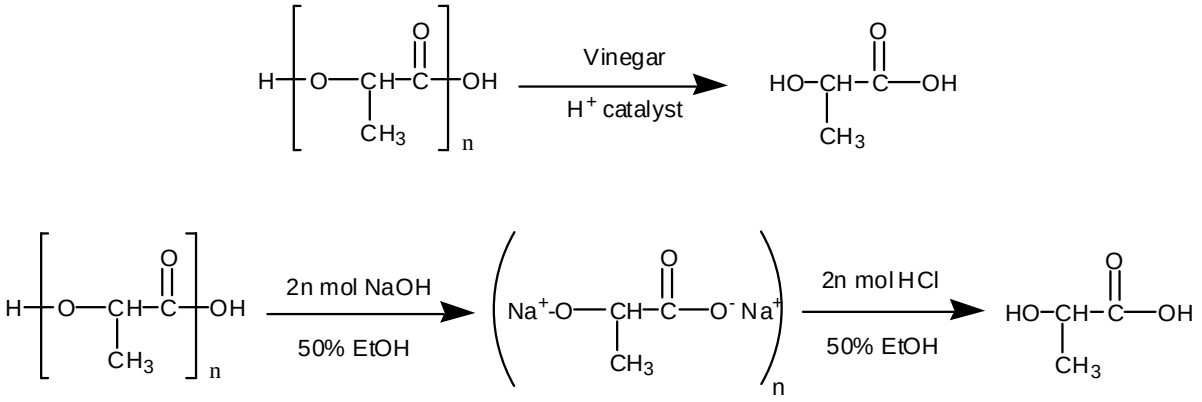

FIG. A1. Schematic representation of the acidic and basic hydrolysis of polylactic acid (PLA).

TABLE AI. Materials for introduction to organic chemistry lab.

Material	Item Quantity
PLA Cup	1
250 mL Erlenmeyer Flask	1
Sodium hydroxide pellets	6 g
50% HCl	15 - 20 mL
Magnetic stir bar	1
Stirring / hotplate	1
Spatula	1
Filter	1
Pipettes / bulb	1
Conc. solution of calcium hydroxide	250 mL per class
Conc. solution of sodium stearate	250 mL per class
Glass plate or bathroom time	1 per student

Estimated lab time: 2 hours

Prelab Preparation:
Basic hydrolysis of PLA

To determine how many moles of sodium hydroxide are required to fully hydrolyze 5.0 of PLA into sodium lactate you need to first determine the number of moles of the residual LA monomer are in the PLA you weighed.

How can you determine the number of moles of LA monomer residue in the PLA you weighed? Hint: What is the molecular weight of the LA monomer residue in PLA? What atoms in the PLA shown below (Fig. A2) are from a single molecule of LA?

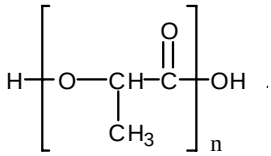

FIG. A2. PLA.

If you weighed 5.0 grams of PLA, how many moles of LA monomer residue do you have? Show your calculations.

Once you determine the number of moles of LA monomer residue in the PLA you have weighed, you now must determine the number of moles of sodium hydroxide that is required to fully hydrolyze the PLA.

If you want to hydrolyze 1 mole of PLA into 1 mole of sodium lactate as shown below (Fig. A3), how many moles of base are required?

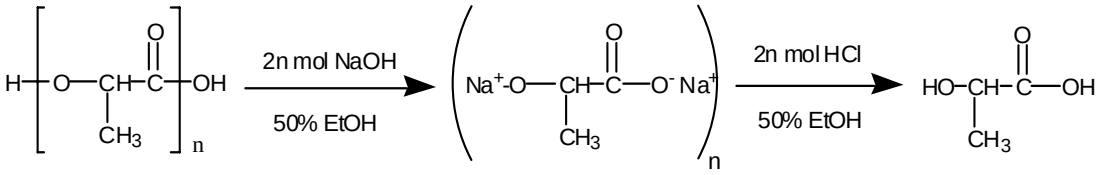

FIG. A3. Sodium lactate.

Now calculate the number of grams of NaOH you will need to fully hydrolyze 5.0 of PLA.

Base Hydrolysis procedure:
Add shredded PLA (5.0 g, 0.07 mol), NaOH (5.6 g, 0.14 mol) and a magnetic stir bar into a 250 mL Erlenmeyer flask. In order for the polymer to completely hydrolyze, a 2:1 molar ratio of the NaOH to the

PLA is needed. Add enough 50% ethanol to cover the contents in the flask. Cover the mouth of the flask with a small watch glass and heat the reaction to a brisk boil with constant stirring for one hour to ensure complete hydrolysis of the PLA. (Alternatively, you can use a household microwave to speed up the process. Microwave the reaction mixture on high for no more than 4 minutes at a time. Allow the reaction to cool for 4 minutes before repeating the process. 4 to 5 cycles are generally required on a 650 Watt household microwave. Use of a microwave with a turntable is recommended.) Cool the reaction in an ice bath and acidify the resulting solution to a pH of 3.8 using 50% HCl using pH meter. Filter the cold solution to remove any residual particulate matter. The filtrate is an aqueous solution of lactic acid and NaCl. Water, ethanol and NaCl can be removed by rotary evaporation followed by vacuum filtration.

Acid Hydrolysis:
Fill a round bottom flask equipped with a reflux condenser ¼ full with shredded PLA. Add a magnetic stir bar and enough *vinegar* to cover the PLA. Wrap the round bottom flask with aluminum foil to ensure uniform and thorough heating. With constant stirring, heat the reaction mixture to reflux using a heating mantle. Hydrolysis of the PLA is complete once a completely transparent yellow solution forms. The reaction is typically complete in one week. Water can be removed by rotary evaporation to afford a concentrate solution of LA with traces of acetic acid.

APPENDIX B

Cups to Cleaners, Trash to Treasure: Converting a PLA cup to LA soap an Introductory Organic Chemistry Laboratory Notes to Instructors

This experiment was developed as a green campus initiative to inform the academic and surrounding communities about the importance of green chemistry and teach members of the community how they can become more environmentally friendly and conscious. In this lab, students will obtain a PLA cup from the school cafeteria and convert the cup into a soap that they will test on soiled bathroom tiles. This lab will teach students useful techniques and instrumentation skills that can be used in other labs. This lab can serve as a replacement to traditional labs offered. This write up will explain how it can replace or supplement the saponification lab: basic hydrolysis of an ester to make soap. The 12 Principles of Green Chemistry will be introduced to the students so that they can apply the principles and learn the importance of practicing them in other applications.

Estimated Lab Time: 1-2 hours

Waste Collection and Disposal: This lab is an excellent example of green chemistry because there is minimal waste. The waste generated from the base hydrolysis procedure is only salt and water, which can be safely disposed of in the sink. The waste from the acid hydrolysis should be collected in a waste jar, but is non-toxic. In both procedures, acid is used. The acid can be either hydrochloric acid or acetic acid. If using acetic acid, no harmful waste is generated.

TABLE BI: Materials for organic chemistry lab.

Item	Additional Information	Hazards	Quantity per Student
PLA cup	Cups can be mass collected or student can bring in own		1
Sodium Hydroxide	Not all students will choose to use this	Corrosive to skin, wear goggles and gloves	~10g
Acetic Acid	Choose this or HCl	Could be Harmful, corrosive, Wear goggles and gloves	~50 mL[a]
Hydrochloric Acid	Choose this or acetic acid	Harmful, corrosive, wear goggles and gloves.	~35 mL[a]
Ethanol	Used as solvent; students only need enough to cover PLA chips	Wear goggles, gloves	~30 mL
Hot Plate w. Magnetic Stirrer			1
50 mL round bottom flask		Surface gets hot	1
Magnetic Stir Bar			1
Ring stand			1
Suction Filter	Used to filter end product		1
Filter Paper			1
Tubing	For filter	Ensure filtering system is set up properly	1
Ice	For cooling product		100 mL Beaker full
20 drum vial	Collect product		1

[a]amount depends on size of cup students choose to use.

Experiment Tips and Safety Concerns:

When using a used PLA cup, it should be rinsed out with water to ensure that no contaminants are present during the reaction. The PLA cup needs to be shredded. At Simmons, we use a paper shredder capable of shredding credit cards and CD's. The cups can also be cut with scissors. The size of the chips of the cup will affect the rate of the reaction. Preliminary results show that the smaller the pieces, the quicker the cups will hydrolyze.

The base hydrolysis reaction is worked up in an acidic solution to create the lactic acid. The acid can either be acetic acid or hydrochloric acid.

Safety: Overall, there are minimal safety concerns in this lab. The use of hydrochloric acid involves the biggest risk for students. HCl is harmful because it has harmful vapors, is corrosive to skin, and is eye irritant. When using HCl, students should work in the fume hood. There is also a small safety concern when working with sodium hydroxide, as well because it is also corrosive to skin when solution is concentrated.

Additional Experimental Notes: When the PLA is added to the base hydrolysis solution, the chips of PLA should go into solution relatively quickly. If not, the student has not performed the correct stoichiometric calculation for adding the appropriate amount of base to react with all of the PLA.

Data: Students can analyze data from the experiment by using ^{1}H and ^{13}C Nuclear Magnetic Resonance and Fourier Transform InfraRed spectroscopy as well as Matrix-Assisted Laser Desorption Ionization – Time-of-Flight Mass Spectrometry.

^{1}H and ^{13}C NMR were measured on a 90 MHz Anasazi EFT NMR instrument. FT-IR were measured on a Digilab Excalibur 3000 FT-IR. MALDI-TOF MS were measured on an Omniflex MALDI-TOF Mass Spectrometer.

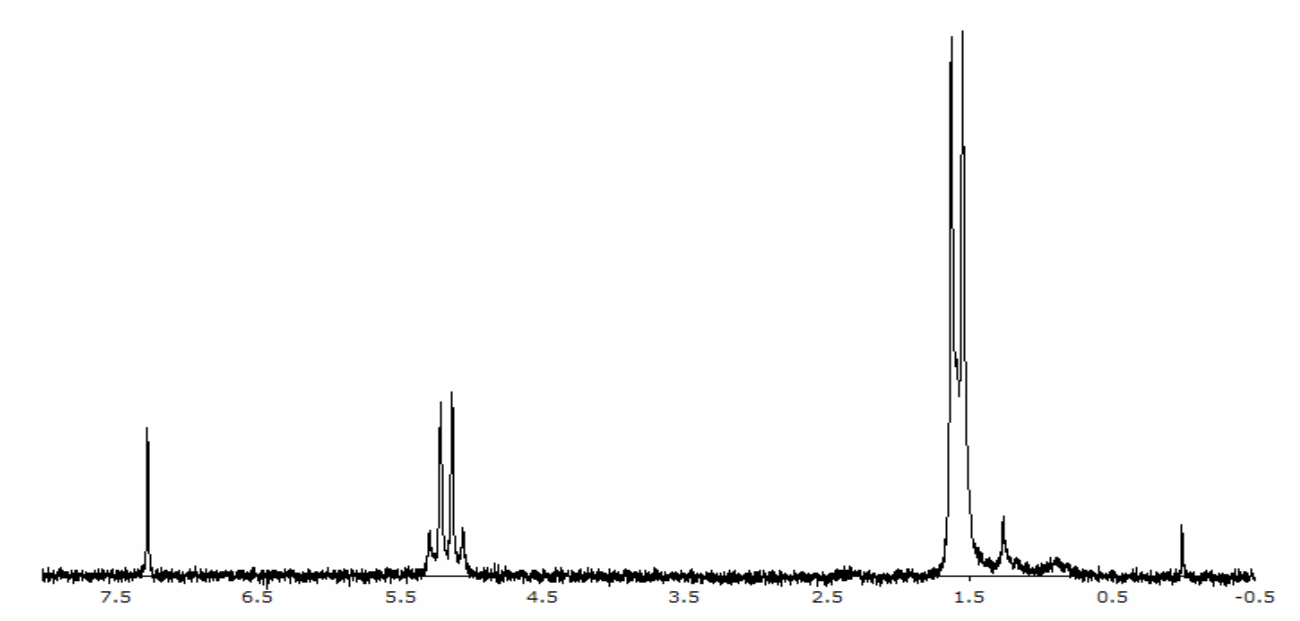

FIG. B1. ^{1}H NMR of PLA from a CUP in $CDCl_3$ with TMS.

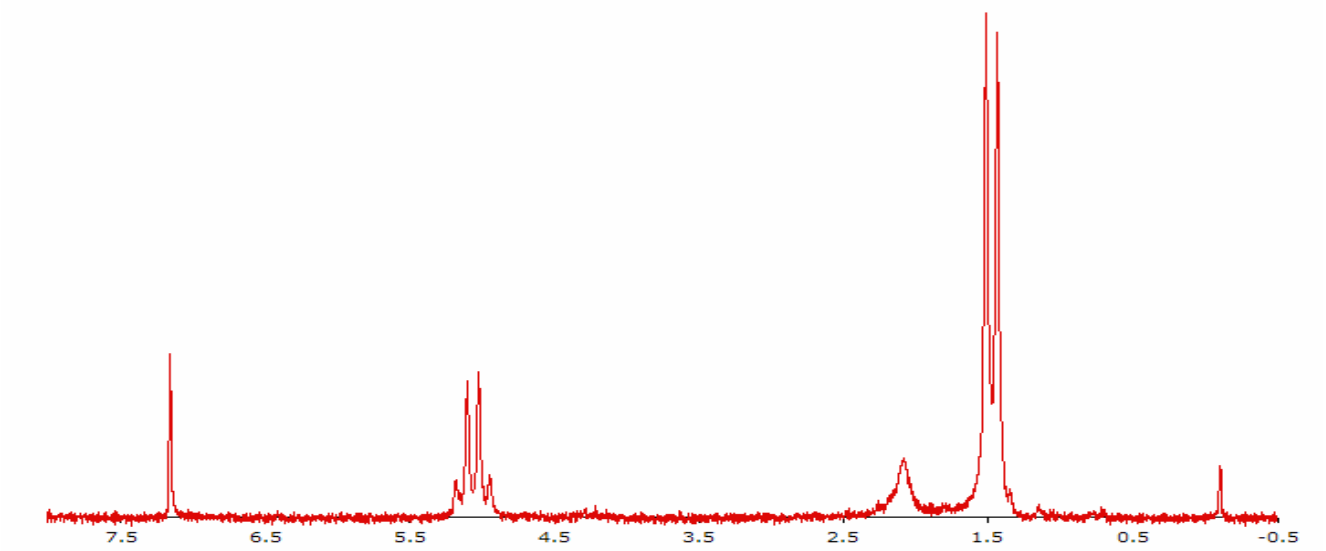

FIG. B2. ^{1}H NMR of solid “PLA” material isolated after *incomplete* acid hydrolysis in $CDCl_3$ with TMS.

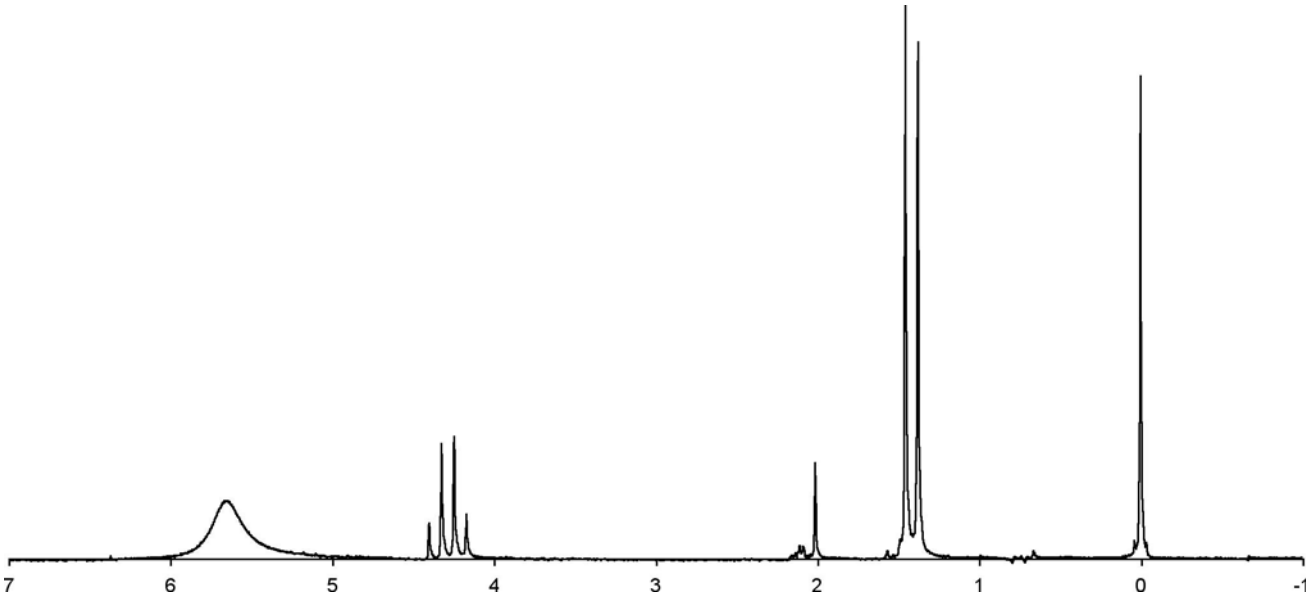

FIG. B3. Complete acid hydrolysis in D6-acetone with TMS.

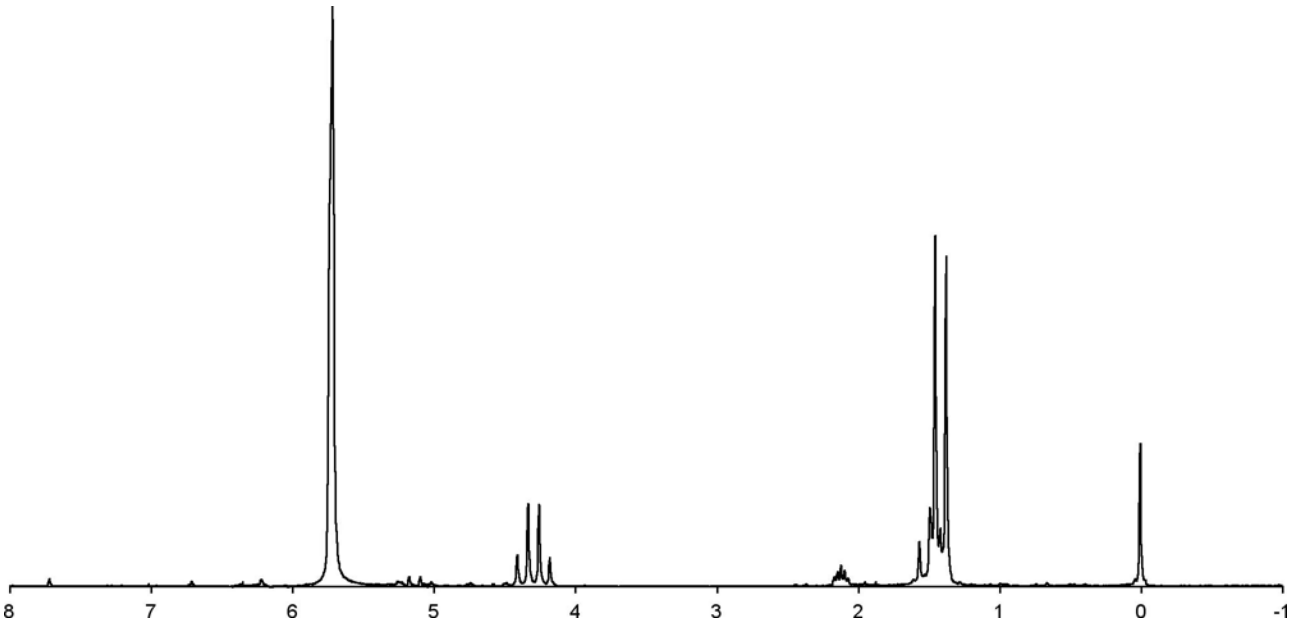

FIG. B4. Complete base hydrolysis in D6-acetone with TMS.

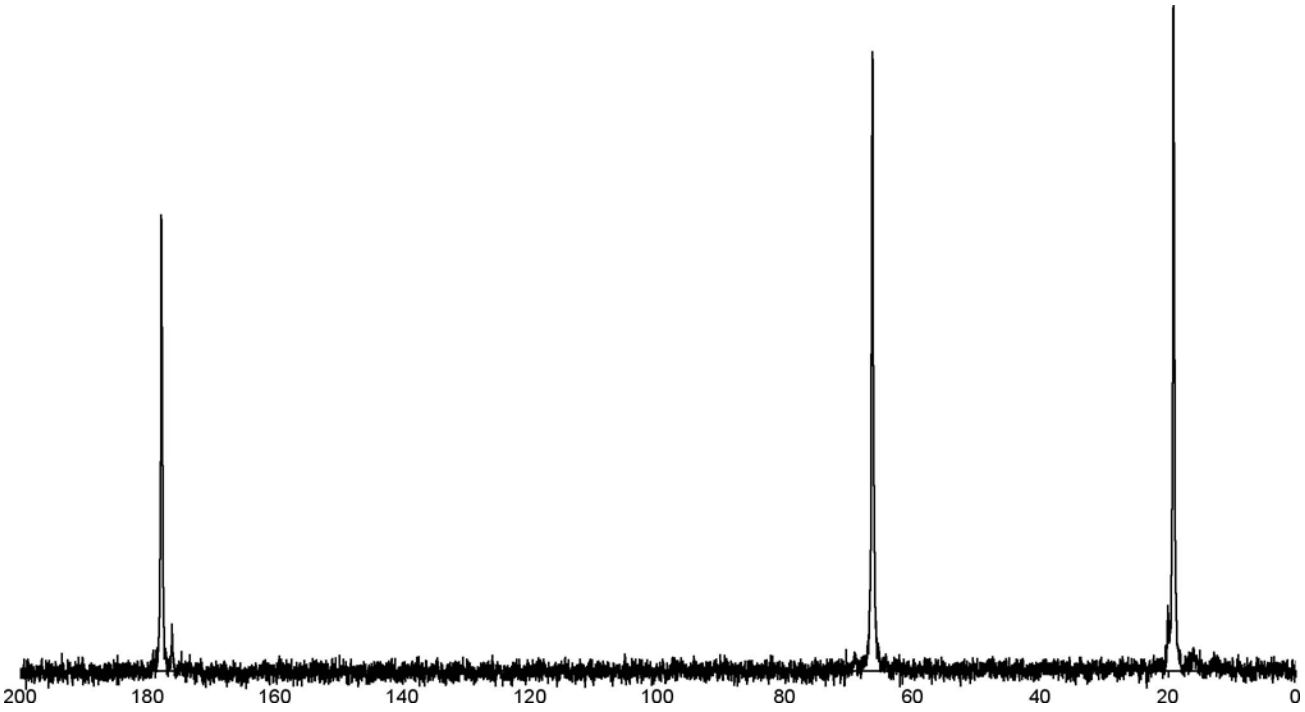

FIG. B5. ^{13}C NMR Spectrum of complete acid hydrolysis (neat).

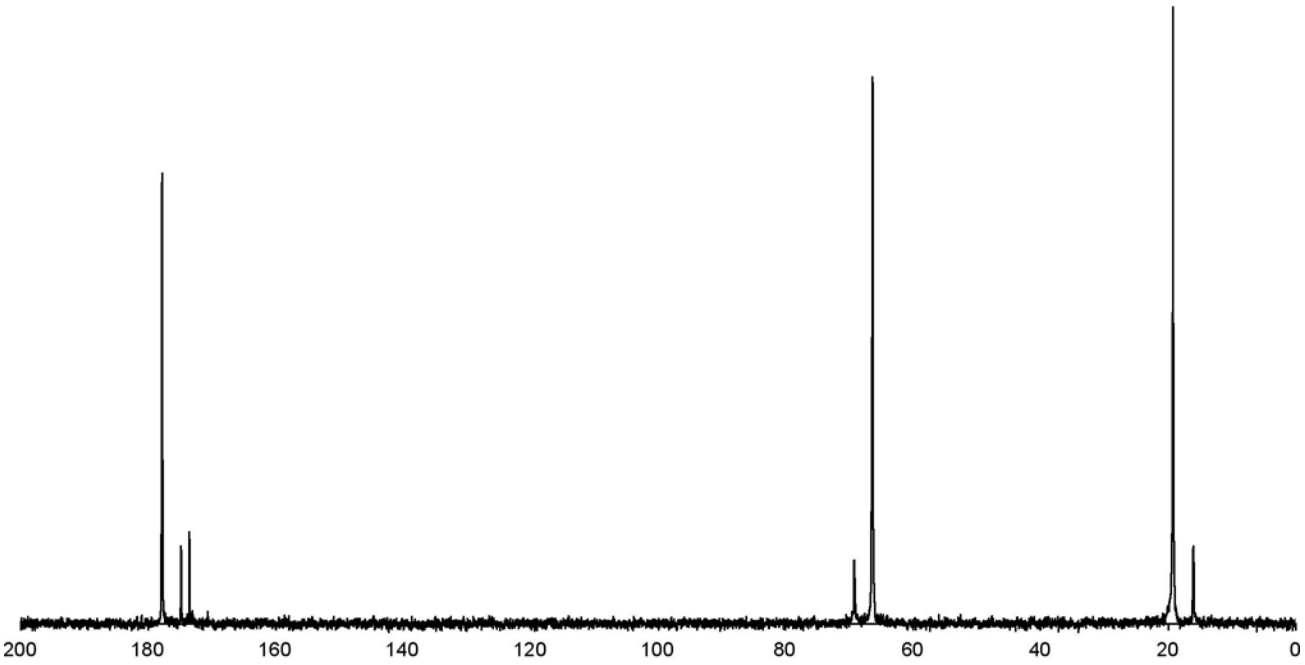

FIG. B6. ^{13}C NMR Spectrum of complete base hydrolysis (neat) traces of diethyl ether.

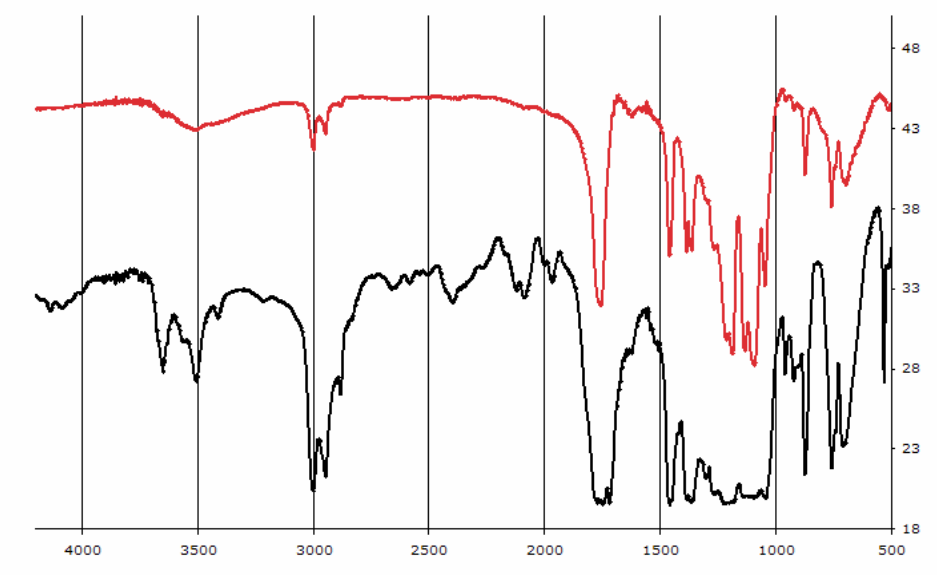

FIG. B7. FTIR – evaporated $CHCl_3$ solution on AgCl plates. Black: PLA cup. Red: solid "PLA" material isolated after *incomplete* acid hydrolysis.

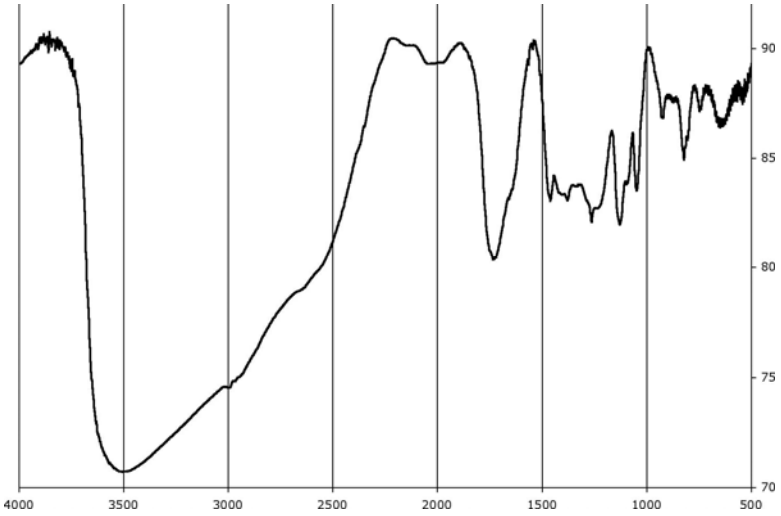

FIG. B8. Complete Acid Hydrolysis.

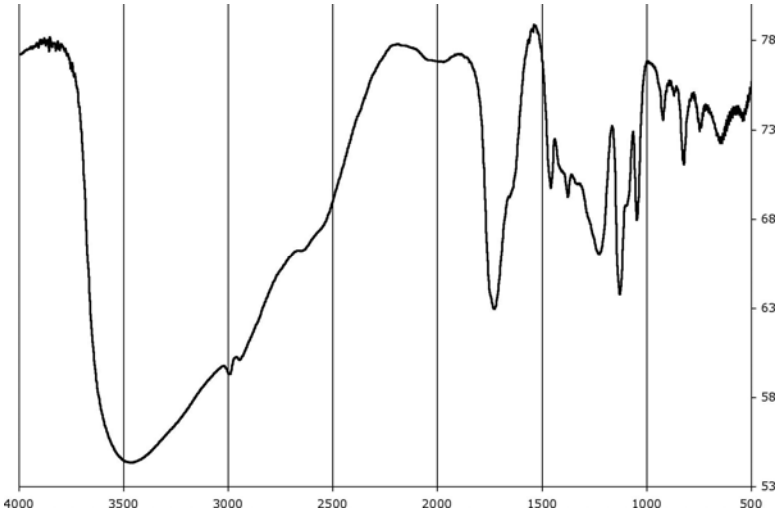

FIG. B9. Complete Base Hydrolysis.

MALDI-TOF MS–
Sample preparation: Solution **A**: 2 mg of PLA in 10µL of THF, Solution **B**: 20 mg of 2,5-dihydroxybenzoic acid in 100 µL of THF. Analyzed 1 µL of a mixture of a 1µL **A** with 10 µL of **B**.

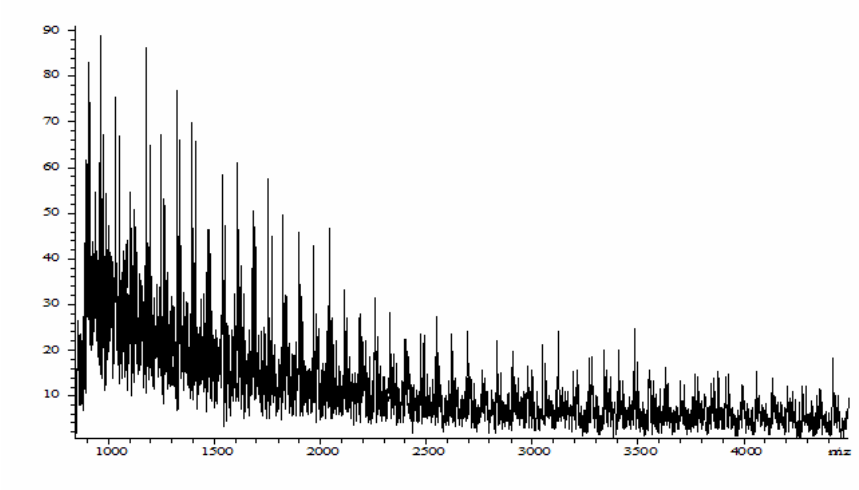

FIG. B10. MALDI-TOF MS– PLA Cup.

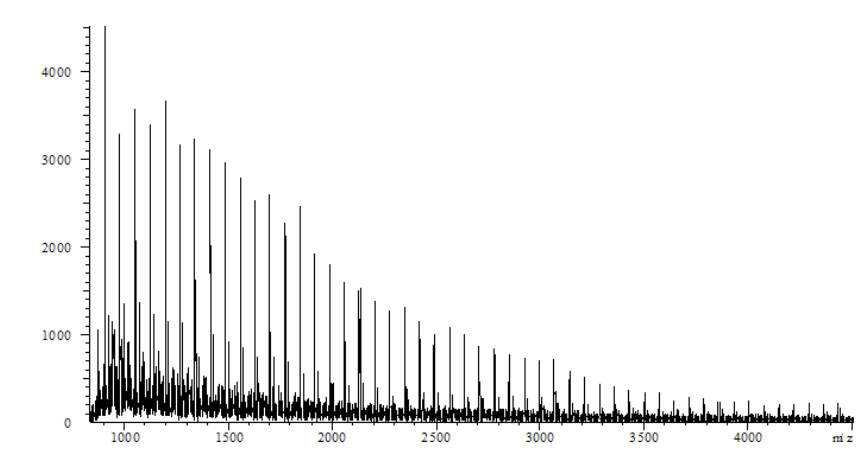

FIG. B11. MALDI-TOF MS– Solid “PLA” material isolated after *incomplete* acid hydrolysis.

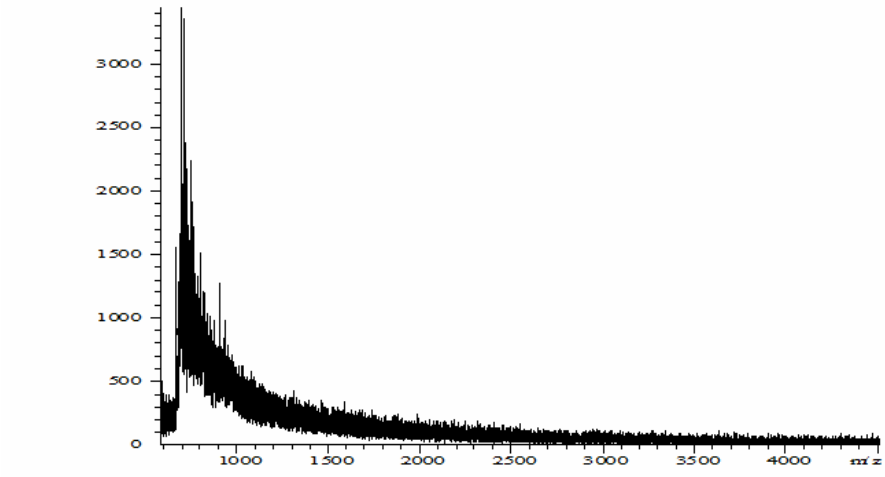

FIG. B12. MALDI-TOF MS– Complete Acid or Base Hydrolysis.

APPENDIX C

Titration of Lactic Acid Solution produced by PLA Depolymerization: A General Organic Biochemistry Laboratory Experiment

In the Cups to Cleaners lab, your group depolymerized polylactic acid (PLA) to produce a solution containing lactic acid (LA). But wait: do you really know that is what you have in your solution? How can you be sure? And how much acid is actually in there?

This laboratory activity is intended to help you answer to these questions. The instructions here lead you through a procedure called acid-base titration, which should provide data which will allow you to be more confident about the contents of the solution. During the titration, you will monitor pH as a solution containing base is gradually added to a small sample of the lactic acid. The way the pH changes with added base will not only allow you to find out how much acid is present, but also will confirm its identity. This is possible because lactic acid is what is considered a weak acid.

Weak acids do not completely ionize in solution. At any given moment only some molecules of these acids have their acidic hydrogens released into the solution. How readily a particular weakly acidic substance gives up its hydrogen in this way is characteristic of that substance. Your titration should provide data we can examine and compare to the accepted behavior of lactic acid. Matching data supports the assertion that your solution actually contains lactic acid.

Experimental Procedure: Standard Buret and pH Meter

The lactic acid (LA) solution should be at a pH of 2 or below before titrating. You will need to use the literature value for the pKa for lactic acid, which is 3.86 (Merck Index, 13/e Merck and Co., Inc., 2001, p.5353).

Hazards/Safety Considerations:
NaOH solution is caustic. Care should be taken to avoid prolonged skin contact or accidental ingestion. Fill the buret with a funnel and with the buret at or below the level of your shoulder.

As always, take general precaution to avoid accidental exposure to any laboratory chemicals.

Materials
Lactic Acid solution, prepared as described in Cups to Cleaners: Trash to Treasure
0.100 M NaOH solution, carbonate-free and standardized if high precision is desired
deionized water
250 mL beaker
stir bar
pH meter and probe, calibrated
buret and funnel
buret clamp and holder (ringstand)
stir plate

Procedure
Aliquot 1 mL (use a volumetric pipet if quantifying yield) of lactic acid solution into the 250-mL beaker. Add sufficient water to allow for proper pH measurement and a stir bar.

Carefully fill the buret with NaOH solution. Check that the stopcock is closed as you add the base. Add base until the level of solution in the buret is around the 5-10 mL mark, then drain a little liquid through the stopcock and into a beaker. This leaves no void between the stopcock and the end of the buret.

Set up the buret on the buret stand and attach the pH probe gently with a clamp. Adjust so there is room underneath the outlet to place the stir plate and beaker containing the lactic acid sample. Lower the pH probe into the sample. Note the initial pH and volume on the buret. Set the sample to stir quietly.

Titrate with base, recording pH for approximately each 0.2 mL of base that is added. Collect data until pH is at least 11.

Experimental Procedure: Vernier Data Acquisition Equipment

Hazards/Safety Considerations:
NaOH solution is caustic. Care should be taken to avoid prolonged skin contact or accidental ingestion.

As always, take general precaution to avoid accidental exposure to any laboratory chemicals.

Materials

Lactic Acid solution, prepared as described in Trash to Treasure
0.100 M NaOH solution, carbonate-free and standardized if high precision is desired
deionized water
250 mL beaker
stir bar
Vernier pH probe, Drop Counter, and data collection interface (LabQuest, LabPro and TI calculator, or computer with Logger Pro software)
Reagent Reservoir or buret and buret clamp
buret holder or ringstand
stir plate

Procedure

Aliquot 1 mL (use a volumetric pipet if quantifying yield) of lactic acid solution into the 250-mL beaker. Add sufficient water to allow for proper pH measurement and a stir bar.

Set up the Reagent Reservoir or buret and funnel with the drop counter directly beneath the outlet.

Carefully fill the reservoir or buret with NaOH solution. Check that the stopcock is closed as you add the base. Add approximately 30 mL of base. Drain a little liquid through the stopcock and into a beaker. This leaves no void between the stopcock and the end of the buret.

Place the buret or Reservoir on the buret stand and adjust so that the drop counter can detect drops that are released, and so there is room underneath the drop counter to place the stir plate and beaker containing the lactic acid sample.

Insert the pH meter through the larger hole in the drop counter and lower into the sample. Note the initial pH. Set the sample to stir quietly.

Establish the pH probe and Drop Counter to the lab acquisition interface (Datalogger, Vernier LabQuest, or computer). When properly set, the device will record a pH value for each drop that passes the drop counter. The Vernier device should plot pH vs. volume in mL.

Carefully adjust the Reservoir or buret to allow drops to pass the drop counter at about 1 drop/second. Collect data until pH is at least 11.

Analysis

The pH data obtained during titration can be used to support the assertion that the sample does indeed include lactic acid, and to determine how much lactic acid is in the original sample from the depolymerization.

1. Generate a graph from your data, with pH plotted vs. volume of base added. Identify the end point of the titration, which is the steepest portion of the plot. (Vernier users who are using Logger Pro software can find this point accurately by taking the first derivative of the data, highlighting the inflection point where the slope of the plot changes).

2. What evidence suggests that lactic acid is actually in the solution?
Weak acids such as lactic acid can be characterized by their pKa values. The pKa value measures the degree to which acidic hydrogens are released when the acid is in a water solution. The pKa is determined from experimental data by finding the pH value at half the volume of titrant required to reach the end point for the titration. At this volume the pH value is equal to the pKa for the acid in the solution.

- What is the volume of base needed to reach the end point for your titration?
- What is the pKa for the acid titrated in your experiment?

Write a paragraph that clearly addresses each question above and draws an appropriate conclusion based on your data.

3. How much lactic acid from the original plastic sample is present in the solution?
The quantity of lactic acid in the sample can be determined from titration data by figuring out how much base was necessary to neutralize all of it. All acid is neutralized at the end point. Your data shows how much base was necessary to reach this point.

- What volume of base was necessary in your experiment?
- How many moles of base are in that much solution, given its concentration?
- How many moles of lactic acid were therefore in the sample you titrated?
- How many moles of lactic acid were in the entire batch of lactic acid generated from the depolymerization?
- What percent of the amount you started with is this?

Write out a paragraph that clearly addresses each question above and draws an appropriate conclusion based on your data.

4. What sorts of things could have happened to cause your data to be misleading? Provide 2 possibilities. For each, explain not only what the error could have been but also the consequence such an error would produce. Be specific and write in complete sentences.

APPENDIX D

Titration of Lactic Acid Solution produced by PLA Depolymerization: A General Organic Biochemistry Laboratory Experiment Instructor Notes

Depolymerization of Polylactic Acid (PLA) performed as described in the "Cups to Cleaners: Trash to Treasure" activity primes students to experience titration as an analytical method with real value. In the General, Organic and Biological (GOB) Chemistry course, students may have only one opportunity to perform a titration. Titrating the lactic acid produced by depolymerization has several advantages over the more incidental titration experience students may otherwise perform. Some of these advantages are especially relevant to the GOB experience.

Students are invested in the titration because they are using it to analyze material they produced in the previous procedure. In this way the titration can be viewed as an analytical method for discovering information they care about. The fact that the material they are analyzing was produced by their own work increases the degree of investment in the activity.

Lactic acid has physical properties which provide students with clear results and straightforward analysis. The solution produced in Cups to Cleaners produces a clear titration curve from a manageable sample size. Experimental pKa values show variation of generally less than 0.1 pH unit and average close to the accepted pKa of 3.86 (Merck Index, 13/e, 2001). Yields are high and reproducible because of the depolymerization reaction in base requires little manipulation of the sample and occurs rapidly and completely. The depolymerization chemistry is straightforward and easy to understand reducing the possibility that inexperienced students will become distracted by the chemical transformation.

Additionally, this titration is amenable to data acquisition using equipment available from Vernier. Drop Counters allow students to collect the titration data in far less time than would be required if titrating by hand. Time for available for meaningful consideration of the concepts involved, rather than preoccupied by repetitive data collection maneuvers, is maximized.

Why does this activity fit the curriculum for GOB?

Lactic acid is a substance worthy of the attention of GOB students. It is an important product of anaerobic metabolism which can be applied to discussions of athletic performance and disease. It also happens to be an alpha-hydroxy acid, which students may encounter in personal care products. There are important roles for lactic acid as a component of food and in food spoilage.

This experience can stimulate discussion about the benefits of new, biodegradable, and nontoxic (green) materials. GOB students are often heading for careers in allied health fields where familiarity with materials is highly relevant. Lactic acid from PLA can stimulate discussion of the principles of Green Chemistry, including use of renewable feedstock, design of safer chemicals, waste prevention, and design for degradation.

APPENDIX E

Testing the Efficacy of Lactic Acid as a Antimicrobial Cleaner: An Introductory Microbiology Experiment

Introduction

Antiseptics are chemicals able to inhibit in vivo sepsis or infection. They do so by simply inhibiting the growth of the infectious agent. Antiseptics chemicals must be nontoxic to allow application to skin and mucous membranes. These chemicals act as disinfectants when used at sufficiently higher concentration levels. The mode of action of antiseptics and disinfectants differs from antibiotics in that they act largely by denaturing proteins.

An assay used in many clinical laboratories to test the potency of antiseptics and disinfectants is a filter paper disc-agar diffusion procedure commonly known as the Kirby-Bauer test. Disc of filter paper impregnated with a possible antiseptic or disinfectant, Lactic acid. The solution will range in concentration levels from ones obtainable in the human body to ones for external use only. The discs are placed on agar plate heavily seeded with test bacterium. When the bacterium is incubated, it will grow in a smooth lawn of confluent growth except in a clear zone around the disc impregnated with the lactic acid solution. The clear growth inhibition zone does not necessarily indicate the degree of microbial susceptibility to the antiseptic or disinfectant nor does it indicate if it appropriate for use in clinical treatment.

When conducting the precisely controlled Kirby-Bauer test, special conditions such as 2 to 5 hour cultures, controlled inoculum size, and short incubation periods are necessary. During observation, the diameter of the clear zone of inhibition surrounding each disc should be measured. Unfortunately, a comparison chart is not available for antiseptics and disinfectants.

Estimated lab time:

Materials

Cultures
Bacteria (24 hour 37°C TS broth cultures)
Escherichia coli (a Gram-negative rod, facultative, found in the intestinal tract of animals, coliform group, can cause diarrhea and serious kidney disease)
Staphylococcus aureus (Gram-positive coccus, a component of normal skin flora, but can cause wound infections, food poisoning and toxic shock syndrome.)
Streptococcus pyogenes (Gram-positive cocci in chains. The cause of strep throat, rheumatic fever, and glomerulonephritis.)
Beakers containing the four concentration levels of lactic acid as antiseptic: 0.5%, 1.0%, 1.5%, & 2.0%.
Beakers containing the four concentration levels of lactic acid as a disinfectant: 30%, 40%, 50%, & 60%.
Mueller-Hinton agar, 6 plates
Sterile cotton swabs, 6
Sterile filter paper discs, 1⁄4” or 1⁄2”, 24
Small forceps, 1
Ruler divide in mm

Experiment Tips and Safety Concerns:

In microbiology laboratory experiments, all materials are potentially infectious and should all times be treated as so. When performing the experiment, students should avoid finger to mouth contact at all times.

Pipetting by mouth should never be performed in order to avoid the danger of ingesting microorganisms or toxic chemicals. Protective clothing should be worn and long hair should be tied back to prevent contaminating cultures. If any individual is immunocompromised for any reason including pregnancy, it is recommended to consult with a physician before performing the experiment. The bench top should be kept clear of any unnecessary items. The bench surface should be cleaned with a disinfectant before and after performing any laboratory experiments. Students should wash hands with soap and water before and after the experiment. If a culture is dropped and broken, the contaminated area should be covered with paper towels and disinfectant is to be poured over the material. After 10 minutes any contaminated material is to be autoclaved. All contaminated material must be put in the proper containers to be autoclaved before disposing.

Waste Collection and Disposal:
All materials should be placed in proper containers for autoclaving before disposal.

Procedure
Filter Paper Disc Technique for Antiseptics and Disinfectants:
1. Divide the underside of six plates of Mueller-Hinton agar into quadrants and label them 1 through 4.
2. Record the four concentration levels of lactic acid as antiseptic: 0.5%, 1.0%, 1.5%, & 2.0%. Record the four concentration levels of lactic acid as a disinfectant: 30%, 40%, 50%, & 60%.
3. Label each cover of the Petri dish with the bacteria: E. coli, S. aureus, and S. pyogenes
4. Suspend the E. coli culture, then insert and moisten a sterile swab, remove excess, followed by streaking the swab in all directions on the surface of the agar plate. Discard swab in appropriate waste container
5. Repeat step 4 with S. aureus, and S. pyogenes
6. Dip the forceps in 95% alcohol and touch to the flame of a Bunsen burner. Allow to air dry.
7. Using the sterile forceps, remove one of the filter paper disc and dip into the lactic acid solution.
8. Repeat step 7 for all the concentrations.
9. Drain each disc thoroughly on a piece of clean absorbent toweling and place them in the center of each quadrant.
10. Repeat steps 5 through 9 for the additional plates of bacteria.
11. Invert the Petri dishes and incubate at 37°C
12. Following incubation observed and measure with a mm ruler the clear area, if any

APPENDIX F

An Experiment for Middle School

Introduction

Polylactic acid (PLA) is a biodegradable polymer derived from lactic acid. It is a highly adaptable material and is made from 100% renewable resource like corn, sugar beets, wheat, and other starch rich products. PLA displays many properties that are better than many petroleum-based plastics, which can be used for many applications.

Polylactic acid (PLA) is completely compostable in commercial composting facilities. PLA can be converted back to monomers, which can then be converted back into polymers. PLA can be biodegraded into water, carbon dioxide, and organic material. PLA can be broken down into its simplest parts so there is no sign of the original product remains.

Materials per Student
Goggles
Plastic gloves
22 oz PLA cup, cover, straw
50 mL ethanol
50 mL H_2O
5.6 g NaOH
20 mL 50% HCl
250 mL Erlenmeyer flask
100 mL graduated cylinder
plastic funnel
filter paper
pH indicator paper
ice
conventional microwave oven

Procedure
1. PUT ON SAFETY GOGGLES AND GLOVES!
2. Break a 22 oz PLA cup into four pieces
3. Shred the cup using a heavy duty paper shredder
4. Using the scale, weigh out 5 g of the shredded cups. Add the 5 g of shredded cup to the 250 mL Erlenmeyer flask
5. Using the graduated cylinder, measure 50 mL of ethanol. Add to the 250 mL Erlenmeyer flask
6. Using the graduated cylinder, measure 50 mL of water. Add to the 250 mL Erlenmeyer flask
7. Add 5.6 grams of NaOH to the Erlenmeyer flask
8. Place the Erlenmeyer flask into a conventional microwave oven. Cover the top of the flask with a watch glass.
9. Heat the flask for 4 intervals of 5 minutes or until the cup has completely dissolved.
10. After the cup is completely dissolved, remove from microwave and let stand for 2-3 minutes.
11. Place in ice bath to cool
12. Use the pH paper to test the pH of the liquid
13. Add HCl until the pH paper turns reddish indicating the liquid is acidic

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FOOTNOTES

[a] LA is used as a calcium chelator in sports drink, a food preservative (suppresses Coliform and Mesentericur group of bacteria), in sugar confectionery to minimize sugar inversion, in the direct acidification of rye or rye-wheat breads and as a butter stabilizer and volumizer. In breweries LA is used during the mashing process and during wort cooking. Acidification of lager beer with LA improves the microbe stability as well as the flavor.

†[a]http://www.ides.com/generics/PLA/PLA_overview.htm

†[b]http://www.natureworksllc.com/news-and-events/press-releases/ingeo-fibers/10-6-05-ingeo-fiber-backgrounder.aspx

†[c]http://www.natureworksllc.com/earth-month-2007/press-materials/technical-overview.aspx